

# Fundamental Formulas of Physics

edited by Donald H. Menzel

GEOMETRICAL OPTICS

PHYSICAL OPTICS

ELECTRON OPTICS

ATOMIC SPECTRA

MOLECULAR SPECTRA

QUANTUM MECHANICS

NUCLEAR THEORY

COSMIC RAYS AND HIGH-ENERGY PHENOMENA

PARTICLE ACCELERATORS

SOLID STATE

THE THEORY OF MAGNETISM

PHYSICAL CHEMISTRY

BASIC FORMULAS OF ASTROPHYSICS

CELESTIAL MECHANICS

METEOROLOGY

BIOPHYSICS

VOLUME TWO



FUNDAMENTAL  
FORMULAS  
OF  
PHYSICS

EDITED BY

DONALD H. MENZEL  
DIRECTOR, HARVARD COLLEGE OBSERVATORY

*In Two Volumes*

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## P R E F A C E

A survey of physical scientists, made several years ago, indicated the need for a comprehensive reference book on the fundamental formulas of mathematical physics. Such a book, the survey showed, should be broad, covering, in addition to basic physics, certain cross-field disciplines where physics touches upon chemistry, astronomy, meteorology, biology, and electronics.

The present volume represents an attempt to fill the indicated need. I am deeply indebted to the individual authors, who have contributed time and effort to select and assemble formulas within their special fields. Each author has had full freedom to organize his material in a form most suitable for the subject matter covered. In consequence, the styles and modes of presentation exhibit wide variety. Some authors considered a mere listing of the basic formulas as giving ample coverage. Others felt the necessity of adding appreciable explanatory text.

The independence of the authors has, inevitably, resulted in a certain amount of overlap. However, since conventional notation may vary for the different fields, the duplication of formulas should be helpful rather than confusing.

In the main, authors have emphasized the significant formulas, without attempting to develop them from basic principles. Apart from this omission, each chapter stands as a brief summary or short textbook of the field represented. In certain instances, the authors have included material not heretofore available.

The book, therefore, should fill needs other than its intended primary function of reference and guide for research. A student may find it a handy aid for review of familiar field or for gaining rapid insight into the techniques of new ones. The teacher will find it a useful guide in the broad field of physics. The chemist, the astronomer, the meteorologist, the biologist, and the engineer should derive valuable aid from the general sections as well as from the cross-field chapters in their specialties. For example, the chapter on Electromagnetic Theory has been designed to meet

the needs of both engineers and physicists. The handy conversion factors facilitate rapid conversion from Gaussian to MKS units or vice versa.

In a work of this magnitude, some errors will have inevitably crept in. I should appreciate it, if readers would call them to my attention.

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FUNDAMENTAL  
FORMULAS  
*of*  
PHYSICS



## Chapter 16

# GEOMETRICAL OPTICS

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### 1. General Considerations

**1.1. Geometrical optics and wave optics.** Light energy is propagated through an optical instrument in the form of a wave motion. Nevertheless, as a consequence of several important theorems, we can, for many purposes, regard light as traversing homogeneous isotropic media in straight lines. In heterogeneous isotropic media light is propagated as a normal congruence of rays in which the direction of motion lies along the normal to the wave front at any given point. In the most general case, i.e., heterogeneous anisotropic media, the direction of motion may be inclined to the wave front. By dealing with a geometry of lines rather than of waves, one can achieve considerable simplification. From this point of view the true wave nature of light enters as a necessary correction to the results of geometrical optics.

**1.2. Media.** Light travels through a vacuum in straight lines at a constant velocity irrespective of color. In material media the speed of light changes to a smaller value and becomes dependent on color. In the process the frequency  $\nu$  and hence the quantum energy  $h\nu$  remain unchanged. The effect of a medium on light is usually characterized by the *index of refraction*, which in the most general case is a function of position, direction, and frequency.

**1.3. Index of refraction.** Let  $n$  be the index of refraction,  $c$  the velocity of light in vacuo, and  $v$  the velocity of light in the medium. Then

$$n = \frac{c}{v} = \frac{\nu\lambda}{v} = \frac{\lambda}{\lambda'} \quad \text{or} \quad \lambda = n\lambda' \quad (1)$$

where  $\lambda'$  is the wavelength in the medium.

$$\lambda = n_i \lambda_i = n_{i+1} \lambda_{i+1} = \dots \text{ etc.} \quad (2)$$

for successive media;  $n = 1$  for a vacuum.

**1.4. Interfaces.** Various kinds of physical media exist. Those of most general use are the transparent homogeneous isotropic substances, which include glass, synthetic resins, cubic crystals, etc. The most usual kinds of anisotropic media in optical applications come from uniaxial and biaxial crystals. Strain introduced mechanically or electrically may alter isotropic substances into anisotropic media.

Because of the physical nature of media, there must exist boundaries or *interfaces* between media. When this interface is a *matte* surface, the resulting reflection of light is called *diffuse*. When the interface is smooth and continuous, the resulting reflection or refraction of light is termed *regular* or sometimes *specular*.

One should note that the physical properties of material media are all a function of temperature. In detailed calculations the effect of temperature must be considered. One should also note that the usual optical instrument is immersed in air, and that the observed indices of refraction of optical glass and crystals are often referred to air under designated conditions.

**1.5. Refraction and reflection. The Fresnel formulas.** When a ray of light passes from one medium into another at a smooth interface, the light energy divides into two parts, one a *reflected* ray, and the other a *refracted* ray. Within a narrow region of disturbance on each side of the interface, secondary wavelets are formed in the backward direction, and a certain amount of energy is returned to the first medium as the reflected ray. The remaining energy goes into the refracted ray in the second medium. Both transmitted and reflected rays are partially polarized in a manner dependent on the *angle of incidence* and on the *angle of refraction*, which are the angles between the ray and normal in the respective media. (Cf. § 1.13.)

For light polarized in the plane of incidence (magnetic vector in the plane of incidence)

$$\frac{I}{I_0} = \frac{\sin^2(i - r)}{\sin^2(i + r)} \quad (1)$$

and for light polarized in a plane perpendicular to the plane of incidence

$$\frac{I}{I_0} = \frac{\tan^2(i - r)}{\tan^2(i + r)} \quad (2)$$

where  $I$  is the intensity of the reflected beam, and  $I_0$  the intensity of the incident beam.

When the light is unpolarized

$$\frac{I}{I_0} = \frac{1}{2} \frac{\sin^2(i-r)}{\sin^2(i+r)} + \frac{1}{2} \cdot \frac{\tan^2(i-r)}{\tan^2(i+r)} \quad (3)$$

For normal incidence whether the light is polarized or unpolarized

$$\frac{I}{I_0} = \left( \frac{n' - n}{n' + n} \right)^2 \quad (4)$$

This formula may be used as an approximation for unpolarized light up to as much as 50 degrees off the normal.

At *Brewster's angle*, defined by  $i = \tan^{-1} n'/n$ , the intensity of the reflected light vanishes for light polarized in a plane perpendicular to the plane of incidence, i.e.,  $\tan^2(i+r) = \infty$ . For unpolarized incident light at Brewster's angle, the intensity of the reflected light, which is now 100 % polarized with its electric vector perpendicular to the plane of incidence, becomes

$$\frac{I}{I_0} = \frac{1}{2} \sin^2(i-r) = \frac{1}{2} \left( \frac{n'^2 - n^2}{n'^2 + n^2} \right)^2 \quad (5)$$

If the incident light is already 100 % polarized at Brewster's angle,

$$\frac{I}{I_0} = \left( \frac{n'^2 - n^2}{n'^2 + n^2} \right)^2 \quad (6)$$

In the latter case for  $n'/n = 1.5$ ,  $I \sim 15$  % of  $I_0$ . For  $n'/n = 1.8$ ,  $I \sim 28$  % of  $I_0$ .

**1.6. Optical path and optical length.** Consider a curve  $S$  through any medium, either homogeneous or heterogeneous, along which light is known to travel between points  $z_1$  and  $z_2$ . The time of transit of the light is given by the line integral

$$t = \int_{z_1}^{z_2} \frac{ds}{v} = \frac{1}{c} \int_{z_1}^{z_2} nds \quad (1)$$

or

$$\overline{ct} = L = \int_{z_1}^{z_2} nds$$

The length  $L$  is called the *optical length* of the path, as opposed to

$$\int_{z_1}^{z_2} ds,$$

which is the *geometrical length*;  $L$  is equal to the geometrical length the light would have traveled in a vacuum in the same time interval.

In a homogeneous medium a geometrical length  $s$  has an associated optical

length  $L = ns$ . Where light travels through a succession of discrete homogeneous media,

$$L = \sum_i n_i s_i$$

where  $s$  is the straight line distance along the path between interfaces.

**1.7. Fermat's principle.** Light passing through a medium follows a path for which the optical length or time of transit is an extremum, i.e., independent of first-order infinitesimal variations of path. The time is said to have a stationary value, and usually is either a maximum or minimum.

$$\delta t = \frac{1}{c} \delta \int_{z_1}^{z_2} n ds = 0 \quad (1)$$

where  $n$  is a function of the space coordinates. Similarly,

$$\delta L = \delta \int_{z_1}^{z_2} n ds = 0 \quad (2)$$

defines the particular path between  $z_1$  and  $z_2$ . For discrete media

$$\delta L = \delta \sum_i n_i s_i = 0 \quad (3)$$

**1.8. Cartesian surfaces and the theorem of Malus.** Consider a meridian cut  $C$  of an interface. The surface  $C$  is to be so chosen that for every point on it in 3-space,  $L = ns + n's' = \text{constant}$  between a given point  $P$  in the first medium of index  $n$  and  $P'$  in the second medium of index  $n'$ . This surface clearly satisfies  $\delta L = 0$  and the higher order differentials are all zero. Hence any ray emitted by  $P_1$  that strikes  $C$  will find its way through  $P'$ . Hence  $P'$  is an image point of the object point  $P$ .

For a single ray originating at  $P$  and refracted through  $P'$  by a refracting surface  $S$ , where  $P'$  is not necessarily an image point, a Cartesian surface  $C$  may be considered tangent to  $S$  at the point of intersection of the refracted ray with  $S$ . By simple construction one can then determine whether the higher order differentials of a neighboring path between  $P$  and  $P'$  are positive or negative with respect to  $C$  where they are zero. If the curve  $S$  is more convex than  $C$  toward the less dense medium,  $L$  will be found to be a maximum.

*Theorem of Malus.* A system of rays normal to a wave front remains normal to a wave front after any number of refractions and reflections. That is, a normal congruence remains a normal congruence.

The combined principles of Fermat and Malus lead to the conclusion that for conjugate foci

$$\sum_i n_i s_i$$

is a constant between object and image points, irrespective of the ray.

A Cartesian surface holds for a point object, point image, and a single interface, defined by  $ns + n's' = \text{constant}$ . Where reflection is involved, the surface is of the second degree and is therefore a conic section. For refraction the Cartesian surface is of the fourth degree, and its meridian cut is called the Cartesian *oval*. When one point lies at infinity, the surface degenerates into a second degree surface.

**1.9. Laws of reflection.** Let  $\lambda, \mu, \nu$  be the direction cosines of a ray before reflection by a surface  $S$ , and  $\lambda', \mu', \nu'$  the direction cosines of the reflected ray. From the variation principle one can show that

$$\left. \begin{aligned} \lambda + \lambda' &= J l \\ \mu + \mu' &= J m \\ \nu + \nu' &= J n \end{aligned} \right\} \quad (1)$$

or 
$$\frac{\lambda + \lambda'}{l} = \frac{\mu + \mu'}{m} = \frac{\nu + \nu'}{n} \quad (2)$$

where  $l, m, n$  are the direction cosines of the normal to  $S$  at the point of reflection of the ray. Also

$$J = 2 \Sigma l \lambda = 2 \Sigma l \lambda' = 2 \cos i = 2 \cos i' \quad (3)$$

$$i = i'; \quad D = 2i \quad (4)$$

where  $D$  is the deviation.

$$\begin{vmatrix} \lambda & \mu & \nu \\ \lambda' & \mu' & \nu' \\ l & m & n \end{vmatrix} = 0 \quad (\text{condition of coplanarity}) \quad (5)$$

The reflected ray therefore lies in the plane of the normal and incident ray.

**1.10. Laws of refraction.** Let  $\lambda, \mu, \nu$  be the direction cosines of a ray before refraction by a surface  $S$ , and  $\lambda', \mu', \nu'$  the direction cosines of the refracted ray. Again from the variation principle one can show that

$$\left. \begin{aligned} n\lambda - n'\lambda' &= J l \\ n\mu - n'\mu' &= J m \\ n\nu - n'\nu' &= J n \end{aligned} \right\} \quad (1)$$

$$\text{or} \quad \frac{n\lambda - n'\lambda'}{l} = \frac{n\mu - n'\mu'}{m} = \frac{nv - n'v'}{n} \quad (2)$$

where  $l, m, n$  are the direction cosines of the normal to  $S$  at the point of refraction. Also

$$J = n \cos i - n' \cos r \quad (3)$$

$$J^2 = n^2 + n'^2 - 2nn' \cos(i - r) \quad (4)$$

$$= n^2 + n'^2 - 2nn' \cos D \quad (5)$$

where  $D$  is the deviation.

$$\cos D = \Sigma \lambda \lambda'$$

$$\begin{vmatrix} \lambda & \mu & \nu \\ \lambda' & \mu' & \nu' \\ l & m & n \end{vmatrix} = 0, \quad (\text{condition of coplanarity}) \quad (6)$$

### 1.11. The fundamental laws of geometrical optics

- The law of the rectilinear propagation of light
- The law of mutual independence of the component parts of a light beam
- The law of regular reflection
- The law of regular refraction

### 1.12. Corollaries of the laws of reflection and refraction

- The incident and reflected rays are equally inclined to any straight line tangent to the surface at the point of incidence.
- The projections of the incident and reflected rays upon any plane containing the normal make equal angles with the normal.
- $n \cos \theta = n' \cos \theta'$ , where  $\theta$  is the angle between the ray and any tangent line.
- $n \sin \psi = n' \sin \psi'$ , where  $\psi$  is the angle between the ray and any normal plane. (Cf. section 5.)

### 1.13. Internal reflection, and Snell's law. The relation

$$n \sin i = n' \sin r \quad (1)$$

is called the optical invariant, and also *Snell's law* after its discoverer. The relationship is valid in the common plane containing the incident and refracted rays and the normal, and follows from § 1.10 above. Note (d) under § 1.12 that a similar relation exists for the oblique refractions.

Where  $n'/n > 1$  and  $\sin r > n/n'$ , no solution exists for  $i$ . This is the case of internal reflection at the interface. The light energy remains 100 % in the same medium and obeys the laws of reflection.

**1.14. Dispersion at a refraction**

$$n \sin i = n' \sin r, \quad (\text{Snell's law}) \tag{1}$$

If  $di = 0$  (entrant white light)

$$dr = \frac{\sin i dn - \sin r dn'}{n' \cos r} \tag{2}$$

For air-glass where  $dn = 0$ ,

$$dr = -\tan r \frac{dn'}{n'}, \quad (\text{in the medium } n') \tag{3}$$

For glass-air where  $dn' = 0$ ,

$$dr = \tan r \frac{dn}{n} \tag{4}$$

where  $i$  and  $r$  are, respectively, the angles of incidence and refraction in the direction of travel of the light. Subsequent refractions determine the final effect for a system as a whole.

**1.15. Deviation**

a. Reflection

$$D = 2i, \quad dD = 2di, \quad (\text{for a single mirror}) \tag{1}$$

If two mirrors are separated by the angle  $\alpha$  and the light strikes each in turn,

$$D = 2\alpha \quad \text{independent of } i \tag{2}$$

b. Refraction

$$\left. \begin{aligned} D &= i - r \\ dD &= di \left( 1 - \frac{n \cos i}{n' \cos r} \right) \end{aligned} \right\} \tag{3}$$

At a glass-air surface and normal incidence,

$$dD = -(n - 1)di \sim -\frac{1}{2}di \tag{4}$$

At a glass-air surface and  $i = 30^\circ$ ,

$$dD = -di \tag{5}$$

At an air-glass surface and normal incidence,

$$dD = \left( 1 - \frac{1}{n} \right) di \sim \frac{1}{3} di \tag{6}$$

At an air-glass surface and  $i = 30^\circ$ ,

$$dD = 0.4di \quad (7)$$

At an air-glass surface and  $i = 90^\circ$ ,

$$dD = di \quad (8)$$

However, the final effect of a deviation depends on the subsequent refractions, as determined by magnification factors along the particular ray. The deviation increases numerically with the angle of incidence at a refraction, a fact that is a direct cause of difficulties in the design of optical systems.

## 2. The Characteristic Function of Hamilton (Eikonal of Bruns) \*

**2.1. The point characteristic,  $V$ .** Here  $V$  is defined as the optical path between points  $x, y, z$  and  $x', y', z'$  in a heterogeneous medium, i.e.,

$$V = \int_{xyz}^{x'y'z'} n ds \quad (1)$$

If both end points of the path are varied, and if  $n$  and  $n'$  are the indices of refraction in the infinitesimal neighborhood of  $x, y, z$  and  $x', y', z'$ , respectively

$$\delta V = -n \Sigma \lambda \delta x + n' \Sigma \lambda' \delta x' \quad (2)$$

$$\text{or} \quad \left. \begin{aligned} \frac{\partial V}{\partial x} &= -n\lambda, & \frac{\partial V}{\partial x'} &= n'\lambda' \\ \frac{\partial V}{\partial y} &= -n\mu, & \frac{\partial V}{\partial y'} &= n'\mu' \\ \frac{\partial V}{\partial z} &= -n\nu, & \frac{\partial V}{\partial z'} &= n'\nu' \end{aligned} \right\} \quad (3)$$

$$\text{and} \quad \Sigma \left( \frac{\partial V}{\partial x} \right)^2 = n^2, \quad \Sigma \left( \frac{\partial V}{\partial x'} \right)^2 = n'^2 \quad (4)$$

Similarly, if  $V$  is defined as the total optical path between a point  $x, y, z$  in an initial medium  $n$  and a point  $x', y', z'$  in a final medium  $n'$ , the above equations continue to apply. The intermediate path may traverse a succession of heterogeneous or discrete homogeneous media, or both.

Thus  $V$  is a function of 12 quantities ( $x, y, z, \lambda, \mu, \nu, x', y', z', \lambda', \mu', \nu'$ )

\* SYNGE, J. L., *Geometrical Optics, an Introduction to Hamilton's Method*, Cambridge University Press, London, 1937.

not all of which are independent. Given any five, we can compute the other five from the above equations.

The importance of the use of  $V$  is that the physical instrument is now replaced by a mathematical function  $V$ , and the behavior of the instrument by the partial derivatives of  $V$ . Knowing the characteristic, one can compute the performance; knowing the performance, one can compute a characteristic containing only a set of constants to be evaluated for a given instrument of that performance. Where  $x, y, z$  is a point source, one has precise information for investigation of the character of the image when  $V$  is known.

*Computation of  $V$ .* Let  $F_i(x_i, y_i, z_i) = 0$  be the equation of the general surface of the instrument separating various homogeneous media. Then the general optical path  $L$  becomes

$$L = ns + \sum_1^{N-1} n_i s_i + n' s' \tag{5}$$

On application of Fermat's principle,  $\delta L = 0$ ,

$$\sum_{i=1}^{N-1} \left( \frac{\partial L}{\partial x_i} \delta x_i + \frac{\partial L}{\partial y_i} \delta y_i + \frac{\partial L}{\partial z_i} \delta z_i \right) = 0 \tag{6}$$

Also, because variations in  $x_i, y_i, z_i$  are confined to the surface  $F_i(x_i, y_i, z_i) = 0$ ,

$$\frac{\partial F}{\partial x_i} \delta x_i + \frac{\partial F}{\partial y_i} \delta y_i + \frac{\partial F_i}{\partial z_i} \delta z_i = 0, \quad (i = 1, 2, \dots, N - 1) \tag{7}$$

If the intermediate points are to be independent of one another, then

$$\left. \begin{aligned} \frac{\partial L}{\partial x_i} &= J_i \frac{\partial F_i}{\partial x_i} \\ \frac{\partial L}{\partial y_i} &= J_i \frac{\partial F_i}{\partial y_i} \\ \frac{\partial L}{\partial z_i} &= J_i \frac{\partial F_i}{\partial z_i} \end{aligned} \right\} (i = 1, 2, \dots, N - 1) \tag{8}$$

These  $4(N - 1)$  equations yield the  $4(N - 1)$  quantities  $x_i, y_i, z_i, J_i$ . When substituted in  $L$ , these quantities yield the relation

$$V(x, y, z, x', y', z') = L, \quad (\text{actual path}) \tag{9}$$

The course of the analytic ray is thus defined.

**2.2. The mixed characteristic,  $W$ .** Here  $W$  is defined as the total optical path between the point  $x, y, z$  in the initial medium  $n$  and the foot of the perpendicular dropped from the origin of coordinates onto the final ray in medium  $n'$ .

$$V = W(x, y, z, \mu', \nu') + n'(\lambda'x' + \mu'y' + \nu'z') \quad (1)$$

From application of the variational principle

$$\left. \begin{aligned} \frac{\partial W}{\partial x} &= -n\lambda & \frac{\partial W}{\partial \mu'} &= -n' \left( y' - \frac{\mu'}{\lambda'} x' \right) \\ \frac{\partial W}{\partial y} &= -n\mu & \frac{\partial W}{\partial \nu'} &= -n' \left( z' - \frac{\nu'}{\lambda'} x' \right) \\ \frac{\partial W}{\partial z} &= -n\nu \end{aligned} \right\} \quad (2)$$

Thus, given  $x, y, z$  (source point) and  $\mu', \nu'$ , the direction of any ray in the final medium, we can obtain at once the equation of that ray in the final medium from the partials of  $W$ .

Then  $W$  may be computed in a fashion quite similar to the method used for computing  $V$  above. Because  $W$  involves fewer unknowns, its calculation is not as difficult as that for  $V$ .

### 2.3. The angle characteristic, $T$

a. Here  $T$  is defined as the total optical path between the foot of the perpendicular dropped onto the initial ray from the origin of coordinates in the first medium  $n$  to the foot of the perpendicular dropped onto the final ray from the origin in the final medium  $n'$ .

$$V = -n \Sigma \lambda x + T(\mu, \nu, \mu', \nu') + n' \Sigma \lambda' x' \quad (1)$$

From application of the variational principle

$$\left. \begin{aligned} \frac{\partial T}{\partial \mu} &= n \left( y - \frac{\mu}{\lambda} x \right), & \frac{\partial T}{\partial \mu'} &= -n' \left( y' - \frac{\mu'}{\lambda'} x' \right) \\ \frac{\partial T}{\partial \nu} &= n \left( z - \frac{\nu}{\lambda} x \right), & \frac{\partial T}{\partial \nu'} &= -n' \left( z' - \frac{\nu'}{\lambda'} x' \right) \end{aligned} \right\} \quad (2)$$

Thus, if  $\mu, \nu, \mu', \nu'$  are assigned, the initial and final rays are known.

The calculation of  $T$  proceeds by application of the variational principle to each pair of adjacent media, inasmuch as the final ray for medium  $i - 1$  becomes the initial ray for the medium  $i$ .

Thus

$$\left. \begin{aligned} \frac{\partial}{\partial \mu_i} (T_{i-1,i} + T_{i,i+1}) &= 0 \\ \frac{\partial}{\partial \nu_i} (T_{i-1,i} + T_{i,i+1}) &= 0 \end{aligned} \right\} \quad (i = 1, 2, \dots, N - 1) \quad (3)$$

$$T = \sum_1^{N-1} T_{i-1,i} \quad (4)$$

for the system as a whole. The  $T$  function is not in its final form until it becomes  $T(\mu, \nu, \mu', \nu')$ .

b. *Translation of origin.* The value of  $T$  is dependent on the choice of origin. If  $T_{\text{new}}$  is to be calculated for a new origin, we have

$$T_{\text{new}} = T_{\text{old}} + a(\lambda' - \lambda) + b(\mu' - \mu) + c(\nu' - \nu) \quad (5)$$

where  $a$ ,  $b$ , and  $c$  are the coordinates of the new origin in the old system.

c. *The value of  $T$  for a spherical surface.* Let

$$F(x, y, z) = x^2 + y^2 + z^2 - R^2 = 0 \quad (6)$$

$$\text{Then } \left. \begin{aligned} T &= \pm R[(n'\lambda' - n\lambda)^2 + (n'\mu' - n\mu)^2 + (n'\nu' - n\nu)^2]^{1/2} \\ &= \pm R[n^2 + n'^2 - 2nn'(\lambda\lambda' + \mu\mu' + \nu\nu')]^{1/2} \end{aligned} \right\} \quad (7)$$

where the origin lies at the center of the sphere. A change of origin may be introduced from b. above. The choice of sign depends on the sense of curvature of  $R$ , with  $T$  reckoned positive from left to right.

d. *The value of  $T$  for a paraboloid of revolution.* Let

$$F(x, y, z) = x - \frac{1}{4F}(y^2 + z^2) = 0 \quad (8)$$

$$L = (n\lambda - n'\lambda')x + (n\mu - n'\mu')y + (n\nu - n'\nu')z \quad (9)$$

$$\delta L = \frac{\delta L}{\partial y} \delta y + \frac{\partial L}{\partial z} \delta z = 0 \quad (10)$$

if the variation takes place on the surface  $F(x, y, z) = 0$ .

$$\left. \begin{aligned} \frac{\partial L}{\partial y} &= (n\lambda - n'\lambda') \frac{\partial x}{\partial y} + (n\mu - n'\mu') = 0 \\ \frac{\partial L}{\partial z} &= (n\lambda - n'\lambda') \frac{\partial x}{\partial z} + (n\nu - n'\nu') = 0 \end{aligned} \right\} \quad (11)$$

$$\frac{\partial x}{\partial y} = \frac{1}{2F} y, \quad \frac{\partial x}{\partial z} = \frac{1}{2F} z \quad (12)$$

$$y = -2F \left( \frac{n\mu - n'\mu'}{n\lambda - n'\lambda'} \right), \quad z = -2F \left( \frac{nv - n'v'}{n\lambda - n'\lambda'} \right) \quad (13)$$

$$x = F \left[ \frac{(n\mu - n'\mu')^2 + (nv - n'v')^2}{(n\lambda - n'\lambda')^2} \right] \quad (14)$$

$$T = -F \left[ \frac{(n\mu - n'\mu')^2 + (nv - n'v')^2}{(n\lambda - n'\lambda')} \right] \quad (15)$$

e. *The value of T for a general ellipsoid.* Let

$$F(x, y, z) = \frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} - 1 = 0 \quad (16)$$

$$L = \Sigma(n\lambda - n'\lambda')x \quad (17)$$

$$y = \frac{b^2}{a^2} \left( \frac{n\mu - n'\mu'}{n\lambda - n'\lambda'} \right) x, \quad z = \frac{c^2}{a^2} \left( \frac{nv - n'v'}{n\lambda - n'\lambda'} \right) x \quad (18)$$

$$x = \pm a \left[ 1 + \frac{b^2}{a^2} \left( \frac{n\mu - n'\mu'}{n\lambda - n'\lambda'} \right)^2 + \frac{c^2}{a^2} \left( \frac{nv - n'v'}{n\lambda - n'\lambda'} \right)^2 \right] \quad (19)$$

$$T = \pm [a^2(n\lambda - n'\lambda')^2 + b^2(n\mu - n'\mu')^2 + c^2(nv - n'v')^2]^{1/2} \quad (20)$$

and similarly for other second-degree solids.

**2.4. The sine condition of Abbe.** An identity among the second partial derivatives of the characteristic function leads to an important general relation that must be satisfied if an elementary surface around a point source is to be imaged accurately into a corresponding elementary surface around the image point. We confine ourselves to an axial source point in an instrument with rotational symmetry.

If we have precise imagery irrespective of the initial ray, then  $y' = my$  and  $z' = mz$ , where  $m$  is the magnification.

$$\left. \begin{aligned} \frac{\partial W}{\partial x} &= -n\lambda & \frac{\partial W}{\partial \mu'} &= -n' \left( y' - \frac{\mu'}{\lambda'} x' \right) \\ \frac{\partial W}{\partial y} &= -n\mu & \frac{\partial W}{\partial v'} &= -n' \left( z' - \frac{v'}{\lambda'} x' \right) \\ \frac{\partial W}{\partial z} &= -nv & & \end{aligned} \right\} \quad (1)$$

If we consider that all rays from the object point combine in the image point, and that the elementary surface and its image are perpendicular to the axis,  $W$  is a function  $W(y, z, \mu', \nu')$  and  $y', z', \mu$ , and  $\nu$  become dependent variables from the above relations. We have

$$\frac{\partial^2 W}{\partial y \partial \mu'} = -n \frac{\partial \mu}{\partial \mu'} = \frac{\partial^2 W}{\partial \mu' \partial y} = -n' \frac{\partial y'}{\partial y} = -n'm \quad (2)$$

$$\frac{\partial^2 W}{\partial z \partial \nu'} = -n \frac{\partial \nu}{\partial \nu'} = \frac{\partial^2 W}{\partial \nu' \partial z} = -n' \frac{\partial z'}{\partial z} = -n'm \quad (3)$$

$$\left. \begin{aligned} \frac{\partial^2 W}{\partial y \partial \nu'} &= -n \frac{\partial \mu}{\partial \nu'} = \frac{\partial^2 W}{\partial \nu' \partial y} = -n' \frac{\partial z'}{\partial y} = 0 \\ \frac{\partial^2 W}{\partial z \partial \mu'} &= -n \frac{\partial \nu}{\partial \mu'} = \frac{\partial^2 W}{\partial \mu' \partial z} = -n' \frac{\partial y'}{\partial z} = 0 \end{aligned} \right\} \quad (4)$$

because of rotational symmetry.

Then 
$$\frac{d\mu}{d\mu'} = \frac{n'}{n} m \quad \text{or} \quad n\mu = n'\mu' m \quad (6)$$

$$\frac{d\nu}{d\nu'} = \frac{n'}{n} m \quad \text{or} \quad n\nu = n'\nu' m \quad (7)$$

where the constant of integration is zero because the angles vanish together.

If  $\theta$  and  $\theta'$  are the respective slope angles of a ray from the object point to the image point,

$$\frac{n \sin \theta}{n' \sin \theta'} = m \quad (8)$$

which is known as the *sine condition* of Abbe. The relationship can also be derived from general principles of thermodynamics.

**2.5. Clausius' equation.** Consider a small line element  $\overline{P_1P_2}$  inclined at an angle  $\varphi$  to the plane normal to the axis of a pencil at  $P_1$  of angular half aperture  $\theta$  (Fig. 1). We wish to examine the conditions that will lead to a sharp image of the line element in image space, i.e., so that  $P_2$  will be sharply imaged.

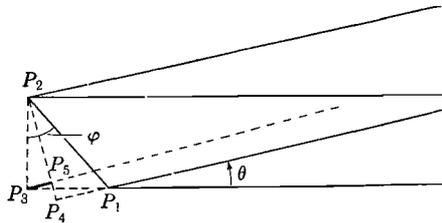


FIGURE 1

We can regard  $\overline{P_2P_3}$  as a portion of a wave front proceeding to the right along the axis of the pencil. Similarly,  $\overline{P_2P_4}$  can be regarded as a portion of another wave front inclined to the first at the angle  $\theta$ . The two paths are related by the increment  $\overline{P_3P_5}$ , the optical length of which must be preserved in the final medium if the inverse construction is to produce a sharp image of the line element.

Thus

$$n l \cos \varphi \sin \theta = n' l' \cos \varphi' \sin \theta' \quad (1)$$

This condition was demonstrated by Clausius on the basis of energy considerations, and is useful in connection with off-axis images in rotationally symmetrical optical systems. The angle  $\varphi$  need not be in the plane of the paper.

**2.6. Heterogeneous isotropic media.** Consider a curve in the medium connecting  $P$  to  $P'$ . Let the parametric equation of the curve be

$$x = x(u), \quad y = y(u), \quad z = z(u) \quad (1)$$

The optical length is

$$L = \int_C n(x, y, z) (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)^{1/2} du \quad (2)$$

$$= \int_C w du, \quad (\text{where } \dot{x} = dx/du, \text{ etc.}) \quad (3)$$

$$\text{where} \quad w = n(x, y, z) (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)^{1/2} = w(x, y, z, \dot{x}, \dot{y}, \dot{z}) \quad (4)$$

If we hold the end points fixed but vary the curve, we have

$$\delta L = \int_u^{u'} \delta w du \quad (5)$$

$$= \int_u^{u'} \left( \Sigma \frac{\partial w}{\partial \dot{x}} \delta \dot{x} + \Sigma \frac{\partial w}{\partial x} \delta x \right) du \quad (6)$$

$$\delta \dot{x} = \delta \frac{dx}{du} = \frac{d}{du} \delta x, \quad \text{etc.} \quad (7)$$

Integration by parts gives

$$\delta L = \left[ \Sigma \frac{\partial w}{\partial \dot{x}} \delta x \right]_u^{u'} - \int_u^{u'} \Sigma \left( \frac{d}{du} \frac{\partial w}{\partial \dot{x}} - \frac{\partial w}{\partial x} \right) \delta x du \quad (8)$$

Because the curves have fixed end points, the first term vanishes. If  $C$  is to be a stationary path, the value of  $L$  must be unchanged in the differential neighborhood of any point on the curve.  $\delta x$ ,  $\delta y$ , and  $\delta z$  are completely

arbitrary, and hence the coefficients must vanish under the integral all along the path. Accordingly,

$$\frac{d}{du} \cdot \frac{\partial w}{\partial \dot{x}} - \frac{\partial w}{\partial x} = 0, \quad (\text{and for } y, z) \tag{9}$$

or

$$\frac{d}{du} \left[ \frac{n\dot{x}}{(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)^{1/2}} \right] - \frac{\partial n}{\partial x} (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)^{1/2} = 0, \quad (y, z) \tag{10}$$

If  $u = s$ , the arc length along  $C$ , from which  $\dot{x}^2 + \dot{y}^2 + \dot{z}^2 = 1$ , the above equations become

$$\frac{d}{ds} \left( n \frac{dx}{ds} \right) - \frac{\partial n}{\partial x} = 0, \quad (y, z) \tag{11}$$

**2.7. Collineation.** A space continuum of points, line, and planes in object space that go into conjugate points, lines, and planes in image space in one to one linear correspondence is called a *collineation*.

Let  $x, y, z$  be the coordinates of a point in object space and  $x', y', z'$  its conjugate in image space with reference to right angle conjugated coordinate systems. Then

$$\left. \begin{aligned} x' &= \frac{\alpha_1 x + \beta_1 y + \gamma_1 z + \delta_1}{\alpha x + \beta y + \gamma z + \delta} \\ y' &= \frac{\alpha_2 x + \beta_2 y + \gamma_2 z + \delta_2}{\alpha x + \beta y + \gamma z + \delta} \\ z' &= \frac{\alpha_3 x + \beta_3 y + \gamma_3 z + \delta_3}{\alpha x + \beta y + \gamma z + \delta} \end{aligned} \right\} \tag{1}$$

This system can be inverted. If the relations were not rational, there would be no one-to-one relationship of object and image space. The denominator must have the same form in order that planes in object space go into planes in image space.

$$A'x' + B'y' + C'z' + D' = 0 \tag{2}$$

$$\rightarrow Ax + By + Cz + D = 0 \tag{3}$$

The inverted solution has the form

$$x = \frac{\alpha'_1 x' + \beta'_1 y' + \gamma'_1 z' + \delta'_1}{\alpha' x' + \beta' y' + \gamma' z' + \delta'}, \text{ etc.} \tag{4}$$

If  $\alpha x + \beta y + \gamma z + \delta = 0$ , then

$$x' = y' = z' = \infty \tag{5}$$

Also, if  $\alpha'x' + \beta'y' + \gamma'z' + \delta' = 0$ , then

$$x = y = z = \infty \quad (6)$$

In the first case,  $\alpha x + \beta y + \gamma z + \delta = 0$  determines a plane conjugate to the plane at infinity in image space. This plane is called the *first focal plane* and lies in object space. The plane  $\alpha'x' + \beta'y' + \gamma'z' + \delta' = 0$  is called the *second focal plane*, and lies in image space. Parallel rays in object space will meet on this focal plane in image space.

In a centered lens system we can set  $z = z' = 0$  without loss of generality. The  $x$  axis becomes the optical axis. Thus for points on the axis

$$x' = \frac{\alpha_1 x + \delta_1}{\alpha x + \delta} \quad (7)$$

Intermediate images will be reducible to this form. If  $\alpha = 0$ , the system is called *telescopic*. In this case

$$x' = \frac{\alpha_1}{\delta} x + \frac{\delta_1}{\delta} \quad (8)$$

When  $\alpha \neq 0$  but  $\alpha = 1$ ,  $x'x + \delta x' - \alpha_1 x - \delta_1 = 0$ , which is of the form

$$(x + a)(x' + b) = \text{constant} \quad (9)$$

A simple change of origin produces the relation  $xx' = \text{constant}$ . Evidently,  $x$  and  $x'$  are measured from the first and second focal points, respectively.

### 3. First Order Relationships

**3.1. Conventions.** Unless specified otherwise for a particular set of equations, we adopt the following conventions, all in reference to a centered rotationally symmetrical optical system.

- a. Light travels from left to right.
- b. An *object distance* is positive relative to a vertex when the object point lies to the left of the vertex.
- c. An *image distance* is positive when the image point lies to the right of the vertex.
- d. A *radius of curvature* is positive when the center of curvature lies to the right of the vertex.
- e. *Slope angles* are positive when the axis must be rotated counterclockwise through less than  $\pi/2$  to become coincident with the ray.
- f. *Angles of incidence and refraction* are positive when the normal must be rotated counterclockwise through less than  $\pi/2$  to bring it into coincidence with the ray.
- g. Distances are positive above the axis.

**3.2. Refraction at a single surface.** The optical path between the source point and image point is simply  $ns + n's'$ , where  $s$  and  $s'$  are the object and image distances, respectively (Fig. 2). Any other paraxial ray from the source point must have the same total optical path to the image point in order that a focus shall exist.

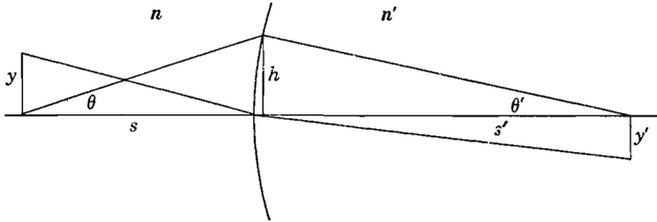


FIGURE 2

If a circle of radius  $s$  is described around the source point, and another circle of radius  $s'$  is described around the image point, one sees that the optical paths of the sagittae must be equated in the following way. (The sagitta of an arc is the depth of the arc from the chord.)

$$\sigma = \frac{1}{2} \cdot \frac{h^2}{R} \tag{1}$$

for the sagitta of a zone  $h$  and radius  $R$ . Then

$$n \left( \frac{1}{2} \cdot \frac{h^2}{s} + \frac{1}{2} \cdot \frac{h^2}{R} \right) + n' \left( -\frac{1}{2} \cdot \frac{h^2}{R} + \frac{1}{2} \cdot \frac{h^2}{s'} \right) = 0 \tag{2}$$

or

$$\frac{n}{s} + \frac{n}{R} - \frac{n'}{R} + \frac{n'}{s'} = 0 \tag{3}$$

Finally,

$$\frac{n}{s} + \frac{n'}{s'} = \frac{n' - n}{R} \tag{4}$$

It is of interest that if object and image distance are referred to the center of curvature, rather than to the vertex, we obtain an analogous formula,

$$\frac{n'}{S} + \frac{n}{S'} = \frac{n' - n}{R} \tag{5}$$

in which the indices on the left become interchanged.

**3.3. Focal points and focal lengths.** If  $s = \infty$ , we find  $n'/s' = (n' - n)/R$ . We define this distance  $s'$  as the *second focal length*, which then is the distance from the vertex or pole of the surface to the *second focal point*, and denote this distance by  $f'$ .

Then

$$f' = \left( \frac{n'}{n' - n} \right) R \quad (1)$$

Similarly, if  $s' = \infty$ , we call  $s$  the *first focal length* of the surface, which is the distance from the *first focal point* to the vertex of the surface, and denote this distance by  $f$ . Then

$$f = \left( \frac{n}{n' - n} \right) R \quad (2)$$

It follows that

$$\frac{f}{n} = \frac{f'}{n'} \quad (3)$$

**3.4. Image formation.** If we consider the construction in Fig. 3, the ray from  $b$  passing through  $C$  must evidently go undeviated through the image point  $b'$ . Then

$$\frac{y'}{y} = - \frac{s' - R}{s + R} = m \quad (1)$$

Also,

$$n \frac{y}{s} = - n' \frac{y'}{s'} \quad (2)$$

or

$$\frac{y'}{y} = - \frac{n}{n'} \frac{s'}{s} = m \quad (3)$$

where  $m$  is called the *lateral magnification*.

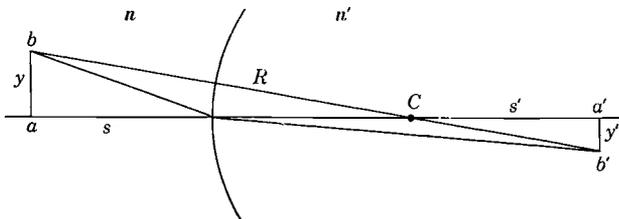


FIGURE 3

**3.5. Lagrange's law** (Known variously as the Helmholtz-Lagrange formula, the Smith-Helmholtz equation, or Helmholtz's equation). In the diagram

$$h = s\theta = -s'\theta' \quad (1)$$

Also,

$$ns'y = -n'sy' \quad (2)$$

or

$$n\theta y = n'\theta'y' \quad (3)$$

This relation applies to any number of successive conjugate images, and is evidently the paraxial expression of the sine condition of Abbe.

**3.6. Principal planes.** The principal planes are that pair of conjugate planes in which object and image are of the same size and on the same side of the optical axis. The lateral magnification for the principal planes is therefore +1. Each point of one plane images into a point on the conjugate plane in 1 to 1 correspondence. Within the accuracy of *Gaussian* optics, both points lie at the same height above the optical axis.

Consider an object  $y = \overline{ab}$  (Fig. 4). A ray from  $b$  parallel to the axis strikes  $H$  at  $P$  and images at  $P'$ . This same ray passes through  $F'$ , which then becomes the *second* focal point. Similarly, the ray  $\overline{bF}$ , if  $F$  is the *first*

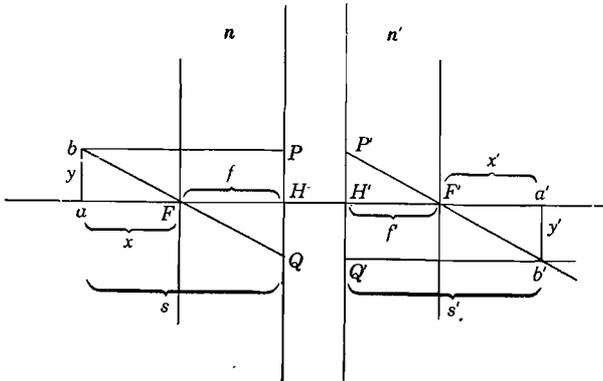


FIGURE 4

focal point, strikes the first principal plane at  $Q$ , emerges at  $Q'$ , and thenceforward remains parallel to the axis. Hence the point  $b'$  where these two rays meet in image space determines the image point of  $b$ . All points of  $y$  are imaged into corresponding points of  $y'$  at a constant lateral magnification  $m$ .

$$\frac{y}{x} = -\frac{HQ}{f} = -\frac{H'Q'}{f} = -\frac{y'}{f} \tag{1}$$

$$\frac{y'}{x'} = -\frac{P'H'}{f'} = -\frac{PH}{f'} = -\frac{y}{f'} \tag{2}$$

$$m = \frac{y'}{y} = -\frac{f}{x} = -\frac{x'}{f'} \tag{3}$$

or 
$$xx' = ff' \tag{4}$$

The above is called *Newton's relation*. We have

$$x = s - f, \quad x' = s' - f' \tag{5}$$

or 
$$\frac{f}{s} + \frac{f'}{s'} = 1 \tag{6}$$

If Lagrange's law is applied to the principal planes, we have

$$n\theta = n'\theta' \quad (7)$$

for any ray of slope  $\theta$  through  $H$ . Let  $\theta$  be determined such that

$$\theta = -\frac{y}{s}, \quad \theta' = -\frac{n}{n'} \cdot \frac{y}{s} \quad (8)$$

$$s'\theta' = y' = -\frac{n}{n'} \cdot \frac{s'}{s} y \quad (9)$$

$$\frac{y'}{y} = m = -\frac{n}{n'} \cdot \frac{s'}{s} = -\frac{f}{x} = -\frac{x'}{f'} \quad (10)$$

Then 
$$f = \frac{nss'}{n's + ns'}, \quad f' = \frac{n'ss'}{n's + ns'} \quad (11)$$

or 
$$\frac{f}{n} = \frac{f'}{n'} \quad (12)$$

(Cf. § 3.3.) For an object at infinity, we have

$$y' = f\theta \quad (13)$$

where  $\theta$  is the off-axis direction of the object point. Similarly,

$$y = -f'\theta' \quad (14)$$

for an image at infinity. The quantity  $f$  is called the *equivalent focal length* of the system in object space, or the *first focal length*, and often the *front focal length*. Similarly, the quantity  $f'$  is called the *equivalent focal length* of the system in image space, or the *second focal length*, and often the *back focal length*. (It should be noted that the terms *front* and *back* focal length are often used at the present time to describe the distance from the first focal point to the front lens vertex, and from the rear lens vertex to the second focal point. This confusion is not desirable, and the terms *front* and *back focal distances* are recommended instead. The terms *front focus* and *back focus* are also used.) Where initial and final media have identical indices, it is clear from the above formula that the two focal lengths are equal.

**3.7. Nodal points.** A ray directed toward the *first nodal point* in object space, by definition, emerges from the *second nodal point* in image space, parallel to its original direction. The nodal points are conjugate to one another. By Lagrange's law

$$n\theta y = n'\theta' y' \quad (1)$$

where  $y$  and  $y'$  are in the nodal planes.

$$\frac{y'}{y} = \frac{n}{n'} \cdot \frac{\theta}{\theta'} = \frac{n}{n'} = -\frac{f}{x} = -\frac{x'}{f'} \tag{2}$$

Therefore 
$$x' = -\frac{n}{n'} f' = -f \tag{3}$$

$$x = -\frac{n'}{n} f = -f' \tag{4}$$

Note that the first nodal point lies to the right of  $F$  by a distance of  $f'$  in Fig. 4, and that the second nodal point lies to the left of  $F'$  by the distance  $f$ . Where initial and final media are identical, the nodal points and principal points coincide.

By determining the position of the second nodal point on an optical bench, one can obtain directly the first equivalent focal length of a system from which the other properties follow.

**3.8. Cardinal points.** The principal points, the focal points and nodal points are the more important cardinal points of an optical system. The determination of the cardinal points of a complex system can be carried out from a knowledge of the cardinal points of the elementary systems from which the complex system is constructed. However, it is usually more expedient to trace a Gaussian ray from infinity on the left to find  $F'$ , and from the right to find  $F$ . To find  $f$ , we note that in a system of  $N$  surfaces

$$m = \frac{y'_N}{y_1} = (-1)^N \frac{n_0}{n_N} \cdot \frac{1}{s_1} \left( \frac{s'_1}{s_2} \right) \left( \frac{s'_2}{s_3} \right) \dots \left( \frac{s'_{N-1}}{s_N} \right) s'_N \tag{1}$$

If we let  $h_i$  be the height of intercept above the axis at the  $i$ th surface, then by similar triangles

$$\frac{y'_N}{y_1} = -\frac{n_0}{n_N} \cdot \frac{1}{s_1} \cdot \frac{h_1}{h_2} \cdot \frac{h_2}{h_3} \dots \frac{h_{N-1}}{h_N} s'_N \tag{2}$$

$$m = \frac{y'_N}{y_1} = -\frac{n_0}{n_N} \cdot \frac{h_1}{h_N} \cdot \frac{s'_N}{s_1} \tag{3}$$

For an infinite object distance, we have

$$y'_N = \frac{n_0}{n_N} \theta \frac{h_1}{h_N} s'_N \tag{4}$$

where  $\theta$  is the slope angle or direction of the object,  $n_0$  the index of object space, and  $n_N$  the index of image space. It is convenient to define  $h_1 = 1$ , in which case all other  $h$ 's are called *relative heights*. Then

$$f = \frac{n_0}{n_N} \cdot \frac{s'_N}{h_N} \tag{5}$$

where  $f$  is the first focal length, or

$$f' = \frac{s'_N}{h_N} \quad (6)$$

where  $f'$  is the second focal length.

When  $F$ ,  $F'$ , and  $f'$  are known from the two ray traces, all other ordinary cardinal properties of the complex system follow. It is important to note that inasmuch as the paraxial ray trace beginning with  $s_1$  refers only to an object point on the axis, the relative heights denoted by  $h_i$  are for an infinitesimally close ray starting out at the same object point. This is simply Lagrange's law again, and indeed

$$n_0 \theta_1 y_1 = n_N \theta'_N y'_N \quad (7)$$

or

$$\frac{n_0 h_1 y_1}{s_1} = - \frac{n_N h'_N y'_N}{s'_N} \quad (8)$$

from which

$$m = \frac{y'_N}{y_1} = - \frac{n_0}{n_N} \cdot \frac{h_1}{h'_N} \cdot \frac{s'_N}{s_1} \quad (9)$$

as above. The ray trace provides the object and image distances throughout the system, and the  $h$  values can be computed by means of the relation

$$h_{i+1} = \frac{s_{i+1}}{s'_i} h_i \quad (10)$$

where  $h_1 = 1$  when convenient. See note p. 408a.

**3.9. The thin lens.** A thin lens is defined to be one whose thickness is negligible compared to the focal length. To Gaussian accuracy we simply set the thickness equal to zero.

$$\frac{n_0}{s_1} + \frac{n_1}{s'_1} = \frac{n_1 - n_0}{R_1} \quad (1)$$

$$\frac{n_1}{s_2} + \frac{n_2}{s'_2} = \frac{n_2 - n_1}{R_2} \quad (2)$$

$$s_2 = -s'_1, \quad n_2 = n_0 = 1 \quad (3)$$

$$\frac{1}{s_1} + \frac{1}{s'_2} = (n_1 - 1) \left( \frac{1}{R_1} - \frac{1}{R_2} \right) \quad (4)$$

If  $s_1 = \infty$ ,  $s'_2 = f' = f$ , and we have

$$\phi = \frac{1}{f} = (n_1 - 1) \left( \frac{1}{R_1} - \frac{1}{R_2} \right) \quad (5)$$

where  $\phi$  is called the *power* of the lens. If now  $s$  and  $s'$  refer to object and image spaces, we have

$$\frac{1}{s} + \frac{1}{s'} = \frac{1}{f} \quad (6)$$

**3.10. The thick lens.** By working through the Gaussian equations above as applied to a lens of finite central thickness  $t$ , one finds that

$$\phi = \frac{1}{f} = (n_1 - 1) \left( \frac{1}{R_1} - \frac{1}{R_2} \right) + \frac{(n_1 - 1)^2}{n_1} \cdot \frac{t}{R_1 R_2} \quad (1)$$

$$\phi d = 1 - \frac{(n_1 - 1)}{n_1} \frac{t}{R_1} \quad (2)$$

where  $d$  is the distance from the second surface to the second focal point, or the back focal distance.

**3.11. Separated thin lenses.** Application of the elementary equations above to the case of separated thin lenses leads to the relations below. The powers of the individual thin lenses are represented by  $\phi_1, \phi_2, \phi_3$  etc. The separations are given by  $d_1, d_2, d_3$ , etc. Let  $d$  be the back focal distance, which then serves to locate the second focal point. Let  $\phi$  be the power of the combined system of lenses, which is the reciprocal of the equivalent focal length.

a. *Two* separated thin lenses

$$\phi = \phi_1 + \phi_2 - d_1 \phi_1 \phi_2 = \phi_1 + h_2 \phi_2 \quad (1)$$

$$\phi d = 1 - d_1 \phi_1 = h_2 \quad (2)$$

b. *Three* separated thin lenses

$$\left. \begin{aligned} \phi &= \phi_1 + \phi_2 + \phi_3 - d_1 \phi_1 \phi_2 - (d_1 + d_2) \phi_1 \phi_3 - d_2 \phi_2 \phi_3 + d_1 d_2 \phi_1 \phi_2 \phi_3 \\ &= \phi_1 + h_2 \phi_2 + h_3 \phi_3 \end{aligned} \right\} \quad (3)$$

$$\phi d = 1 - (d_1 + d_2) \phi_1 - d_2 \phi_2 + d_1 d_2 \phi_1 \phi_2 = h_3 \quad (4)$$

c. *Four* separated thin lenses

$$\left. \begin{aligned} \phi &= \phi_1 + \phi_2 + \phi_3 + \phi_4 - d_1 \phi_1 \phi_2 - (d_1 + d_2) \phi_1 \phi_3 - (d_1 + d_2 + d_3) \phi_1 \phi_4 \\ &\quad - d_2 \phi_2 \phi_3 - (d_2 + d_3) \phi_2 \phi_4 + d_1 d_2 \phi_1 \phi_2 \phi_3 + d_1 (d_2 + d_3) \phi_1 \phi_2 \phi_4 \\ &\quad + (d_1 + d_2) d_3 \phi_1 \phi_3 \phi_4 + d_2 d_3 \phi_2 \phi_3 \phi_4 - d_1 d_2 d_3 \phi_1 \phi_2 \phi_3 \phi_4 \\ &= \phi_1 + h_2 \phi_2 + h_3 \phi_3 + h_4 \phi_4 \end{aligned} \right\} \quad (5)$$

$$\left. \begin{aligned} \phi d &= 1 - (d_1 + d_2 + d_3) \phi_1 - (d_2 + d_3) \phi_2 - d_3 \phi_3 + d_1 (d_2 + d_3) \phi_1 \phi_2 \\ &\quad + (d_1 + d_2) d_3 \phi_1 \phi_3 + d_2 d_3 \phi_2 \phi_3 - d_1 d_2 d_3 \phi_1 \phi_2 \phi_3 = h_4 \end{aligned} \right\} \quad (6)$$

The corresponding expressions for five or more separated thin lenses follow readily, but serve no purpose in being reproduced here. If the above formulas are applied from right to left in order to locate the first focal point,

the positions of both principal points then become established. Inasmuch as  $\phi$  in air is the same for both first and second focal lengths, all the formulas for  $\phi$  must possess symmetrical properties.

**3.12. Chromatic aberration.** The index of refraction of any material medium is a function of wavelength. Accordingly, it is important to ascertain the dependence of the Gaussian properties of an optical system on wavelength.

a. The *single* thin lens 
$$\frac{1}{f} = (n-1) \left( \frac{1}{R_1} - \frac{1}{R_2} \right) \quad (1)$$

Differentiating logarithmically, we have

$$\frac{df}{f} = -\frac{dn}{n-1} = -\frac{1}{\nu} = -\frac{d\phi}{\phi} \quad (2)$$

$\nu$  is defined as  $(n_D - 1)/(n_F - n_C)$ , and is called the Abbe number, or the reciprocal dispersion of the glass. The negative sign indicates that the focal length is less for blue light than for red. In the case of ordinary crown glass for which  $\nu \sim 60$

$$df = -\frac{1}{60} f \quad (3)$$

between the red and blue focus.

b. *Two* separated thin lenses.

$$\phi = \phi_1 + \phi_2 - d_1\phi_1\phi_2 \quad (4) \quad \phi d = 1 - d_1\phi_1 = h_2 \quad (5)$$

Differentially, 
$$d\phi = d\phi_1 + d\phi_2 - d_1\phi_1 d\phi_2 - d_1\phi_2 d\phi_1 \quad (6)$$

$$= \frac{\phi_1}{\nu_1} + \frac{\phi_2}{\nu_2} - d_1\phi_1\phi_2 \left( \frac{1}{\nu_1} + \frac{1}{\nu_2} \right) \quad (7)$$

In general, one knows  $\phi$  and desires that  $d\phi = 0$ . Then  $\phi_1$  and  $\phi_2$  can be determined in terms of  $\phi$ . If this is carried out, one finds

$$d\phi = 0 \rightarrow d_1 = \frac{\nu_1 f_1 + \nu_2 f_2}{\nu_1 + \nu_2} \quad (8) \quad \phi = \left( \frac{\nu_1}{\nu_1 + \nu_2} \right) \phi_1 + \left( \frac{\nu_2}{\nu_1 + \nu_2} \right) \phi_2 \quad (9a)$$

and

$$\phi_1 = \left( \frac{\nu_1 + \nu_2 - \nu_2/h_2}{\nu_1 - \nu_2/h_2} \right) \phi \quad (9b) \quad \phi_2 = - \left( \frac{\nu_2/h_2}{\nu_1 - \nu_2/h_2} \right) \phi \quad (9c)$$

If  $\nu_1 = \nu_2$ , then

$$d_1 = \frac{1}{2}(f_1 + f_2) \quad (10)$$

It should be noted that the achromatization of  $\phi$  applies only to the size of the image and not to its location. For example, when the object distance is infinite,  $y'_2 = f \tan \theta$ , where  $\theta$  is the field angle off-axis. If  $df = 0$ , then  $dy'_2$  will be zero also. Hence achromatization of  $\phi$  for the case of two simple lenses at the proper separation stabilizes the size of the image but not its position.

Sometimes one desires to achromatize  $d$  instead of  $\phi$ , by selection of the proper  $\nu_2$  and  $\phi_2$  to go with a given  $\phi_1$ ,  $\nu_1$ , and  $d_1$ .

$$dd = 0 \rightarrow \frac{\phi_1}{\nu_1} + h_2^2 \frac{\phi_2}{\nu_2} = 0 \tag{11}$$

The introduction of the  $h^2$  shows that the color contribution of a lens to the system is weighted by the square of the relative height.

$$\phi = \phi_1 + h_2 \phi_2 \tag{12}$$

which leads to 
$$\phi_1 = \left( \frac{\nu_1}{\nu_1 - \nu_2/h_2} \right) \phi \tag{13}$$

$$\phi_2 = -\frac{1}{h_2} \left( \frac{\nu_2/h_2}{\nu_1 - \nu_2/h_2} \right) \phi \tag{14}$$

It is clear that when  $h_2 = \nu_2/\nu_1$ , the denominator is zero, and the solution loses practical significance.

In the case of 2 thin lenses,  $d$  and  $\phi$  cannot simultaneously be stabilized for color, unless the separation vanishes. For if  $d\phi$  and  $dd$  are both zero, then  $d(\phi d) = 0$ . But

$$d(\phi d) = -d_1 d\phi_1 \tag{15}$$

For the simple lens,  $d\phi_1 \neq 0$  and hence the only solution is for  $d_1 = 0$ ,  $h_2 = 1$ .

$$\phi_1 = \frac{\nu_1}{\nu_1 - \nu_2} \phi \tag{16}$$

$$\phi_2 = -\frac{\nu_2}{\nu_2 - \nu_2} \phi \tag{17}$$

These expressions are applicable, then, to the ordinary contact achromatized doublet.

c. *Separated doublets.* Let us consider that at least the first component can be made of two or more elements in contact. The first component can have a net power of  $\phi_1$  still, and when achromatized,  $d\phi_1 = 0$ . Then  $d(\phi d) = 0$ , even when  $d_1 \neq 0$ . But

$$d\phi = d\phi_1 + d\phi_2 - d_1\phi_1 d\phi_2 - d_1\phi_2 d\phi_1 \tag{18}$$

$$= d\phi_2(1 - d_1\phi_1) \tag{19}$$

$$= h_2 d\phi_2 \tag{20}$$

Hence, if  $d\phi = 0$ ,  $d\phi_2 = 0$  also. The result is that if two separated components yield a system stabilized for both size and position of image, the individual components must be separately achromatized.

d. *Three separated thin lenses.* In the case of three separated thin lenses we have more quantities at our disposal, and it is possible to achromatize the system for both position and size of image without achromatizing the individual elements.

If both the equivalent focal length and the back focal distance are achromatized,  $\phi d$  is also achromatized. Under § 3.11b we need only to differentiate. When we accomplish this operation, we find

$$\frac{\phi_1}{v_1(d_2 - d_1 d_2 \phi_1)} = \frac{-\phi_2}{v_2(d_1 + d_2 - d_1 d_2 \phi_2)} = \frac{(\phi d)\phi_3}{v_3(d_1 - d_1^2 \phi_1)} \quad (21)$$

When the above two relations are satisfied, the simple triplet will be fully achromatized.

e. *The general relations for a rotationally symmetrical system\*.* The fundamental equation of Gaussian optics given in § 3.2 can be rearranged in the form

$$Q_{si} = n_{i-1} \left( \frac{1}{R_i} + \frac{1}{s_i} \right) = n_i \left( \frac{1}{R_i} - \frac{1}{s'_i} \right) \quad (22)$$

$Q_{si}$  is called the *optical invariant*. Let

$$k_i = k_1 + \sum_1^{i-1} \frac{d_j}{n_j h_j h_{j+1}} \quad (23)$$

a relation whose significance will be more apparent below (§ 4.5). Then the respective conditions for the absence of chromatic aberration for the position and size of the image are found to be

$$\sum_{i=1}^N h_i^2 Q_{si} \left( \frac{dn_i}{n_i} - \frac{dn_{i-1}}{n_{i-1}} \right) = 0 \quad (24)$$

$$\sum_{i=1}^N k_i h_i^2 Q_{si} \left( \frac{dn_i}{n_i} - \frac{dn_{i-1}}{n_{i-1}} \right) = 0 \quad (25)$$

In these expressions  $dn_i$  is the increment in index between chosen wave lengths, such as  $(n_F - n_C)$ , and  $n_i$  is the mean index for the wavelength region of interest. For the above purpose  $k_1$  is an arbitrarily chosen quantity,

\* MERTÉ, W., RICHTER, R. and VON ROHR, M., *Das photographische Objektiv (Handbuch der wissenschaftlichen und angewandten Photographie, Bd. 1)*, Julius Springer, Vienna, 1932, pp. 235-238.

which, however, below will be identified by the relation  $k_1 = t_1(s_1 - t_1)/s_1$ , where  $t_1$  is the distance of the entrance pupil (§ 4.3f) from the front lens vertex. As before,  $h_i$  is the relative height.

**3.13. Secondary spectrum.** The discussions under § 3.12 refer only to the first derivative. Now, however, we must examine the higher-order variation. Consider the simple doublet, which already has been achromatized through the first order of approximation.

$$\phi = \phi_1 + \phi_2 \tag{1}$$

$$\frac{d\phi}{d\lambda} = \frac{d\phi_1}{d\lambda} + \frac{d\phi_2}{d\lambda} = 0 \tag{2}$$

$$= \frac{dn_1/d\lambda}{(n_1 - 1)}\phi_1 + \frac{dn_2/d\lambda}{(n_2 - 1)}\phi_2 \tag{3}$$

$$\left. \begin{aligned} \frac{d^2\phi}{d\lambda^2} = & \frac{(dn_1/d\lambda)^2}{(n_1 - 1)^2}\phi_1 + \frac{d^2n_1/d\lambda^2}{(n_1 - 1)}\phi_1 - \frac{(dn_1/d\lambda)^2}{(n_1 - 1)^2}\phi_1 + \frac{(dn_2/d\lambda)^2}{(n_2 - 1)^2}\phi_2 \\ & + \frac{d^2n_2/d\lambda^2}{(n_2 - 1)}\phi_2 - \frac{(dn_2/d\lambda)^2}{(n_2 - 1)^2}\phi_2 \end{aligned} \right\} \tag{4}$$

We find

$$\frac{d^2\phi}{d\lambda^2} = \frac{d^2n_1/d\lambda^2}{(n_1 - 1)}\phi_1 + \frac{d^2n_2/d\lambda^2}{(n_2 - 1)}\phi_2 \tag{5}$$

from which

$$\frac{(\nu_1 - \nu_2)}{\phi} \frac{d^2\phi}{d\lambda^2} = \frac{d^2n_1/d\lambda^2}{dn_1/d\lambda} - \frac{d^2n_2/d\lambda^2}{dn_2/d\lambda} = 0 \tag{6}$$

From this expression it is clear that when two glasses of widely different  $\nu$  values are combined, the second derivative must bear a constant ratio to the first derivative, if the *secondary spectrum* is to be eliminated.

Customarily in glass catalogs, the first and second derivatives are replaced by their equivalents in differences, namely, by

$$(n_{A'} - n_C)/(n_C - n_F), \quad (n_g - n_h)/(n_C - n_F), \quad \text{etc.}$$

These partial dispersion ratios must then match at both ends of the spectrum if full elimination of the secondary spectrum is to be achieved.

**3.14. Dispersion formulas.** The function  $n(\lambda)$  has been given a number of forms, some empirical and some derived from the theory of dispersion. One of the more familiar of such formulas is that given by Hartmann.

$$n = n_0 + \frac{A}{(\lambda - \lambda_0)^a} \tag{1}$$

where  $n_0$ ,  $A$ ,  $\lambda_0$ , and  $a$  are constants to be determined from observed values

over a wide spectral range. The term  $a$  has been assigned the value of 1.2 for best fit, though  $a = 1.0$  is far more convenient.

$$\frac{dn}{d\lambda} = - \frac{A}{(\lambda - \lambda_0)^2} \quad (2)$$

$$\frac{d^2n}{d\lambda^2} = + \frac{2A}{(\lambda - \lambda_0)^3} \quad (3)$$

The requirement that the secondary spectrum vanish is simply that

$$\lambda_{0_1} = \lambda_{0_2} \quad (4)$$

Perrin \* has computed values of  $\lambda_0$  for all the well-known varieties of optical glass, and has found several pairs with reduced secondary spectrum. Such pairs are characterized by quite small values of  $(\nu_1 - \nu_2)$  so that the individual lens powers are rather considerable.

The Hartmann formula is inconvenient in several ways. First of all, the wavelength  $\lambda$  is tied up within the expression. The derivatives become more complicated functions, rather than simpler ones. Furthermore, the  $\lambda_0$  has on particular utility from a physical point of view and lies in the ultraviolet.

The same objections can be applied to *Sellmeier's equation*, which is

$$n^2 = 1 + \frac{A\lambda^2}{\lambda^2 - \lambda_0^2} \quad (5)$$

Sellmeier's equation is founded in theory, and holds over quite a complete spectral range, even where there are several absorption boundaries.

The objections can be overcome by a modification of a formula due to Cauchy. The *Cauchy formula* is

$$n = A + B \frac{1}{\lambda^2} + C \frac{1}{\lambda^4} + \dots \quad (6)$$

Here the value of  $A$  is  $n$  for  $\lambda = \infty$ , and again of no utility. Also, the derivatives retain the wavelength, though in more explicit form than in Hartmann's formula. Let

$$n_0 = A + B \frac{1}{\lambda_0^2} + C \frac{1}{\lambda_0^4} + \dots \quad (7)$$

Then we can write

$$n = n_0 + \alpha\tilde{\omega} + \beta\tilde{\omega}^2 + \gamma\tilde{\omega}^3 + \dots \quad (8)$$

$$\tilde{\omega} = \frac{1/\lambda^2 - 1/\lambda_0^2}{1/\lambda_F^2 - 1/\lambda_C^2} \quad (9)$$

and where  $\alpha$ ,  $\beta$ ,  $\gamma$ , etc., are to be determined by a least-squares solution from the observed data.

\* PERRIN, F., "A Study of Harting's Criterion for Complete Achromatism," *J. Opt. Soc. Am.*, **28**, 86-93 (1938).

Use of the power series form implies that an arbitrarily close fit can be made to the observed dispersion curve, provided enough constants are used. The formula is useful in that the derivatives with respect to  $\tilde{\omega}$  are simple series also. If a given lens aberration is rendered independent of  $\tilde{\omega}$ , it also is necessarily independent of  $\lambda$ . Hence, in optical formulas  $\tilde{\omega}$  can be employed in simple expansions. In particular the back focal distance can be expressed

$$s'_N = s'_N(0) + a\tilde{\omega} + b\tilde{\omega}^2 + c\tilde{\omega}^3 + \dots \tag{10}$$

The coefficient  $a$  is called the coefficient of *primary spectrum*,  $b$  the coefficient of *secondary spectrum*,  $c$  the coefficient of *tertiary spectrum*, etc. Such a formula holds for a system of almost any complexity. In combinations of ordinary glasses, one can bring  $a$  to zero in the usual process of achromatization. For contact achromats

$$b = -\frac{(\beta_1/\alpha_1 - \beta_2/\alpha_2)}{\nu_1 - \nu_2} \tag{11}$$

If  $b$  is to vanish, the glass pairs must obey the requirements

$$\frac{\beta_1}{\alpha_1} = \frac{\beta_2}{\alpha_2} \tag{12}$$

and

$$(\nu_1 - \nu_2) \gg 0 \tag{13}$$

If  $(\nu_1 - \nu_2)$  is too small, the curvatures are excessive.

In most ordinary combinations of glasses  $b$  is nearly constant. Its magnitude can be reduced by certain optical arrangements, such as the Petzval portrait type lens that consists of separated positive components with an attendant strongly curved field, or by more elaborate systems. A few glass pairs exist that have  $b = 0$ , but the powers are such as to limit the over-all aperture ratio of the system.

The particular form of  $\tilde{\omega}$  is a matter of convenience. For most applications in the visual range, one can take  $\lambda_0 = 5500$  angstroms, and use  $F$  at 4861 and  $C$  at 6563. Then

	$\tilde{\omega}$	$\tilde{\omega}^2$
$h$	1.466 754	2.151 367
$G'$	1.048 364	1.099 067
$g$	1.025 708	1.052 077
$F$	0.484 741	0.234 974
$e$	0.025 006	0.000 625
$d$	-0.214 239	0.045 898
$D$	-0.223 183	0.049 811
$C$	-0.515 259	0.265 492
$A'$	-0.843 706	0.711 840

The least-squares solution for a glass with observed values for all the designated wavelengths takes the following form.

$$A = \sum_i n_i, \quad B = \sum_i n_i \tilde{\omega}_i, \quad C = \sum_i n_i \tilde{\omega}_i^2$$

$$n_0 = 0.235\ 325A + 0.111\ 817B - 0.244\ 154C$$

$$\alpha = 0.111\ 817A + 0.431\ 333B - 0.352\ 630C$$

$$\beta = -0.244\ 154A - 0.352\ 630B + 0.533\ 273C$$

Typical dispersion formulas and residuals are

$$\text{BK-7:} \quad n = 1.518\ 035 + 0.008\ 163\tilde{\omega} - 0.000\ 131\tilde{\omega}^2 \quad (14)$$

$$\bar{\nu} = \frac{n_0 - 1}{\alpha} = 63.46, \quad \frac{\beta}{\alpha} = -0.0160$$

$$\text{F-2:} \quad n = 1.623\ 648 + 0.017\ 212\tilde{\omega} + 0.000\ 784\tilde{\omega}^2 \quad (15)$$

$$\bar{\nu} = 36.23, \quad \frac{\beta}{\alpha} = +0.0455$$

	h	G'	g	F	e	d	D	C	A'
(O—C) BK-7:	6	—4	—4	—5	0	5	4	6	—7
F-2:	10	—6	—7	—7	3	4	7	5	—9

where the residuals are in units of the fifth decimal place. The magnitude of the residuals is caused partially by the extent of the wavelength range fitted in the least-squares solution. However, it is clear also from the trend of the residuals that inclusion of the  $\gamma\tilde{\omega}^3$  term in the least squares solution would render the residuals as small as  $\pm 1$  in the fifth place, from 4047 to 7682.

A doublet made of BK-7 and F-2 glasses would have a secondary spectrum

$$b = \frac{0.0455 + 0.0160}{27.23} = 0.002\ 259 \quad (16)$$

$$\Delta s'_N = +0.002\ 259\tilde{\omega}^2 + \dots \quad (17)$$

where  $\Delta s'_N$  is in units of the focal length.

Herzberger\* has introduced a new form for the dispersion formulas, derived from the near constancy for the value of  $b$ , or more strictly, from the relationship

$$\frac{\beta}{\alpha} = k_1\bar{\nu} + k_2 \quad (18)$$

\* HERZBERGER, M., "The Dispersion of Optical Glass," *J. Op. Soc. Am.*, **32**, 70-77 (1942).

This formula is given by Herzberger as

$$\mu = \mu_0 + \mu_1\lambda^2 + \frac{\mu_2}{\lambda^2 - 0.035} + \frac{\mu_3}{(\lambda^2 - 0.035)^2} \quad (19)$$

where  $\lambda$  is the wavelength measured in *microns*,  $\mu = n - 1$ , and  $\mu_0, \mu_1, \mu_2$ , and  $\mu_3$  are four constants depending on the material. For unusual glasses, crystals, and rare-earth glasses the linear relationship for  $\beta/\alpha$  must be modified. In terms of the partial dispersions

$$P_\lambda = A_1\nu + A_2 + A_3\rho_A + A_4\rho_h \quad (20)$$

where the  $A_i$  are universal functions of the wavelength, and  $\rho_A$  and  $\rho_h$  are constants. Each  $A_i$  has the equivalent form

$$A_i = \alpha_0 + \alpha_1\lambda^2 + \frac{\alpha_2}{\lambda^2 - 0.035} + \frac{\alpha_3}{(\lambda^2 - 0.035)^2} \quad (21)$$

The superposition of the coefficients of  $\lambda^2$ , etc., lead to the values of  $\mu_0, \mu_1$ , etc.

Herzberger shows that the (O - C) residuals are mostly zero, or  $\pm 1$  in the fifth decimal place from  $\lambda = 0.400$  to  $\lambda = 1\mu$ , almost irrespective of the material. The  $\tilde{\omega}$  function above has larger residuals for the unusual materials, though with any dispersion formula an (O - C) plot can always be employed as a differential correction.

The  $\tilde{\omega}$  function expanded about the wavelength of best performance of a given instrument permits ready inspection of the variations of the aberrations with color. The fact that  $(\tilde{\omega}_F - \tilde{\omega}_C) = 1$  gives a ready measure of the blue-red variation.

#### 4. Oblique Refraction

**4.1. First-order theory.** Paraxial or first-order theory involves refraction in the immediate neighborhood of the optical axis. The equivalence of complex and simple systems through the use of the principal planes and focal points arises basically from the linear character of the refractions.

The introduction of rays that are considerably inclined to the optical axis, or more general still, of *skew* rays that do not even intersect the optical axis, brings about wide departures from the Gaussian laws. The departure may be expanded in series development around the Gaussian quantities. Because of rotational symmetry this expansion assumes only odd powers, and the successive stages of approximation are often referred to as *first-order theory*, *third-order theory*, *fifth-order theory*, etc.

The most general expansion of the problem of refraction of a light ray through an optical system involves a function of five variables, namely,  $\mu, \nu, \gamma, z, \tilde{\omega}$ , where  $\mu$  and  $\nu$  are direction cosines of the ray,  $\gamma$  and  $z$  the intercept on a reference plane normal to the axis, and  $\tilde{\omega}$  is the function of the wavelength referred to in 3.14.

Explicitly, we have

$$\left. \begin{aligned} y_{i+1} &= y_{i+1}(\mu_i, \nu_i, y_i, z_i, \tilde{\omega}_i) \\ z_{i+1} &= z_{i+1}(\mu_i, \nu_i, y_i, z_i, \tilde{\omega}_i) \\ \mu_{i+1} &= \mu_{i+1}(\mu_i, \nu_i, y_i, z_i, \tilde{\omega}_i) \\ \nu_{i+1} &= \nu_{i+1}(\mu_i, \nu_i, y_i, z_i, \tilde{\omega}_i) \end{aligned} \right\} (1)$$

For rotationally symmetrical systems we must have a symmetry of expression in such a way that  $y \rightleftharpoons z$  and  $\mu \rightleftharpoons \nu$ . Also, if rotational variables are used in the power series expansions, such as

$$r = \mu^2 + \nu^2, \quad s = y^2 + z^2, \quad t = \mu y + \nu z \quad (2)$$

we must find that the several orders use  $r, s, t$  in every combination.

The explicit expansion through the third order is given below for the case where the reference plane is the tangent plane at the  $i$ th surface, where  $n_i$  is the index of refraction after the  $i$ th surface,  $y_i$  and  $z_i$  are intercepts in the tangent plane, and  $\mu_i$  and  $\nu_i$  are the direction cosines of the initial ray before refraction. Let  $N_i = n_{i-1}/n_i$  and  $c_i = 1/R_i$ , where  $R_i$  is the radius of curvature. Here  $S_i$  is an aspheric coefficient that vanishes for a spherical surface;  $d_i$  is the vertex to vertex separation of the  $i$ th and the  $(i+1)$ th surface.

$$\overbrace{\begin{array}{ll} \mu_{i+1} = & y_{i+1} = \\ [\mu_i] = N_i & [\mu_i] = N_i d_i \\ [y_i] = (N_i - 1)c_i & [y_i] = 1 + (N_i - 1)c_i d_i \\ [\mu_i^3] = 0 & [\mu_i^3] = \frac{1}{2}N_i^3 d_i \\ [\mu_i \nu_i^2] = 0 & [\mu_i \nu_i^2] = \frac{1}{2}N_i^3 d_i \\ [\mu_i^2 y_i] = \frac{1}{2}N_i(N_i - 1)c_i & [\mu_i^2 y_i] = \frac{1}{2}N_i(N_i - 1)(3N_i + 1)c_i d_i \\ [\nu_i^2 y_i] = \frac{1}{2}N_i(N_i - 1)c_i & [\nu_i^2 y_i] = \frac{1}{2}N_i(N_i - 1)(N_i + 1)c_i d_i \\ [\mu_i \nu_i z_i] = N_i^2(N_i - 1)c_i d_i \\ [\mu_i y_i^2] = \frac{1}{2}(N_i - 1)(2N_i + 1)c_i^2 & [\mu_i y_i^2] = -\frac{1}{2}(N_i - 1)c_i \\ & \quad + \frac{1}{2}(N_i - 1)(3N_i^2 - N_i + 1)c_i^2 d_i \\ [\mu_i z_i^2] = \frac{1}{2}(N_i - 1)c_i^2 & [\mu_i z_i^2] = -\frac{1}{2}(N_i - 1)c_i \\ & \quad + \frac{1}{2}(N_i - 1)(3N_i^2 - N_i + 1)c_i^2 d_i \\ [\nu_i y_i z_i] = N_i(N_i - 1)c_i^2 & [\nu_i y_i z_i] = N_i^2(N_i - 1)c_i^2 d_i \\ [y_i^3] = \frac{1}{2}(N_i - 1)S_i & [y_i^3] = \frac{1}{2}(N_i - 1)S_i d_i \\ & \quad + \frac{1}{2}N_i(N_i - 1)c_i^3 \\ & \quad + \frac{1}{2}N_i(N_i - 1)c_i^3 \\ [y_i z_i^2] = \frac{1}{2}(N_i - 1)S_i & [y_i z_i^2] = \frac{1}{2}(N_i - 1)S_i d_i \\ & \quad + \frac{1}{2}N_i(N_i - 1)c_i^3 \\ & \quad + \frac{1}{2}(N_i - 1)(N_i^2 - N_i + 1)c_i^3 d_i \\ & \quad - \frac{1}{2}(N_i - 1)c_i^2 \end{array}} (3)$$

Equivalent expressions for  $\nu_{i+1}$  and  $z_{i+1}$  are obtained by an interchange of  $\mu, \nu$  and  $y, z$ . The bracketed expressions are the coefficients of the power term enclosed. The notation is useful for saving cumbersome symbols.

The explicit expressions are given here only through the third order. The fifth order has been derived, but is much too lengthy for inclusion here. In general, the explicit expressions have only a limited range of usefulness. Where a number of surfaces are involved, the insertion of successive series into one another becomes a formidable task. However, the author has solved a number of interesting problems in this way, even in the fifth order. The complexity of the procedure is compensated partly by the explicit nature of the results.

For more complex systems one must work in successive stages of approximation. Here one uses the important relations of the first order to reduce the number of corrective terms of the third order. The first order is calculated, and the numerical results used in the calculation of the third order. The results in the first and third can then be applied to the evaluation of the fifth order, a process not often attempted in this particular way.

Apart from the general development of the aberrations of an optical system, one can separate out two branches admitting of specialized treatment. The first branch involves a series expansion in all powers of the aperture but linear in the sine of the field angle. These terms are included in the sine condition of Abbe, which has already been discussed. Evaluation is most often accomplished by ray tracing, rather than by series development, at least in the fifth and higher orders. The other branch involves a series expansion in all powers of the field angle but linear in the aperture. This second branch is treated immediately below.

**4.2. Oblique refraction of elementary pencils.** The first-order expansion in the angular aperture of a narrow pencil of rays around a central *chief ray* or *principal ray* of finite inclination to the normal to a surface at point of contact leads to the existence of two foci along the refracted pencil. If the pencil is in a meridional section of a surface, the focus of this *tangential* fan can be determined. If the pencil is perpendicular to the meridional section, the focus of this *sagittal* fan can also be determined. In general the foci do not coincide, and only by controlled design can they be made to coincide in image space. The difference between the tangential and sagittal or radial foci along the chief ray is often called the *astigmatic difference*, and the halfway point between the two is called the *mean focus*.

If  $\tau$  and  $\sigma$  are the respective tangential and radial object distances *along*

the ray from the actual point of refraction on the surface, and if  $\tau'$  and  $\sigma'$  are the corresponding image distances, we have

$$\frac{n_{i-1} \cos^2 i_i}{\tau_i} + \frac{n_i \cos^2 r_i}{\tau'_i} = \frac{n_i \cos r_i - n_{i-1} \cos i_i}{R_i} \quad (1)$$

$$\frac{n_{i-1}}{\sigma_i} + \frac{n_i}{\sigma'_i} = \frac{n_i \cos r_i - n_{i-1} \cos i_i}{R_i} \quad (2)$$

where  $i$  and  $r$  are the angles of incidence and refraction, respectively.

These highly important relations are a generalization of the paraxial expressions. It is clear that when  $i$  and  $r$  go to zero, the two expressions coalesce and become identical with the basic paraxial formula. The expressions may be applied to any meridional ray through a system in order to determine the foci of the particular pencil.

In the relations above the transfer equations between surfaces are

$$\tau_{i+1} = -\tau'_i + \delta_i \quad (3)$$

$$\sigma_{i+1} = -\sigma'_i + \delta_i \quad (4)$$

where

$$\delta_i = (R_{i+1} - R_i + d_i) \cos \theta'_i + R_i \cos r_i - R_{i+1} \cos i_{i+1} \quad (5)$$

Here again  $d_i$  is taken to be the axial separation between the vertices of the  $i$ th and  $(i+1)$ th surfaces, and  $\theta'_i$  is the slope angle of the ray after refraction at the  $i$ th surface;  $\delta_i$  is the separation *along* the ray.

There is another way of finding the final  $\sigma'_N$  in cases where  $\tau'_N$  is not required. An auxiliary line connecting  $\sigma$  and  $\sigma'$  for a single surface can be shown to contain the center of curvature of the surface. This line is called the axis of sagittal symmetry, and becomes an auxiliary optical axis of the refraction. If one calls the angle between this auxiliary axis and the optical axis  $\varphi$ , the apparent height of the  $\sigma'$  focus can be multiplied throughout the system because of similar triangles, and one finds

$$\tan \varphi_N = \frac{\left( \prod_1^{N-1} a_i \right) \tan \theta_1}{1 - \left[ \sum_1^{N-1} b_i \prod_1^{i-1} a_j \right] \tan \theta_1} \quad (6)$$

where  $\theta_1$  is the direction of the object relative to the optical axis, the object taken here to lie at infinity. In the above

$$a_i = \frac{K_i}{J_i}, \quad b_i = \frac{\cos \theta'_i}{J_i} \quad (7)$$

where 
$$J_i = K_i + \sin \theta'_i, \quad \text{and} \quad K_i = \frac{R_i \sin r_i}{R_{i+1} - R_i + d_i} \quad (8)$$

The angle  $\varphi_N$  is the angular subtense of  $\sigma'_N$  as seen from the center of curvature of the last surface. Hence,

$$(-s'_N + d'_N) \tan \theta_N = (-R_N + d'_N) \tan \varphi_N = h'_N \quad (9)$$

where  $s'_N$  is the axial intercept of the final ray in image space, relative to the vertex of  $R_N$ , in accord with the conventions of § 3.1. The coordinates  $d'_N$  and  $h'_N$  locate the position of the final  $\sigma'_N$  focus in image space relative to the vertex of  $R_N$ . The formula requires about half of the computing time of the first formula given for finding  $\sigma'_N$ . However, the second method is not applicable where any one  $\sin r$  is nearly zero or zero.

**4.3. The Seidel aberrations\*.** Ludwig von Seidel first worked out convenient expressions for the third-order aberrations of an optical system, and it has been customary to designate the five independent aberrations of the third order as the *Seidel* aberrations.

a. *Spherical aberration.* This aberration refers to the improper union, near the image point, of rays that originate from an object point. Rays outside the paraxial region intersect the optical axis progressively farther from the paraxial focus according to the angular aperture of the initial pencil. Spherical aberration ordinarily can be evaluated on the optical axis where other aberrations are zero, but is present off the axis as well.

b. *Coma.* This aberration refers to the variation of magnification of rays in a pencil outside the paraxial region. The image point of intersection of any particular ray on the focal plane will vary in height according to the ray. A comatic pattern is produced by the combined meridional and skew rays in the form of circles tangent within a pair of straight envelope lines 60 degrees inclined to one another. The apex of the pattern lies at the paraxial magnification, if not too far from the axis. The largest circle within the envelope lines arises from the extreme rays of the pencil from the object point, the pencil taken as having a circular cross section. The so-called *upper* and *lower rim rays* in the meridional plane lie farthest from the apex, and in fact intersect. Indeed, the single circle for the cross section of the pencil maps twice around for the corresponding circle in the image. Coma

\* HERZBERGER, M., *Strahlenoptik*, Julius Springer, Berlin, 1931; also numerous papers. MERTÉ, W., RICHTER, R., and VON ROHR, M., *Das photographische Objektiv (Handbuch der wissenschaftlichen und angewandten Photographie, Bd. 1)*, Julius Springer, Vienna, 1932. WHITTAKER, E. T., *The Theory of Optical Instruments*, Cambridge University Press, London, 1907.

is an unsymmetrical aberration. Seidel coma varies as the square of the aperture and linearly with field angle. The spherical aberration and coma together are combined within the sine condition of Abbe, which within the Seidel region simply become the third-order expansion of the sine condition in series form.

c. *Astigmatism.* This aberration refers to lack of coincidence of the  $\tau'_N$  and  $\sigma'_N$  foci, described in §4.2. A point source images into two focal lines at right angles to one another. The tangential focus produces a tangential line, i.e., a line element perpendicular to the meridional plane. The radial or sagittal focus produces a radial line, i.e., a line element directed toward the optical axis and lying in the meridional plane. The astigmatism is measured by the separation of the focal lines, or by the diameter of the mean image for a given angular aperture of the system. The mean image is circular if the image forming pencil is of circular cross section, though in practice diffraction often produces a cross instead of a circle for the image.

d. *Curvature of field.* This aberration refers to the departure of the mean focus of an oblique pencil from a flat focal plane. The mean image in a rotationally symmetrical system lies on a surface that in the third order is spherical and tangent at its vertex to the paraxial focal plane. A flat field is simply a focal surface of infinite contact radius.

e. *Distortion.* This aberration refers to a displacement of an image point, even though sharply defined, from where it should be if the object plane were mapped at a constant magnification onto the image plane. A square reseau in an object plane ought to map into a square reseau in the conjugate image plane. If the image point is displaced outward, the distortion is called the *pincushion* type. If the image point is displaced inward, the distortion is called the *barrel* type.

f. *Stops.* A description of Seidel optics cannot be complete without introducing the concept of *stops*. The *aperture stop* limits the diameter of the bundle of rays admitted to the system. This stop may lie internally in the system. The *entrance pupil* is the image of the aperture stop in object space, and the *exit pupil* is the corresponding image in image space. If a system has a number of real stops formed by the clear apertures of the successive surfaces, the entrance pupil is the stop image in object space subtending the smallest angle as seen from the object point. Most often, the aperture stop is designed into a system, and may be simply an aperture in a metal sheet, or formed by a variable iris diaphragm.

The *principal ray* of a system passes through the center of the entrance pupil from any assigned object point. For symmetrical aberrations the principal ray remains central within the refracted pencils. For comatic aberrations, the principal ray may be shifted away from the rest of the light in the image. For these reasons the principal ray assumes particular importance in the calculation of the Seidel aberrations.

**4.4. The Seidel third-order expressions.** The equations of §4.2 for the  $\tau'$  and  $\sigma'$  foci are exact for a specific pencil. If the final foci coincide, the pencil becomes stigmatic. If a variety of pencils over the aperture of a system are separately stigmatic, the optical system becomes corrected over a finite aperture.

The development is too lengthy to be reproduced here. However, through the third order the cosines of §4.2 are expanded in terms of  $i$  and  $r$ . By tracing a paraxial ray through the center of the entrance pupil, i.e., a chief ray, one can express  $i$  and  $r$  in terms of the stop location for a given surface. The astigmatic difference in image space for the  $i$ th surface becomes the astigmatic difference in object space for the  $(i + 1)$ th surface. The equations of §4.2 can be arranged in such a way as to have the intermediate terms cancel out. Then one arrives at the following.

*Zinken-Sommer's condition.* Let

$$Q_{si} = n_{i-1} \left( \frac{1}{R_i} + \frac{1}{s_i} \right) = n_i \left( \frac{1}{R_i} - \frac{1}{s'_i} \right) \quad (1)$$

$$Q_{ti} = n_{i-1} \left( \frac{1}{R_i} + \frac{1}{t_i} \right) = n_i \left( \frac{1}{R_i} - \frac{1}{t'_i} \right) \quad (2)$$

where  $s_i$  refers to the object distance and  $t_i$  to the object distance of the stop from a surface. Then Zinken-Sommer's condition for the absence of astigmatism in an elementary pencil around a chosen chief ray becomes

$$\sum \left( \frac{Q_{ti}}{Q_{ti} - Q_{si}} \right)^2 \left( \frac{1}{n_{i-1}s_i} + \frac{1}{ns'_i} \right) = 0 \quad (3)$$

In the original notation of Seidel there is a different choice of conventions from those adopted here. Optical conventions vary so widely that readers must always be alert to avoid error.

Zinken-Sommer's condition contain  $Q_{ti}$ , which involves the stop position at each surface. By a transformation due to Seidel, the  $Q_{ti}$  can be replaced by an equivalent involving more desirable quantities. Zinken-Sommer's condition can be written in the form

$$\sum_i \left[ 1 + Q_{si} h_i^2 \sum_1^{i-1} \frac{d_j}{n_j h_j h_{j+1}} + \frac{Q_{si} h_i^2}{h_1^2 (Q_{t1} - Q_{s1})} \right]^2 \left( \frac{1}{n_{i-1} s_i} + \frac{1}{n_i s'_i} \right) = 0 \quad (4)$$

This expression is still simply a condition for the elimination of astigmatism along a narrow pencil through the center of the entrance pupil, which is located at a distance of  $t_1$  from the vertex of  $R_1$ . However,  $t_1$  and hence  $Q_{t1}$  can be made to vary over an arbitrarily large range. If the coefficients of  $1/(Q_{t1} - Q_{s1})^2$  and  $1/(Q_{t1} - Q_{s1})$  vanish independently, the correction becomes independent of the stop position. The coefficient of  $1/(Q_{t1} - Q_{s1})^2$  is identifiable with the condition for absence of spherical aberration, the coefficient  $1/(Q_{t1} - Q_{s1})$  with the absence of coma, and the remaining constant term with astigmatism itself. Hence, Zinken-Sommer's condition in the revised form contains all in one the basic requirements for a corrected optical system through the third order of approximation.

*Flatness of field.* The equations of § 4.2 can be recast into a requirement that the image lie in a plane surface when the object lies in a plane. One finds

$$\sum_i \left[ \left( \frac{Q_{ti}}{Q_{ti} - Q_{si}} \right)^2 \left( \frac{1}{n_{i-1} s_i} + \frac{1}{n_i s'_i} \right) + \frac{1}{R_i} \left( \frac{1}{n_{i-1}} - \frac{1}{n_i} \right) \right] = 0 \quad (5)$$

The first part is Zinken-Sommer's condition, which in a corrected instrument can be made to vanish. In the absence of astigmatism, therefore, we have the condition for *flatness of field*,

$$P = \sum_i \frac{1}{R_i} \left( \frac{1}{n_{i-1}} - \frac{1}{n_i} \right) = 0 \quad (6)$$

This relation is known as Petzval's condition for flatness of field, a criterion that is valid only in the absence of astigmatism. For finite values of  $P$ , a solution of the entire summation may still have a given pencil produce a mean focus on a flat image plane, but such a system cannot be satisfied simultaneously for spherical aberration, coma, and astigmatism, though any two can be zero.

For a group of thin lenses, whether separated or not,

$$P = \sum_i \frac{\phi_i}{n_i} = -\frac{1}{\rho_P} \quad (7)$$

where  $\rho_P$  is the radius of curvature of the so-called *Petzval surface*. If the astigmatism is zero,  $\rho_P$  is the radius of curvature of the focal surface itself. In the case of the general system

$$\frac{3}{\rho_{\sigma'}} - \frac{1}{\rho_{\tau}} = \frac{2}{\rho_P} \quad (8)$$

or 
$$\frac{1}{2} \left( \frac{1}{\rho_{\sigma'}} + \frac{1}{\rho_{\tau'}} \right) + \left( \frac{1}{\rho_{\sigma'}} - \frac{1}{\rho_{\tau'}} \right) = \frac{1}{\rho_P} \tag{9}$$

$$\frac{1}{\rho_f} \quad \text{Astigmatism}$$

where  $\rho_f$  is the radius of curvature of the mean focal surface,  $\rho_{\tau'}$  of the tangential image surface, and  $\rho_{\sigma'}$  of the radial or sagittal image surface. The sign of the radius follows the same conventions of § 3.1.

*Distortion.* The condition for the absence of distortion takes the form

$$\left. \begin{aligned} \sum_i \frac{Q_{ti}}{h_i^2 Q_{si} (Q_{ti} - Q_{si})} \\ \left[ \frac{Q_{ti}^2}{(Q_{ti} - Q_{si})^2} \left( \frac{1}{n_{i-1} s_i} + \frac{1}{n_i s'_i} \right) + \frac{1}{R_i} \left( \frac{1}{n_{i-1}} - \frac{1}{n_i} \right) \right] = 0 \end{aligned} \right\} \tag{10}$$

Seidel's five third-order conditions can then be written in the condensed form :

$$\left. \begin{aligned} \text{spherical aberration : } & \sum \Theta_i = 0 \\ \text{coma : } & \sum \Theta_i U_i = 0 \\ \text{astigmatism : } & \sum \Theta_i U_i^2 = 0 \\ \text{Petzval : } & \sum P_i = 0 \\ \text{distortion : } & \sum \{ \Theta_i U_i^3 + P_i U_i \} = 0 \end{aligned} \right\} \tag{11}$$

where 
$$U_i = \frac{1}{Q_{si} h_i^2} \left( 1 + Q_{si} h_i^2 \sum_1^{i-1} \frac{d_j}{n_j h_j h_{j+1}} \right) \tag{12}$$

$$\Theta = Q_{si}^2 h_i^4 \left( \frac{1}{n_{i-1} s_i} + \frac{1}{n_i s'_i} \right) \tag{13}$$

The reader is referred to Merté \* for evaluation of the image errors when any of the above five conditions is not satisfied.

**4.5. Seidel's conditions in the Schwarzschild-Kohlschütter form<sup>+</sup>**

$$K_i = n_{i-1} \left( \frac{1}{R_i} + \frac{1}{s_i} \right) = n_i \left( \frac{1}{R_i} - \frac{1}{s'_i} \right) = Q_{si} \tag{1}$$

$$s_{i+1} = -s'_i + d_i, \quad h_1 = \frac{s_1}{s_1 - t_1}, \quad k_1 = \frac{t_1}{h_1} \tag{2}$$

\* MERTÉ *et al.*, *Das photographische Objektiv*, Julius Springer, Vienna, 1932, pp. 235-238.

<sup>+</sup> SCHWARZSCHILD, K., *Mitteilungen der Göttingen Sternwarte*, IX-XI (1905).

$$\frac{h_{i+1}}{h_i} = \frac{s_{i+1}}{-s'_i} = \left(1 - \frac{1}{s'_i} d_i\right) \quad (3)$$

$$k_{i+1} = k_1 + \sum_{j=1}^i \frac{d_j}{n_j h_j h_{j+1}}, \quad (kc)_i = k_i + \frac{1}{h_i^2 K_i} \quad (4)$$

$$f_i = \frac{1}{s_i} + \frac{1}{R_i} - \frac{1}{s'_i} \quad (5)$$

$$B_i = \frac{1}{2} h_i^4 K_i f_i \left(\frac{1}{s_i} + \frac{1}{s'_i}\right) \quad (6)$$

$$F_i = (kc)_i B_i \quad (7)$$

$$C_i = (kc)_i^2 B_i = (kc)_i F_i \quad (8)$$

$$P_i = \frac{1}{R_i} \left(\frac{1}{n_{i-1}} - \frac{1}{n_i}\right) \quad (9)$$

$$E_i = (kc)_i \left(C_i + \frac{1}{2} P_i\right) \quad (10)$$

$$\text{spherical aberration : } B = \sum_1^N B_i$$

$$\text{coma : } F = \sum_1^N F_i$$

$$\text{astigmatism : } C = \sum_1^N C_i$$

$$\text{Petzval : } P = \sum_1^N P_i$$

$$\text{distortion : } E_i = \sum_1^N E_i$$

$$\left. \vphantom{\begin{matrix} B \\ F \\ C \\ P \\ E_i \end{matrix}} \right\} (11)$$

### 5. Ray-Tracing Equations

Apart from the approximate analysis of the performance of an optical system indicated by equations of Sec. 4., one finds it almost always necessary to trace selected rays through an optical system as a final check on its merit or for further information on its deficiencies. There are many forms of ray-tracing equations, some adapted to logarithmic computing, some to the hand calculator, and some to the automatic calculating equipment that is now making its appearance in the optical field. Typical formulations are given below.

**5.1. Meridional rays** \*. The basic data are to be tabulated in advance in a notebook or some separate page to be used throughout the computation of any number of rays. It is necessary to tabulate only five quantities per surface otherwise, though quite often more quantities are written down to increase the information afforded by the ray.

- a. Given  $\sin i_i$ , find  $\sin r_i$  from

$$\sin r_i = N_i \sin i_i \quad (1)$$

- b. Find  $i_i$  and  $r_i$  from trigonometric tables (2)

- c. Find  $\theta_i$  from the relation

$$\theta_i = \theta_{i-1} + r_i - i_i \quad (3)$$

- d. Find  $\sin \theta_i$  from tables. (4)

- e. Find  $\sin i_{i+1}$  from the relation

$$\sin i_{i+1} = M_i \sin r_i + L_i \sin \theta_i \quad (5)$$

Proceed to the next surface. The auxiliary quantities  $M_i$ ,  $L_i$ , and  $N_i$  are calculated once and for all from the relations

$$M_i = \frac{R_i}{R_{i+1}} \quad (6)$$

$$L_i = 1 - M_i + \frac{d_i}{R_{i+1}} \quad (7)$$

$$N_i = \frac{n_{i-1}}{n_i} \quad (8)$$

\* COMRIE, L. J., *Proc. Phys. Soc.*, **52**, 246-252 (1940). BAKER, J. G., *Design and Development of an Automatically Focusing Distortionless Telephoto, and Related Lenses for High Altitude Aerial Reconnaissance*, OSRD Report 6017, Library of Congress microfilms.

**5.2. Skew rays.** \* The following equations have merit because of their symmetrical form, and because the same basic data can be used that have already been calculated before the meridional rays are traced. There are a number of other forms used for skew ray tracing, but space does not permit the detailed treatment that would be necessary for the formulas to be immediately applicable. The formulas below make use of square root solutions instead of the natural functions.

Given  $(l_i, m_i, n_i, \bar{Y}_i, \bar{Z}_i, M_i, L_i, N_i)$  at surface  $i$ , where  $M, L$ , and  $N$  are from the separately tabulated basic data,  $l, m$ , and  $n$  are the direction cosines of the normal to the surface at point of intercept of the ray, and  $\bar{Y}_i$  and  $\bar{Z}_i$  are auxiliary quantities.

a. Find  $\bar{Y}'_i = N_i \bar{Y}_i$  (1)

$$\bar{Z}'_i = N_i \bar{Z}_i \quad (2)$$

b. Find  $A_i = m_i \bar{Y}'_i + n_i \bar{Z}'_i$  (3)

$$B_i = l_i^2 - (\bar{Y}'_i)^2 - (\bar{Z}'_i)^2 \quad (4)$$

$$\lambda_i = -A_i + \sqrt{A_i^2 + B_i} \quad (5)$$

$$\mu_i = \frac{1}{l_i} (m_i \lambda_i + \bar{Y}'_i) \quad (6)$$

$$\nu_i = \frac{1}{l_i} (n_i \lambda_i + \bar{Z}'_i) \quad (7)$$

c. Find  $\bar{Y}_{i+1} = M_i \bar{Y}'_i + L_i \mu_i$  (8)

$$\bar{Z}_{i+1} = M_i \bar{Z}'_i + L_i \nu_i \quad (9)$$

d. Find  $C_{i+1} = \mu_i \bar{Y}_{i+1} + \nu_i \bar{Z}_{i+1}$  (10)

$$D_{i+1} = \lambda_i^2 - \bar{Y}_{i+1}^2 - \bar{Z}_{i+1}^2 \quad (11)$$

$$l_{i+1} = C_{i+1} + \sqrt{C_{i+1}^2 + D_{i+1}} \quad (12)$$

$$m_{i+1} = \frac{1}{\lambda_i} (\mu_i l_i - \bar{Y}_{i+1}) \quad (13)$$

$$n_{i+1} = \frac{1}{\lambda_i} (\nu_i l_i - \bar{Z}_{i+1}) \quad (14)$$

\* BAKER, J. G., *loc. cit.*

The cycle is now complete and ready for the next surface. The usual check on the direction cosines of the ray after refraction and on the direction cosines of the normal in step d. can be applied. The starting equations at surface 1 involve finding the first  $l$ ,  $m$ , and  $n$ , and the first  $\bar{Y}$  and  $\bar{Z}$ . The ending equations at surface  $N$  involve finding the intercept of the ray with the adopted image plane from a knowledge of  $l_N$ ,  $m_N$ ,  $n_N$ ,  $\lambda_N$ ,  $\mu_N$ , and  $\nu_N$ . When needed,

$$\bar{Y}_i = (l_i \mu_{i-1} - m_i \lambda_{i-1}) \quad (15)$$

$$\bar{Z}_i = (l_i \nu_{i-1} - n_i \lambda_{i-1}) \quad (16)$$

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NOTE : The longitudinal magnification  $\gamma$  is defined by

$$\gamma = \frac{ds'_N}{ds_1} \quad (11),$$

where  $ds_1$  and  $ds'_N$  are displacements of infinitesimal magnitude in the vicinity of the object and image points considered as changes in  $s_1$  and  $s'_N$  respectively. From a treatment similar to that above, we find

$$\gamma = - \frac{n_o}{n_N} \left( \frac{s'_N{}^2}{s_1^2} \right) \left( \frac{h_1}{h_N} \right)^2 \quad (12)$$

from which

$$\frac{\gamma}{m} = \left( \frac{s'_N}{s_1} \right) \left( \frac{h_1}{h_N} \right) \quad (13)$$

for finite object and image distances.



## Chapter 17

### PHYSICAL OPTICS

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Geometrical optics considers light as being made up of rays. Color or wavelength enters as a special parameter to distinguish one ray from another in a medium whose physical properties are not independent of wavelength. Physical optics, on the other hand, treats of properties of light in much greater detail. The interference of light, for example, can be explained only in terms of the basic vibrations. The rays enter, if at all, merely as indicating the direction of propagation of energy in the medium. Physical optics, like hydrodynamics and acoustics, depends for its solutions on certain prescribed boundary conditions, which the wave equation or its appropriate solutions must fulfil. Also, since light is electromagnetic in character, its basic properties go back to the fundamental equations of Maxwell. Relativity, and special relativity in particular, are also related to this problem, since certain properties depend upon the interpretation of matter in motion with velocities that may be a considerable fraction of the velocity of light. The formulas selected have been chosen largely from the standpoint of utility—utility, that is, for the laboratory scientist as well as for the student of theoretical phases.

The following symbols are not standard, and are not explained in the text :

- $a, b, d$  slit width, length, and separation (between centers)
- $A, W$  absorptance and radiant emittance of a surface
- $B, D$  distances from source to diffracting screen, and from diffracting screen to point of observation
- $E, R, E'$  complex amplitudes of incident, reflected, and refracted waves
- $e, o$  (as subscripts) extraordinary and ordinary components in double refraction
- $I$  intensity (flux per unit area)
- $l$  geometrical path length

$m$	order of interference
$M$	molecular weight
$n$	refractive index
$s, p$ (as subscripts)	refer to light polarized perpendicular and parallel to the plane of incidence
$t$	thickness of a plane-parallel plate
$v$	wave velocity
$\alpha$	absorption coefficient, grazing angle of incidence
$\delta$	phase difference, phase change
$\Delta$	path difference (retardation)
$\epsilon$	dielectric constant
$\zeta$	angle of astronomical aberration
$\theta$	angle of diffraction
$\kappa$	absorption index
$\mu$	permeability, electric or magnetic moment
$\xi$	angle of rotation of plane of polarization
$\rho$	reflectance of a surface
$\sigma$	wave number
$\tau$	transmittance
$\phi, \phi'$	angles of incidence and refraction
$\psi$	azimuth of plane-polarized light

## 1. Propagation of Light in Free Space

### 1.1. Wave equation

$$\nabla^2 E = \frac{\mu\epsilon}{C^2} \cdot \frac{\partial^2 E}{\partial t^2} = \frac{1}{v^2} \cdot \frac{\partial^2 E}{\partial t^2} \quad (1)$$

( $C = 1$  in mks units;  $C = c$  in Gaussian units)

The general solution is (Chap. 1, § 5.20)

$$E = f(s - vt) + g(s + vt) \quad (2)$$

For a monochromatic plane wave, the wave normal having the direction cosines  $l$ ,  $m$ , and  $n$ ,

$$E = E_0 e^{2\pi i \nu [t - (lx + my + nz)/v] + i\delta}, \quad (lx + my + nz = s) \quad (3)$$

or

$$E = E_0 \sin \left[ 2\pi \nu \left( t - \frac{lx + my + nz}{v} \right) + \delta \right] \quad (4)$$

Wave traveling in the direction  $+x$ , phase constant zero at origin,

$$E = E_0 \sin 2\pi \nu \left( t - \frac{x}{v} \right) \quad (5)$$

Since  $\nu = 1/T$  and  $v = \nu\lambda$ ,

$$E = E_0 \sin 2\pi \left( \frac{t}{T} - \frac{x}{\lambda} \right) \quad (6)$$

### 1.2. Plane-polarized wave

$$E_y = E_{0y} \sin 2\pi\nu \left( t - \frac{x}{v} \right) \quad (1)$$

$$H_z = H_{0z} \sin 2\pi\nu \left( t - \frac{x}{v} \right) \quad (2)$$

**1.3. Elliptically polarized wave.** Combination of the two plane-polarized waves

$$E_y = E_{0y} \sin 2\pi\nu \left( t - \frac{x}{v} \right) \quad \text{and} \quad E_z = E_{0z} \sin \left[ 2\pi\nu \left( t - \frac{x}{v} \right) + \delta \right] \quad (1)$$

gives, at one value of  $x$ ,

$$\sin^2 \delta = \frac{E_y^2}{E_{0y}^2} - \frac{2E_y E_z}{E_{0y} E_{0z}} \cos \delta + \frac{E_z^2}{E_{0z}^2} \quad (2)$$

an ellipse in the  $y, z$  plane.

**1.4. Poynting vector.** The instantaneous rate of flow of energy across unit area placed normal to the direction of flow,

$$\mathbf{\Pi} = \frac{C}{4\pi} \left[ \mathbf{E} \times \mathbf{H} \right] \quad (1)$$

**1.5. Intensity.** In vacuum,  $E = H$ , so

$$\Pi = \frac{C}{4\pi} E_y^2, \quad I = \frac{C}{8\pi} E_{0y}^2 \quad (1)$$

for a plane-polarized wave. For the elliptically polarized wave of § 1.3,

$$I = \frac{C}{8\pi} (E_{0y}^2 + E_{0z}^2) \quad (2)$$

For an unpolarized wave of amplitude  $E_0$ ,

$$I = \frac{C}{4\pi} E_0^2 \quad (3)$$

For  $N$  such waves having random phases,

$$I = N \frac{C}{4\pi} E_0^2 \quad (4)$$

**1.6. Partially polarized light.** If the preferential polarization is in the  $y$  direction,

$$P = \frac{I_y - I_z}{I_y + I_z} \quad (1)$$

gives the fraction of admixed plane-polarized light (proportional polarization).

### 1.7. Light quanta

energy of a photon =  $h\nu$ ,      velocity =  $c$

momentum =  $\frac{h\nu}{c} = \frac{h}{\lambda}$       rest mass = 0

## 2. Interference

**2.1. Two beams of light.** Difference in optical path is

$$\Delta = \sum n_i l_i - \sum n_j l_j \quad (1)$$

Phase difference is

$$\delta = \frac{2\pi}{\lambda} \Delta \quad (2)$$

$$I = E_0^2 + E_0'^2 + 2E_0E_0' \cos \delta \quad (3)$$

When  $E_0 = E_0'$ ,

$$I = 4E_0^2 \cos^2 \frac{\delta}{2} \quad (4)$$

**2.2. Double-source experiments.** For Young's double slit, condition for maxima is

$$d \sin \theta = m\lambda \quad (1)$$

and linear separation of successive fringes is

$$y_1 = \frac{D\lambda}{d} \quad (2)$$

For Fresnel biprism

$$y_1 = \frac{(B + D)\lambda}{2B(n - 1)\alpha} \quad (3)$$

where  $\alpha$  = prism angle.

For Fresnel mirrors

$$y_1 = \frac{(B + D)\lambda}{2B\alpha} \quad (4)$$

where  $\alpha$  = angle between mirrors.

**2.3. Fringes of equal inclination.** For reflected fringes,

$$I = \frac{4\rho \sin^2 \delta/2}{(1-\rho)^2 + 4\rho \sin^2 \delta/2} \quad (1)$$

For transmitted fringes,

$$I = \frac{(1-\rho)^2}{(1-\rho)^2 + 4\rho \sin^2 \delta/2} \quad (2)$$

$$\delta = \frac{4\pi nt \cos \phi'}{\lambda} \quad (3)$$

For maxima in reflected light,

$$2nt \cos \phi' = (m + \frac{1}{2})\lambda \quad (4)$$

**2.4. Fringes of equal thickness.** At normal incidence, maxima in reflected light,

$$2nt = (m + \frac{1}{2})\lambda \quad (1)$$

Newton's rings

$$r_m^2 = \frac{r(m + \frac{1}{2})\lambda}{n} \quad (2)$$

where  $r_m$  = radius of  $m$ th bright fringe,  $r$  = radius of lens surface.

**2.5. Michelson interferometer.** When the interferometer is adjusted for circular fringes, maxima are

$$2t \cos \phi = m\lambda \quad (1)$$

Fringe shift (number of fringes) due to a displacement  $t' - t$  of one mirror :

$$m' - m = \frac{2(t' - t)}{\lambda} \quad (2)$$

Fringe shift caused by insertion of a thin lamina of index  $n$  and thickness  $t$  :

$$m' - m = \frac{2(n - n_a)t}{\lambda} \quad (3)$$

where  $n_a$  = refractive index of air. Visibility of fringes is

$$V = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}} \quad (4)$$

**2.6. Fabry-Perot interferometer.**

$$I = \frac{\tau^2}{1 - 2\rho \cos \delta + \rho^2} = \frac{\tau^2}{(1 - \rho)^2} \cdot \frac{1}{1 + \frac{4\rho}{(1 - \rho)^2} \sin^2 \frac{\delta}{2}} \quad (1)$$

$$m\lambda = 2t \cos \phi \approx 2t \left( 1 - \frac{r_i^2}{2f^2} \right) \quad (2)$$

where  $f$  = focal length of camera lens. Spectral range is

$$\Delta\lambda_1 = \frac{\lambda}{m} = \frac{\lambda^2}{2t}, \quad \Delta\sigma_1 = \frac{1}{2t} \quad (3)$$

Ratio of fringe width at half maximum to fringe separation\*

$$2\gamma_h = \frac{1 - \rho}{\pi\rho^{1/2}} + \frac{1}{24} \left( \frac{1 - \rho}{\rho^{1/2}} \right)^3 \quad (4)$$

Resolving power +

$$\frac{\lambda}{\Delta\lambda} = 3.0 \frac{m\rho^{1/2}}{1 - \rho} \quad (5)$$

Dispersion

$$\frac{d\theta}{d\lambda} = \frac{m}{2t \sin \phi} = \frac{1}{\lambda \tan \phi}, \quad \frac{\Delta y}{\Delta\lambda} = \frac{f^2}{r\lambda} \quad (6)$$

Comparison of  $\lambda$ 's with sliding interferometer

$$\lambda_1 - \lambda_2 = \frac{\lambda_1 \lambda_2}{2d} = \frac{\lambda_{av}^2}{2d} \quad (7)$$

where  $d$  = distance one mirror is moved between coincidences.

### 2.7. Lummer-Gehrcke plate. Maxima

$$m\lambda = 2nt \cos \phi' = 2t\sqrt{n^2 - \sin^2 \phi} \quad (1)$$

$$\Delta\lambda_1 = \frac{m\lambda^2}{m^2\lambda - 4t^2n(dn/n\lambda)} \quad (2)$$

$$\frac{d\theta}{d\lambda} = \frac{2\lambda n(dn/d\lambda) - 2(n^2 - \sin^2 \phi)}{\lambda \sin 2\phi} \quad (3)$$

$$\frac{\lambda}{\Delta\lambda} = \frac{l}{\lambda \sin \phi} \left( n^2 - \sin^2 \phi - \lambda n \frac{dn}{d\lambda} \right) \quad (4)$$

where  $l$  = length of the plate.

### 2.8. Diffraction grating

$$I = \frac{\sin^2 \alpha}{\alpha^2} \cdot \frac{\sin^2 N\beta}{\sin^2 \beta} \quad (1)$$

where  $\alpha = (\pi a \sin \theta)/\lambda$ ,  $\beta = (\pi d \sin \theta)/\lambda$ . Principal maxima

$$m\lambda = d(\sin \phi + \sin \theta) \quad (2)$$

\* MEISSNER, K. W., *J. Opt. Soc. Am.*, 31, 414 (1941).

+ BIRGE, R. T., Private communication.

$$\frac{d\theta}{d\lambda} = \frac{m}{d \cos \theta} \quad (3)$$

$$\frac{\lambda}{\Delta\lambda} = mN \quad (4)$$

Concave grating, radius  $r$ ,

$$\cos \phi \left( \frac{\cos \phi}{r_1} - \frac{1}{r} \right) + \cos \theta \left( \frac{1}{r} - \frac{\cos \theta}{r_2} \right) = 0 \quad (5)$$

$$\frac{1}{r_1} + \frac{1}{r_3} = \frac{\cos \phi + \cos \theta}{r} \quad (6)$$

where  $r_1$  = distance of slit,  $r_2$  = distance of image (first focal line),  $r_3$  = distance of second focal line.

**2.9. Echelon grating.** Transmission echelon; maxima

$$m\lambda = (n - 1)t - a\theta \quad (1)$$

$$\Delta\lambda_1 = \frac{\lambda}{Ct} \quad (2)$$

where  $C = [(n - 1)/\lambda] - dn/d\lambda$ .

$$\frac{d\theta}{d\lambda} = C \frac{t}{a} \quad (3)$$

$$\frac{\lambda}{\Delta\lambda} = NCt \quad (4)$$

Reflection echelon

$$m\lambda = 2t - a\theta \quad (5)$$

The other equations are the same, with  $C = 2/\lambda$ .

**2.10. Low-reflection coatings.** Single, homogeneous layer of index  $n_1$ , deposited on glass of index  $n$ , to a thickness  $t = \lambda/4n_1$ :

$$\rho = \frac{n_1^2 - n}{n_1^2 + n}, \quad \rho = 0 \text{ when } n_1 = \sqrt{n} \quad (1)$$

Two layers,\* the one next to the air having index  $n_1$  and thickness  $\lambda/4n_1$ , that next to the glass having index  $n_2$  and thickness  $\lambda/4n_2$ :

$$\rho = \left( \frac{n_1^2 n - n_2^2}{n_1^2 n + n_2^2} \right)^2, \quad \rho = 0 \text{ when } n_1^2 n = n_2^2 \quad (2)$$

\* VACISEK, A., *J. Opt. Soc. Am.*, **37**, 623 (1947).

### 3. Diffraction

**3.1. Fraunhofer diffraction by a rectangular aperture.** For parallel light incident normally,

$$I = I_0 \frac{\sin^2 \beta}{\beta^2} \frac{\sin^2 \gamma}{\gamma^2} \quad (1)$$

where  $\beta = (\pi a \sin \theta)/\lambda$ , with  $\theta$  measured in a plane perpendicular to  $b$ ;  $\gamma = (\pi b \sin \Omega)/\lambda$ , with  $\Omega$  measured in a plane perpendicular to  $a$ . Single slit, having  $b \gg a$ ,

$$I = I_0 \frac{\sin^2 \beta}{\beta^2}, \quad \beta = \frac{\pi a(\sin \phi + \sin \theta)}{\lambda} \quad (2)$$

for oblique incidence at the angle  $\phi$ . Zeros of intensity occur at  $\beta = \pi, 2\pi, 3\pi, \dots$ ; maxima at  $\tan \beta = \beta$ ; first zero at  $\sin \theta_1 = \lambda/a$ .

### 3.2. Chromatic resolving power of prisms and gratings

$$\frac{\lambda}{\Delta\lambda} = t \frac{dn}{d\lambda} \quad (1)$$

for prism, or prisms, with total length of base  $t$ .

$$\frac{\lambda}{\Delta\lambda} = mN = \frac{Nd(\sin \phi + \sin \theta)}{\lambda} \quad (2)$$

for grating, where  $Nd =$  total width of grating.

### 3.3. Fraunhofer diffraction by a circular aperture

$$I = I_0 \left( \frac{2J_1(\alpha)}{\alpha} \right)^2, \quad \alpha = \frac{2\pi r \sin \theta}{\lambda} \quad (1)$$

where  $J_1 =$  Bessel function of order unity (Chap. 1, § 9.2).

$$\sin \theta_1 = 1.220 \frac{\lambda}{2r} \quad (2)$$

at first zero of intensity.

### 3.4. Resolving power of a telescope

$$\theta_1 = 1.220 \frac{\lambda}{2r} \text{ radians} \quad (1)$$

where  $r =$  radius of objective lens.

$$\theta_1 = \frac{14.1}{2r} \text{ seconds of arc} \quad (2)$$

where  $r$  is in centimeters.

**3.5. Resolving power of a microscope.** Smallest separation of two points resolved :

$$x = \frac{\lambda}{2n \sin \phi} = \frac{\lambda}{2(\text{numerical aperture})} \quad (1)$$

where  $\phi$  = half-angle subtended at object by objective lens.

### 3.6. Fraunhofer diffraction by $N$ equidistant slits

$$I = I_0 \frac{\sin^2 \beta}{\beta^2} \cdot \frac{\sin^2 N\gamma}{\sin^2 \gamma} \quad (1)$$

where  $\beta = (\pi a \sin \theta)/\lambda$ ,  $\gamma = (\pi d \sin \theta)/\lambda$ .

$$I = I_0 \frac{\sin^2 \beta}{\beta^2} \cos^2 \gamma \quad (2)$$

for double slit.

$$d(\sin \phi + \sin \theta) = m\lambda$$

at maxima.

$$\frac{\gamma}{\beta} = \frac{d}{a} = \text{an integer} \quad (3)$$

is the condition for missing orders.

### 3.7. Diffraction of x rays by crystals

$$2d \sin \alpha = m\lambda, \quad (\text{Bragg's law}) \quad (1)$$

where  $d$  = separation of atomic planes,  $\alpha$  = grazing angle of incidence and diffraction. More accurately, \*

$$m\lambda = 2d\sqrt{n^2 - 1 + \sin^2 \alpha} \approx 2d\left(1 - \frac{1-n}{\lambda^2} \cdot \frac{4d^2}{m^2}\right) \sin^2 \alpha \quad (2)$$

For a cubic crystal, lattice constant  $c$ ,

$$\sin \alpha = \frac{\lambda}{2c} \left[ (mh)^2 + (mk)^2 + (ml)^2 \right]^{1/2} \quad (3)$$

where  $h, k, l$  = Miller indexes. +

### 3.8. Kirchhoff's formulation of Huygens' principle

$$4\pi E_P = \iint \left\{ \cos(n, r) \frac{\partial}{\partial r} \left[ \frac{E(t - r/v)}{r} \right] - \frac{1}{r} \cdot \frac{\partial}{\partial n} \left[ E \left( t - \frac{r}{v} \right) \right] \right\} dS \quad (1)$$

\* VALASEK, J., *Theoretical and Experimental Optics*, John Wiley & Sons, Inc., New York, 1949, p. 191.

+ *Ibid.*, p. 419.

where  $(n, r)$  is the angle between the *inward* normal to the surface element  $dS$  and the radius vector  $r$  from  $P$  to  $dS$ . For plane waves incident normally on an aperture in a screen,\*

$$E_P = \frac{iE_0}{4\pi} \iint \left[ \frac{2\pi}{\lambda} \cdot \frac{e^{-ikr}}{r} (1 + \cos \theta) - i \frac{e^{-ikr}}{r^2} \cos \theta \right] dS \quad (2)$$

The second term may be neglected for optical waves.

### 3.9. Fresnel half-period zones

$$r_m = \sqrt{mD\lambda + \frac{m^2}{4}\lambda^2} \approx \sqrt{mD\lambda} \quad (1)$$

Intensity on the axis of a circular aperture.

$$I = \frac{E_1}{2} + \frac{E_m}{2} \quad (2)$$

approaches  $E_1/2$  as  $m \rightarrow \infty$ .

### 3.10. Fresnel integrals

$$x = \int_0^v \cos \frac{\pi v^2}{2} dv, \quad y = \int_0^v \sin \frac{\pi v^2}{2} dv \quad (1)$$

where  $v = l\sqrt{2B/[D\lambda(B+D)]}$ , and  $l$  is the distance along the screen.

## 4. Emission and absorption

### 4.1. Kirchhoff's law of radiation

$$\frac{W}{A} = W_b \quad (1)$$

where  $W_b$  = radiant emittance of a black body at the same temperature at which  $W$  and  $A$  are measured.

### 4.2. Blackbody radiation laws

$$W_\nu d\nu = \frac{C_1 \nu^3}{c^4} (e^{h\nu/kT} - 1)^{-1} d\nu, \quad (\text{Planck's law}) \quad (1)$$

$$W_\lambda d\lambda = \frac{C_1}{\lambda^5} (e^{C_2/\lambda T} - 1)^{-1} d\lambda \quad (2)$$

where  $C_1 = 2\pi hc^2$ ,  $C_2 = hc/k$

\* *Ibid.*, p. 185.

$$\lambda_{\max} T = \frac{C_2}{4.965}, \quad (\text{Wien's displacement law}) \quad (3)$$

$$W_b = CT^4, \quad (\text{Stefan-Boltzmann law}) \quad (4)$$

### 4.3. Exponential law of absorption

$$I = I_0 \tau^x = I_0 e^{-\alpha x}, \quad (\text{Bouguer's law}) \quad (1)$$

$$I = I_0 e^{-\alpha [C]x} \quad (\text{Beer's law}) \quad (2)$$

where  $[C]$  = concentration of a solution.

### 4.4. Bohr's frequency condition

$$h\nu = E_1 - E_2, \quad \sigma = T_2 - T_1 = \frac{E_1 - E_2}{hc} \quad (1)$$

### 4.5. Intensities of spectral lines

$$I = N_n A_{nm} h\nu_{nm}, \quad (\text{emission lines}) \quad (1)$$

where  $N_n$  = number of atoms in initial (upper) state, and  $A_{nm}$  = spontaneous transition probability.

$$\alpha = N_m B_{nm} h\nu_{nm}, \quad (\text{absorption lines}) \quad (2)$$

where  $N_m$  = number of atoms in initial (lower) state, and  $B_{nm}$  = induced transition probability.

$$B_{nm} = \frac{c^3}{8\pi h\nu_{nm}^3} \cdot \frac{g_n}{g_m} A_{nm} \quad (3)$$

where  $g_n, g_m$  = statistical weights of upper and lower states.\*

## 5. Reflection

### 5.1. Fresnel's equations

$$\left. \begin{aligned} \frac{R_s}{E_s} &= -\frac{\sin(\phi - \phi')}{\sin(\phi + \phi')} \\ \frac{R_p}{E_p} &= \frac{\tan(\phi - \phi')}{\tan(\phi + \phi')} \\ \frac{E'_s}{E_s} &= \frac{2 \sin \phi' \cos \phi}{\sin(\phi + \phi')} \\ \frac{E'_p}{E_p} &= \frac{2 \sin \phi' \cos \phi}{\sin(\phi + \phi') \cos(\phi - \phi')} \end{aligned} \right\} (1)$$

\* HERZBERG, G., *Atomic Spectra and Atomic Structure*, Prentice-Hall, Inc., New York, 1937, Chap. 4.

The signs conform to the convention that corresponding phases are as seen by an observer looking *against* the light, whether incident, reflected, or refracted. This leads to an apparent inconsistency in the signs of  $R_s/E_s$  and  $R_p/E_p$  at  $\phi = 0$ . It cannot be avoided, however, without introducing other difficulties.

**5.2. Stokes' amplitude relations.** Reversal of the rays makes  $\phi'$  the angle of incidence, and  $\phi$  the angle of refraction. Using the subscript 1 for the reversed rays,

$$\frac{R_1}{E_1} = -\frac{R}{E} \quad (1)$$

for both  $s$  and  $p$  components; also

$$\frac{E'}{E} \frac{E'_1}{E_1} = 1 - \left(\frac{R}{E}\right)^2 \quad (2)$$

### 5.3. Reflectance of dielectrics

$$\rho_s = \left(\frac{R_s}{E_s}\right)^2, \quad \rho_p = \left(\frac{R_p}{E_p}\right)^2 \quad (1)$$

At normal incidence ( $\phi = 0$ ),

$$\rho = \left(\frac{n-1}{n+1}\right)^2 \quad (2)$$

for both  $s$  and  $p$  components.

### 5.4. Azimuth of reflected plane-polarized light

$$\tan \psi = \frac{R_p}{R_s} = -\frac{E_p}{E_s} \frac{\cos(\phi + \phi')}{\cos(\phi - \phi')} \quad (1)$$

for dielectrics;  $\psi$  = angle between  $R$  and the normal to the plane of incidence.

### 5.5. Transmittance of dielectrics

$$\frac{E'_s}{E_s} = 1 + \frac{R_s}{E_s}, \quad \frac{E'_p}{E_p} = 1 + \frac{R_p/E_p}{n} \quad (1)$$

$$\left(\frac{R}{E}\right)^2 + n\left(\frac{E'}{E}\right)^2 \frac{\cos \phi'}{\cos \phi} = 1 \quad (2)$$

applies to both the  $s$  and  $p$  components.

$$\tau = \left(\frac{E'}{E}\right)^2 = \frac{1 - \rho}{n(\cos \phi' / \cos \phi)} \quad (3)$$

**5.6. Polarization by a pile of plates.** For unpolarized incident light, the proportional polarization (Sec. 1.6) caused by  $2m$  surfaces ( $m$  plates) is

$$P = \frac{\rho_s - \rho_p}{\rho_s + \rho_p + 2(2m - 1)\rho_s\rho_p} \quad (1)$$

for reflected light

$$P = \frac{m(\rho_s - \rho_p)}{1 + (m - 1)(\rho_s + \rho_p) - (2m - 1)\rho_s\rho_p} \quad (2)$$

for transmitted light

$$P = \frac{m\rho_s}{1 + (m - 1)\rho_s} \quad (3)$$

for light transmitted at the polarizing angle ( $\rho_p = 0$ ).\*

**5.7. Phase change at total internal reflection**

$$\left. \begin{aligned} \tan \frac{\delta_s}{2} &= \frac{\sqrt{n^2 \sin^2 \phi - 1}}{n \cos \phi} \\ \tan \frac{\delta_p}{2} &= \frac{n \sqrt{n^2 \sin^2 \phi - 1}}{\cos \phi} \end{aligned} \right\} \quad (1)$$

**5.8. Fresnel's rhomb.** The angle of incidence at each of the two internal reflections is determined by

$$\tan \frac{\delta_p - \delta_s}{2} = \frac{\cos \phi \sqrt{n^2 \sin^2 \phi - 1}}{n \sin^2 \phi} = 45^\circ \quad (1)$$

Maximum possible phase change at a single reflection is given by

$$\tan \left( \frac{\delta_p - \delta_s}{2} \right)_{\max} = \frac{n^2 - 1}{2n} \quad (2)$$

This occurs at the angle of incidence  $\phi_m$  such that

$$\sin \phi_m = \sqrt{\frac{2}{n^2 + 1}} \quad (3)$$

**5.9. Penetration into the rare medium in total reflection**

$$E' = C e^{-(2\pi/\lambda)z \sqrt{n^2 \sin^2 \phi - 1}} e^{2\pi i \nu(t - x n \sin \phi/c)} \quad (1)$$

where the  $x, y$  plane is a totally reflecting surface, and the  $x, z$  plane is a plane of incidence.

\* GEIGER, H. and SCHEEL, K. (eds.), *Handbuch der Physik*, Vol. 20, "Licht als Wellenbewegung," Julius Springer, Berlin, 1928, p. 217.

**5.10. Electrical and optical constants of metals.** For perpendicular incidence in the  $+z$  direction,

$$I_0 e^{-4\pi\kappa_0 z/\lambda_0} = I_0 e^{-4\pi\kappa z/\lambda} \quad (1)$$

defines  $\kappa$ ,  $\kappa_0$ , where  $\lambda =$  wavelength in metal,  $\lambda_0 =$  wavelength in vacuum.

$$\left. \begin{aligned} \epsilon' &= \epsilon - i \frac{2\sigma}{\nu} = n^2(1 - i\kappa)^2, \quad (\text{complex dielectric constant}) \\ \epsilon &= n^2(1 - \kappa^2) = n^2 - \kappa_0^2 \\ \frac{\sigma}{\nu} &= n^2\kappa = n\kappa_0 \end{aligned} \right\} (2)$$

### 5.11. Reflectance of metals \*

$$\left. \begin{aligned} \rho_s &= \frac{a^2 + b^2 - 2a \cos \phi + \cos^2 \phi}{a^2 + b^2 + 2a \cos \phi + \cos^2 \phi} \\ \rho_p &= \rho_s \left( \frac{a^2 + b^2 - 2a \sin \phi \tan \phi + \sin^2 \phi \tan^2 \phi}{a^2 + b^2 + 2a \sin \phi \tan \phi + \sin^2 \phi \tan^2 \phi} \right) \end{aligned} \right\} (1)$$

where

$$\left. \begin{aligned} a^2 &= \frac{1}{2} \left\{ \sqrt{[n^2(1 - \kappa^2) - \sin^2 \phi]^2 + 4n^4\kappa^2} + n^2(1 - \kappa^2) - \sin^2 \phi \right\} \\ b^2 &= \frac{1}{2} \left\{ \sqrt{[n^2(1 - \kappa^2) - \sin^2 \phi]^2 + 4n^4\kappa^2} - n^2(1 - \kappa^2) + \sin^2 \phi \right\} \end{aligned} \right\} (2)$$

Useful approximate expressions are +

$$\rho_p = \frac{(n - 1/\cos \phi)^2 + n^2\kappa^2}{(n + 1/\cos \phi)^2 + n^2\kappa^2} \quad (3)$$

$$\rho_s = \frac{(n - \cos \phi)^2 + n^2\kappa^2}{(n + \cos \phi)^2 + n^2\kappa^2} \quad (4)$$

At normal incidence, the exact expressions become

$$\rho = \frac{(n - 1)^2 + n^2\kappa^2}{(n + 1)^2 + n^2\kappa^2} = \frac{(n - 1)^2 + \kappa_0^2}{(n + 1)^2 + \kappa_0^2} \quad (5)$$

\* GEIGER, H. and SCHEEL, K. (eds.), *Handbuch der Physik*, Vol. 20, "Licht als Wellenbewegung," Julius Springer, Berlin, 1928, p. 242.

+ WIEN, W. and HARMS, F., *Handbuch der Experimentallphysik*, Vol. 18, "Wellenoptik und Polarisation," Akademische Verlagsgesellschaft, Leipzig, 1928, p. 164.

### 5.12. Phase changes and azimuth for metals

$$\tan \delta_s = -\frac{2b \cos \phi}{a^2 + b^2 - \cos^2 \phi} \quad (1)$$

where  $a^2$  and  $b^2$  are defined in § 5.11.

$$\tan \delta_p = \frac{2b \cos \phi (a^2 + b^2 - \sin^2 \phi)}{a^2 + b^2 - n^4(1 + \kappa^2)^2 \cos^2 \phi} \quad (2)$$

$$\tan \Delta = \frac{2b \sin \phi \tan \phi}{\sin^2 \phi \tan^2 \phi - a^2 - b^2} \quad (3)$$

where  $\Delta = \delta_p - \delta_s$ .

$$\tan \psi e^{i\Delta} = -\frac{E_p \cos(\phi + \phi')}{E_s \cos(\phi - \phi')} \quad (4)$$

### 5.13. Determination of the optical constants \*

$$\left. \begin{aligned} n^2 &= f^2 \tan^2 \phi \cos(\beta + \alpha) \cos(\beta - \alpha) \\ n^2 \kappa^2 &= f^2 \tan^2 \phi \sin(\beta + \alpha) \sin(\beta - \alpha) \\ \kappa^2 &= \tan(\beta + \alpha) \tan(\beta - \alpha) \end{aligned} \right\} (1)$$

where

$$\begin{aligned} \sin 2\alpha &= \frac{\sin 2\phi \sin \Delta \sin 2\psi}{1 - \cos 2\phi \cos \Delta \sin 2\psi} \\ \sin \beta &= \frac{\sin \phi \sin \Delta \sin 2\psi}{(1 - \cos 2\phi \cos \Delta \sin 2\psi)(1 - \cos \Delta \sin 2\psi)^{1/2}} \\ f^2 &= \frac{1 - \cos 2\phi \cos \Delta \sin 2\psi}{1 - \cos \Delta \sin 2\psi} \end{aligned}$$

Using the principal angle of incidence  $\bar{\phi}$  (for which  $\Delta = 90^\circ$ ) and the principal azimuth  $\bar{\psi}$ , these simplify to

$$\left. \begin{aligned} \sin 2\bar{\alpha} &= \sin 2\bar{\phi} \sin 2\bar{\psi} \\ \sin \bar{\beta} &= \sin \bar{\phi} \sin 2\bar{\psi} \\ f^2 &= 1 \end{aligned} \right\} (2)$$

The approximate equations used by Drude are

$$\left. \begin{aligned} \kappa &= \tan 2\bar{\psi} \\ n\sqrt{1 + \kappa^2} &= \sin \bar{\phi} \tan \bar{\phi} \end{aligned} \right\} (3)$$

\* GEIGER, H. and SCHEEL, K. (eds.), *Handbuch der Physik*, Vol. 20, "Licht als Wellenbewegung," Julius Springer, Berlin, 1928, p. 244.

## 6. Scattering and dispersion

### 6.1. Dipole scattering \*

$$E_s = \frac{8\pi N e^4}{3m^2 c^4 [(\nu_0/\nu)^2 - 1]^2} \quad (1)$$

where  $E_s$  = total light energy scattered per unit incident intensity;  $N$  = number of dipoles of charge  $e$ , mass  $m$ , natural frequency  $\nu_0$ .

### 6.2. Rayleigh scattering formula

$$E_s = \frac{8\pi N e^4 \nu^4}{3m^2 c^4 \nu_0^4}, \quad (\nu \ll \nu_0) \quad (1)$$

### 6.3. Thomson scattering formula

$$E_s = \frac{8\pi N e^4}{3m^2 c^4}, \quad (\nu \gg \nu_0) \quad (1)$$

**6.4. Scattering by dielectric spheres.** Case  $r \ll \lambda$  (Rayleigh scattering):

$$E_s = 24\pi^3 N \left( \frac{n^2 - 1}{n^2 + 2} \right)^2 \frac{V^2}{\lambda^4} \quad (1)$$

where  $n$  = refractive index of the spheres relative to the surrounding medium;  $V = \frac{4}{3}\pi r^3$ .

$$I_s = \frac{9\pi^2 N}{2D^2} \left( \frac{n^2 - 1}{n^2 + 2} \right)^2 \frac{V^2}{\lambda^4} (1 + \cos^2 \theta), \quad (\text{unpolarized incident light}) \quad (2)$$

where  $I_s$  = relative intensity scattered at angle  $\theta$  with incident beam;  $D$  = distance from scattering spheres to observer. +

The degree of polarization of scattered light is ×

$$P = \frac{\sin^2 \theta}{1 + \cos^2 \theta} \quad (3)$$

Case  $r \geq \lambda$ :

$$E_s = \frac{N\lambda^2}{2\pi} \sum_{k=1}^{\infty} \frac{a_k^2 + p_k^2}{2k + 1} \quad (4)$$

where  $a_k$  and  $p_k$  are complex functions of  $2\pi r/\lambda$ . □

\* VALASEK, J., *Theoretical and Experimental Optics*, John Wiley & Sons, Inc., New York, 1949, p. 332.

+ SINCLAIR, D., *J. Opt. Soc. Am.*, **37**, 476 (1947).

× BORN, M., *Optik*, Edwards Bros., Inc., Ann Arbor, Mich., 1943, p. 294.

□ MIE, G., *Ann. Physik*, **25**, 377 (1908).

### 6.5. Scattering by absorbing spheres \*

$$E_t = \frac{N\lambda^2}{2\pi} \operatorname{Re} \sum_{k=1}^{\infty} (-1)^k i (a_k + p_k) \quad (1)$$

where  $\operatorname{Re}$  = real part;  $E_t$  includes energy removed by both absorption and scattering.

### 6.6. Scattering and refractive index †

$$n - 1 = \frac{1}{2\pi} \sqrt{N} \lambda^2 \sqrt{E_s} \quad (1)$$

### 6.7. Refractivity ×

$$r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{\rho} \approx m_1 r_1 + m_2 r_2 + \dots + m_s r_s, \quad (\text{specific refractivity}) \quad (1)$$

where  $s$  = number of substances of specific refractivity  $r_i$ .

$$Mr = C_1 + \frac{C_2}{T}, \quad (\text{molecular refractivity}) \quad (2)$$

where  $C_1 = 4\pi N_0 \mu^2 / 9k$ ,  $\mu$  = dipole moment of molecule,  $k$  = Boltzmann constant,  $N_0$  = Avogadro number.

### 6.8. Dispersion of gases

$$\left. \begin{aligned} n^2(1 - \kappa^2) &= 1 + \sum_i \frac{\rho_i(v_i^2 - v^2)}{4\pi^2(v_i^2 - v^2)^2 + (v\gamma_i)^2} \\ &= 1 + \sum_i \frac{K_i \lambda^2 (\lambda^2 - \lambda_i^2)}{(\lambda^2 - \lambda_i^2)^2 + g_i \lambda^2} \end{aligned} \right\} \quad (1)$$

$$2n^2\kappa = \sum_i \frac{\rho_i v \gamma_i}{8\pi^2(v_i^2 - v^2)^2 + 2\pi(v\gamma_i)^2} = \frac{K_i \sqrt{g_i} \lambda^3}{(\lambda^2 - \lambda_i^2)^2 + g_i \lambda^2} \quad (2)$$

where  $\rho_i = 4\pi N_i e_i^2 / m_i$ ,  $K_i = N_i e_i^2 \lambda_i^2 / \pi m_i c^2$ ,  $\gamma_i$  = damping coefficient in  $E = E_0 e^{-\gamma_i t / 2} e^{2\pi i \nu_i t}$  and  $g_i = \lambda_i^4 \gamma_i^2 / 4\pi^2 c^2$ .

\* SINCLAIR, D., *op. cit.*, p. 476.

† JENKINS, F. A. and WHITE, H. E., *Fundamentals of Optics*, 2d ed., McGraw-Hill Book Company, Inc., New York, 1950, p. 459.

× VALASEK, J., *Theoretical and Experimental Optics*, John Wiley & Sons, Inc., New York, 1949, p. 234.

In the immediate neighborhood of an absorption frequency  $\nu_0$ ,\*

$$\left. \begin{aligned} n^2(1 - \kappa^2) &\approx n_0^2 + \frac{1}{2\nu_0} \cdot \frac{\rho_0(\nu_0 - \nu)}{(\nu_0 - \nu)^2 + (\gamma_0/4\pi)^2} \\ 2n^2\kappa &\approx \frac{\gamma_0}{8\pi\nu_0} \cdot \frac{\rho_0}{(\nu_0 - \nu)^2 + (\gamma_0/4\pi)^2} \end{aligned} \right\} \quad (3)$$

### 6.9. Dispersion of solids and liquids

$$n - 1 = C + \frac{C'}{\lambda^2}, \quad (\text{Cauchy's formula}) \quad (1)$$

$$n^2 - 1 = C_1 + \frac{C_2\lambda^2}{\lambda^2 - \lambda_0^2}, \quad (\text{Sellmeier's formula}) \quad (2)$$

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha = \frac{Ne^2}{3\pi m} \sum_i \frac{\rho_i}{\nu_i^2 - \nu^2} \quad (3)$$

in transparent regions, and where  $\alpha$  = polarizability ( $\mu = \alpha E$ ).<sup>+</sup>

### 6.10. Dispersion of metals $\times$

$$\left. \begin{aligned} n^2(1 - \kappa^2) &= 1 - \frac{4\pi\sigma}{g} \cdot \frac{1}{1 + 4\pi^2\nu^2/g^2} + \sum_i \frac{\rho_i(\nu_i^2 - \nu^2)}{4\pi^2(\nu_i^2 - \nu^2)^2 + (\nu\gamma_i)^2} \\ 2n^2\kappa &= \frac{2\sigma}{\nu} \cdot \frac{1}{1 + 4\pi^2\nu^2/g^2} + \sum_i \frac{\rho_i\nu\gamma_i}{8\pi^3(\nu_i^2 - \nu^2)^2 + 2\pi(\nu\gamma_i)^2} \end{aligned} \right\} \quad (1)$$

### 6.11. Quantum theory of dispersion $\square$

$$n^2 - 1 = 8\pi B \sum_{i, i'} \frac{\nu_{i, i'} P_{i, i'}^2}{h(\nu_{i, i'}^2 - \nu^2)} e^{-E_i^0/kT} \quad (1)$$

$$B = \frac{N}{\sum_i e^{-E_i^0/kT}} \quad (2)$$

\* BORN, M., *Optik*, Edwards Bros., Inc., Ann Arbor, Mich., 1943, p. 478.

<sup>+</sup> *Ibid.*, p. 503.

$\times$  SLATER, J. C. and FRANK, N. H., *Introduction to Theoretical Physics*, McGraw-Hill Book Company, Inc., 1933, p. 282.

$\square$  VAN VLECK, J. H., *Theory of Electric and Magnetic Susceptibilities*, Clarendon Press, Oxford, 1932, p. 361.

### 7. Crystal Optics

#### 7.1. Principal dielectric constants and refractive indices

$$\left. \begin{aligned} D_x &= \epsilon_x E_x, \quad D_y = \epsilon_y E_y, \quad D_z = \epsilon_z E_z, \quad (\epsilon_x < \epsilon_y < \epsilon_z) \\ n_a &= \frac{c}{v_a} = \sqrt{\epsilon_x}, \quad n_b = \frac{c}{v_b} = \sqrt{\epsilon_y}, \quad n_c = \frac{c}{v_c} = \sqrt{\epsilon_z} \end{aligned} \right\} \quad (1)$$

#### 7.2. Normal ellipsoid

$$\frac{x^2}{\epsilon_x} + \frac{y^2}{\epsilon_y} + \frac{z^2}{\epsilon_z} = 1 \quad (1)$$

Any plane section of the ellipsoid is an ellipse, and the two normal velocities of light traveling perpendicular to this section, for which the  $E$  vibrations are parallel to the major and minor axes of the ellipse, respectively, are inversely proportional to the length of these axes.

#### 7.3. Normal velocity surface

$$\frac{l^2}{v_n^2 - v_a^2} + \frac{m^2}{v_n^2 - v_b^2} + \frac{n^2}{v_n^2 - v_c^2} = 0 \quad (1)$$

where  $v_n$  = velocity along the wave normal,  $l, m, n$  = direction cosines of the wave normal.

#### 7.4. Ray velocity surface

$$\frac{v_a^2 p^2}{v_r^2 - v_a^2} + \frac{v_b^2 q^2}{v_r^2 - v_b^2} + \frac{v_c^2 r^2}{v_r^2 - v_c^2} = 0 \quad (1)$$

where  $v_r$  = velocity along the ray,  $p, q, r$  = direction cosines of the ray.

#### 7.5. Directions of the axes

$$\text{Optic axes : } l = \pm \sqrt{\frac{v_a^2 - v_b^2}{v_a^2 - v_c^2}}, \quad \text{Ray axes : } p = \pm \frac{v_c}{v_b} l \quad (1)$$

#### 7.6. Production and analysis of elliptically polarized light

$$\left. \begin{aligned} E'_e &= E \cos \theta, \quad I_e = E^2 \cos^2 \theta \\ E'_o &= E \sin \theta, \quad I_o = E^2 \sin^2 \theta \end{aligned} \right\} \text{(law of Malus)} \quad (1)$$

$$\delta = \frac{2\pi}{\lambda} t(n_e - n_o) \quad (2)$$

Quarter-wave plate

$$\delta = \frac{\pi}{2}, \quad t = \frac{\lambda}{4(n_e - n_o)} \quad (3)$$

Babinet compensator

$$\delta = \frac{2\pi}{\lambda} (t_1 - t_2) (n_e - n_o), \quad \tan \psi = \frac{E_p}{E_s} \quad (4)$$

is the ratio of the components of the ellipse parallel and perpendicular to the optic axis of one of the wedges. The angle  $\psi$  is measured when the analyzer is set for complete extinction at the minima.

**7.7. Interference of polarized light.** For a thin sheet of doubly refracting material between polarizer and analyzer, with its principal section at the angle  $\alpha$  with the plane of transmission of the polarizer,

$$I_{\perp} = E^2 \sin^2 2\alpha \sin^2 \frac{\delta}{2} \quad (\text{analyzer crossed}) \quad (1)$$

$$I_{\parallel} = E^2 \left( 1 - \sin^2 2\alpha \sin^2 \frac{\delta}{2} \right), \quad (\text{analyzer parallel}) \quad (2)$$

## 7.8. Rotation of the plane of polarization

Solutions

$$\xi = [\xi] C = [\xi] l p d \quad (1)$$

where  $[\xi]$  = specific rotation,  $C$  = concentration (g/cm<sup>3</sup>),  $p$  = per cent concentration (wt %),  $d$  = density.

Crystals

$$\xi = [\xi] l \quad (2)$$

Specific rotation \*

$$[\xi] = \frac{\pi}{\lambda} (n_r - n_l) = \frac{\pi G}{\lambda n^2} \quad (3)$$

where  $n_r$ ,  $n_l$  = refractive indexes for right- and left-handed circular components. Dispersion of the rotation †

$$[\xi] = \sum_i \frac{K_i}{\lambda^2 - \lambda_i^2}, \quad K_i = \frac{4\pi}{c} \frac{N_i g_i e_i^2 \lambda_i^2}{m_i} \quad (4)$$

## 8. Magneto-optics and Electro-optics

**8.1. Normal Zeeman effect.** For light linearly polarized parallel to the magnetic field,

$$\nu = \nu_0$$

\* BORN, M., *Optik*, Edwards Bros., Inc., Ann Arbor, Mich., 1943, p. 418.

† FÖRSTERLING, K., *Lehrbuch der Optik*, S. Hirzel, Leipzig, 1928, p. 198.

For light circularly polarized in the plane perpendicular to the magnetic field,

$$\left. \begin{aligned} \nu &= \nu_0 \pm \frac{eH}{4\pi mc} \\ \Delta\sigma &= \frac{\Delta\nu}{c} = 4.670 \times 10^{-5}H \end{aligned} \right\} (1)$$

where  $H$  is in oersteds.

**8.2. Anomalous Zeeman effect**

$$\nu = \nu_0 + (M'g' - M''g'') \frac{eH}{4\pi mc} \quad (1)$$

where  $M' = M''$  for light linearly polarized parallel to  $H$ , and  $M' = M'' \pm 1$  for light circularly polarized perpendicular to  $H$ .

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (\text{Landé } g \text{ formula})$$

**8.3. Quadratic Zeeman effect.** Due to the component of the magnetic moment perpendicular to  $J$ , \*

$$\left. \begin{aligned} \nu &= \nu_0 + (M'g' - M''g'') \frac{eH}{4\pi mc} + \frac{he^2H^2}{16\pi^2m^2c^2} \\ &\times \left\{ \frac{[f(J',M')]^2}{h\nu(J',J'+1)} + \frac{[f(J'-1,M')]^2}{h\nu(J',J'-1)} \right. \\ &\left. - \frac{[f(J'',M'')]^2}{h\nu(J'',J''+1)} - \frac{[f(J''-1,M'')]^2}{h\nu(J'',J''-1)} \right\} \end{aligned} \right\} (1)$$

Due to the diamagnetic term,

$$\nu = \nu_0 + \frac{e^2H^2a_0n^4}{8mc^2} \quad (2)$$

for light linearly polarized parallel to  $H$ .

$$\nu = \nu_0 \pm \frac{eH}{4\pi mc} + \frac{e^2H^2a_0n^4}{4mc^2} \quad (3)$$

for light circularly polarized perpendicular to  $H$ . +

\* VAN VLECK, J. H., *Theory of Electric and Magnetic Susceptibilities*, Clarendon Press, Oxford, 1932, p. 173.

+ VAN VLECK, J. H., *op. cit.*, p. 178.

#### 8.4. Faraday effect

$$\left. \begin{aligned} \xi &= \omega H l \\ \omega &= \frac{\pi(n_l - n_r)}{\lambda H}, \quad (\text{Verdet constant}) \\ \omega &= -\frac{e\lambda_0}{2mc^2} \cdot \frac{dn}{d\lambda}, \quad (\text{classical Becquerel formula}) \\ \omega &= \frac{\pi}{\lambda} \cdot \frac{n^2 + 2}{3n} N f \end{aligned} \right\} (1)$$

Here  $f = f_0 + (1/kT)f_1$ , where  $f_0$  and  $f_1$  are molecular constants.\*

#### 8.5. Cotton-Mouton effect +

$$\left. \begin{aligned} \delta &= \frac{n_o - n_e}{\lambda} l = C l H^2 \\ n_o - n_e &= H^2 N \frac{n^2 + 2}{6n} \left( 3b + f^2 N \frac{n^2 + 2}{3n^2} \right) \end{aligned} \right\} (1)$$

Here  $b = b_0 + (1/kT)b_1 + (1/k^2T^2)b_2$ , where  $b_0$ ,  $b_1$ , and  $b_2$  are molecular constants.

$$C = C_0 + \frac{1}{T} C_1 + \frac{1}{T^2} C_2, \quad (\text{Cotton-Mouton constant})$$

#### 8.6. Stark effect × For hydrogen and hydrogen-like orbits,

$$\sigma = \sigma_0 - \frac{3Eh}{8\pi^2 m Z e c} [n'(n'_\xi - n'_\eta) - n''(n''_\xi - n''_\eta)] \quad (1)$$

where  $n_\xi, n_\eta =$  parabolic quantum numbers.

For many-electron atoms

$$\sigma = \sigma_0 - C E^2 \quad (2)$$

#### 8.7. Kerr electro-optic effect □

$$\left. \begin{aligned} \delta &= 2\pi B l E^2 \\ B &= \frac{n_o - n_e}{\lambda E^2}, \quad (\text{Kerr constant}) \\ B &= N \frac{n^2 + 2}{6n} \left( \frac{\epsilon + 2}{3} \right)^2 \frac{3b}{\lambda} \end{aligned} \right\} (1)$$

\* BORN, M., *Optik*, Edwards Bros., Inc., Ann Arbor, Mich., 1943, p. 356.

+ BORN, M., *Optik*, Edwards Bros., Inc., Ann Arbor, Mich., 1943, p. 362.

× RUARK, A. E., and UREY, H. C., *Atoms, Molecules, and Quanta*, McGraw-Hill Book Company, Inc., 1930, p. 153.

□ BORN, M., *op. cit.*, p. 367.

## 9. Optics of Moving Bodies

### 9.1. Doppler effect

$$\nu' = \nu \frac{\sqrt{1 - v^2/c^2}}{1 - (v/c) \cos \theta} \quad (1)$$

where  $\theta$  = angle between direction of observation and direction of motion.  
Reflection from a moving mirror

$$\nu' = \nu \frac{1 + (v/c) \cos \phi}{1 - (v/c) \cos \phi} \quad (2)$$

### 9.2. Astronomical aberration

$$\sin \zeta = \frac{|v|}{c} \quad (1)$$

### 9.3. Fresnel dragging coefficient

$$v = \frac{c}{n} \pm v' \left( \frac{n^2 - 1}{n^2} - \frac{\lambda}{n} \cdot \frac{dn}{d\lambda} \right) \quad (1)$$

where  $v$  = observed wave velocity of light,  $v'$  = velocity of medium,  
 $\lambda$  = wavelength in vacuum.

### 9.4. Michelson-Morley experiment

$$\delta = \frac{2\pi l}{\lambda} \cdot \frac{v^2}{c^2} \quad (1)$$

This is doubled when the interferometer is turned through  $90^\circ$ .

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## Chapter 18

### ELECTRON OPTICS

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Although electron optics has certain features peculiar to itself, largely because its "lenses" and "prisms" are built to control the passage of electrons rather than light waves, a large part of the subject has close analogy to the field of light optics. In certain aspects, geometrical or ray optics are useful; in others only the application of the electron equivalent of physical optics will suffice to explain the phenomena.

The formulas here given are those that will prove most useful for description of the focusing properties and path deflections of practical electron optical systems, such as electron guns, electron microscopes, image tubes, and deflection fields. Formulas for the field distributions, focal lengths, and aberrations of characteristic electrode configurations and lenses supplement the more general formulas of electron optics. The personal experience of the author has been the primary guide for the selection—an experience gained from the computation of a wide variety of electron-optical systems, particularly in the fields of electron microscopy and television.

#### Symbols Employed in Formulas

- $A$  magnetic vector potential
- $A_z, A_r, A_\theta$  components of magnetic vector potential in polar coordinates
- $a = e/(2m_0c^2)$ , relativistic correction constant
- $b = -r'/r + 1/(2z)$  [Eq. (5.6)]
- $b_z, b_r$  components of magnetic induction
- $B$  magnetic induction along axis or in plane of symmetry
- $c$  velocity of light
- $c = -r'/r$ , "convergence" [Eq. (5.5)]
- $C$  integration constant of electron path ( $\sqrt{2em_0} C =$  angular momentum in zero magnetic field)

- $C_1, C_2, C_3$  coefficients of chromatic aberration [Eq. (10.2)]  
 $d$  "half-width" of refractive field; separation of electrodes  
 $e$  Napierian base 2.718...  
 $-e$  charge of the electron  
 $E$  electric field  
 $f, f_o, f_i$  focal length (object-side, image-side) of complete lens field  
 $f_n, f_{on}, f_{in}$  focal length (object-side, image-side) of lens field terminated by  $n$ th focal point  
 $h_o, h_i$  distance of (object-side, image-side) principal plane from plane of symmetry of electron lens  
 $i$   $\sqrt{-1}$   
 $I$  electric current  
 $i$  (*subscript*) referring to the image plane  
 $k$  Boltzmann constant [Eq. (1.4)]  
 $k$   $\sqrt{\frac{e}{8m\Phi}} B_{\max} d, \sqrt{\frac{3}{16} \left(\frac{\Phi'}{\Phi}\right)_{\max}} d$  = lens strength parameter of magnetic and electrostatic lenses, respectively  
 $l$  length of field  
 $m$  mass of the electron  
 $m_o$  rest mass of the electron  
 $M$  magnification  
 $n$  integer, 1, 2, 3, ...  
 $n$  index of refraction [Eqs. (1.1) and (1.2)]  
 $N$  magnetic flux  
 $o$  (*subscript*) referring to object plane or starting point  
 $r$  distance of electron from axis of symmetry  
 $r_a, r_i, r_o$  distance from axis in "aperture plane," image plane, object plane  
 $r_\alpha(z), r_\gamma(z)$  solutions of paraxial ray equation with initial conditions  
 $r_\alpha(z_o) = 0, \quad r_\alpha'(z_o) = 1; \quad r_\gamma(z_o) = 1, \quad r_\gamma(z_a) = 0$   
 $r_{\alpha a} \quad r_\alpha(z_a)$   
 $R$  radius of curvature  
 $R = r\Phi^{1/4}$  [Eq. (5.4)]  
 $S_1 \dots S_8$  coefficients of geometric aberration  
 $t$  time  
 $T$  absolute temperature  
 $u$  object distance (from object-side principal plane to object plane)

- $v$  image distance (from image-side principal plane to image plane)  
 $v$  velocity of electron [Eq. (1.2)]  
 $w = x + iy = re^{i\theta}$   
 $w_a, w_i, w_o' = x_a + iy_a, x_i + iy_i, (x_o + iy_o)e^{ix_i} =$  coordinates in aperture, image, and object plane, the last referred to rotated frame of reference  
 $x$  coordinate parallel to axis of symmetry in two-dimensional fields  
 $x, y, z$  rectangular coordinates  
 $Y = y\Phi^{1/4}$   
 $z$  coordinate parallel to axis in axially symmetric field  
 $z_n$  distance of  $n$ th (real) focal point from plane of symmetry  
 $z_f$  distance of (generally virtual) focal point of complete field from plane of symmetry  
 $\alpha$  aperture angle; inclination with respect to axis  
 $\delta$  variation  
 $\Delta r_i, \Delta\Phi, \dots$  increment of  $r_i, \Phi, \dots$   
 $\theta$  azimuthal angle of electron  
 $\mu$  permeability  
 $\pi$  3.1416...  
 $\chi$  angle between electron path and magnetic vector potential [Eq. (1.2)]  
 $\chi = \int_{z_0}^z \sqrt{\frac{e}{8m\Phi}} B dz$   
 $\varphi$  electric potential, so normalized that  $e\varphi$  is kinetic energy of electron in question  
 $\varphi^* = \varphi + a\varphi^2 =$  "effective" electric potential  
 $\varphi^{**}$  "equivalent potential" in presence of magnetic field [Eq. (4.1)]  
 $\Phi$  electric potential along axis of symmetry  
 $\Phi^* = \Phi + a\Phi^2 =$  "effective" axial electric potential

*Superscripts :*

- $r'$  first derivative of  $r$  with respect to  $z$  or  $x$  (coordinate parallel to axis of symmetry)  
 $r''$  second derivative of  $r$  with respect to  $z$  or  $x$   
 $r^{(n)}$   $n$ th derivative of  $r$  with respect to  $z$  or  $x$   
 $\dot{r}$  first derivative of  $r$  with respect to  $t$   
 $\ddot{r}$  second derivative of  $r$  with respect to  $t$   
 $\bar{w}$  complex conjugate of  $w$

## 1. General Laws of Electron Optics

### 1.1. Fermat's principle for electron optics

$$\delta \int_{P_1}^{P_2} n ds = 0 \quad (1)$$

for the path of an electron between the terminal points  $P_1$  and  $P_2$ , where  $ds$  is an element of path and  $n$  is the refractive index for the electron.

### 1.2. Index of refraction of electron optics \*

$$n = \frac{mv}{m_0c} - \frac{eA}{m_0c} \cos \chi = \sqrt{\frac{2e\varphi^*}{m_0c^2}} - \frac{eA}{m_0c} \cos \chi \quad (1)$$

where  $\chi$  is the angle between the path of the electron and the magnetic vector potential  $A$ .

### 1.3. Law of Helmholtz-Lagrange for axially symmetric fields

$$\sqrt{\Phi_o} r_o \alpha_o = \sqrt{\Phi_i} r_i \alpha_i \quad (1)$$

where  $\alpha_o, \alpha_i$  are the apertures of the imaging pencils, which are assumed to be small, and  $r_i/r_o$  is the magnification.

### 1.4. Upper limit to the current density $j$ in a beam cross section at potential $\Phi$ and with aperture angle $\alpha$ †

$$\frac{j}{j_o} = \left( \frac{e\Phi}{kT} + 1 \right) \sin^2 \alpha \quad (1)$$

where  $j_o$  is the current density at the emitting cathode,  $T$  is the cathode temperature, and  $k$  is Boltzmann's constant.  $\Phi$  is measured with respect to the cathode.

### 1.5. General lens equation

$$\frac{f_i}{v} - \frac{f_o}{u} = 1; \quad \frac{f_i}{f_o} = \sqrt{\frac{\Phi_i}{\Phi_o}}; \quad \sqrt{\frac{\Phi_o}{\Phi_i}} \frac{v}{u} = M \quad (1)$$

\* GLASER, W., "Geometric-Optical Imaging by Electron Rays," *Z. Physik*, **80**, 451-464 (1933). PICT, J., *Einführung in die Theorie der Elektronenoptik*, J. A. Barth, Leipzig, 1939.

† LANGMUIR, D. B., "Limitations of Cathode-Ray Tubes," *Proc. IRE*, **25**, 977-991 (1937).

## 2. Axially Symmetric Fields

### 2.1. Differential equations of the axially symmetric field in free space

$$\frac{\partial^2 \varphi}{\partial z^2} + \frac{1}{r} \cdot \frac{\partial}{\partial r} \left( r \frac{\partial \varphi}{\partial r} \right) = 0; \quad \frac{\partial b_z}{\partial z} + \frac{1}{r} \cdot \frac{\partial}{\partial r} (r b_r) = 0 \quad (1)$$

### 2.2. Potential distribution in axially symmetric electric field

$$\varphi(z, r) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(n!)^2} \Phi^{(2n)}(z) \left( \frac{r}{2} \right)^{2n} = \Phi - \frac{1}{4} \Phi'' r^2 + \frac{1}{64} \Phi^{IV} r^4 - \dots \quad (1)$$

### 2.3. Behavior of equipotential surfaces on axis

Radius of curvature :

$$R = \frac{2\Phi'}{\Phi''} \quad (1)$$

Vertex half-angle of equipotential cone at saddle point :

$$\alpha_s = \arctan \sqrt{2} = 54^\circ 44' \quad (2)$$

### 2.4. Magnetic vector potential in axially symmetric field

$$A = A_\theta(z, r) = \frac{N}{2\pi r} \quad (1)$$

where  $N$  is the magnetic flux through a circle of radius  $r$  in the azimuthal plane defined by  $z$ .

### 2.5. Field distribution in axially symmetric magnetic field

$$\left. \begin{aligned} b_z(r, z) &= \frac{1}{r} \cdot \frac{\partial(rA_\theta)}{\partial r} = \sum_{n=0}^{\infty} \frac{(-1)^n}{(n!)^2} B^{(2n)}(z) \left( \frac{r}{2} \right)^{2n} \\ &= B(z) - \frac{1}{4} B''(z) r^2 + \dots \\ b_r(r, z) &= -\frac{\partial A_\theta}{\partial z} = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!(n-1)!} B^{(2n-1)} \left( \frac{r}{2} \right)^{2n-1} \\ &= -\frac{1}{2} B'(z) r + \frac{1}{16} B^{III}(z) r^3 - \dots \end{aligned} \right\} \quad (1)$$

### 3. Specific Axially Symmetric Fields

**3.1. Electric field.** For a field of aperture of radius  $R$  and potential  $\Phi_A$  located at  $z = 0$ , separating fields  $-\Phi'(-\infty) = E_0$  and  $-\Phi'(\infty) = E_i$ ,

$$\Phi(z) = \Phi_A - \frac{E_0 + E_i}{2} z + \frac{R}{\pi} (E_0 - E_i) \left( \frac{z}{R} \arctan \frac{z}{R} + 1 \right) \quad (1)$$

**3.2. Electric field.** For a field between two coaxial cylinders of equal radius  $R$  at potentials  $\Phi_o(z < 0)$  and  $\Phi_i(z > 0)$ ,

$$\left. \begin{aligned} \Phi(z) &= \frac{\Phi_i + \Phi_o}{2} + \frac{\Phi_i - \Phi_o}{\pi} \int_0^\infty \frac{\sin(kz)}{J_0(ikR)} \cdot \frac{dk}{k} * \\ &\cong \frac{\Phi_i + \Phi_o}{2} + \frac{\Phi_i - \Phi_o}{2} \tanh \left( \frac{1.315z}{R} \right) + \end{aligned} \right\} \quad (1)$$

**3.3. Magnetic field.** For a field of single wire loop of radius  $R$  at  $z = 0$ ,

$$B(z) = \frac{2\pi\mu IR^2}{(z^2 + R^2)^{3/2}} \quad (1)$$

**3.4. Magnetic field.** For a coil with  $nI$  ampere turns enclosed by infinitely permeable shell with narrow circular gap, and radius of inner surface of magnetic material  $R$ ,

$$B(z) \cong 2\pi\mu nI \cdot \frac{1.315}{R} \operatorname{sech}^2 \left( \frac{1.315z}{R} \right) \quad (1)$$

## 4. Path Equation in Axially Symmetric Field

### 4.1. General path equation in axially symmetric field

$$r'' = \frac{1 + r'^2}{2\varphi^{**}} \left( \frac{\partial\varphi^{**}}{\partial r} - r' \frac{\partial\varphi^{**}}{\partial z} \right) \quad (1)$$

with 
$$\varphi^{**} = \varphi^* - \left( \frac{C}{r} + \sqrt{\frac{e}{2m_0}} A \right)^2$$

and 
$$C = \frac{r^2\theta'\sqrt{\varphi^*}}{\sqrt{r'^2 + r^2\theta'^2 + 1}} - \sqrt{\frac{e}{2m_0}} rA_\theta, \quad (\text{constant of integration})$$

Here  $\sqrt{2em_0} C$  is the angular momentum of the electron about the axis

\* MORTON, G. A. and RAMBERG, E. G., "Electron Optics of an Image Tube," *Physics*, **7**, 451-459 (1936).

+ BERTRAM, S., "Determination of the Axial Potential Distribution in Axially Symmetric Electrostatic Fields," *Proc. IRE*, **13**, 496-502 (1942). GRAY, F., "Electrostatic Electron Optics," *Bell System Tech. J.*, **18**, 1-31 (1939).

for zero magnetic field ( $A_\theta = 0$ ). The azimuth of the electron is given by

$$\theta = \theta_0 + \int_{z_0}^z \frac{\frac{C}{r} + \sqrt{\frac{e}{2m_0}} A_\theta}{\sqrt{\varphi^* - \left(\frac{C}{r} + \sqrt{\frac{e}{2m_0}} A_\theta\right)^2}} \frac{\sqrt{1+r'^2}}{r} dz \quad (2)$$

**5. Paraxial Path Equations** (for  $e\Phi \ll m_0c^2$ )

(See § 5.7 for arbitrary electron energies.)

**5.1. General paraxial path equation**

$$r'' = -r' \frac{\Phi'}{2\Phi} - r \left( \frac{\Phi''}{4\Phi} + \frac{eB^2}{8m_0\Phi} - \frac{C^2}{\Phi r^4} \right) \quad (1)$$

with 
$$C = r^2 \left( \sqrt{\Phi} \theta' - \sqrt{\frac{e}{8m_0}} B \right)$$

**5.2. Azimuth of electron**

$$\theta = \theta_0 + \int_{z_0}^z \left( \frac{C}{r^2 \sqrt{\Phi}} + \sqrt{\frac{e}{8m_0\Phi}} B \right) dz \quad (1)$$

**5.3. Paraxial path equation for path crossing axis ( $C = 0$ )**

$$\left. \begin{aligned} r'' &= -r' \frac{\Phi'}{2\Phi} - r \left( \frac{\Phi''}{4\Phi} + \frac{eB^2}{8m_0\Phi} \right) \\ \theta &= \theta_0 + \chi = \theta_0 + \int_{z_0}^z \sqrt{\frac{e}{8m_0\Phi}} B dz \end{aligned} \right\} \quad (1)$$

**5.4. Paraxial ray equation for variable  $R = r\Phi^{1/4}$  (for  $C = 0$ ) \***

$$-R'' = R \left[ \frac{3}{16} \left( \frac{\Phi'}{\Phi} \right)^2 + \frac{eB^2}{8m_0\Phi} \right] \quad (1)$$

**5.5. Paraxial ray equation in electric field for variable  $c = -r'/r$  ( $C = 0$ )**

$$c' = c^2 - \frac{\Phi'}{2\Phi} c + \frac{\Phi''}{4\Phi} \quad (1)$$

with 
$$r = r_0 e^{-\int_{z_0}^z c dz}$$

\* PICTH, J., "Contributions to the Theory of Geometric Electron Optics," *Ann. Physik*, 15, 926-964 (1932).

**5.6. Paraxial ray equation in electric field for variable  $b = -r'/r + 1/(2z)$  (finite at surface of flat cathode) ( $C = 0$ )\***

$$b' = b^2 - b \left( \frac{1}{z} + \frac{\Phi'}{2\Phi} \right) + \frac{\Phi''}{4\Phi} + \frac{1}{2z} \left( \frac{\Phi'}{2\Phi} - \frac{1}{2z} \right) \quad (1)$$

with 
$$r = r_0 \sqrt{\frac{z}{z_0}} e^{-\int_{z_0}^z b \, dz}$$

**5.7. Paraxial ray equation in electric field for arbitrarily high voltage +**

$$\left. \begin{aligned} r'' &= -r' \frac{\Phi'}{2\Phi} \frac{1 + 2a\Phi}{1 + a\Phi} \\ &- r \left( \frac{\Phi''}{4\Phi} \frac{1 + 2a\Phi}{1 + a\Phi} + \frac{eB^2}{8m_0(1 + a\Phi)\Phi} - \frac{C^2}{r^4(1 + a\Phi)\Phi} \right) \end{aligned} \right\} \quad (1)$$

with 
$$C = r^2 \left( \theta' \sqrt{\Phi + a\Phi^2} - \sqrt{\frac{e}{8m_0} B} \right)$$

## 6. Electron Paths in Uniform Fields ( $e\Phi \ll m_0c^2$ )

**6.1. Path in uniform electrostatic field  $-\Phi'$  parallel to  $z$  axis.**

For electron with initial energy  $e\Phi_0$  making an initial angle  $\alpha_0$  with  $z$  axis in  $yz$  plane,

$$y - y_0 = \frac{\Phi_0}{\Phi'} \left[ -\sin 2\alpha_0 \pm 2 \sin \alpha_0 \sqrt{\cos^2 \alpha_0 + \frac{\Phi'}{\Phi_0} (z - z_0)} \right] \quad (1)$$

**6.2. Path in uniform magnetic field.** For  $B = B_z$  with initial energy  $e\Phi_0$ , initial angle  $\alpha_0$  with respect to  $z$  axis, and azimuth  $\theta_0$  with respect to  $x$  axis,

$$\left. \begin{aligned} x - x_0 &= R \left[ \sin \left( \frac{z - z_0}{R} \tan \alpha_0 + \theta_0 \right) - \sin \theta_0 \right] \\ y - y_0 &= -R \left[ \cos \left( \frac{z - z_0}{R} \tan \alpha_0 + \theta_0 \right) - \cos \theta_0 \right] \\ R &= \frac{1}{B} \sqrt{\frac{2m_0\Phi_0}{e}} \sin \alpha_0, \quad \frac{z - z_0}{R} \tan \alpha_0 = \frac{eB}{m_0} (t - t_0) \end{aligned} \right\} \quad (1)$$

\* MORTON, G. A. and RAMBERG, E. G., "Electron Optics of an Image Tube," *Physics*, **7**, 451-459 (1936).

+ RAMBERG, E. G., "Variation of Axial Aberrations of Electron Lenses with Lens Strength," *J. Appl. Phys.*, **13**, 582-594 (1942).

**6.3. Path in crossed electric and magnetic field,  $-\Phi' = E_y, B = B_z$**

$$\left. \begin{aligned}
 x - x_0 = -\frac{\Phi'}{B} t - \frac{m_0}{eB} \dot{y}_0 + \frac{m_0}{eB} \sqrt{\left(\dot{x}_0 + \frac{\Phi'}{B}\right)^2 + \dot{y}_0^2} \\
 \times \sin\left(\frac{eB}{m_0} t + \arctan \frac{\dot{y}_0}{\Phi'/B + \dot{x}_0}\right)
 \end{aligned} \right\} (1)$$

$$\left. \begin{aligned}
 y - y_0 = \frac{m_0}{eB} \left(\frac{\Phi'}{B} + \dot{x}_0\right) - \frac{m_0}{eB} \sqrt{\left(\dot{x}_0 + \frac{\Phi'}{B}\right)^2 + \dot{y}_0^2} \\
 \times \cos\left(\frac{eB}{m_0} t + \arctan \frac{\dot{y}_0}{\Phi'/B + \dot{x}_0}\right)
 \end{aligned} \right\} (2)$$

$$z - z_0 = \dot{z}_0 t$$

where  $\dot{x}_0, \dot{y}_0, \dot{z}_0$  are components of initial velocity.

**7. Focal Lengths of Weak Lenses \* ( $e\Phi \ll m_0 c^2$ )**

**7.1. General formula for focal length of a weak lens**

$$\frac{1}{f_o} = \sqrt{\frac{\Phi_i}{\Phi_o}} \int_{z_o}^{z_i} \left[ \frac{3}{16} \left(\frac{\Phi'}{\Phi}\right)^2 + \frac{eB^2}{8m_0\Phi} \right] dz, \quad f_i = \sqrt{\frac{\Phi_i}{\Phi_o}} f_o \quad (1)$$

**7.2. Focal length of aperture lens (§ 3.1)**

$$\frac{1}{f_o} = \frac{E_o - E_i}{4\Phi_A} \quad (1)$$

**7.3. Focal length of electric field between coaxial cylinders (§ 3.2)**

$$\frac{1}{f_o} = \frac{1}{4} \sqrt{\frac{\Phi_i}{\Phi_o}} \frac{(\Phi_i - \Phi_o)^2}{(\Phi_i + \Phi_o)} \frac{1.315}{R} \quad (1)$$

**7.4. Focal length of magnetic field of single wire loop (§ 3.3)**

$$\frac{1}{f} = \frac{3\pi^3}{16} \frac{e\mu^2}{m_0} \frac{I^2}{R} \frac{1}{\Phi} \quad (1)$$

\* REBSCH, R. and SCHNEIDER, W., "Aperture Defect of Weak Electron Lenses," *Z. Physik*, **107**, 138-143 (1937).

### 7.5. Focal length of magnetic gap lens (§ 3.4)

$$\frac{1}{f} = \frac{2\pi^2}{3} \frac{e\mu^2}{m_o} \frac{n^2 I^2 \cdot 1.315}{R\Phi} \quad (1)$$

### 7.6. Focal length of lens consisting of two apertures at potential $\Phi_o$ and $\Phi_i$ , separated by a distance $d$ (radius of apertures $\ll d$ ) \*

$$\frac{1}{f_o} = \frac{3}{8d} \left(1 - \sqrt{\frac{\Phi_o}{\Phi_i}}\right) \left(\frac{\Phi_i}{\Phi_o} - 1\right) \quad \frac{1}{f_i} = \frac{3}{8d} \left(\sqrt{\frac{\Phi_i}{\Phi_o}} - 1\right) \left(1 - \frac{\Phi_o}{\Phi_i}\right) \quad (1)$$

The position of the principal planes relative to the plane of symmetry is given by

$$h_o = -\frac{d}{2} - \frac{4d\Phi_o}{3(\Phi_i - \Phi_o)} \quad h_i = \frac{d}{2} - \frac{4d\Phi_i}{3(\Phi_i - \Phi_o)} \quad (2)$$

## 8. Cardinal Points of Strong Lenses ( $e\Phi \ll m_o c^2$ )

**8.1. Strong lens.** Let  $r_\beta(z)$  represent a path incident parallel to the axis from  $-\infty$ , and let  $r_\delta(z)$  represent one incident parallel to the axis from  $+\infty$ . Then the positions of the focal points relative to the plane of symmetry of the lens field and the focal lengths are given by the following expressions :

$z_{in}$  =  $n$ th image-side focal point [ $n$ th point for which  $r_\beta(z) = 0$ , counted from the side of incidence]

$z_{on}$  =  $n$ th object-side focal point [ $n$ th point for which  $r_\delta(z) = 0$ ]

$f_{in} = -r_\beta(-\infty)/r'_\beta(z_{in})$  = focal length corresponding to  $n$ th image-side focal point

$f_{on} = r_\delta(\infty)/r'_\delta(z_{on})$  = focal length corresponding to  $n$ th object-side focal point

$z_{if} = (z - r_\beta/r'_\beta)_{z \rightarrow \infty}$  = image-side focal point of complete field

$z_{of} = (z - r_\delta/r'_\delta)_{z \rightarrow -\infty}$  = object-side focal point of complete field

$f_i = -r_\beta(-\infty)/r'_\beta(\infty)$  = image-side focal length of complete field

$f_o = r_\delta(\infty)/r'_\delta(-\infty)$  = object-side focal length of complete field

For a symmetrical magnetic or (generally) equipotential lens

$$z_n = z_{in} = -z_{on}, \quad f_n = f_{in} = f_{on}, \quad z_f = z_{if} = -z_{of}, \quad f = f_i = f_o$$

\* GANS, R., "Electron Paths in Electron-Optical Systems," *Z. tech. Physik*, **18**, 41-48 (1937).

**8.2. Uniform magnetic field, cut off sharply at  $z = \pm d$  \***

$$B = B_m, \quad |z| < d; \quad B = 0, \quad |z| > d; \quad k^2 = \frac{eB_m^2}{8m_0\Phi} d^2$$

$$\left. \begin{aligned} z_n &= d \left[ \frac{\pi}{2k} (2n-1) - 1 \right] \\ \frac{1}{f_n} &= (-1)^{n-1} \frac{k}{d} \end{aligned} \right\} [k \geq (\pi/4) (2n-1)] \quad (1)$$

$$z_f = d \left( 1 + \frac{\cot 2k}{k} \right), \quad \frac{1}{f} = \frac{k}{d} \sin 2k$$

**8.3. "Bell-shaped" magnetic field. +**

with 
$$B = \frac{B_m}{1 + (z/d)^2}, \quad k^2 = \frac{eB_m^2}{8m_0\Phi} d^2,$$

$$z_n = -d \cot \frac{n\pi}{\sqrt{k^2 + 1}}, \quad (k \geq \sqrt{n^2 - 1}) \quad (1)$$

$$\frac{1}{f_n} = \frac{(-1)^{n-1}}{d} \sin \frac{n\pi}{\sqrt{k^2 + 1}}$$

$$z_f = d\sqrt{k^2 + 1} \cot \pi\sqrt{k^2 + 1}$$

$$\frac{1}{f} = -\frac{1}{d\sqrt{k^2 + 1}} \sin \pi\sqrt{k^2 + 1}$$

**8.4. Electric field  $\Phi = \Phi_m e^{(4/\sqrt{3})k \arctan z/d}$  ×**

$$\left. \begin{aligned} z_{in} &= -z_{on} = -d \cot \frac{n\pi}{\sqrt{k^2 + 1}} \\ \frac{1}{f_{in}} &= \frac{(-1)^{n-1}}{d} e^{-(k/\sqrt{3})(n\pi/\sqrt{k^2+1})} \sin \frac{n\pi}{\sqrt{k^2 + 1}} \\ \frac{1}{f_{on}} &= \frac{(-1)^{n-1}}{d} e^{(k/\sqrt{3})(n\pi/\sqrt{k^2+1})} \sin \frac{n\pi}{\sqrt{k^2 + 1}} \end{aligned} \right\} (k \geq \sqrt{n^2 - 1}) \quad (1)$$

\* LENZ, F., "Computation of Optical Parameters of Magnetic Lenses of Generalized Bell-Type," *Z. angew. Physik*, **2**, 337-340 (1950).

+ GLASER, W., "Exact Calculation of Magnetic Lenses with the Field Distribution  $H = H_0/[1 + (z/a)^2]$ ," *Z. Physik*, **117**, 285-315 (1941).

× HUTTER, R. G. E., "Rigorous Treatment of the Electrostatic Immersion Lens Whose Axial Potential Distribution is Given by  $\Phi(z) = \Phi_0 e^{K \arctan z}$ ," *J. Appl. Phys.*, **16**, 678-699 (1945).

$$z_{if} = -z_{of} = d\sqrt{k^2 + 1} \cot \pi\sqrt{k^2 + 1}$$

$$\frac{1}{f_i} = -\frac{e^{-\pi k/\sqrt{3}}}{d\sqrt{k^2 + 1}} \sin \pi\sqrt{k^2 + 1}, \quad \frac{1}{f_o} = -\frac{e^{\pi k/\sqrt{3}}}{d\sqrt{k^2 + 1}} \sin \pi\sqrt{k^2 + 1}$$

**9. Electron Mirrors \* ( $e\Phi \ll m_o c^2$ )**

**9.1. Paraxial ray equations**

$$\dot{z} = \pm \sqrt{\frac{2e\Phi}{m_o}}, \quad \dot{r} = -\frac{e\Phi''}{2m_o} r \tag{1}$$

**9.2. Displacement of electron.** For electron leaving point  $z_o, r_o$  with inclination  $\alpha_o$  to axis after reflection by uniform retarding field  $-\Phi' = \Phi_o/d$ ,

$$r(z_o) = 2d \sin 2\alpha_o \tag{1}$$

**9.3. Approximate formula for focal length of an electron mirror**

$$\frac{1}{f} = \frac{1}{2\sqrt{\Phi_o}} \int_{z_u}^{\infty} \frac{\Phi''}{\sqrt{\Phi}} dz - \frac{1}{8\sqrt{\Phi_o}} \int_{z_u}^{\infty} \frac{\Phi''}{\sqrt{\Phi}} dz \cdot \int_{z_u}^{\infty} \frac{dz}{\sqrt{\Phi}} \int_z^{\infty} \frac{\Phi''}{\sqrt{\Phi}} dz \tag{1}$$

Here  $z_u$  is determined by the condition  $\Phi(z_u) = 0$ .

**10. Aberrations ( $e\Phi \ll m_o c^2$ )**

**10.1. Geometric aberrations of the third order +**

$$\Delta w_i = (S_1 + iS_2)(w_o')^2 \bar{w}_o' + S_3 w_o' \bar{w}_o' w_a + (S_4 + iS_5) (w_o')^2 \bar{w}_a \left. \begin{array}{l} \\ \\ \end{array} \right\} \tag{1}$$

$$+ (S_6 - iS_7) \bar{w}_o' w_a^2 + 2(S_6 + iS_7) w_o' w_a \bar{w}_a + S_8 \bar{w}_a w_a^2$$

Here  $w_i = r_i e^{i\theta_i}$ ,  $w_a = r_a e^{i\theta_a}$ ,  $w_o' = r_o e^{i(\theta_o + \chi)}$  represent the coordinates of a particular electron path in the image, aperture, and object planes, respectively. The image plane is the paraxial (Gaussian) image plane, the aperture plane is any (eventually also virtual) plane parallel to the image plane, such that the space between aperture plane and image plane is field-free;  $\Delta w_i$  is the deviation of the actual intersection of the electron path with the image plane from that calculated by the paraxial ray equations,

\* PICTH, J., *Einführung in die Theorie der Elektronenoptik*, J. A. Barth, Leipzig, 1939. RECKNAGEL, A., "The Theory of the Electron Mirror," *Z. Physik*, **104**, 381-394 (1937).

+ GLASER, W., "Theory of the Electron Microscope," *Z. Physik*, **83**, 103-122 (1933).

retaining terms of the third order in the radial coordinates. The several aberration coefficients are correlated with individual aberrations as follows :  $S_1$ , distortion ;  $S_2$ , anisotropic distortion ;  $S_3$ , curvature of field ;  $S_4$ , astigmatism ;  $S_5$ , anisotropic astigmatism ;  $S_6$ , coma ;  $S_7$ , anisotropic coma ;  $S_8$ , aperture defect or spherical aberration.

**10.2. Chromatic aberrations \***

$$\Delta w_i = (C_1 + iC_2)w_o' + C_3w_a \tag{1}$$

$$C_1 = -\frac{M\Delta\Phi}{\sqrt{\Phi_o}} \int_{z_o}^{z_i} \left[ \frac{\Phi'}{2\Phi^{3/2}} r_\alpha r_\gamma' + \left( \frac{\Phi''}{4\Phi^{3/2}} + \frac{eB^2}{8m_o\Phi^{3/2}} \right) r_\alpha r_\gamma \right] dz$$

$$C_2 = -\frac{M\Delta\Phi}{2} \int_{z_o}^{z_i} \sqrt{\frac{e}{8m_o\Phi^3}} B dz$$

$$C_3 = -\frac{M\Delta\Phi}{r_{\alpha a} \sqrt{\Phi_o}} \int_{z_o}^{z_i} \left[ \frac{3}{8} \frac{(\Phi')^2}{\Phi^{5/2}} + \frac{eB^2}{8m_o\Phi^{3/2}} \right] r_\alpha^2 dz$$

Here  $C_1$  is the coefficient of chromatic difference in magnification,  $C_2$  is that of chromatic difference in rotation, and  $C_3$  is that of chromatic difference in image position ;  $\Delta w_i$  denotes the shift in the intersection of a particular electron ray with the (fixed) Gaussian image plane if the energy of the electron is increased by  $e\Delta\Phi$  without changing its position or direction of motion at the object plane.

**10.3. General formula for aperture defect +**

$$S_8 = \frac{M}{16r_{\alpha a}^3 \sqrt{\Phi_o}} \int_{z_o}^{z_i} \Phi^{-3/2} r_\alpha^4 \left[ U + 4V \frac{r_\alpha'}{r_\alpha} + 2W \frac{r_\alpha'^2}{r_\alpha^2} \right] dz \tag{1}$$

$$U = \frac{5(\Phi'')^2}{4} + \frac{5(\Phi')^4}{24\Phi^2} + \frac{e\Phi(B')^2}{m_o} + \frac{3e^2B^4}{8m_o^2} + \frac{35e(\Phi')^2B^2}{16m_o\Phi} - \frac{3e\Phi'BB'}{m_o}$$

$$V = \frac{7(\Phi')^3}{6\Phi} - \frac{e\Phi'B^2}{2m_o}, \quad W = -\frac{3(\Phi')^2}{4} - \frac{e\Phi B^2}{2m_o}$$

**10.4. Aperture defect of weak lens ×**

$$S_8 = v \left\{ \int_{z_o}^{z_i} \left[ \frac{5}{64} \left( \frac{\Phi''}{\Phi} \right)^2 + \frac{e}{8m_o} \frac{(B')^2}{\Phi} \right] dz \right\} \tag{1}$$

\* WENDT, G., "Chromatic Aberration of Electron-Optical Imaging Systems," *Z. Physik*, 116, 436-443 (1940).

+ SCHERZER, O., "Calculation of Third-Order Aberrations by the Path Method," in BUSCH, H. and BRÜCHE, E., *Beiträge zur Elektronenoptik*, J. A. Barth, Leipzig, 1937.

× REBSCH, R. and SCHNEIDER, W., "Aperture Defect of Weak Electron Lenses," *Z. Physik*, 107, 138-143 (1937).

**10.5. Aperture defect of bell-shaped magnetic field** (§ 8.3)\* (for large magnification,  $|M| \gg 1$ ). With

$$\Delta r_i = Cf_o M \alpha_o^3 = S_8 r_a^3,$$

$$\left. \begin{aligned} \frac{Cf_o}{d} = \frac{n\pi}{4} \frac{k^2}{(k^2 + 1)^{3/2}} \csc^4 \frac{n\pi}{\sqrt{k^2 + 1}} - \frac{1}{4} \cdot \frac{4k^2 - 3}{4k^2 + 3} \\ \times \cot \frac{n\pi}{\sqrt{k^2 + 1}} \csc^2 \frac{n\pi}{\sqrt{k^2 + 1}} \end{aligned} \right\} (1)$$

**10.6. Aperture defect of uniform magnetic and electric field**

$$\Delta r_i = -\frac{\pi}{B} \sqrt{\frac{2m_o \Phi_o}{e}} \alpha_o^3 \sqrt{\frac{\Phi_o}{\Phi_i}} \quad (1)$$

**10.7. Aperture defect of uniform electric field of length  $l$**

$$\Delta r_i = \frac{l\Phi_o}{\Phi_i - \Phi_o} \left( 1 - 2 \sqrt{\frac{\Phi_o}{\Phi_i} + \frac{\Phi_o}{\Phi_i}} \right) \alpha_o^3 \quad (1)$$

**10.8. Chromatic aberration of weak unipotential electrostatic lens** +

$$C_3 = -2M \frac{\Delta\Phi}{\Phi}, \quad (|M| \gg 1) \quad (1)$$

**10.9. Chromatic aberration of a magnetic lens for large magnification** +

$$|C_3| \leq \left| M \frac{\Delta\Phi}{\Phi} \right| \quad (1)$$

where the equality sign applies to a weak lens.

**10.10. Chromatic aberration of uniform magnetic and electric field**

$$\Delta r_i = \frac{\pi}{B} \sqrt{\frac{2m_o}{e\Phi_i}} \Delta\Phi \alpha_o \quad (1)$$

**10.11. Relativistic aberration of weak electrostatic unipotential**

\* GLASER, W., "Exact Calculation of Magnetic Lenses with the Field Distribution  $H = H_o/[1 + (z/a)^2]$ ," *Z. Physik*, **117**, 285-315 (1941).

+ GLASER, W., "Chromatic Aberration of Electron Lenses," *Z. Physik*, **116**, 56-67 (1940).

**lens.** Diffusion of axial image point as applied voltage is increased from zero to  $\Phi_A$ , keeping all voltage ratios constant for  $|M| \gg 1$ .

$$\Delta r_i = -\frac{2}{3} a \Phi_A M f_o \alpha_o \tag{1}$$

**11. Symmetrical Two-Dimensional Fields** ( $e\Phi \ll m_o c^2$ )

$$\left. \begin{aligned} \frac{\partial \varphi}{\partial z} &\equiv 0, \quad b_z \equiv 0, \quad \varphi(x, y) = \varphi(x, -y) \\ b_x(x, y) &= b_x(x, -y), \quad b_y(x, y) = -b_y(x, -y) \end{aligned} \right\} \tag{1}$$

**11.1. Field distributions**

$$\varphi(x, y) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n)!} \Phi^{(2n)}(x) y^{2n} = \Phi(x) - \frac{1}{2} \Phi''(x) y^2 + \frac{1}{24} \Phi^{IV}(x) y^4 - \dots \tag{2}$$

Radius of curvature of equipotentials on axis

$$R = \frac{\Phi'}{\Phi''} \tag{3}$$

Vertex half-angle of equipotential wedge at saddle point

$$\alpha_s = \arctan 1 = 45^\circ \tag{4}$$

$$b_x(x, y) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n)!} B^{(2n)}(x) y^{2n} = B(x) - \frac{1}{2} B''(x) y^2 + \dots \tag{5}$$

$$b_y(x, y) = \sum_{n=1}^{\infty} \frac{(-1)^n}{(2n-1)!} B^{(2n-1)}(x) y^{2n-1} = -B' y + \frac{1}{6} B^{III} y^3 - \dots \tag{6}$$

**11.2. Paraxial path equation in electric field**

$$y'' = -\frac{\Phi'}{2\Phi} y' - \frac{\Phi''}{2\Phi} y \quad \text{or} \quad Y'' = -\left[ \frac{3}{16} \left( \frac{\Phi'}{\Phi} \right)^2 + \frac{\Phi''}{4\Phi} \right] Y \tag{1}$$

where  $Y = y\Phi^{1/4}$ .

**11.3. Paraxial path equations in magnetic field**

$$y'' = -\sqrt{\frac{e}{2m_o\Phi}} z' B, \quad z'' = \sqrt{\frac{e}{2m_o\Phi}} (yB' + y'B) \tag{1}$$

**11.4. Focal length of weak electric cylinder lens**

$$\frac{1}{f_o} = \frac{7}{16} \sqrt{\frac{4\Phi_i}{\Phi_o}} \int_{x_o}^{x_i} \left( \frac{\Phi'}{\Phi} \right)^2 dx \tag{1}$$

### 11.5. Focal length of weak slit lens

$$\frac{1}{f} = \frac{E_o - E_i}{2\Phi_A} \quad (1)$$

### 11.6. Focal length and displacement of focal point in $z$ direction for weak magnetic cylinder lens

$$\frac{1}{f} = \frac{e}{2m_o\Phi} \int_{x_o}^{x_i} B^2 dx, \quad z_f = y_o \sqrt{\frac{e}{2m_o\Phi} \int_{x_o}^{x_i} B dx} \quad (1)$$

## 12. Deflecting Fields \* ( $e\Phi \ll m_o c^2$ )

$$\left. \begin{aligned} \frac{\partial\varphi}{\partial z} &\equiv 0, \quad b_z \equiv 0, \quad \varphi(x,y) - \Phi_o = \Phi_o - \varphi(x,-y), \\ b_x(x,y) &= -b_x(x,-y), \quad b_y(x,y) = b_y(x,-y) \\ E &= -\left(\frac{\partial\varphi}{\partial y}\right)_{y=0}, \quad B = b_y(x,0) \end{aligned} \right\} \quad (1)$$

### 12.1. Field distribution in two-dimensional deflecting fields

$$\varphi(x,y) = \Phi_o + \sum_{n=0}^{\infty} \frac{(-1)^{n+1}}{(2n+1)!} E^{(2n)}(x)y^{2n+1} = \Phi_o - Ey + \frac{1}{6} E''y^3 - \dots \quad (1)$$

$$b_y(x,y) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n)!} B^{(2n)}(x)y^{2n} = B - \frac{1}{2} B''y^2 + \dots \quad (2)$$

$$b_x(x,y) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)!} B^{(2n+1)}(x)y^{2n+1} = B'y - \frac{1}{6} B''''y^3 + \dots \quad (3)$$

### 12.2. Deflection by electric field for electron incident in midplane (deflection assumed small)

$$y(x) = -\frac{1}{2\Phi_o} \int_0^x d\xi \int_0^\xi E(\zeta) d\zeta \quad (1)$$

For a uniform field of length  $l$  whose mid-point is a distance  $L$  from the screen, the deflection becomes

$$y\left(\frac{l}{2} + L\right) = -\frac{E l L}{2\Phi_o} \quad (2)$$

### 12.3. Deflection by magnetic field of length $l$

$$\sin \alpha = - \int_0^x \frac{eB}{m_0 v} dx$$

in the  $x, z$  plane with apparent point of origin of the deflected ray at

$$x_c = l - \cot \alpha_l \int_0^l \tan \alpha dx \quad (2)$$

For a uniform magnetic deflecting field,

$$\sin \alpha_l = - \sqrt{\frac{e}{2m_0 \Phi^*}} Bl, \quad x_c = \frac{\tan \alpha_l / 2}{\sin \alpha_l} l \quad (3)$$

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## Chapter 19

### ATOMIC SPECTRA

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#### 1. The Bohr Frequency Relation

##### 1.1. Basic combination principle

$$\bar{\nu} = \left( \frac{E_1 - E_2}{h} \right) \text{ sec}^{-1} \quad (1)$$

where  $\bar{\nu}$  is the frequency, in vibrations per second, of the emitted spectral line;  $h$  is Planck's constant,  $E_1$  and  $E_2$  are the atomic energies (in ergs) involved in the transition giving rise to a spectral line.

$$\nu = \frac{\bar{\nu}}{c} = \frac{1}{\lambda} = \left( \frac{E_1}{hc} - \frac{E_2}{hc} \right) \text{ cm}^{-1} \quad (2)$$

where  $c$  is the velocity of light;  $\nu$  is the wave number of the observed spectral line, i.e., the number of waves per cm expressed in  $\text{cm}^{-1}$ ; \*  $\lambda$  is the wavelength of the observed line, expressed in cm;

$$\frac{E_1}{hc} \quad \text{and} \quad \frac{E_2}{hc}$$

are the spectroscopic energy levels. (Ref. 3, p. 1.)

#### 2. Series Formulas

##### 2.1. The Rydberg equation

$$\nu_n = \nu_\infty - \frac{R}{(n + \mu)^2} \quad (1)$$

where  $\nu_n$  is the wave number of the observed line [called  $\nu$  in Eq. (2) of

\* The Joint Commission for Spectroscopy has recommended that the unit of wave number hitherto described as  $\text{cm}^{-1}$  be named *kayser* with the abbreviation K, and that the symbol  $\sigma$  be used for wave number instead of  $\nu$ . See Trans. Joint Commission for Spectroscopy, *J. Opt. Soc. Am.*, **43**, 411 (1953).

§ 1.1];  $\nu_\infty$  is the limit of the series;  $R$  is the Rydberg constant;  $\mu$  is a constant;  $n$  takes integral values only. When  $\mu = 0$  and  $n = 2, 3, 4, 5, \dots, \infty$  this equation reduces to Balmer's formula for hydrogen (see below).

Rydberg's more general formula

$$\nu_n = \frac{R}{(n_1 + \mu_1)} - \frac{R}{(n_2 + \mu_2)} \quad (2)$$

If  $\mu_1 = 0, \mu_2 = 0, n_1 = 2, n_2 = 3, 4, 5$  this reduces to the hydrogen series formula

$$\nu_n = \frac{R}{n_1^2} - \frac{R}{n_2^2} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{as follows :} \quad (3)$$

Lyman series

$$\nu_n = R \left( \frac{1}{1^2} - \frac{1}{n_2^2} \right), \quad (n_2 = 2, 3, 4, \dots) \quad (4)$$

Balmer series

$$\nu_n = R \left( \frac{1}{2^2} - \frac{1}{n_2^2} \right), \quad (n_2 = 3, 4, 5, \dots) \quad (5)$$

Paschen series

$$\nu_n = R \left( \frac{1}{3^2} - \frac{1}{n_2^2} \right), \quad (n_2 = 4, 5, 6, \dots) \quad (6)$$

**2.2. The Ritz combination principle.** From the formulas for the Lyman, Balmer, and Paschen series it may be seen that the fixed terms of the equations for the Balmer, Paschen, etc. series are the first, second, etc., running terms of the Lyman series. This is known as the Ritz combination principle as it applies to hydrogen. Predictions of new series from this principle have been verified in many spectra.

If the sharp and principal series of the alkali metals are represented, respectively, by the equations

$$\text{Sharp} \quad \nu_n = 1 \text{ } ^2\text{P}^0 - n \text{ } ^2\text{S}, \quad (n = 2, 3, 4) \quad (1)$$

$$\text{Principal} \quad \nu_n = 1 \text{ } ^2\text{S} - n \text{ } ^2\text{P}^0, \quad (n = 2, 3, 4) \quad (2)$$

the series predicted by Ritz are obtained by changing the fixed terms  $1 \text{ } ^2\text{P}^0$ , to  $2 \text{ } ^2\text{P}^0, 3 \text{ } ^2\text{P}^0$ , etc., and  $1 \text{ } ^2\text{S}$  to  $2 \text{ } ^2\text{S}, 3 \text{ } ^2\text{S}$  etc. The resulting equations are as follows :

Combination sharp series

$$2 \text{ } ^2\text{P}^0 - n \text{ } ^2\text{S}, \quad (n = 3, 4, 5, \dots) \quad (3)$$

$$3 \text{ } ^2\text{P}^0 - n \text{ } ^2\text{S}, \quad (n = 4, 5, 6, \dots) \quad (4)$$

Combination principal series

$$2\ ^2S - n\ ^2P_0, \quad (n = 3, 4, 5) \tag{5}$$

$$3\ ^2S - n\ ^2P_0, \quad (n = 4, 5, 6) \tag{6}$$

Similarly, diffuse or fundamental series are predicted from the combinations  $^2P_0 - ^2D$ , and  $^2D - ^2F_0$ , respectively. Series among terms of different multiplicities are known in many spectra. (Ref. 37, p. 15.)

**2.3. The Ritz formula.** By expressing the Rydberg formula for hydrogen as

$$\nu_n = R \left( \frac{1}{p^2} - \frac{1}{q^2} \right) \tag{1}$$

with  $p$  and  $q$  as functions involving the order numbers  $n$ , Ritz obtained  $p$  and  $q$  in the form of infinite series.

$$p = n_1 + a_1 + \frac{b_1}{n_1^2} + \frac{c_1}{n_1^4} + \frac{d_1}{n_1^6} + \dots \tag{2}$$

$$q = n_2 + a_2 + \frac{b_2}{n_2^2} + \frac{c_2}{n_2^4} + \frac{d_2}{n_2^6} + \dots \tag{3}$$

By using only the first two terms, the Ritz formula becomes identical with Rydberg's general formula, which is now considered only a close approximation. Two useful forms of the Rydberg-Ritz formula are

$$\nu_n = T_1 - T_n = T_1 - \frac{R}{(n + a + b/n^2)^2} \tag{4}$$

where  $T_n$  is the running term and  $T_1$  the fixed term. Here  $n$  is an integer,  $T_n$  denotes the absolute term value, i.e., the difference between  $E_1/hc$  and  $E_2/hc$  in Eq. (2) of § 1.1, and the ionization limit of the series, and

$$T_n = \frac{R}{(n + a + bT_n)^2} \tag{5}$$

The solution of these equations gives the limit of the series.

**2.4. The Hicks formula.** Hicks expressed the denominator of Rydberg's equation as a series

$$n + \mu + \frac{a}{n} + \frac{b}{n^2} + \frac{c}{n^3} + \dots \tag{1}$$

The formula then becomes (Ref. 37, pp. 16-22)

$$\nu_n = \nu_\infty - \frac{R}{(n + \mu + a/n + b/n^2 + c/n^3 + \dots)^2} \tag{2}$$

Shenstone has suggested a method of solving an extended Ritz formula, and illustrated it in Cu II :

$$T_n = \frac{4R}{(n + \mu + \alpha T_n + \beta T_n^2)} \quad (3)$$

In all the series formulas,  $R$  is used for arc spectra,  $4R$  for first spark spectra,  $9R$  for second spark spectra, etc. Shenstone's formula is of the form of the Ritz formula given above, with one term added, and with  $4R$  used because it is applied to the *first spark* spectrum of Cu.

Let  $x_1, x_2, x_3, x_4$  be the fractional parts of the denominators when the correct limit is chosen

$$\frac{x_1 - x_2}{T_1 - T_2}, \quad \frac{x_2 - x_3}{T_2 - T_3}, \quad \frac{x_3 - x_4}{T_3 - T_4} \quad (4)$$

and let  $y_1, y_2, y_3$  be defined by the equation

$$\frac{y_1 - y_2}{y_2 - y_3} = \frac{T_1 - T_3}{T_2 - T_4} \quad (5)$$

$T_1, T_2$ , etc., are running values of the limit used as approximations to derive the final value. The right-hand side of this equation depends on observed quantities only; the left depends on the limit chosen, and can be varied by varying the limit.

The constants may then be found from the intermediate equations : (Ref. 36)

$$\left. \begin{aligned} y_1 - y_2 &= \beta(T_1 - T_3) \\ y_1 &= \alpha + \beta(T_1 + T_2) \\ x_1 &= \mu + \alpha T_1 + \beta T_1^2 \end{aligned} \right\} \quad (6)$$

### 3. The Sommerfeld Fine Structure Constant for Hydrogen-like Spectra

**3.1. Energy states.** Energy states of an atomic system consisting of a nucleus and a single electron are given by

$$\frac{E(n, l, j)}{hc} = \mu c^2 \left[ 1 + \frac{\alpha^2 Z^2}{(n - j - \frac{1}{2} + \sqrt{(j + \frac{1}{2})^2 - \alpha^2 Z^2})^2} \right]^{-1/2} - \mu c^2 \quad (1)$$

where  $E/hc$  is the level value in  $\text{cm}^{-1}$ , and the term with  $\alpha^2$  arises from electron spin and relativity corrections.

$$\alpha = \frac{2\pi e^2}{hc} \quad (2)$$

is the Sommerfeld fine-structure constant, where  $c$  is the velocity of light,  $h$  is Planck's constant,  $e$  is the electronic charge,  $Z$  is the atomic number.

$$\mu = \frac{Mm}{M+m} \quad (3)$$

is the reduced mass,  $M$  being the mass of the nucleus, and  $m$  the mass of the electron.

Each electron is characterized by the quantum numbers  $n$ ,  $l$ , and  $j$ . The quantum number  $j$  gives the total angular momentum of each electron, the resultant of the orbital moment  $l$ , and the spin moment  $s$ . The unit of momentum is  $\hbar/2\pi$ .  $n$  has the integral values 1, 2, etc. For energy levels, where the properties of more than one electron are considered, the vector sums of these quantities are used, i.e.,  $J, L, S$  replace  $j, l, s$ , capitals denoting the vector sums of the small characters. Here  $L = 0, 1, 2, \dots$ , to  $n-1$ ;  $J = L + \frac{1}{2}$ , and  $L - \frac{1}{2}$ , but for  $L = 0$ ,  $J = \frac{1}{2}$  only. By using the first terms of the expansion, Eq. (1) becomes

$$\frac{E(n, l, j)}{hc} = \frac{RZ^2}{n^2(1+m/M)} + \frac{R\alpha^2 Z^4}{n^3(1+m/M)} \left( \frac{3}{4n} - \frac{1}{j + \frac{1}{2}} \right) \quad (4)$$

$$R = \frac{2\pi^2 m e^4}{h^3 c} \quad (5)$$

where  $R$  is the Rydberg constant. (Ref. 3, p. 218; Refs. 6, 7, 8, 9, 10, 11; Ref. 37, pp. 117, 147.)

## 4. Coupling

**4.1. *LS* or Russell-Saunders coupling.** The terms of a spectrum are made up of groups of related energy levels. Hund has shown what terms may be expected from the different configurations which the valence electrons of the atom assume when it is excited. In addition to the total quantum number  $n$ , which tells which shell it is in, each electron is specified by the quantum numbers  $l$  ( $= 0, 1, 2, 3, \dots$  for  $s, p, d, f, \dots$  electrons) and  $s$  ( $= \pm \frac{1}{2}$  which states the number of units of quantized angular momenta associated with their orbital revolutions and axial rotations). Any level  ${}^n T_J$  represents quantitatively one of the resultants obtained by adding vectorially the orbital and axial angular momenta of the electrons composing a particular configuration. Thus  $L = 0, 1, 2, 3$ , for  $S, P, D, F, \dots$  terms; and  $S = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$  for singlets, doublets, triplets,  $\dots$ . The inner quantum numbers,  $J$ ,

which represent mechanically the resultant angular momentum of the atom, are limited by the relations

$$J_{\max} = L + S$$

$$J_{\min} = L - S$$

and all intermediate values differing by unity are included. The multiplicity,

$$r = 2S + 1$$

With the orbital motions of two electrons coupled together to give a resultant  $L^*$ , and the spins of the same electron coupled together to form  $S^*$ , both  $L^*$  and  $S^*$  will in turn be coupled to form  $J^*$ . The quantum conditions imposed upon this coupling are that  $J^* = \sqrt{J(J+1)}$  and that  $J$  take non-negative integral values. The  $g$ -values calculated from Eq. (3) of § 6.1 hold for  $LS$  coupling. (Ref. 37, pp. 184-186.)

*jj*-coupling. In this type of coupling the interaction between the spin of each electron and its own orbit is greater than the interactions between the two spins and the two orbits, respectively, i.e.,  $L$  and  $S$  are no longer constants, and the formula for Landé  $g$ -values does not hold. (Refs. 17, 18; Ref. 37, p. 196.)

*jl*-coupling. This intermediate coupling is conspicuous in the spectra of the inert gases. Perturbations of  $g$ -values caused by configuration interaction, and various types of coupling, are well known in a number of spectra. (Refs. 15, 20, 21, 33.)

## 5. Line Intensities

### 5.1. Doublets. Lines due to ${}^2S - {}^2P^o$ transitions

Designation	${}^2S_{0\frac{1}{2}}$
${}^2P^o_{1\frac{1}{2}}$	$x_1$
${}^2P^o_{0\frac{1}{2}}$	$x_2$

Here  $x_1$  and  $x_2$  are the observed lines. The quantum weights of the  ${}^2P$  levels are  $2J + 1$ . For  ${}^2P^o_{1\frac{1}{2}}$ ,  $J = 1\frac{1}{2}$  and the quantum weight is 4. For  ${}^2P^o_{0\frac{1}{2}}$ ,  $J = 0\frac{1}{2}$  and the quantum weight is 2. The ratio of the intensities of the lines  $x_1$  and  $x_2$  is proportional to  $2J + 1$ , i.e., 4:2 or 2:1.

This example is oversimplified, and for multiplets of more than two lines the following sum rules must be taken into account.

1. The sum of the intensities of all lines of a multiplet which start from a common initial level is proportional to the quantum weight  $(2J + 1)$  of the initial level.

2. The sum of the intensities of all lines of a multiplet which end on a common final level is proportional to the quantum weight  $(2J + 1)$  of the final level.

A Fourier analysis of precessing electron orbits in conjunction with the sum rules leads to the following formulas for intensities.

For transitions  $(L - 1) \rightarrow L$   $\left\{ \begin{array}{l} {}^3P - {}^3D \text{ multiplets for example,} \\ \text{transitions } 1 \rightarrow 2, L = 2 \end{array} \right\}$

$(J - 1) \rightarrow J$ :

$$I = \frac{B(L+J+S+1)(L+J+S)(L+J-S)(L+J-S-1)}{J} \quad \left. \begin{array}{l} J = 2 \rightarrow 3 \\ 1 \rightarrow 2 \\ 0 \rightarrow 1 \end{array} \right\} \quad (1)$$

$J \rightarrow J$ :

$$I = \frac{-B(L+J+S+1)(L+J-S)(L-J+S)(L-J-S-1)(2J+1)}{J(J+1)} \quad \left. \begin{array}{l} J = 2 \rightarrow 2 \\ 1 \rightarrow 1 \end{array} \right\} \quad (2)$$

$(J + 1) \rightarrow J$ :

$$I = \frac{B(L-J+S)(L-J+S-1)(L-J-S-1)(L-J-S-2)}{J+1} \quad J = 1 \quad (3)$$

For transitions  $L \rightarrow L$  ( $D - D$  multiplets for example,  $L = 2$ ) the equations are

$(J - 1) \rightarrow J$ :

$$I = \frac{-A(L+J+S+1)(L+J-S)(L-J+S+1)(L-J-S)}{J} \quad (4)$$

$J \rightarrow J$ :

$$I = \frac{A[L(L+1)+J(J+1)-S(S+1)]^2(2J+1)}{J(J+1)} \quad (5)$$

$(J + 1) \rightarrow J$ :

$$I = \frac{-A(L+J-S+2)(L+J-S+1)(L-J+S)(L-J-S-1)}{(J+1)} \quad (6)$$

The constants  $A$  and  $B$  may be omitted, since they apply to temperature corrections and to Einstein's  $\nu^4$  correction, which will be very small for multiplets of narrow separation.

The relative theoretical intensities in a  ${}^3P - {}^3D$  multiplet can be determined from these formulas as follows.

	${}^3D_3$	${}^3D_2$	${}^3D_1$	<i>Sum</i>	<i>Ratio</i>
${}^3P_2$	168	30	2	200	5
${}^3P_1$		90	30	120	3
${}^3P_0$			40	40	1
<i>Sum</i>	168	120	72		
<i>Ratio</i>	7	5	3		

$L = 1$  for a P term;  $L = 2$  for a D term.  $L = 2$  in Eqs. (1), (2), and (3).

The subscripts 3, 2, 1 and 2, 1, 0 represent the  $J$  values, or inner quantum numbers, for  ${}^3D$  and  ${}^3P$  terms respectively.  $S = 1$  for triplet terms, the superscript denoting the multiplicity,  $2S + 1$  (3 in this case).

In Eq. (1)  $J$  has the values 3, 2, 1, giving the intensities along the main diagonals of the multiplet: 168, 90, 40. In Eq. (2)  $J$  has the values 2, 1, giving the intensities of the first satellite lines in the multiplet: 30, 30. In Eq. (3)  $J = 1$ , giving the intensity of the second satellite line in the multiplet: 2. (Ref. 37, pp. 120, 204-206.)

Russell gives the quantum formulas for theoretical intensities for unperturbed  $LS$  coupling, in the following form:

Ordinary multiplets (SP, PD, etc.)

$$x = \frac{(r + k - n + 1)(r + k - n)(k - n + 1)(k - n)}{r + k - 2n + 1} \quad (7)$$

$$y = \frac{2(r + k - 2n)(r + k - n)n(k - n)(r - n)}{(r + k - 2n + 1)(r + k - 2n - 1)} \quad (8)$$

$$z = \frac{(r - n)(r - n - 1)n(n + 1)}{r + k - 2n - 1} \quad (9)$$

$s = rk(k^2 - 1)$ ;  $x$  denotes the intensity of a line in the principal diagonal of the multiplet;  $y$  denotes the intensity of a line that is one of the first satellites;  $z$  denotes the intensity of a line that is one of the second satellites;  $s$  is the sum of the intensities of all the lines of the multiplet;  $r$  is the multiplicity;  $k$  has the values 2, 3, 4, 5 for the combinations SP, PP, PD, DD, etc.;  $n$  is the number of the line in the diagonal to which it belongs. The leading line of the multiplet is always  $x_1$ .

Along with these formulas he gives tables of theoretical intensities for multiplicities 2 to 11 and for term types as far as I terms. (Refs. 5, 12, 29, 30, 34, 35.)

## 6. Theoretical Zeeman Patterns

**6.1. Landé splitting factor.** An external magnetic field causes each energy level to be split up into  $(2J + 1)$  sublevels. When the field is weak enough, these sublevels will be equidistant and lie symmetrically around the original position of the level without field. The distance between them is proportional to the field strength  $H$ . Since  $H$  is the same for all levels of a given atom it is convenient to express the Zeeman splitting in terms of the Lorentz unit  $L$  (in  $\text{cm}^{-1}$ ).

$$L = \frac{He}{4\pi mc^2} = \Delta\nu \quad (1)$$

Here  $e$  is the charge on the electron in electrostatic units,  $m$  is the mass of the electron, and  $c$  is the velocity of light.

Expressed (in  $\text{cm}^{-1}$ ) in terms of the normal Zeeman triplet this reduces to

$$\Delta\nu = \frac{\mu}{J} m = gm \quad (2)$$

The distance between the sublevels expressed in Lorentz units is denoted by  $g$ , the Landé splitting factor. The  $g$ -factor represents the ratio of the magnetic to the mechanical moment of the state, the former expressed in Bohr magnetons,  $he/4\pi mc$ ; the latter in units  $h/2\pi$ . It must be noted that  $m$  in Eq. (2) is the magnetic quantum number and must not be confused with the  $m$  used in the denominator of Eq. (1) and in the expression defining the Bohr magneton. (Ref. 37, pp. 52, 53, 157, 158; Ref. 22.)

The quantity  $g$  is expressed as a function of the quantum numbers which describe spectroscopic energy levels and terms,

$$g = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)} \quad (3)$$

For details of the theory and calculation of  $g$ -values see BACK, E. and LANDÉ, A., *Zeemaneffekt und Multiplettstruktur der Spektrallinien*, Julius Springer, Berlin, 1925, p. 42; also KIESS, C. C. and MEGGERS, W. F., *Bur. Standards J. Research*, RP 23, 1, 641-684 (1928); MEGGERS, W. F., "Zeeman Effect," *Enc. Britannica*, 1953, 4 pp.

**6.2. The Paschen-Back effect.** In a very strong magnetic field, the coupling between all the individual magnetic vectors may be broken down, regardless of the original coupling scheme, so that each part will quantize separately with the field  $H$ . Equation (3) of § 6.1 does not hold, owing to the Paschen-Back interaction, in which the magnetic levels are displaced from

their  $LS$ -coupling positions. The displacement  $\epsilon$  is given by the equation :

$$\epsilon = \frac{I^2}{\delta} \quad (1)$$

where  $\delta$  is the distance between the two repelling levels, and  $I$ , the interaction factor is

$$I = \left[ \frac{(J-L+S)(J+L-S)(L+S+1+J)(L+S+1-J)}{4J^2(2J-1)(2J+1)} \right]^{1/2} (J^2 - M^2)^{1/2} \quad (2)$$

Values of  $I$  and  $I^2$  for all term combinations likely to be affected by Paschen-Back interaction have been tabulated by Catalán. (Refs. 13, 14, 15, 19, 23; Ref. 37, p. 231.)

**6.3. Pauli's  $g$ -sum rule.** This rule is that out of all the states arising from a given electron configuration the sum of the  $g$ -factors for levels with the same  $J$ -value is a constant independent of the coupling scheme. (Refs. 25, 31; Ref. 37, p. 222.)

## 7. Nuclear Magnetic Moments

**7.1. Hyperfine structure.** Approximate formulas for the calculation of nuclear magnetic moments from observed hyperfine structure separations.

For  $s$ -electrons

$$g(I) = \frac{3a}{8R\alpha^2} \cdot \frac{n_0^3}{Z_i Z_0^2} \cdot \frac{1838}{\kappa(\frac{1}{2}, Z_i)} \quad (1)$$

For non  $s$ -electrons

$$g(I) = \frac{aZ_i}{\Delta\nu} \cdot \frac{j(j+1)(l+\frac{1}{2})}{l(l+1)} \cdot \frac{\lambda(l, Z_i)}{\kappa(j, Z_i)} \cdot 1838 \quad (2)$$

where  $I$  is the nuclear moment in units  $h/2\pi$ ;  $g(I)$ , the nuclear  $g$ -value, is the ratio of the magnetic to the mechanical moment of the nucleus, the former expressed in "proton magnetons"  $eh/4\pi Mc$ , where  $M$  is the mass of the proton. For a single electron  $a$  is used instead of  $A$ , where  $A$  is equal to the distance between two adjacent hyperfine levels divided by the largest of their  $F$ -values and counted positive when the larger  $F$  value belongs to the higher energy,  $F$  being the fine structure quantum number, the resultant of  $I$  and  $J$ ;  $J$  the inner quantum number is the vector sum of  $j$ ;  $L$  the azimuthal quantum number is the vector sum of  $l$ ; and  $a$  = the interval factor for hyperfine structure.  $R$  is the Rydberg constant;  $\alpha$  is the Sommerfeld fine-structure constant;  $n_0$  is the Rydberg denominator or effective principal quantum number;  $Z_0$  is the effective nuclear charge of the outer region of the

atom;  $Z_0 = 1$  for a neutral atom, 2 for a singly ionized atom, etc.;  $Z_i$  is the average effective nuclear charge of the inner region of the atom;  $Z_i = Z$  for  $s$ -electrons;  $Z_i = Z - 4$  for  $p$ -electrons;  $\kappa(j, Z_i)$  is the relativity correction by which the equation for the hyperfine structure must be multiplied;  $\lambda(l, Z_i)$  is the relativity correction by which the equation for the multiplet separation  $\Delta\nu$  must be multiplied; where  $\Delta\nu$  is the spin doublet separation for fine structure. (Ref. 16.)

## 8. Formulas for the Refraction and Dispersion of Air for the Visible Spectrum

**8.1. Meggers' and Peters' formula.** Complete sets of observations made with dry air at atmospheric pressure and at temperatures of 0, 15, and 30° C are closely represented by the following dispersion formulas.

$$(n - 1)_0 \times 10^7 = 2875.66 + \frac{13.412}{\lambda^2 \times 10^{-8}} + \frac{0.3777}{\lambda^4 \times 10^{-16}} \quad (1)$$

$$(n - 1)_{15} \times 10^7 = 2726.43 + \frac{12.288}{\lambda^2 \times 10^{-8}} + \frac{0.3555}{\lambda^4 \times 10^{-16}} \quad (2)$$

$$(n - 1)_{30} \times 10^7 = 2589.72 + \frac{12.259}{\lambda^2 \times 10^{-8}} + \frac{0.2576}{\lambda^4 \times 10^{-16}} \quad (3)$$

where  $\lambda$  = wavelength in air expressed in angstroms;  $(n - 1) \times 10^7$  = refractivity. (Ref. 28.)

Tabular values of  $(n - 1) \times 10^7$  and of  $\lambda(n - 1) \times 10^7$  per angstrom (2000 Å to 7000 Å), and per 10 Å (7000 Å to 10000 Å) for normal pressure and 15° C, from the above formulas are given in the standard table used to convert wavelengths in air to wave numbers *in vacuo*, e.g., KAYSER, H., *Tabelle der Schwingungszahlen*, rev. ed. (prepared by Meggers, W. F.), Edwards Bros., Inc., Ann Arbor, Mich., 1944. (See also Ref. 1.)

For wave numbers of infrared spectral lines beyond 10000 Å see Ref. 2.

**8.2. Perard's equation.** Perard's equation for CO<sub>2</sub>-free dry air is

$$(n - 1)10^6 = \left[ 288.02 + \frac{1.478}{\lambda^2} + \frac{0.0316}{\lambda^4} \right] \times \frac{h(1 + \beta h)}{760(1 + 760\beta)} \cdot \frac{1}{1 + 0.003716\theta} \quad (1)$$

where  $\lambda$  = wavelength in air (microns),  $h$  = pressure (mm),  $\theta$  = temperature (°C),  $\beta = 2.4 \times 10^{-6}$  (which can be taken as zero without appreciable error). (Ref. 32.)

**8.3. The formula of Barrell and Sears.** Barrell and Sears give the following equation for the refractivity of moist, normal air.

$$(n_{t,p,f} - 1)10^6 = \left[ 0.378,125 + \frac{0.002,141,4}{\lambda^2} + \frac{0.000,017,93}{\lambda^4} \right] \times p \frac{\{1 + (1.049 - 0.0157t)p \times 10^{-6}\}}{1 + 0.003,661t} - \left[ 0.0624 - \frac{0.000,680}{\lambda^2} \right] \frac{f}{1 + 0.003,661t} \quad (1)$$

This equation is applicable to ranges of temperature  $t = 10$ -30° C, and pressure  $p = 720$ -800 mm. The quantity  $(n_{t,p,f} - 1)$  represents the refractivity of atmospheric air containing water vapor at pressure  $f$  mm, and  $\lambda$  is the wavelength in normal air expressed in microns. (Ref. 4.)

The formula of Kösters and Lampe is

$$(n_{t,p} - 1)10^6 = \left[ 268.036 + \frac{1.476}{\lambda^2} + \frac{0.01803}{\lambda^4} \right] \frac{p}{760} \cdot \frac{1 + 20\alpha}{1 + \alpha t} \quad (2)$$

where  $\lambda$  refers to the wavelength *in vacuo*,  $\alpha$  assumed to be 0.00367. Their results refer to dry, CO<sub>2</sub>-free air for the visible spectrum (exact range not specified). The equation is intended to apply only to small departures of temperature and pressure from 20° C and 760 mm, respectively. (Ref. 24.)

From recent study of the spectrum of Hg<sup>198</sup>, Meggers concludes that "the unique properties of Hg<sup>198</sup> force the conclusion that a progressive scientific world will soon adopt the wavelength of green radiation (5461 Å) from Hg<sup>198</sup> as the ultimate standard of length." Accurately measured relative wavelengths in this spectrum tested by the combination principle, indicate that a revision of the dispersion formulas is necessary. (Refs. 26, 27.)

Barrell\* has recently derived a new formula representing the arithmetical mean of data from three different laboratories, as follows :

$$(n - 1)10^6 = 272.729 + (1.4814/\lambda_s^2) + (0.02039/\lambda_s^4) \dots$$

where  $\lambda_s$  = wavelength in standard air, expressed in microns.

At the 1952 meeting of the Joint International Commission for Spectroscopy, Edlén<sup>+</sup> proposed a solution to this problem by suggesting that the

\* H. BARRELL, *J. Opt. Soc. Am.*, **41**, 297 (1951).

+ B. EDLÉN, *J. Opt. Soc. Am.*, **43**, 339 (1953).

empirical Cauchy formulas previously used be replaced by a dispersion formula of the Sellmeier type, which has physical meaning :

$$n - 1 = \sum A_i(\sigma_i^2 - \sigma^2)^{-1}$$

where  $\sigma_i$  are resonance frequencies of the gas. He adopts as the formula that gives the " best representation of the observed values :"

$$(n - 1)10^8 = 6432.8 + \frac{2,949,810}{146 - \sigma^2} + \frac{25,540}{41 - \sigma^2}$$

$\sigma$  being the vacuum wave number expressed in  $\mu^{-1}$ . " In order to preserve the usefulness of Kayser's *Tabelle der Schwingungszahlen*," he provides a table of corrections to be applied to the wave numbers given in Kayser.

The Joint Commission for Spectroscopy\* has recommended the use of the tables of Edlén for correcting wavelengths in standard air to wavelengths in vacuum. (Ref. 38.)

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## Chapter 20

# MOLECULAR SPECTRA

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### 1. General Remarks

The motions in a molecule are determined by its Schrödinger equation (see § 1.3 of Chapter 21). The eigenvalues of the Schrödinger equation are the stationary energy values of the system. To a usually satisfactory approximation the energy can be resolved into a sum of contributions due to electronic motion, vibration, and rotation.

$$E = E_e + E_v + E_r \quad (1)$$

The observed spectra correspond to transitions between these energy levels according to the Bohr frequency condition

$$h\nu = E' - E'' \quad (2)$$

where the ' and '' refer to the upper and lower states, respectively, and where  $\nu$  is the wave number.

The transition probabilities are determined by the eigenfunctions of the Schrödinger equation by way of the matrix elements of the dipole moment ( $p$ ) or other quantities considered, e.g.,

$$\int \psi' p \psi''^* d\tau$$

### 2. Rotation and Rotation Spectra

#### 2.1. Diatomic and linear polyatomic molecules

a. *Moments of inertia.* The moment of inertia about an axis perpendicular to the figure axis is defined by

$$I_B = \sum m_i r_i^2 \quad (1)$$

where  $m_i$  stands for the mass of an individual nucleus, and  $r_i$  for its distance from the center of mass. The moment of inertia about the figure axis  $I_A$  is very small.

For the special case of a diatomic molecule we have

$$I_B = \mu r^2 \quad (2)$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

is the "reduced mass," and  $r$  is the internuclear distance.

b. *Energy levels.* The rotational energy levels of the rigid diatomic or linear polyatomic molecule are given by the expression

$$\frac{E_r}{hc} = F(J) = BJ(J+1) \quad (3)$$

where  $E_r$  is the rotational energy (in ergs) and  $F(J)$  is the rotational term value (in  $\text{cm}^{-1}$ ). The rotational constant  $B$  is given by

$$B = \frac{h}{8\pi^2 c I_B} = \frac{27.98_{30} \times 10^{-40}}{I_B}$$

$J$  is the rotational quantum number corresponding to the angular momentum  $\mathbf{J}$  whose magnitude is

$$\frac{h}{2\pi} \sqrt{J(J+1)} \approx \frac{h}{2\pi} J$$

For the nonrigid diatomic or linear polyatomic molecule we have

$$\frac{E_r}{hc} = F(J) = BJ(J+1) - DJ^2(J+1)^2 + \dots \quad (4)$$

where  $D$  is a rotational constant representing the influence of the centrifugal forces. In the case of a diatomic molecule of vibrational frequency  $\omega$  (in  $\text{cm}^{-1}$ ), the constant  $D$ , in a first approximation, is given by

$$D = \frac{4B^3}{\omega^2}$$

In a polyatomic molecule,  $D$  depends in general on all the vibrational frequencies of the molecule.

c. *Eigenfunctions.* The rotational eigenfunctions of a diatomic or linear polyatomic molecule are the so-called surface harmonics

$$\psi_r = N_r P_J^{|M|}(\cos \vartheta) e^{iM\varphi} \quad (5)$$

where  $\varphi$  is the azimuth of the line connecting the mass point to the origin, taken about the  $z$  axis;  $\vartheta$  is the angle between this line and the  $z$  axis;  $M$  is a second quantum number (the so-called magnetic quantum number) which takes the values  $M = J, J-1, J-2, \dots, -J$ , and which represents

in units  $h/2\pi$  the component of the angular momentum  $J$  in the direction of the  $z$  axis;  $P_J^{|M|}(\cos \vartheta)$  is a function of the angle  $\vartheta$ , the so-called associated Legendre function (§ 8.11 of Chapter 1);  $N_r$  is a normalization constant.

The probability of finding the system oriented in the direction  $(\vartheta, \varphi)$  is

$$\psi_r \psi_r^* = N_r^2 [P_J^{|M|}(\cos \vartheta)]^2 \quad (6)$$

that is, the probability is independent of  $\varphi$ .

d. *Symmetry properties.* A rotational level is called positive or negative (+ or -) depending on whether the total eigenfunction  $\psi$  remains unaltered or changes its sign by reflection of all the particles (electrons and nuclei) at the origin (inversion). In addition, if the molecule has a center of symmetry, a rotational level is symmetric (*s*) or antisymmetric (*a*) depending on whether or not the total eigenfunction  $\psi$  of the system (apart from the nuclear spin function) remains unchanged or changes sign, when all nuclei on one side of the center are simultaneously exchanged with the corresponding ones on the other side.

e. *Statistical weight.* The statistical weight  $g$  of a rotational state is dependent on two factors

$$g = g_J \times g_I \quad (7)$$

where  $g_J$  depends on the over-all rotation of the molecule and is equal to the number of possible orientations of  $J$  in a magnetic field

$$g_J = 2J + 1$$

and  $g_I$  depends on the nuclear spins, and, if the molecule has a center of symmetry, on the statistics of the nuclei.

For molecules without a center of symmetry we have

$$g_I = (2I_1 + 1)(2I_2 + 1) \dots$$

where  $I_1, I_2, \dots$  are the spins of the individual nuclei. Since in this case  $g_I$  is the same for all rotational levels, it can, for most purposes, be omitted.

If the molecule has a center of symmetry and if the number of pairs of identical nuclei following Fermi statistics is odd (while the number of pairs of identical nuclei following Bose statistics is even or odd), the statistical weight due to the nuclear spins is

$$g_I^s = \frac{1}{2}[(2I_X + 1)^2(2I_Y + 1)^2(2I_Z + 1)^2 - (2I_X + 1)(2I_Y + 1)(2I_Z + 1)\dots]$$

for the symmetric rotational levels (§ 2.1d), and

$$g_I^a = \frac{1}{2}[(2I_X + 1)^2(2I_Y + 1)^2(2I_Z + 1)^2 + (2I_X + 1)(2I_Y + 1)(2I_Z + 1)\dots]$$

for the antisymmetric rotational levels. If the number of pairs of identical nuclei following Fermi statistics is even, the situation is reversed. Here  $X, Y, Z, \dots$  refer to the different pairs of nuclei.

If only one pair of identical nuclei has a nonzero nuclear spin  $I$ , the ratio of the statistical weights of the symmetric to the antisymmetric rotational levels becomes simply  $(I+1)I$  or  $I/(I+1)$ , depending on whether the nuclei follow Bose or Fermi statistics.

f. *Thermal distribution of rotational levels.* The population  $N_J$  of the various rotational levels is given by the general formula

$$N_J = \frac{N}{Q_r} g_I (2J+1) e^{-BJ(J+1)hc/kT} \quad (8)$$

Here  $T$  is the absolute temperature and  $k$  the Boltzmann constant,  $B$  is the rotational constant, as defined in § 2.1b,  $g_I$  is the statistical weight due to the nuclear spin, as discussed in § 2.1e, and  $Q_r$  is the rotational partition function

$$Q_r = \sum g_I (2J+1) e^{-BJ(J+1)hc/kT}$$

g. *Pure rotation spectrum.* A pure rotation spectrum in the far infrared or microwave region can occur only in molecules with a permanent dipole moment, that is, in molecules without a center of symmetry. The selection rules are

$$+ \leftrightarrow -, \quad + \leftarrow | \rightarrow +, \quad - \leftarrow | \rightarrow -$$

that is, positive levels combine only with negative levels, and

$$\Delta J = J' - J'' = 1$$

where  $J'$  and  $J''$  are the rotational quantum numbers of the upper and lower states, respectively. Accordingly, the wave-numbers of the pure rotation spectrum are given by the formula

$$\nu = 2B(J+1) - 4D(J+1)^3 + \dots \quad (9)$$

where  $D \ll B$  (§ 2.1b) and  $J$  stands for  $J''$ .

A Raman spectrum can occur only if the polarizability of the molecule changes during the transition. This is the case for the rotation of diatomic and linear polyatomic molecules, whether or not there is a center of symmetry. The selection rules referring to the symmetry of the rotational states (§ 2.1d) are

$$+ \leftrightarrow +, \quad - \leftrightarrow -, \quad + \leftarrow | \rightarrow -$$

and

$$s \leftrightarrow s, \quad a \leftrightarrow a, \quad s \leftarrow | \rightarrow a$$

that is, positive levels combine only with positive, negative only with negative, symmetric only with symmetric, and antisymmetric only with antisymmetric levels. The selection rule for the rotational quantum number is

$$\Delta J = 0, \pm 2 \quad (10)$$

that is, besides the undisplaced line ( $\Delta J = 0$ ) one observes two lines both with  $\Delta J = J' - J'' = +2$ , one with the lower state as the initial state (Stokes line) and one with the upper state as the initial state (anti-Stokes line).

The wave number shifts are given by the formula

$$|\Delta\nu| = (4B - 6D)(J + \frac{3}{2}) - 8D(J + \frac{3}{2})^3 \quad (11)$$

or, since always  $D \ll B$ , to a very good approximation

$$|\Delta\nu| = 4B(J + \frac{3}{2}) \quad (12)$$

where  $J$ , as always, stands for  $J''$ , the rotational quantum number of the lower state involved.

For molecules with a center of symmetry, corresponding to the alternation of statistical weights for the symmetric and antisymmetric rotational levels, an alternation of intensities will occur. If the spins of all nuclei with the possible exception of the one at the center are zero, alternate lines will be missing.

## 2.2. Symmetric top molecules

a. *Moments of inertia.* A symmetric top molecule is characterized by the fact that two of its principal moments of inertia are the same ( $I_B$ ), and that the third ( $I_A$ ) is of the same order of magnitude. The axis of the third moment of inertia is called the figure axis of the molecule. If  $I_A < I_B$ , we speak of a prolate symmetric top; if  $I_A > I_B$ , of an oblate symmetric top.

b. *Energy levels.* The rotational energy levels of a rigid symmetric top molecule are given by the expression

$$\frac{E_r}{hc} = F(J, K) = B J(J + 1) + (A - B)K^2 \quad (1)$$

Here  $E_r$  is the rotational energy (in ergs),  $F(J, K)$  the rotational term value (in  $\text{cm}^{-1}$ );  $A$  and  $B$  are rotational constants given by

$$B = \frac{h}{8\pi^2 c I_B}, \quad A = \frac{h}{8\pi^2 c I_A}$$

and  $J$  and  $K$  are rotational quantum numbers. Here  $J$  corresponds to the total angular momentum  $\mathbf{J}$ , and  $K$  corresponds to the component of  $\mathbf{J}$  in the

direction of the figure axis; therefore  $J = K, K + 1, K + 2, \dots$ . All rotational levels with  $K > 0$  are doubly degenerate.

For the nonrigid symmetric top molecule, the energy formula is

$$\left. \begin{aligned} \frac{E_r}{hc} &= F(J, K) \\ &= BJ(J + 1) + (A - B)K^2 - D_J J^2(J + 1)^2 \\ &\quad - D_{JK}J(J + 1)K^2 - D_K K^4 + \dots \end{aligned} \right\} \quad (2)$$

where  $D_J$ ,  $D_{JK}$ , and  $D_K$  are rotational constants corresponding to  $D$  in the linear molecule (§ 2.1b).

c. *Eigenfunctions.* The rotational eigenfunctions of the symmetric top are given by

$$\psi_r = \theta_{JKM}(\vartheta) \cdot e^{iK\chi} \cdot e^{iM\varphi} \quad (3)$$

Here  $\vartheta$ ,  $\varphi$ , and  $\chi$  are the so-called Eulerian angles,  $\vartheta$  is the angle of the figure axis of the top with the fixed  $z$  axis,  $\varphi$  is the azimuthal angle about the  $z$  axis, and  $\chi$  is the azimuthal angle measuring the rotation about the figure axis;  $J$  and  $K$  are rotational quantum numbers as defined in (§ 2.2b);  $M$  is the magnetic quantum number which gives the component of  $J$  in the direction of the  $z$  axis in units  $h/2\pi$  and can have the values  $J, J - 1, \dots, -J$ . The function  $\theta_{JKM}(\vartheta)$  depends in a somewhat complicated way on the angle  $\vartheta$ ; it contains the so-called Jacobi (hypergeometric) polynomials (see § 10.7 of Chapter 1).

d. *Symmetry properties.* In the nonplanar symmetric top molecule a reflection of all particles at the origin (inversion) leads to a configuration which cannot also be obtained by rotation of the molecule. Corresponding to these two configurations of the molecule, each rotational level  $J, K$  is doubly degenerate as long as the potential hill separating the two configurations is infinitely high. For a finite potential hill, a splitting occurs into two sublevels which have opposite symmetry with respect to an inversion. The eigenfunctions of these sublevels contain equal contributions from the positive and negative "original" levels (inversion doubling).

For  $K > 0$  the  $K$  degeneracy exists in addition to the inversion doubling, so that each level with a given  $J$  and  $K (> 0)$  consists of four sublevels.

In the planar symmetric top molecule no inversion doubling occurs. Each rotational level  $J, K (> 0)$  consists of two sublevels either both positive or both negative with respect to inversion.

For molecules which are symmetrical tops due to their symmetry, additional symmetry properties arise corresponding to the property sym-

metric-antisymmetric in linear molecules. Levels belonging to different species are distinguished by symbols  $A$ ,  $E$ , etc.

e. *Statistical weights.* In the symmetric top molecule the statistical weight of a rotational state due to the over-all rotation is

$$g_{JK} = 2J + 1, \quad \text{for } K = 0$$

$$g_{JK} = 2(2J + 1), \quad \text{for } K > 0$$

For molecules without symmetry the statistical weight due to the nuclear spin is

$$g_I = (2I_1 + 1)(2I_2 + 1)(2I_3 + 1) \dots$$

In this case  $g_I$  contributes only a constant factor to the total statistical weight

$$g = g_{JK} \times g_I$$

and can usually be omitted.

If the molecule has symmetry, rotational levels of different species have different statistical weights depending on spin and statistics of the identical nuclei. If, for instance, the figure axis of the molecule is a threefold axis of rotation, in a totally symmetric vibrational and electronic state the levels with  $K = 0, 3, 6, 9, \dots (A)$  have

$$g_I = \frac{1}{3}(2I + 1)(4I^2 + 4I + 3)$$

while those with  $K = 1, 2, 4, 5, 7, 8, \dots (E)$  have

$$g_I = \frac{1}{3}(2I + 1)(4I^2 + 4I)$$

If the spin of all the identical nuclei is zero, the levels with  $K = 1, 2, 4, 5, 7, 8, \dots$  are entirely missing.

f. *Thermal distribution of rotational levels.* The population of the various rotational levels (using the same notation as in (§ 2.1f) is given by

$$N_{JK} = \frac{N}{Q_r} g_I g_{JK} e^{-[BJ(J+1) + (A-B)K^2]hc/kT} \quad (4)$$

where

$$Q_r = \sum_{J,K} g_I g_{JK} e^{-[BJ(J+1) + (A-B)K^2]hc/kT}$$

and  $g_{JK}$  and  $g_I$  are given in § 2.2e.

g. *Pure rotation spectrum.* A pure rotation spectrum in the far infrared and microwave region can occur only if the molecule has a permanent dipole moment. For the accidental symmetric top the selection rules are

$$\Delta K = 0, \pm 1; \quad \Delta J = 0, \pm 1; \quad + \leftrightarrow -, \quad + \leftarrow \rightarrow +, \quad - \leftarrow \rightarrow -$$

For a molecule which is a symmetric top because of its symmetry the same selection rules hold, but  $\Delta K = \pm 1$  is excluded. In addition, only states having the same species of the rotational eigenfunction combine with one another (e.g.,  $A \leftrightarrow A$ ,  $E \leftrightarrow E$ ,  $A \leftarrow \rightarrow E$  for molecules with a threefold axis of symmetry).

The wave-numbers of the pure rotation lines when the molecule has an axis of symmetry are given in a first approximation by the formula

$$\nu = 2B(J + 1) \quad (5)$$

or, if centrifugal stretching is taken into account,

$$\nu = 2B(J + 1) - 2D_{KJ}K^2(J + 1) - 4D_J(J + 1)^3 \quad (6)$$

(For definition of the constants  $B$ ,  $D_{KJ}$ , and  $D_J$ , see § 2.2b).

For the rotational Raman spectrum, in the case of the accidental symmetric top the selection rules are

$$\Delta J = 0, \pm 1, \pm 2; \quad \Delta K = 0, \pm 1, \pm 2$$

and

$$+ \leftrightarrow +, \quad - \leftrightarrow -, \quad + \leftarrow \rightarrow -$$

If the molecule is a symmetric top because of its symmetry, the same selection rules apply except that transitions with  $\Delta K = \pm 1, \pm 2$  are no longer possible and, those with  $\Delta J = \pm 1$  occur only for  $K \neq 0$ . In this case the Raman lines form two branches on either side of the undisplaced line with the displacements

$$|\Delta\nu| = F(J + 2, K) - F(J, K) = 6B + 4BJ, \quad J = 0, 1, \dots \text{ (S-branches)}$$

and

$$|\Delta\nu| = F(J + 1, K) - F(J, K) = 2B + 2BJ, \quad J = 1, 2, \dots \text{ (R-branches)}$$

neglecting centrifugal stretching terms.

### 2.3. Spherical top molecules

a. *Moment of inertia and energy levels.* A spherical top is defined as a rotating body in which all three principal moments of inertia are equal, that is,

$$I_A = I_B = I_C = I$$

The energy levels of a spherical top molecule are therefore given by (compare § 2.2b)

$$\frac{E_r}{hc} = F(J) = BJ(J+1), \quad B = \frac{h}{8\pi^2cI} \quad (1)$$

b. *Symmetry properties and statistical weights.* In the case of a spherical top, the distinction between positive and negative rotational levels can be ignored since they always occur in close pairs, and in no case of spherical top molecules has the inversion doubling been resolved.

The statistical weight of a given rotational level due to the over-all rotation is

$$g_J = (2J+1)^2$$

and that due to the nuclear spin is

$$g_I = (2I_1 + 1)(2I_2 + 1)(2I_3 + 1) \dots$$

For molecules that are spherical tops on account of their symmetry there are additional symmetry properties, e.g., *A*, *E*, and *F* for tetrahedral molecules. The over-all statistical weight is then a product of  $(2J+1)$  times a factor that depends in a complicated way both on  $J$  and the spin of the identical nuclei (ref. 10).

c. *Pure rotation spectrum.* Molecules which are spherical tops on account of their symmetry have no pure rotation spectrum in the infrared because they have no permanent dipole moment. Accidental spherical top molecules may have a permanent dipole moment and, consequently, a pure rotation spectrum. The selection rule is

$$\Delta J = 0, \pm 1$$

leading to the same wave-number formula as for linear molecules (§ 2.1g).

Molecules which are spherical tops on account of their symmetry have no pure rotational Raman spectrum, since the polarizability does not change during the rotation. In accidental spherical top molecules a rotational Raman spectrum may occur. The selection rule is

$$\Delta J = 0, \pm 1, \pm 2$$

The Raman displacements are the same as those of a symmetric top molecule (§ 2.2h).

## 2.4. Asymmetric top molecules

a. *Moments of inertia.* The asymmetric top molecule is defined as one in which all three principal moments of inertia are different from each other.

$$I_A \neq I_B \neq I_C \quad (I_A < I_B < I_C)$$

b. *Energy levels.* The energy levels of the asymmetric top are represented by the formula

$$F(J_\tau) = \frac{1}{2}(B + C)J(J + 1) + [A - \frac{1}{2}(B + C)]W_\tau \quad (1)$$

Here  $A = h/8\pi^2cI_A$ ,  $B = h/8\pi^2cI_B$ ,  $C = h/8\pi^2cI_C$ . The symbol  $\tau$  numbers the  $2J + 1$  levels of a given  $J$  in the order of their energy, i.e.,

$$\tau = -J, -J + 1, \dots, +J$$

and  $W_\tau$  are the roots of algebraic equations containing  $A$ ,  $B$ , and  $C$ . For the lowest values of  $J$  one has

$$J = 0: \quad W_0 = 0$$

$$J = 1: \quad W_\tau = 0 \\ W_\tau^2 - 2W_\tau + (1 - b^2) = 0$$

$$J = 2: \quad W_\tau - 1 + 3b = 0 \\ W_\tau - 1 - 3b = 0 \\ W_\tau - 4 = 0 \\ W_\tau^2 - 4W_\tau - 12b^2 = 0$$

$$J = 3: \quad W_\tau - 4 = 0 \\ W_\tau^2 - 4W_\tau - 60b^2 = 0 \\ W_\tau^2 - (10 - 6b)W_\tau + (9 - 54b - 15b^2) = 0 \\ W_\tau^2 - (10 + 6b)W_\tau + (9 + 54b - 15b^2) = 0$$

$$J = 4: \quad W_\tau^2 - 10(1 - b)W_\tau + (9 - 90b - 63b^2) = 0 \\ W_\tau^2 - 10(1 + b)W_\tau + (9 + 90b - 63b^2) = 0 \\ W_\tau^2 - 20W_\tau + (64 - 28b^2) = 0 \\ W_\tau^3 - 20W_\tau^2 + (64 - 208b^2)W_\tau + 2880b^2 = 0$$

Here  $b$  stands for

$$b = \frac{C - B}{2[A - \frac{1}{2}(B + C)]}$$

For higher values of  $J$  see (Refs. 7, 12, 14, 18).

The average of the levels with a certain  $J$  follows accurately (neglecting centrifugal stretching) the formula for the simple rotator with an average rotational constant, that is,

$$\frac{\sum J F(J_\tau)}{2J + 1} = \frac{1}{3}(A + B + C)J(J + 1) \quad (2)$$

When two of the three principal moments of inertia are nearly equal, the formulas for the symmetric top can be applied (see § 2.2*b*) if the average of the two corresponding rotational constants ( $B$  and  $C$  or  $A$  and  $B$ ) is used in place of  $B$ .

c. *Symmetry properties.* Apart from the symmetry property positive-negative with respect to inversion, which is unimportant for asymmetric top molecules, the rotational levels are distinguished by the behavior of their eigenfunctions with respect to rotations by  $180^\circ$  about the axes of largest and smallest moment of inertia ( $C_2^c$  and  $C_2^a$ ). There are thus four different types (species) of rotational levels, briefly described by  $++$ ,  $+ -$ ,  $- +$ , and  $--$ , where the first sign refers to the behavior of the rotational eigenfunction with respect to  $C_2^c$ , the second to the behavior with respect to  $C_2^a$ .

The highest level ( $J_{+J}$ ) of each set with a given  $J$  is always  $+$  with respect to  $C_2^c$ , the two next are  $-$ , the two next  $+$ , and so on. The lowest level ( $J_{-J}$ ) of each set with a given  $J$  is always  $+$  with respect to  $C_2^a$ , the two next  $-$ , the two next  $+$ , and so on.

If an asymmetric top molecule has elements of symmetry, the eigenfunctions have additional symmetry properties corresponding to the exchange of identical nuclei, e.g.,  $A$  and  $B$  (similar to  $a$  and  $s$  of linear molecules) for molecules with one twofold axis and  $A, B_1, B_2, B_3$  for molecules with three twofold axes.

d. *Statistical weights.* For the asymmetric top molecule the statistical weight of a rotational level  $J_r$  due to the over-all rotation of the molecule is

$$g_J = 2J + 1$$

If the molecule has no axis of symmetry, the statistical weight due to the nuclear spins is

$$g_I = (2I_1 + 1)(2I_2 + 1)(2I_3 + 1) \dots$$

If the molecule has one twofold axis of symmetry, the dependence of the statistical weights of the symmetric and antisymmetric rotational levels on the spins and statistics of the identical nuclei is the same as in linear molecules (§ 2.1*e*). If there are three axes of symmetry, more complex relations hold (Ref. 10).

e. *Pure rotation spectrum.* Asymmetric top molecules in general have a permanent dipole moment, and therefore have a pure rotation spectrum in the far infrared or microwave region. The selection rule for  $J$  is

$$\Delta J = 0, \pm 1$$

If the molecule has no symmetry the only further restriction is that levels of the same species do not combine with each other

$$++ \leftrightarrow ++, \quad +- \leftrightarrow +-, \quad -+ \leftrightarrow -+, \quad -- \leftrightarrow --$$

If the molecule has an axis of symmetry, only those rotational levels can combine with one another whose eigenfunctions have the same behavior with respect to a rotation by  $180^\circ$  about this axis, and opposite behavior with respect to similar rotations about the other two axes. Thus if the dipole moment lies in the axis of least moment of inertia ( $a$  axis) only the transitions

$$++ \leftrightarrow +- \quad \text{and} \quad +- \leftrightarrow --$$

can take place. If the dipole moment lies in the axis of intermediate moment of inertia ( $b$  axis) only the transitions

$$++ \leftrightarrow -- \quad \text{and} \quad +- \leftrightarrow -+$$

can take place. If the dipole moment lies in the axis of largest moment of inertia ( $c$  axis), only the transitions

$$++ \leftrightarrow +- \quad \text{and} \quad -+ \leftrightarrow --$$

can take place.

f. *Raman spectrum.* The polarizability of an asymmetric top molecule in general changes during the rotation, and therefore as a rule a rotational Raman spectrum will occur. The selection rule for  $J$  is

$$\Delta J = 0, \pm 1, \pm 2$$

If the molecule has no symmetry, transitions between levels of any of the symmetry types ( $++$ ,  $+-$ ,  $-+$ ,  $--$ ) can occur. If the molecule has at least one twofold axis of symmetry, only levels of the same species can combine with each other, that is

$$++ \leftrightarrow ++, \quad +- \leftrightarrow +-, \quad -+ \leftrightarrow -+, \quad -- \leftrightarrow --$$

## 2.5. Effect of external fields

a. *Zeeman effect.* In an external magnetic field of intensity  $H$ , a state of angular momentum  $J$  is split into  $2J + 1$  components of energy

$$W = W_0 - \bar{\mu}_H H \quad (1)$$

where  $W_0$  is the energy without field and  $\bar{\mu}_H$  the mean value of the component of the magnetic moment of the molecule in the field direction. If the

magnetic moment is due to the orbital motion of the electrons (orbital angular momentum =  $\Lambda h/2\pi$  (see § 5.1), one has

$$\bar{\mu}_H = \frac{\Lambda^2}{J(J+1)} M\mu_0$$

where

$$M = J, J-1, \dots, -J$$

is the quantum number of the component of  $J$  in the field direction, and where

$$\mu_0 = \frac{e}{2mc} \cdot \frac{h}{2\pi}$$

is the Bohr magneton. If the magnetic moment is due to the electron spin only ( $S \neq 0, \Lambda = 0$ ) one has

$$\bar{\mu}_H = 2M_S\mu_0$$

where

$$M_S = S, S-1, \dots, -S$$

If both orbital motion and electron spin are contributing to  $\bar{\mu}_H$  more complicated formulas hold (Ref. 9). If the orbital and the spin angular momentum of the electrons is zero ( $\Lambda = 0, S = 0$ ) as is usual for the electronic ground states of molecules, one has

$$\bar{\mu}_H = g_r M\mu_{0n}$$

where

$$\mu_{0n} = \frac{e}{2m_p c} \cdot \frac{h}{2\pi}$$

is the nuclear magneton ( $m_p =$  mass of proton) and where  $g_r$  is a number of order 1 characteristic of the particular molecular state.

The selection rule for the quantum number  $M$  is

$$\Delta M = 0, \pm 1 \quad (M = 0 \leftarrow 1 \rightarrow M = 0 \text{ for } \Delta J = 0)$$

where  $\Delta M = 0$  applies when the field is parallel to the electric vector of the incident radiation,  $\Delta M = \pm 1$  when it is perpendicular to this vector. From these formulas it follows that for  $\Lambda = 0, S = 0$  in a magnetic field the lines of the rotation spectrum split into three components whose spacing is (in  $\text{cm}^{-1}$ )

$$\Delta\nu = \frac{g_r \mu_{0n}}{hc} H \quad (2)$$

Transitions between the Zeeman levels without change of rotational level may occur as magnetic dipole radiations. Their wave number is

$$\nu = \frac{g_r \mu_{0n} H}{hc} \quad (3)$$

b. *Stark effect.* In an electric field (of intensity  $E$ ) the values of  $M$  are the same as in a magnetic field (§ 2.5a) but levels with the same  $|M|$  coincide. Thus there is a splitting into only  $J + 1$  or  $J + \frac{1}{2}$  component levels (depending on whether  $J$  is integral or half integral). The energies of these levels are given by

$$W = W_0 - \bar{\mu}_E E \quad (4)$$

where  $\bar{\mu}_E$  is the mean component of the *electric* dipole moment in the field direction. For molecules without permanent dipole moment

$$\bar{\mu}_E = a_{JM} E$$

For linear or symmetric top molecules with a permanent dipole moment  $\mu$ ,

$$\bar{\mu}_E = + \frac{\mu M k}{J(J+1)} - \frac{4\pi^2 I_0 \mu^2 E}{h^2} \left\{ \frac{(J^2 - M^2)(J^2 - K^2)}{J^3(2J-1)(2J+1)} - \frac{[(J+1)^2 - M^2][(J+1)^2 - K^2]}{(J+1)^3(2J+1)(2J+3)} \right\}$$

Here  $k = \pm K$ . For diatomic molecules  $K$  must be replaced by  $\Lambda$ , for linear polyatomic molecules by  $l$  (see Ref. 10). If  $K$  (or  $\Lambda$  or  $l$ ) is zero the preceding equation simplifies to

$$\bar{\mu}_E = - \frac{4\pi^2 I_0 \mu^2 E}{h^2} \left[ \frac{J(J+1) - 3M^2}{J(J+1)(2J-1)(2J+3)} \right]$$

that is, only a quadratic, no linear Stark effect occurs.

The same selection rule applies for  $M$  as in the case of the Zeeman effect. But the line splittings in the rotation spectrum are not as simple.

### 2.6. Hyperfine structure (influence of nuclear spin).

If one of the nuclei of the molecule has a nonzero spin  $I$ , the total angular momentum  $F$  will be the vector sum of  $J$  and  $I$ . The corresponding quantum numbers are

$$F = J + I, \quad J + I - 1, \quad \dots, \quad |J - I|$$

For  $J > I$  there is thus a splitting into  $2I + 1$  hyperfine structure components. The magnitude of the splitting depends on the interaction of the nuclear spin with the rest of the molecule.

For purely magnetic interaction the energies of the component levels are given (Ref. 8) by

$$W = W_0 + \left( \frac{aK^2}{J(J+1)} + b \right) [F(F+1) - J(J+1) - I(I+1)] \quad (1)$$

where  $a$  and  $b$  are constants depending on the nuclear magnetic moment

and the magnetic moment due to rotation (§ 2.5a). According to this formula the separation of successive levels is proportional to  $F + 1$  ("interval rule").

If the nucleus of spin  $I \neq 0$  has an electric quadrupole moment, a hyperfine structure splitting arises on account of the electrostatic interaction with the electric field produced by the other nuclei and the electrons at the position of the nucleus considered. This interaction energy is usually much larger than the magnetic interaction energy. For diatomic, linear polyatomic, and symmetric top molecules, the energy levels are given to a first, good approximation by

$$W = W_0 + e^2qQ \left( \frac{3K^2}{J(J+1)} - 1 \right) \frac{\frac{3}{8}G(G+1) - \frac{1}{2}I(I+1)J(J+1)}{I(2I-1)(2J-1)(2J+3)} \quad (2)$$

where  $Q$  is the quadrupole moment of the nucleus in  $\text{cm}^2$ ,  $eq$  is the average inhomogeneity of the electrostatic field at the position of the nucleus in the direction of the  $z$  axis

$$eq = \left( \frac{\partial^2 V}{\partial z^2} \right)_{\text{average}} = \int \frac{3z^2 - r^2}{r^5} de$$

and where

$$G = F(F+1) - I(I+1) - J(J+1)$$

Higher approximations and the case of molecules with two nuclei having a nonzero quadrupole moment have been considered by Bardeen and Townes (Ref. 1).

Transitions between the hyperfine structure levels follow the selection rules

$$\Delta F = 0, \pm 1; \quad F = 0 \leftarrow 1 \rightarrow F = 0$$

For more details see Gordy (Ref. 6).

In a magnetic field each component level of the hyperfine structure splits into  $2F + 1$  components distinguished by

$$M_F = F, \quad F-1, \quad \dots, \quad -F$$

The energy in the field is obtained from the first equation in (§ 2.5a) by substituting

$$\bar{\mu}_H = g_F M_F \mu_{0n}$$

where (Ref. 11),

$$g_F = \frac{[F(F+1) + J(J+1) - I(I+1)]g_r + [F(F+1) + I(I+1) - J(J+1)]g_I}{2F(F+1)}$$

and  $g_r$  and  $g_I$  are rotational and nuclear  $g$ -factors (for  $g_r$  see § 2.5a). The selection rule for  $M_F$  is

$$\Delta M_F = 0, \pm 1$$

### 3. Vibration and Vibration Spectra

#### 3.1. Diatomic molecules

a. *Energy levels.* The vibrational energy levels of a diatomic molecule can be represented by the formula

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \omega_e z_e(v + \frac{1}{2})^4 + \dots \quad (1)$$

where  $v$  is the vibrational quantum number which assumes the values 0, 1, 2, ..., and where  $\omega_e$  is, apart from a factor  $c$ , the vibrational frequency for infinitesimal amplitude. One has in general  $\omega_e z_e \ll \omega_e y_e \ll \omega_e x_e \ll \omega_e$  and frequently  $\omega_e z_e \approx 0$  and  $\omega_e y_e \approx 0$ . The frequency  $\omega_e$  is related to the force constant  $k_e$  in the equilibrium position by the relation

$$\omega_e = \frac{v_{\text{osc}}}{c} = \frac{1}{2\pi c} \sqrt{\frac{k_e}{\mu}}$$

or 
$$k_e = 4\pi^2 \mu c^2 \omega_e^2 = 5.8883 \times 10^{-2} \mu_A \omega_e^2 \text{ dyne/cm}$$

where  $\mu$  and  $\mu_A (= \mu N_A)$  stand for the reduced mass in grams and in atomic weight units ( $0^{16} = 16$ ), respectively.

The zero-point vibrational energy of a diatomic molecule is

$$G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e + \frac{1}{8}\omega_e y_e + \frac{1}{16}\omega_e z_e + \dots \quad (2)$$

If the vibrational energy is measured relative to the lowest level the vibrational formula may be written

$$G_0(v) = \omega_0 v - \omega_0 x_0 v^2 + \omega_0 y_0 v^3 + \omega_0 z_0 v^4 \dots \quad (3)$$

If higher powers of  $(v + \frac{1}{2})$  are negligible, the vibrational constants  $\omega_e$ ,  $\omega_e x_e$ , etc. are related to the constants  $\omega_0$ ,  $\omega_0 x_0$ , etc. by the formulas

$$\left. \begin{aligned} \omega_e z_e &= \omega_0 z_0 \\ \omega_e y_e &= \omega_0 y_0 - 2\omega_0 z_0 \\ \omega_e x_e &= \omega_0 x_0 + \frac{3}{2}\omega_0 y_0 - \frac{3}{2}\omega_0 z_0 \\ \omega_e &= \omega_0 + \omega_0 x_0 + \frac{3}{4}\omega_0 y_0 - \frac{1}{2}\omega_0 z_0 \end{aligned} \right\} \quad (4)$$

The separation of successive vibrational levels is

$$\left. \begin{aligned} \Delta G_{v+\frac{1}{2}} &= G(v+1) - G(v) = G_0(v+1) - G_0(v) \\ &= (\omega_e - \omega_e x_e + \omega_e y_e + \omega_e z_e) - (2\omega_e x_e - 3\omega_e y_e - 4\omega_e z_e)(v + \frac{1}{2}) \\ &\quad + (3\omega_e y_e + 6\omega_e z_e)(v + \frac{1}{2})^2 + 4\omega_e z_e(v + \frac{1}{2})^3 \\ &= (\omega_0 - \omega_0 x_0 + \omega_0 y_0 + \omega_0 z_0) - (2\omega_0 x_0 - 3\omega_0 y_0 - 4\omega_0 z_0)v \\ &\quad + (3\omega_0 y_0 + 6\omega_0 z_0)v^2 + 4\omega_0 z_0 v^3 \end{aligned} \right\} \quad (5)$$

b. *Potential functions and dissociation energy.* For a harmonic oscillator the potential energy is given by

$$V = \frac{1}{2}kx^2 \quad (6)$$

where  $k$  is the force constant (§ 3.1a) and  $x = r - r_e$  is the displacement from the equilibrium position ( $r_e$ ). If anharmonicity is taken into account the potential energy may be represented by a power series

$$V = \frac{1}{2}kx^2(1 + a_1x + a_2x^2 + \dots) \quad (7)$$

or, if large internuclear distances are considered, by a Morse function

$$V(r - r_e) = D_e[1 - e^{-\beta(r-r_e)}]^2 \quad (8)$$

Here  $D_e$  is the dissociation energy referred to the minimum of the potential energy and

$$\beta = \sqrt{\frac{2\pi^2c\mu}{D_e h}} \omega_e = 1.2177 \times 10^7 \omega_e \sqrt{\frac{\mu_A}{D_e}}$$

where  $\mu_A$  is in atomic weight units ( $O^{16} = 16$ ) and  $D_e$  is in  $\text{cm}^{-1}$ .

The dissociation energies  $D_e$  and  $D_0$  are the energies required to dissociate the molecule from the minimum and from the lowest vibrational level, respectively. Therefore

$$D_e = D_0 + G(0)$$

Quite generally  $D_0$  is given by

$$D_0 = \sum_v \Delta G_{v+\frac{1}{2}}$$

If the Morse function is a good approximation, the cubic and quartic terms in the energy expression vanish ( $\omega_e y_e = \omega_e z_e \approx 0$ ) and

$$D_0 = \frac{\omega_0^2}{4\omega_0 x_0}, \quad D_e = \frac{\omega_e^2}{4\omega_e x_e}$$

This approximation is frequently very poor.

c. *Eigenfunctions.* As long as the anharmonicity of the vibration is small, the vibrational eigenfunctions are approximated by the harmonic oscillator eigenfunctions. These are the Hermite orthogonal functions

$$\psi_v(x) = N_v e^{-\frac{1}{2}\alpha x^2} H_v(\sqrt{\alpha}x) \quad (9)$$

where  $N_v$  is a normalization factor,  $H_v(\sqrt{\alpha}x)$  the Hermite polynomial of the  $v$ th degree (see § 12.1 of Chapter 1), and

$$\alpha = \frac{4\pi^2\mu\nu_{\text{osc}}}{h} = \frac{2\pi\sqrt{\mu k}}{h}$$

For the anharmonic oscillator eigenfunctions see Refs. 3 and 5.

d. *Selection rules and spectrum.* An infrared vibration spectrum can occur only if the molecule has no center of symmetry, that is, if it does not consist of two like nuclei. A vibrational Raman spectrum occurs for both symmetrical and asymmetrical molecules. For the harmonic oscillator the selection rule for the vibrational quantum number is (both in the Raman effect and the infrared)

$$\Delta v = \pm 1$$

For the anharmonic oscillator no strict selection rule exists, but transitions with  $\Delta v = 1$  are much stronger than those with  $\Delta v = 2$ , those with  $\Delta v = 2$  much stronger than those with  $\Delta v = 3$ , and so on.

Absorption of light by the molecule in the ground state produces a series of bands whose wave numbers correspond to the energies of successive vibrational levels

$$\left. \begin{aligned} \nu_{\text{abs}} &= G(v) - G(0) \\ &= \omega_e \left[ \left( v + \frac{1}{2} \right) - \frac{1}{2} \right] - \omega_e x_e \left[ \left( v + \frac{1}{2} \right)^2 - \frac{1}{4} \right] + \omega_e y_e \left[ \left( v + \frac{1}{2} \right)^3 - \frac{1}{8} \right] + \dots \\ &= G_0(v) = \omega_0 v - \omega_0 x_0 v^2 + \omega_0 y_0 v^3 + \dots \end{aligned} \right\} \quad (10)$$

The same formula holds for the displacements observed in the Raman spectrum.

e. *Isotope effect.* The vibrational constants of an isotopic molecule [designated by the superscript (*i*)] are related to those of the "normal" molecule by the formulas

$$\omega_e^{(i)} = \rho \omega_e, \quad \omega_e^{(i)} x_e^{(i)} = \rho^2 \omega_e x_e, \quad \omega_e^{(i)} y_e^{(i)} = \rho^3 \omega_e y_e, \quad \dots \quad (11)$$

where

$$\rho = \sqrt{\frac{\mu}{\mu^{(i)}}}$$

and  $\mu$  and  $\mu^{(i)}$  are the reduced masses (see § 2.1a) of the "normal" and the isotopic molecules, respectively. The vibrational absorption bands of an isotopic molecule are given by the formula (see § 3.1d).

$$\left. \begin{aligned} \nu_{\text{abs}}^{(i)} &= \rho \omega_e \left[ \left( v + \frac{1}{2} \right) - \frac{1}{2} \right] - \rho^2 \omega_e x_e \left[ \left( v + \frac{1}{2} \right)^2 - \frac{1}{4} \right] \\ &\quad + \rho^3 \omega_e y_e \left[ \left( v + \frac{1}{2} \right)^3 - \frac{1}{8} \right] + \dots \end{aligned} \right\} \quad (12)$$

The vibrational isotope shift is therefore

$$\left. \begin{aligned} \Delta \nu &= \nu_{\text{abs}} - \nu_{\text{abs}}^{(i)} \\ &= \omega_e (1 - \rho) v - \omega_e x_e (1 - \rho^2) (v^2 + v) \\ &\quad + \omega_e y_e (1 - \rho^3) (v^3 + \frac{3}{2} v^2 + \frac{3}{4} v) + \dots \end{aligned} \right\} \quad (13)$$

If  $\rho$  is close to one, the vibrational isotope shift is approximately given by the expression

$$\Delta\nu = (1 - \rho)v\Delta G_{v+\frac{1}{2}} \quad (14)$$

### 3.2. Polyatomic molecules

a. *Normal vibrations and normal coordinates.* The potential and kinetic energies of a system of  $N$  particles of masses  $m_i$  for small displacements from the equilibrium position are given by

$$V = \frac{1}{2} \sum_{ij} k_{ij} q_i q_j \quad (1)$$

and

$$T = \frac{1}{2} \sum_{ij} b_{ij} \dot{q}_i \dot{q}_j \quad (2)$$

where the  $q_i$  may either be  $3N$  Cartesian displacement coordinates or, for nonlinear molecules,  $3N - 6$ , for linear molecules,  $3N - 5$  internal displacement coordinates such as changes of internuclear distances. The  $k_{ij}$  ( $= k_{ji}$ ) are force constants, the  $b_{ij}$  ( $= b_{ji}$ ) are constants depending on the masses and geometrical parameters of the molecule. By the linear transformation

$$q_i = c_{i1}\xi_1 + c_{i2}\xi_2 + c_{i3}\xi_3 + \dots$$

new coordinates  $\xi_i$ , so-called normal coordinates, can be formed such that both  $V$  and  $T$  are sums of squares.

$$V = \frac{1}{2}(\lambda_1\xi_1^2 + \lambda_2\xi_2^2 + \lambda_3\xi_3^2 + \dots) \quad (3)$$

$$T = \frac{1}{2}(\dot{\xi}_1^2 + \dot{\xi}_2^2 + \dot{\xi}_3^2 + \dots) \quad (4)$$

that is, the motion in the molecule in this approximation may be considered as a superposition of  $3N$  or  $3N - 6$  or  $3N - 5$  independent harmonic oscillators described by the normal coordinates  $\xi_i$  such that

$$\xi_i = \xi_i^0 \cos(2\pi\nu_i t + \varphi_i)$$

In each such normal vibration all nuclei in the molecule carry out simple harmonic motions about their respective equilibrium positions with one and the same frequency  $\nu_i$  which is related to  $\lambda_i$  by

$$\lambda_i = 4\pi^2\nu_i^2 \quad (5)$$

The  $\lambda_i$ , that is, the frequencies of the different normal vibrations, are determined by the secular equation :

$$\begin{vmatrix} k_{11} - b_{11}\lambda & k_{12} - b_{12}\lambda & k_{13} - b_{13}\lambda & \dots \\ k_{21} - b_{21}\lambda & k_{22} - b_{22}\lambda & k_{23} - b_{23}\lambda & \dots \\ k_{31} - b_{31}\lambda & k_{32} - b_{32}\lambda & k_{33} - b_{33}\lambda & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix} = 0 \quad (6)$$

If Cartesian coordinates are used, six or five of the  $\lambda_i$  are found to be zero depending on whether the molecule is nonlinear or linear, respectively. These zero roots correspond to the nongenuine normal vibrations (null vibrations) : the translations and rotations. When two or three  $\lambda_i$  are equal, we have doubly or triply degenerate normal vibrations.

The form of a given normal vibration  $\xi_j$  can be obtained from the transformation equations by putting all other  $\xi_i$  equal to zero. The coefficients  $c_{ij}$  are the minors of the above determinant.

*Special cases.* The general relation between the force constants and the frequencies of the normal vibrations is given by the determinantal equation (6) above. In the most general case there are  $\frac{1}{2}n(n+1)$  force constants, ( $n = 3N - 6$  or  $3N - 5$ ) while there are only  $n$  normal frequencies.

If the molecule has symmetry the normal vibrations also have certain symmetry properties. For a given molecular symmetry there are a number of symmetry types (or species) of the normal vibrations. For example, if the molecule has a single plane of symmetry there are two species of normal vibrations, those that are symmetric with respect to that plane and those that are antisymmetric with respect to it. They are designated  $A'$  and  $A''$ , respectively. For a molecule with two mutually perpendicular planes of symmetry there are four species which may be characterized by  $++$ ,  $--$ ,  $+-$ ,  $-+$  where the two signs indicate the behavior with respect to the two planes. These four species are designated  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$ , respectively. For other cases see Ref. 10.

In the case of a symmetrical molecule, if the original coordinates are appropriately chosen (symmetry coordinates) the secular determinant can be factored into as many smaller determinants as there are different species. The degree of each of these subdeterminants, that is, the number  $f_j$  of vibrations of the particular species  $j$  can be readily obtained from the number of the various atoms in the molecule. The number of force constants belonging to each species is  $\frac{1}{2}f_j(f_j + 1)$  and therefore the total number of force constants is  $\sum \frac{1}{2}f_j(f_j + 1)$  which is smaller, often much smaller, than  $\frac{1}{2}n(n+1)$ . But even then the number of force constants is in general larger than the number of normal frequencies.

In order to reduce the number of unknown force constants, often simplifying assumptions are made about the restoring forces in the molecule. The assumption most often used is that of valence forces, that is, of a strong restoring force in the line of every valence bond and a weaker one opposing a change of the angle between two valence bonds connecting one atom with two others.

Thus, if in nonlinear symmetric  $XY_2$  molecules  $k_1$  is the force constant of the  $XY$  bond and  $k_\delta$  the force constant of the  $Y-X-Y$  angle, the following simple relations between the frequencies and force constants are obtained by solving the corresponding secular equations :

$$\left. \begin{aligned} 4\pi^2(\nu_1^2 + \nu_2^2) &= \left(1 + \frac{2m_Y}{m_X} \cos^2 \alpha\right) \frac{k_1}{m_Y} + \frac{2}{m_Y} \left(1 + \frac{2m_Y}{m_X} \sin^2 \alpha\right) \frac{k_\delta}{l^2} \\ 16\pi^4 \nu_1^2 \nu_2^2 &= 2 \left(1 + \frac{2m_Y}{m_X}\right) \frac{k_1}{m_Y^2} \cdot \frac{k_\delta}{l^2} \\ 4\pi^2 \nu_3^2 &= \left(1 + \frac{2m_Y}{m_X} \sin^2 \alpha\right) \frac{k_1}{m_Y} \end{aligned} \right\} \quad (7)$$

Here  $m_X$  and  $m_Y$  are the masses of the atoms  $X$  and  $Y$ ,  $\alpha$  is half the  $Y-X-Y$  angle, and  $l$  is the  $XY$  distance.

For linear symmetric  $XY_2$ , one finds

$$\left. \begin{aligned} 4\pi^2 \nu_1^2 &= \frac{k_1}{m_Y} \\ 4\pi^2 \nu_2^2 &= \frac{2}{m_Y} \left(1 + \frac{2m_Y}{m_X}\right) \frac{k_\delta}{l^2} \\ 4\pi^2 \nu_3^2 &= \left(1 + \frac{2m_Y}{m_X}\right) \frac{k_1}{m_Y} \end{aligned} \right\} \quad (8)$$

For linear  $XYZ$  molecules, if  $k_1$  and  $k_2$  are the force constants,  $l_1$  and  $l_2$  the lengths of the  $XY$  and  $YZ$  bonds, one finds

$$\left. \begin{aligned} 4\pi^2(\nu_1^2 + \nu_3^2) &= k_1 \left(\frac{1}{m_X} + \frac{1}{m_Y}\right) + k_2 \left(\frac{1}{m_Y} + \frac{1}{m_Z}\right) \\ 16\pi^4 \nu_1^2 \nu_3^2 &= \frac{m_X + m_Y + m_Z}{m_X m_Y m_Z} k_1 k_2 \\ 4\pi^2 \nu_2^2 &= \frac{1}{l_1^2 l_2^2} \left(\frac{l_1^2}{m_Z} + \frac{l_2^2}{m_X} + \frac{(l_1 + l_2)^2}{m_Y}\right) k_\delta \end{aligned} \right\} \quad (9)$$

b. *Energy levels.* In the approximation in which the normal vibrations

are well defined, that is, when the potential energy contains only quadratic terms the vibrational energy is simply

$$G(v_1, v_2, v_3, \dots) = \sum \omega_i (v_i + \frac{1}{2}) \quad (10)$$

where  $v_i$  is the vibrational quantum number of the  $i$ th normal vibration and  $\omega_i = \nu_i/c$ . If the potential energy contains higher powers, that is

$$2V = \sum_i \sum_j k_{ij} q_i q_j + \sum_i \sum_j \sum_k f_{ijk} q_i q_j q_k + \sum_i \sum_j \sum_k \sum_l g_{ijkl} q_i q_j q_k q_l + \dots$$

and if there are no degenerate vibrations, the vibrational energy becomes

$$G(v_1, v_2, v_3, \dots) = \sum_i \omega_i (v_i + \frac{1}{2}) + \sum_i \sum_{k \geq i} x_{ik} (v_i + \frac{1}{2}) (v_k + \frac{1}{2}) + \dots \quad (11)$$

Here the anharmonicity constants  $x_{ik}$  are small compared to the  $\omega_i$  if the deviations from a quadratic potential are small; the  $\omega_i$  are now the (classical) vibrational frequencies in  $\text{cm}^{-1}$  for infinitesimal amplitudes (so-called zero-order frequencies).

The zero-point vibrational energy is

$$G(0, 0, \dots) = \frac{1}{2} \sum_i \omega_i + \frac{1}{4} \sum_i \sum_{k \geq i} x_{ik} \quad (12)$$

Referred to this lowest energy level the vibrational energy may also be written

$$G_0(v_1, v_2, \dots) = \sum_i \omega_i^0 v_i + \sum_i \sum_{k \geq i} x_{ik}^0 v_i v_k + \dots \quad (13)$$

where

$$\omega_i^0 = \omega_i + x_{ii} + \frac{1}{2} \sum_{k \neq i} x_{ik} + \dots$$

The wave numbers of the 1-0 bands, the so-called fundamentals, are given by

$$\nu_i = \omega_i^0 + x_{ii}^0 = \omega_i + 2x_{ii} + \frac{1}{2} \sum_{k \neq i} x_{ik} + \dots$$

where  $x_{ik} = x_{ki}$ , and, if higher powers are neglected,  $x_{ik}^0 = x_{ik}$ .

If degenerate normal vibrations are present the previous energy formula has to be replaced by

$$G(v_1, v_2, \dots) = \left. \begin{aligned} & \sum_i \omega_i \left( v_i + \frac{d_i}{2} \right) + \sum_i \sum_{k \geq i} x_{ik} \left( v_i + \frac{d_i}{2} \right) \left( v_k + \frac{d_k}{2} \right) \\ & + \sum_i \sum_{k \geq i} g_{ik} l_i l_k + \dots \end{aligned} \right\} \quad (14)$$

In this equation  $d_i$  is the degree of degeneracy; the  $l_i$  are integral numbers which assume the values

$$l_i = v_i, \quad v_i - 2, \quad v_i - 4, \quad \dots \quad 1 \text{ or } 0$$

and the  $g_{ik}$  are constants of the order of the  $x_{ik}$  (not to be confused with the potential constants  $g_{ijkl}$ ).

The zero-point energy in the presence of degenerate vibrations is

$$G(0,0,\dots) = \sum_i \omega_i \frac{d_i}{2} + \sum_i \sum_{k \geq i} x_{ik} \frac{d_i d_k}{4} \dots \quad (15)$$

The vibrational energy referred to the lowest vibrational energy level is

$$G_0(v_1, v_2, \dots) = \sum_i \omega_i^0 v_i + \sum_i \sum_{k \geq i} x_{ik}^0 v_i v_k + \sum_i \sum_{k \geq i} g_{ik} l_i l_k + \dots \quad (16)$$

where

$$\omega_i^0 = \omega_i + x_{ii} d_i + \frac{1}{2} \sum_{k \neq i} x_{ik} d_k + \dots$$

and where  $x_{ik}^0 = x_{ik}$ , if higher powers are neglected. The fundamentals are

$$v_i = \omega_i^0 + x_{ii} + g_{ii} = \omega_i + x_{ii}(1 + d_i) + \frac{1}{2} \sum_{k \neq i} x_{ik} d_k + g_{ii}$$

where, as previously,  $x_{ik} = x_{ki}$ .

c. *Eigenfunctions.* The total vibrational eigenfunction of a polyatomic molecule is, to a first approximation, the product of  $3N - 6$ , or, in the case of a linear molecule,  $3N - 5$ , harmonic oscillator functions (§ 3.1c).

$$\psi_v = \prod \psi_i(\xi_i) = \prod N_{v_i} e^{-\frac{1}{2}\alpha_i \xi_i^2} H_{v_i}(\sqrt{\alpha_i} \xi_i) \quad (17)$$

where  $\alpha_i = 2\pi c \omega_i / h$ .

d. *Selection rules, vibration spectra.* In the harmonic oscillator approximation, the only allowed transitions are those in which one vibration changes its vibrational quantum by one unit, i.e.,

$$\Delta v_i = \pm 1, \quad \Delta v_k = 0$$

If the anharmonicity of the vibrations is taken into account also transitions in which  $v_i$  changes by several units or in which several  $v_i$  change will occur. But they are in general less intense than the fundamentals.

If the molecule has symmetry, certain rigorous selection rules for vibrational transitions hold irrespective of the degree of anharmonicity. Quite generally a vibrational transition  $v' \longleftrightarrow v''$  is allowed in the infrared when there is at least one component of the dipole moment  $M$  that has the same

species (i.e., the same behavior with respect to the symmetry operations permitted by the symmetry of the molecule) as the product  $\psi_v'\psi_v''$ . A vibrational transition  $v' \longleftrightarrow v''$  is allowed in the Raman effect if at least one component of the polarizability tensor has the same species as the product  $\psi_v'\psi_v''$ .

As a result, for example, for molecules with a center of symmetry, transitions that are allowed in the infrared are forbidden in the Raman spectrum, and those allowed in the Raman spectrum are forbidden in the infrared.

A table of the species of the components of the dipole moment and of the polarizability for the more important point groups is given in Ref. 10.

For molecules for which the inversion doubling (§ 2.2d) is not negligible the additional selection rule has to be taken into account that in the infrared only sublevels of opposite parity can combine with one another ( $+ \longleftrightarrow -$ ), whereas in the Raman effect only sublevels of the same parity can combine with one another ( $+ \longleftrightarrow +$ ,  $- \longleftrightarrow -$ ).

c. *Isotope effect.* For two isotopic molecules the product of the  $\omega^{(i)}/\omega$  values for all vibrations of a given symmetry type is independent of the potential constants and depends only on the masses of the atoms and the geometrical structure of the molecule according to the following formula (Teller-Redlich product rule) :

$$\left. \frac{\omega_1^{(i)}\omega_2^{(i)}}{\omega_1\omega_2} \cdots \frac{\omega_f^{(i)}}{\omega_f} \right\} = \sqrt{\left(\frac{m_1}{m_1^{(i)}}\right)^\alpha \left(\frac{m_2}{m_2^{(i)}}\right)^\beta \cdots \left(\frac{M^{(i)}}{M}\right)^t \left(\frac{I_x^{(i)}}{I_x}\right)^{\delta x} \left(\frac{I_y^{(i)}}{I_y}\right)^{\delta y} \left(\frac{I_z^{(i)}}{I_z}\right)^{\delta z}} \right\} \quad (18)$$

Here quantities with the superscript  $(i)$  refer to one of the isotopic molecules, quantities without superscript to the other;  $\omega_1, \omega_2, \dots, \omega_f$  are the zero order frequencies of the  $f$  (genuine) vibrations of the symmetry type considered;  $m_1, m_2, \dots$  are the masses of the representative atoms of the various sets (each set consisting of those identical atoms that are transformed into one another by the symmetry operations permitted by the molecule);  $\alpha, \beta, \dots$  are the numbers of vibrations (inclusive of nongenuine vibrations) that each set contributes to the symmetry type considered;  $M$  is the total mass of the molecule;  $t$  is the number of translations of the symmetry type considered;  $I_x, I_y, I_z$  are the moments of inertia about the  $x, y,$  and  $z$  axes;  $\delta x, \delta y, \delta z$  are 1 or 0 depending on whether or not the rotation about the  $x, y,$  or  $z$  axis is a nongenuine vibration of the symmetry type considered. Both on the left and right hand side (in  $\alpha, \beta, \dots, t, \delta x, \delta y, \delta z$ ) a degenerate vibration is counted only once.

#### 4. Interaction of Rotation and Vibration : Rotation-Vibration Spectra

##### 4.1. Diatomic molecules

a. *Energy levels.* The interaction of rotation and vibration causes the rotational energy of a vibrating molecule to be somewhat different from that of a nonvibrating molecule. One has for the term values of the rotating vibrator

$$T = G(v) + F_v(J) \quad (1)$$

where  $G(v)$  is given by the previous formula (§ 3.1a) and where

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2 + \dots$$

Here

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \dots$$

and

$$D_v = D_e + \beta_e(v + \frac{1}{2}) + \dots$$

The constants  $B_e$  and  $D_e$  refer to the equilibrium position and are defined by formulas entirely similar to those previously given for  $B$  and  $D$  (§ 2.1b). The constants  $\alpha_e$  and  $\beta_e$  are small compared to  $B_e$  and  $D_e$ , respectively, and are determined by the form of the potential function.

b. *Selection rules and spectrum.* For rotation-vibration spectra the same selection rules apply as for the pure rotation and the pure vibration spectrum separately. Therefore the vibrational quantum number can change by

$$\Delta v = \pm 1, \pm 2, \dots$$

with  $\Delta v = \pm 1$  giving by far the strongest transitions. The selection rules for the rotational quantum number, assuming that there is no electronic angular momentum about the internuclear axis, are, in the case of infrared transitions

$$\Delta J = J' - J'' = \pm 1$$

and in the case of Raman transitions

$$\Delta J = J' - J'' = 0, \pm 2$$

Hence in the infrared a rotation-vibration band consists of two branches, an  $R$  branch ( $\Delta J = +1$ ) and a  $P$  branch ( $\Delta J = -1$ ) which are given by (neglecting small terms in  $D'$  and  $D''$ )

$$\nu_R = \nu_0 + 2B_v' + (3B_v' - B_v'')J + (B_v' - B_v'')J^2 \quad (J = 0, 1, \dots)$$

$$\nu_P = \nu_0 - (B_v' + B_v'')J + (B_v' - B_v'')J^2 \quad (J = 1, 2, \dots)$$

Here  $\nu_0$ , the vibrational energy difference between the two states (band origin), is given by  $\nu_{\text{abs}}$  in § 3.1d;  $J$  is the rotational quantum number  $J''$  of the lower state.

In the Raman effect a rotation-vibration band consists of three branches, an *S* branch ( $\Delta J = +2$ ), an *O* branch ( $\Delta J = -2$ ), and a *Q* branch ( $\Delta J = 0$ ). Formulas for these branches may be found in Ref. 9.

c. *Combination differences and combination sums.* The combination differences

$$\begin{aligned} R(J-1) - P(J+1) &= F_v''(J+1) - F_v''(J-1) = \Delta_2 F''(J) \\ &= (4B_v'' - 6D_v'')(J + \frac{1}{2}) - 8D_v''(J + \frac{1}{2})^3 \end{aligned}$$

$$\begin{aligned} R(J) - P(J) &= F_v'(J+1) - F_v'(J-1) = \Delta_2 F'(J) \\ &= (4B_v' - 6D_v')(J + \frac{1}{2}) - 8D_v'(J + \frac{1}{2})^3 \end{aligned}$$

are used to separate the rotational energy levels of the upper and lower vibrational states and to determine the rotational constants.

The combination sums

$$R(J-1) + P(J) = 2\nu_0 + 2(B_v' - B_v'')J^2 - 2(D_v' - D_v'')J^2(J^2 + 1)$$

are used to determine the band origins (zero lines) and the differences ( $B_v' - B_v''$ ) and ( $D_v' - D_v''$ ) of the rotational constants.

Similar combination relations apply to the *S* and *O* branches observed in the Raman effect.

## 4.2. Linear polyatomic molecules

a. *Energy levels.* The rotational term values of a vibrating linear polyatomic molecule are given by the same formula as those of diatomic molecules (§ 4.1) except that  $B_v$  depends now on the vibrational quantum numbers of all the vibrations. We have

$$B_{[v]} = B_{v_1 v_2 v_3 \dots} = B_e - \sum \alpha_i \left( v_i + \frac{d_i}{2} \right) \quad (1)$$

where the  $\alpha_i$  are small constants similar to  $\alpha_e$  for diatomic molecules and where  $d_i$  is the degeneracy of the vibration  $i$ . Here  $B_e$  is the rotational constant for the equilibrium position and is given by

$$B_e = \frac{h}{8\pi^2 c I_e}$$

where  $I_e$  is the moment of inertia in the equilibrium position. The rotational constant  $B_{000\dots}$ , obtainable from the pure rotation spectrum, for the lowest vibrational level is given by

$$B_{[0]} = B_{000\dots} = B_e - \sum \alpha_i \frac{d_i}{2}$$

Vibrational levels with  $l = 1, 2, \dots$ , ( $\Pi, \Delta, \dots$  vibrational levels) are doubly degenerate (§ 3.2a). With increasing rotation a splitting of this degeneracy arises ( $l$ -type doubling). As a result there are two rotational term series with slightly different rotational constants,  $B_v^c$  and  $B_v^d$ . The splitting is given by

$$\Delta\nu = q_i J(J+1) = (B_v^c - B_v^d) J(J+1) \quad (2)$$

The splitting constant  $q_i$  for a given perpendicular vibration  $\nu_i$  is of the same order as  $\alpha_i$ . For detailed formulas see Ref. 15. The two levels of a given  $J$  have opposite parity (+, -).

b. *Selection rules and spectrum.* The selection rules for rotation-vibration spectra of linear polyatomic molecules are the same as for diatomic molecules (§ 4.1b) if the quantum number  $l$  of the vibrational angular momentum is zero in both the upper and lower states, i.e., if  $l' = l'' = 0$ . In this case the same two branches occur.

If  $l'$  or  $l''$  or both are different from zero, in addition to the transitions discussed in § 4.1b, in the infrared, transitions with  $\Delta J = 0$  occur; in the Raman effect, transitions with  $\Delta J = \pm 1$  occur. That is, the selection rules are

$$\Delta J = 0, \pm 1 \quad (\text{infrared})$$

$$\Delta J = 0, \pm 1, \pm 2 \quad (\text{Raman effect})$$

At the same time the symmetry selection rules

$$+ \longleftrightarrow -, \quad s \longleftrightarrow a \quad (\text{infrared})$$

$$+ \longleftrightarrow +, \quad - \longleftrightarrow -, \quad S \longleftrightarrow \quad (\text{Raman effect})$$

must be obeyed.

The additional possibility  $\Delta J = 0$  in the infrared gives rise to a  $Q$  branch whose formula is

$$\nu_Q = \nu_0 + (B' - B'')J + (B' - B'')J^2 \quad (3)$$

In the Raman spectrum in such cases  $P$  and  $R$  branches in addition to the  $S$ ,  $O$ , and  $Q$  branches can occur.

According to the preceding selection rules, when  $l_i$  is different from zero a transition between the two components of an  $l$ -type doublet can occur. Such transitions occur in the microwave region and are represented by the formula

$$\nu = q_i J(J+1) \quad (4)$$

### 4.3. Symmetric top molecules

a. *Energy levels.* As for linear molecules, the term values of a vibrating symmetric top molecule can be represented as the sum of vibrational and rotational term values

$$T = G(v_1, v_2, v_3, \dots) + F_{[v]}(J, K) \quad (1)$$

In the case of a nondegenerate vibrational level and neglecting the effect of centrifugal forces, the rotational term values are given by

$$F_{[v]}(J, K) = B_{[v]}J(J+1) + (A_{[v]} - B_{[v]})K^2 \quad (2)$$

where  $[v]$  stands for the set of vibrational quantum numbers  $v_1, v_2, v_3, \dots$  and where

$$B_{[v]} = B_e - \sum \alpha_i^B \left( v_i + \frac{d_i}{2} \right) + \dots$$

$$A_{[v]} = A_e - \sum \alpha_i^A \left( v_i + \frac{d_i}{2} \right) + \dots$$

The  $\alpha_i^B$  and  $\alpha_i^A$  are constants similar to  $\alpha_e$  of diatomic molecules and

$$B_e = \frac{h}{8\pi^2 c I_B^e} \quad \text{and} \quad A_e = \frac{h}{8\pi^2 c I_A^e}$$

are the rotational constants corresponding to the equilibrium position.

In a degenerate vibrational level the Coriolis interaction of the degenerate components causes an additional term

$$-2A_{[v]} \sum_i (\pm \zeta_i l_i) K \quad (3)$$

which has to be added to the previous expression for  $F_{[v]}(J, K)$ . Here  $\zeta_i$  is a constant,  $0 \leq \zeta_i \leq 1$ , measuring the magnitude of the vibrational angular momentum of the degenerate vibration  $\nu_i$  in units  $h/2\pi$  and  $l_i = v_i, v_i - 2, \dots, 1$  or  $0$  is the azimuthal quantum number of the degenerate vibration. For a state in which only one degenerate vibration is singly excited ( $l_i = 1$ ) the additional term is

$$\mp 2A_{[v]} \zeta_i K$$

leading to an increasing splitting of the degeneracy with increasing  $K$ .

The individual  $\zeta_i$  are complicated functions of the potential constants and other parameters of the molecule. But the sums of the  $\zeta_i$  of all vibrations of a given species are independent of the potential constants. For example, for axial  $XY_3$  molecules (pyramidal or planar)

$$\zeta_3 + \zeta_4 = \frac{I_A}{2I_B} - 1 = \frac{B}{2A} - 1$$

for axial  $XYZ_3$  molecules

$$\zeta_4 + \zeta_5 + \zeta_6 = \frac{I_A}{2I_B} = \frac{B}{2A}$$

for axial  $WXYZ_3$  molecules

$$\zeta_5 + \zeta_6 + \zeta_7 + \zeta_8 = \frac{I_A}{2I_B} + 1 = \frac{B}{2A} + 1$$

For  $X_2Y_6$  molecules of point group  $D_{3h}$  or  $D_{3d}$

$$\zeta_7 + \zeta_8 + \zeta_9 = 0, \quad \text{and} \quad \zeta_{10} + \zeta_{11} + \zeta_{12} = \frac{I_A}{2I_B} = \frac{B}{2A}$$

b. *Selection rules and spectrum.*

*Infrared.* The selection rules for the vibrational quantum numbers are the same as for the pure vibration spectrum. If the molecule is a symmetric top on account of its symmetry, the (vibrational) transition moment can be only either parallel or perpendicular to the figure axis. For an accidental symmetric top any orientation with regard to the figure axis is possible.

If the transition is parallel to the figure axis ( $\parallel$  band), the selection rules for the rotational quantum numbers are

$$\Delta K = 0, \quad \Delta J = 0, \pm 1 \quad (\Delta J = 0 \text{ forbidden for } K = 0)$$

and if the transition moment is perpendicular to the figure axis ( $\perp$  band)

$$\Delta K = \pm 1, \quad \Delta J = 0, \pm 1$$

If the transition moment has a general direction with respect to the figure axis, changes of the rotational quantum numbers allowed by either set of selection rules may occur, i.e., the resulting band has both a  $\parallel$  and a  $\perp$  component (hybrid band).

Both  $\parallel$  and  $\perp$  bands consist of a number of subbands corresponding to the different values of  $K$ . Each subband consists of a  $P$ , a  $Q$  and an  $R$  branch corresponding to  $\Delta J = -1, 0$ , and  $+1$ , respectively, similar to the bands of linear molecules.

The zero lines of the subbands of a  $\parallel$  band or of the  $\parallel$  component of a hybrid band are given by

$$\nu_0^{\text{sub}} = \nu_0 + [(A_{[v]}' - A_{[v]}'') - (B_{[v]}' - B_{[v]}'')]K^2 \quad (4)$$

those of a  $\perp$  band or of the  $\perp$  component of a hybrid band are given by

$$\left. \begin{aligned} \nu_0^{\text{sub}} = \nu_0 + (A_{[v]}' - B_{[v]}') \pm 2(A_{[v]}' - B_{[v]}')K \\ + [(A_{[v]}' - B_{[v]}') - (A_{[v]}'' - B_{[v]}'')]K^2 \end{aligned} \right\} (5)$$

Here it is assumed that both states involved are nondegenerate or, if degenerate, of such a nature that the effect of Coriolis forces can be neglected. If this is not the case the term  $-2A_{[v]} \Sigma (\pm \zeta_i l_i) K$  has to be added to the energy formula, and the subband formulas are correspondingly changed. For example, if the upper state is degenerate with  $\zeta_i \neq 0$ ,  $l_i = 1$ , and the lower state nondegenerate, the subbands of the resulting  $\perp$  band are given by

$$\left. \begin{aligned} \nu_0^{\text{sub}} = \nu_0 + [A_{[v]}'(1 - 2\zeta_i) - B_{[v]}' ] \pm 2[A_{[v]}'(1 - \zeta_i) - B_{[v]}' ] K \\ + [(A_{[v]}' - B_{[v]}') - (A_v'' - B_v'')] K^2 \end{aligned} \right\} \quad (6)$$

where the upper sign holds for  $\Delta K = +1$  and the lower for  $\Delta K = -1$ . Neglecting the dependence of  $A$  and  $B$  on the  $\nu_i$ , the spacing of the subbands is  $2[A(1 - \zeta_i) - B]$  instead of  $2(A - B)$  for a nondegenerate upper state.

The intensities of the lines in absorption are given by the expression

$$I(J, K) = CA_{KJ} \nu g_{KJ} e^{-F(K, J)hc/kT} \quad (7)$$

where the statistical weight factors  $g_{KJ}$  are the same as those given in § 2.2e and the intensity factors  $A_{KJ}$  are

$$\left. \begin{aligned} \Delta J = +1: \quad A_{KJ} &= \frac{(J+1)^2 - K^2}{(J+1)(2J+1)} \\ \Delta J = 0: \quad A_{KJ} &= \frac{K^2}{J(J+1)} \\ \Delta J = -1: \quad A_{KJ} &= \frac{J^2 - K^2}{J(2J+1)} \end{aligned} \right\} \quad (\Delta K = 0) \quad (8)$$

$$\left. \begin{aligned} \Delta J = +1: \quad A_{KJ} &= \frac{(J+2 \pm K)(J+1 \pm K)}{(J+1)(2J+1)} \\ \Delta J = 0: \quad A_{KJ} &= \frac{(J+1 \pm K)(J \mp K)}{J(J+1)} \\ \Delta J = -1: \quad A_{KJ} &= \frac{(J-1 \mp K)(J \mp K)}{J(2J+1)} \end{aligned} \right\} \quad (\Delta K = \pm 1) \quad (9)$$

Here  $K$  and  $J$  refer to the rotational quantum numbers of the lower state. For  $K = 0$ ,  $\Delta K = +1$  the values given by the formulas have to be multiplied by 2.

*Raman effect.* The vibrational selection rules are again the same as for the pure vibration spectrum (§ 3.2d). In the most general case of an accidental symmetric top with arbitrary orientation of the polarizability ellipsoid

with respect to the momental ellipsoid the selection rules for the rotational quantum numbers are

$$\Delta K = 0, \pm 1, \pm 2; \quad \Delta J = 0, \pm 1, \pm 2 \quad (J' + J'' \geq 2)$$

If the molecule has symmetry and if therefore the figure axis coincides with one of the symmetry axes, only certain components of the matrix elements of the polarizability  $\alpha$  are different from zero and only certain of the above transitions can occur.

For vibrational transitions for which only  $[\alpha_{zz}]^{nm}$  or  $[\alpha_{xx} + \alpha_{yy}]^{nm}$  or both are different from zero, only  $\Delta K = 0$  occurs. Here it is assumed that the  $z$  axis is the figure axis;  $[\alpha_{zz}]^{nm}$  stands for the integral  $\int \alpha_{zz} \psi_n \psi_m^* dt$ , and similarly in other cases. For axial molecules  $\Delta K = 0$  applies to all transitions for which  $\psi_n \psi_m^*$  is totally symmetric. For vibrational transitions for which only  $[\alpha_{xz}]^{nm}$  or  $[\alpha_{yz}]^{nm}$  or both are different from zero, only  $\Delta K = \pm 1$  applies, and for vibrational transitions for which only  $[\alpha_{xx} - \alpha_{yy}]^{nm}$  or  $[\alpha_{xy}]^{nm}$  or both are different from zero,  $\Delta K = \pm 2$  applies.

*Inversion spectrum.* The inversion doubling which occurs for all non-planar molecules (§ 2.2d) is usually negligibly small. But for molecules like  $\text{NH}_3$  for which the two configurations obtained by inversion are separated by only a comparatively small potential barrier, an appreciable doubling arises. The rotational constants in the two component levels are slightly different, that is, one has

$$\left. \begin{aligned} F_{[v]}^s(J, K) &= B_{[v]}^s J(J+1) + (A_{[v]}^s - B_{[v]}^s) K^2 + \dots \\ F_{[v]}^a(J, K) &= B_{[v]}^a J(J+1) + (A_{[v]}^a - B_{[v]}^a) K^2 + \dots \end{aligned} \right\} \quad (10)$$

where the superscripts  $s$  and  $a$  refer to the levels whose vibrational eigenfunctions are symmetric and antisymmetric with respect to the inversion. Transitions from one set of levels to the other occur in the microwave region, the selection rules being

$$\Delta J = 0, \quad \Delta K = 0, \quad K \neq 0$$

The resulting lines are therefore given by the formula

$$\left. \begin{aligned} \nu &= \nu_0 + (B_{[v]}^s - B_{[v]}^a) J(J+1) \\ &+ [(A_{[v]}^s - A_{[v]}^a) - (B_{[v]}^s - B_{[v]}^a)] K^2 + \dots \end{aligned} \right\} \quad (11)$$

where  $\nu_0$  is the inversion splitting for zero rotation. Slight deviations of the observed microwave spectra from this formula can be accounted for by adding higher (quartic) terms to it.

#### 4.4. Spherical top molecules

a. *Energy levels.*—The energy of a vibrating spherical top is the sum of the vibrational energy  $G(v_1, v_2, v_3, \dots)$  and the rotational energy

$$F_{[v]}(J) = B_{[v]}J(J+1) + \dots \quad (1)$$

where

$$B_{[v]} = B_e - \sum \alpha_i B \left( v_i + \frac{d_i}{2} \right) + \dots$$

For a molecule that is a spherical top on account of its symmetry (e.g.,  $\text{CH}_4$ ) doubly and triply degenerate vibrational levels occur. In the case of the latter (but not of the former) the Coriolis interaction produces a splitting into three sets of levels given by

$$\left. \begin{aligned} F_{[v]}^+(J) &= B_{[v]}J(J+1) + 2B_{[v]}\zeta_i(J+1) \\ F_{[v]}^0(J) &= B_{[v]}J(J+1) \\ F_{[v]}^-(J) &= B_{[v]}J(J+1) - 2B_{[v]}\zeta_i J \end{aligned} \right\} \quad (2)$$

where  $\zeta_i$  is a constant giving the vibrational angular momentum in units  $h/2\pi$  (compare § 4.3a).

b. *Selection rules and spectrum.* For the accidental spherical top the selection rules for  $J$  are the same as for the symmetric top, both in the infrared and the Raman effect (§ 4.3b). For a molecule that is a spherical top on account of its symmetry, additional rules apply.

In the infrared the most common vibrational transitions are  $F_2 - A_1$ . Of the three components of the upper state the  $F^+$  levels combine with the lower state only with  $\Delta J = -1$ , the  $F_0$  levels only with  $\Delta J = 0$  and the  $F^-$  levels only with  $\Delta J = +1$ . Therefore  $F_2 - A_1$  bands have only three branches represented by the formulas

$$\left. \begin{aligned} R(J) &= \nu_0 + 2B_{[v]}' - 2B_{[v]}'\zeta_i + (3B_{[v]}' - B_{[v]}'' - 2B_{[v]}'\zeta_i)J \\ &\quad + (B_{[v]}' - B_{[v]}'')J^2 \\ Q(J) &= \nu_0 + (B_{[v]}' - B_{[v]}'')J + (B_{[v]}' - B_{[v]}'')J^2 \\ P(J) &= \nu_0 - (B_{[v]}' + B_{[v]}'' - 2B_{[v]}'\zeta_i)J + (B_{[v]}' - B_{[v]}'')J^2 \end{aligned} \right\} \quad (3)$$

In the Raman effect, for  $A_1 - A_1$  vibrational transitions only  $\Delta J = 0$  occurs, that is, only a  $Q$  branch. But in  $F_2 - A_1$  vibrational transitions all five  $\Delta J$  values are possible for each of the three sublevels of the  $F_2$  state; the resulting bands therefore consist of fifteen branches.

### 4.5. Asymmetric top molecules

a. *Energy levels.* To a good approximation the rotational energy levels of a vibrating asymmetric top molecule are obtained from those of the non-vibrating asymmetric top molecule (§ 2.4b) by substituting effective values of the various rotational constants corresponding to the vibrational level considered, that is

$$F_{[v]}(J_\tau) = \frac{1}{2}(B_{[v]} + C_{[v]})J(J+1) + [A_{[v]} - \frac{1}{2}(B_{[v]} + C_{[v]})]W_\tau^{[v]} \quad (1)$$

where

$$A_{[v]} = A_e - \sum \alpha_i^A (v_i + \frac{1}{2})$$

$$B_{[v]} = B_e - \sum \alpha_i^B (v_i + \frac{1}{2})$$

$$C_{[v]} = C_e - \sum \alpha_i^C (v_i + \frac{1}{2})$$

and where the quantities  $W_\tau^{[v]}$  are given by equations similar to those in (§ 2.4b), except that the constants  $A, B, C$  are to be replaced by  $A_{[v]}, B_{[v]}$ , and  $C_{[v]}$ .

b. *Selection rules and spectrum.* The selection rules for the rotation-vibration spectra of asymmetric top molecules are the same as those for the vibration and the rotation spectra separately, except that it is now the direction of the *change* of dipole moment and *change* of polarizability that determines the infrared and Raman transitions respectively. The fine structure of the bands is always very complicated and cannot be represented by simple formulas, except if the molecule approaches the limiting case of a symmetric top ( $A \simeq B$  or  $C \simeq B$ ). For more details see Ref. 10.

### 4.6. Molecules with internal rotation

#### a. Energy levels

*Free rotation.* When one part of a symmetric top molecule can rotate freely relative to the other about the figure axis, the following term has to be added to the ordinary rotational energy  $F(J, K)$

$$F_t(k_1, k) = \frac{A_1 A_2}{A} \left( k_1 - k \frac{A}{A_1} \right)^2 \quad (1)$$

Here  $A_1$  and  $A_2$  are the rotational constants corresponding to the partial moments of inertia  $I_A^{(1)}$  and  $I_A^{(2)}$ ;  $k (= \pm K)$  is the quantum number of the component of the total angular momentum  $\mathbf{J}$  about the top axis;  $k_1$  is the quantum number of the angular momentum of part 1 [moment of inertia  $I_A^{(1)}$ ] of the molecule and assumes the values

$$k_1 = 0, \pm 1, \pm 2, \dots$$

For molecules with  $I_{A_1} = I_{A_2}$  or  $\frac{A}{A_1} = \frac{1}{2}$  the term  $F_t$  simplifies to

$$F_t(k_1, k) = A(2k_1 - k)^2 = A(k_1 - k_2)^2 = AK_i^2 \quad (2)$$

where  $K_i = |k_1 - k_2|$  is the quantum number of internal rotation.

*Hindered rotation.* The limiting case of hindered rotation is that of torsional oscillation in a periodic potential field with  $n$  potential minima

$$V(\chi) = V \left( \chi \pm \frac{2\pi}{n} \right) \quad (3)$$

If a cosine form is assumed for the hindering potential

$$V = \frac{1}{2}V_0(1 - \cos n\chi)$$

the energy levels in the neighborhood of the minima for large  $V_0$  are those of a harmonic oscillator :

$$G(v_t) = \omega_t(v_t + \frac{1}{2}) \quad (4)$$

where the torsional frequency  $\omega_t$  is given by

$$\omega_t = n \sqrt{\frac{V_0 A_1 A_2}{A}}$$

or, for a molecule with two equal parts

$$\omega_t = 2n\sqrt{V_0 A}$$

For small values of  $V_0$  the vibrational motion of the molecule becomes a hindered rotation. The energy levels corresponding to this intermediate case can be found qualitatively by interpolation between those of the two limiting cases, free rotation and torsional oscillation (Ref. 10). Quantitative discussions of this intermediate case have been given in Refs. 4, 13, 16, and 17.

b. *Infrared spectrum.* For symmetrical molecules there is no pure rotation spectrum corresponding to free rotation. For the vibration-rotation spectrum the selection rules for the quantum number  $K_i$  of the internal rotation are  $\Delta K_i = 0$  for  $\Delta K = 0$  and  $\Delta K_i = \pm 1$  for  $\Delta K = \pm 1$ . As a consequence the  $\parallel$  bands of a symmetric top molecule are not affected by the presence of internal rotation, while in the  $\perp$  bands each of the line-like  $Q$  branches is split into a number of nearly equidistant "lines" of spacing  $2B$ .

In slightly asymmetric molecules the internal rotation is infrared active.

For the pure internal rotation spectrum the selection rules are

$$\Delta J = 0, \pm 1, \quad \Delta K = \pm 1, \quad \Delta K_1 = \pm 1, \quad \Delta K_2 = 0$$

where  $K_1 = |k_1|$ , and  $K_2 = |k_2|$ . Therefore the  $Q$  "lines" of the free internal rotation spectrum form the double series

$$\nu = A_1 - B \mp 2BK \pm 2A_1K_1 \quad (5)$$

where the upper signs hold for positive  $\Delta K$  and  $\Delta K_1$ , the lower signs for negative  $\Delta K$  and  $\Delta K_1$ .

For the rotation-vibration spectrum we have in the case of  $\parallel$  bands ( $\Delta K = 0$ ) the selection rule

$$\Delta K_1 = 0, \quad \Delta K_2 = 0$$

and in the case of  $\perp$  bands ( $\Delta K = \pm 1$ )

$$\Delta K_1 = \pm 1, \quad \Delta K_2 = 0 \quad \text{or} \quad \Delta K_1 = 0, \quad \Delta K_2 = \pm 1$$

depending on whether the dipole moment of the vibrational transition is in part 1 or part 2 of the molecule. The structure of the  $\parallel$  bands is therefore not affected by the presence of internal rotation, while in the  $\perp$  bands each subband corresponding to a given  $K$  and  $\Delta K$  is resolved into a number of sub-subbands corresponding to the different  $K_1$  values and  $\Delta K_1 = \pm 1$  or to the different  $K_2$  values and  $\Delta K_2 = \pm 1$  depending on whether the oscillating dipole moment is in part 1 or part 2. For  $\Delta K_1 = \pm 1$  the spacing of the sub-subbands is  $2A_1$ , for  $\Delta K_2 = \pm 1$  it is  $2A_2$ .

## 5. Electronic States and Electronic Transitions

**5.1. Total energy and electronic energy.** The energy of a molecule may be written as the sum of electronic, vibrational, and rotational energy (Section 1):

$$E = E_e + E_v + E_r$$

or in wave number units (term values)

$$T = T_e + G + F$$

The total eigenfunction can be expressed as

$$\psi = \psi_e \psi_v \psi_r \quad (1)$$

where  $\psi_e$  is the electronic eigenfunction,  $\psi_v$  the vibrational eigenfunction, and  $\psi_r$  the rotational eigenfunction.

The different electronic states of a molecule are characterized by certain quantum numbers and symmetry properties of their eigenfunctions. For diatomic and linear polyatomic molecules the orbital angular momentum  $\Lambda$  about the internuclear axis is defined and has the magnitude  $\Lambda h/2\pi$ , where  $\Lambda$  is the corresponding quantum number which can assume only integral values. Depending on whether  $\Lambda = 0, 1, 2, \dots$ , we distinguish  $\Sigma, \Pi, \Delta, \dots$  states. For nonlinear molecules different types (species) of electronic states arise depending on the symmetry properties of the nuclear frame. For example, for molecules with two mutually perpendicular planes of symmetry there are four types of electronic states,  $A_1, A_2, B_1$ , and  $B_2$  (see § 3.2a). These species are precisely the same as those of the vibrational levels (see the tables in Ref. 10).

Each electronic state has a multiplicity  $(2S + 1)$  depending on the value of the quantum number  $S$  of the resultant electron spin of the molecule.

No general formulas for the energies of the electronic states of a molecule can be given except for those states in which one electron is excited to orbitals of increasing principal quantum number  $n$ . In this case one has to a good approximation

$$T_e = A - \frac{R}{(n - a)^2} \quad (2)$$

where  $A$  is the ionization potential,  $R$  the Rydberg constant, and  $a$  the Rydberg correction.

## 5.2. Interaction of rotation and electronic motion in diatomic and linear polyatomic molecules

a. *Multiplet splitting.* The total angular momentum  $\mathbf{J}$  is the vector sum of the angular momentum of the nuclear frame, the electronic orbital angular momentum  $\mathbf{A}$ , and the electron spin  $\mathbf{S}$ . The total angular momentum apart from spin is designated  $\mathbf{K}$ .\* For the corresponding quantum numbers we have

$$J = K + S, \quad K + S - 1, \quad \dots, \quad |K - S|$$

The interaction of rotation and electron spin (which increases with increasing rotation) causes a variation of the multiplet splitting with  $K$  or  $J$ .

\* In a recent report, the Joint Commission for Spectroscopy [*J. Opt. Soc. Am.*, **43**, 416 (1953)] recommends  $N$  in place of  $K$  as a designation of angular momentum apart from spin and of the corresponding quantum number.

The following formulas give the rotational term values for some important cases referring to diatomic and linear polyatomic molecules :

${}^2\Sigma$  states ( $\Lambda = 0, S = \frac{1}{2}$ )

$$\left. \begin{aligned} F_1(K) &= B_v K(K+1) + \frac{1}{2}\gamma K \\ F_2(K) &= B_v K(K+1) - \frac{1}{2}\gamma(K+1) \end{aligned} \right\} (1)$$

Here  $F_1(K)$  and  $F_2(K)$  refer to the levels with  $J = K + \frac{1}{2}$  and  $J = K - \frac{1}{2}$ , respectively, and  $\gamma$  is a small coupling constant ( $\gamma \ll B_v$ ).

${}^3\Sigma$  states ( $\Lambda = 0, S = 1$ ) (Schlapp's formula)

$$\left. \begin{aligned} F_1(K) &= B_v K(K+1) + (2K+3)B_v - \lambda \\ &\quad - \sqrt{(2K+3)^2 B_v^2 + \lambda^2 - 2\lambda B_v} + \gamma(K+1) \\ F_2(K) &= B_v K(K+1) \\ F_3(K) &= B_v K(K+1) - (2K-1)B_v - \lambda \\ &\quad + \sqrt{(2K-1)^2 B_v^2 + \lambda^2 - 2\lambda B_v} - \gamma K \end{aligned} \right\} (2)$$

Here  $F_1(K)$ ,  $F_2(K)$ ,  $F_3(K)$  refer to the levels with  $J = K + 1$ ,  $J = K$ , and  $J = K - 1$ , respectively, and  $\lambda$  and  $\gamma$  are small coupling constants.

${}^2\Pi, {}^2\Delta, \dots$  states ( $\Lambda = 1, 2, \dots, S = \frac{1}{2}$ ) (Hill and Van Vleck's formula)

$$\left. \begin{aligned} F_1(J) &= B_v[(J + \frac{1}{2})^2 - \Lambda^2 - \frac{1}{2}\sqrt{4(J + \frac{1}{2})^2 + Y(Y-4)\Lambda^2}] - D_v J^4 \\ F_2(J) &= B_v[(J + \frac{1}{2})^2 - \Lambda^2 + \frac{1}{2}\sqrt{4(J + \frac{1}{2})^2 + Y(Y-4)\Lambda^2}] \\ &\quad - D_v(J+1)^4 \end{aligned} \right\} (3)$$

Here  $Y = A/B_v$ , where the coupling constant  $A$  is a measure of the strength of the coupling between the spin  $S$  and the orbital angular momentum  $\Lambda$ ;  $F_1(J)$  is the term series that forms for large rotation the levels with  $J = K + \frac{1}{2}$ , while  $F_2(J)$  forms for large rotation the levels with  $J = K - \frac{1}{2}$ .

b. *Lambda-type doubling.* The  $\Pi, \Delta, \dots$  states of diatomic and linear polyatomic molecules are doubly **degenerate** if the molecule is not rotating. In the rotating molecule the interaction of rotation and electronic motion causes a splitting of this degeneracy which in general increases with increasing rotation ( $\Lambda$ -type doubling). The rotational levels of the two term series, distinguished by superscripts  $c$  and  $d$ , are in the case of a  ${}^1\Pi$  state

$$F_c(J) = B_v^c J(J+1) + \dots, \quad F_d(J) = B_v^d J(J+1) + \dots$$

that is, the splitting is given by

$$\Delta\nu_{cd} = (B_v^c - B_v^d)J(J+1) = qJ(J+1) \quad (4)$$

where the splitting constant  $q$  depends on the position of nearby  $\Sigma$  states. For  $\Delta$  states the splitting is usually negligibly small.

**5.3. Selection rules and spectrum.** A transition between the electronic states  $i$  and  $k$  is allowed as dipole radiation if there is at least one component of the dipole moment  $M_x$ ,  $M_y$ , or  $M_z$  which has the same symmetry properties as the product of the electronic eigenfunctions  $\psi_e^i \psi_e^{k*}$ . The electronic selection rules therefore are of the same form as the vibrational selection rules. The symmetry of the products  $\psi_e^i \psi_e^{k*}$  can be determined from tables given in Ref. 19 or in Ref. 10, though the latter were originally prepared for vibrational transitions.

For diatomic and linear polyatomic molecules the selection rule

$$\Delta\Lambda = 0, \pm 1$$

results from the above general rule.

a. *Vibrational structure.* The totality of vibrational transitions for a given electronic transition is a band system. The wave numbers of the bands of a band system are represented by the formula

$$\nu = \nu_e + G'(v_1', v_2', \dots) - G''(v_1'', v_2'', \dots) \quad (1)$$

or in the case of diatomic molecules

$$\nu = \nu_e + \omega_e'(v' + \frac{1}{2}) - \omega_e'x_e'(v' + \frac{1}{2})^2 + \dots - [\omega_e''(v'' + \frac{1}{2}) - \omega_e''x_e''(v'' + \frac{1}{2})^2 + \dots] \quad \left. \vphantom{\nu} \right\} (2)$$

where  $\nu_e = T_e' - T_e''$  is the origin of the band system.

Which vibrational transitions are possible and what intensities they have is determined by the integral

$$\int \psi_v' \psi_v'' d\tau_v$$

To a good approximation the relative intensities of the various vibrational transitions are proportional to the square of this integral. Only those vibrational transitions are possible for which the product  $\psi_v' \psi_v''$  is symmetric with respect to all symmetry operations permitted by the symmetry of the molecule.

b. *Rotational structure.* The rotational structure of the individual vibrational transitions (bands) of an electronic transition is essentially the same as that of rotation-vibration bands (Section 4) as long as there is no spin

splitting. If spin splitting is present, additional selection rules apply; for example, for diatomic and linear polyatomic molecules, if  $K$  the angular momentum apart from spin is defined, one has

$$\Delta K = 0, \pm 1$$

For  $\Sigma - \Sigma$  transitions  $\Delta K = 0$  does not occur. For details about the formulas for the branches in such cases see Ref. 9.

c. *Microwave spectra.* Transitions between individual multiplet components of a given electronic state can occur as magnetic dipole radiation. They give rise to absorption lines (bands) in the microwave region. For example, for a  ${}^3\Sigma$  state the wave numbers of the transitions between the triplet components of a given  $K$  are

$$\nu = F_2(K) - F_1(K) \quad \text{and} \quad \nu = F_2(K) - F_3(K) \quad (3)$$

where the  $F_i(K)$  are given in § 5.2a.

Transitions between the  $\Lambda$  doublet components of  $\Pi$ ,  $\Delta$ , ... states are possible as dipole radiation and are likely to be observed in the microwave region. The formula for such lines would be

$$\nu = F_c(J) - F_d(J) = qJ(J + 1) \quad (4)$$

where  $q$  is the  $\Lambda$  doubling constant (§ 5.2b).

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## Chapter 21

# QUANTUM MECHANICS

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The collection of formulas given below has been assembled on the premise that the reader already has some familiarity with the subject matter of quantum mechanics. The collection is intended to be complete, except that selection rules are omitted here since they are included in Chapter 19. The formalism of quantized field theory is so abstruse that no attempt was made to condense it into formulas for this book.

### 1. Equations of Quantum Mechanics

**1.1. Old quantum theory.** The energy  $E$ , circular frequency  $\nu$ , and angular frequency  $\omega$  of a light quantum are related by

$$E = h\nu = \hbar\omega, \quad \hbar \equiv h/2\pi \quad (1)$$

where  $h$  is Planck's constant. Since  $E = pc$ , where  $p$  is the momentum and  $c$  the speed of light, we also have

$$p = h/\lambda = \hbar k \quad (2)$$

where  $\lambda$  is the wavelength and  $k = 2\pi/\lambda$  is the wave number.

The Planck distribution formula for the electromagnetic energy density per unit angular frequency range within a cavity at temperature  $T$  is

$$\frac{\hbar\omega^3}{\pi^2 c^3 (e^{\hbar\omega/kT} - 1)} \quad (3)$$

where  $k$  is Boltzmann's constant.

The Bohr-Wilson-Sommerfeld quantization rule for a cyclic variable  $q$  and its canonical momentum  $p$  is

$$\oint p dq = nh \quad (4)$$

where the integral is over one cycle and  $n$  is a positive integer, called the quantum number.

If a quantum of wavelength  $\lambda$  is scattered by an electron of mass  $m$  through an angle  $\theta$ , the wavelength  $\lambda'$  after scattering is (Compton effect)

$$\lambda' = \lambda + \frac{h}{mc} (1 - \cos \theta) \quad (5)$$

**1.2. Uncertainty principle.** A coordinate  $q$  and its canonically conjugate momentum  $p$  cannot both be measured precisely; the uncertainties in their values are related by the Heisenberg uncertainty principle

$$\Delta q \cdot \Delta p \gtrsim \hbar \quad (1)$$

The same relation holds between an angular coordinate  $\phi$  and the component of angular momentum  $J$  perpendicular to the plane of  $\phi$ , and between the time  $t$  of observation and the energy  $E$  of the system observed.

$$\Delta \phi \cdot \Delta J \gtrsim \hbar, \quad \Delta t \cdot \Delta E \gtrsim \hbar \quad (2)$$

Expressed in terms of a space wave packet of wave number  $k$ , or a time wave packet of angular frequency  $\omega$

$$\Delta x \cdot \Delta k \gtrsim 1, \quad \Delta t \cdot \Delta \omega \gtrsim 1 \quad (3)$$

For an electron,  $E = p^2/2m = \hbar\omega$ , the de Broglie relation is  $p = \hbar k$ , and the group velocity of the packet is

$$v_g = \frac{d\omega}{dk} = \frac{p}{m} \quad (4)$$

**1.3. Schrödinger wave equation.** The classical relation that the total energy  $E$  is the sum of the kinetic energy  $p^2/2\mu$  and the potential energy  $V(\mathbf{r}, t)$  of a particle of mass  $\mu$ , can be transcribed into quantum mechanics by substituting

$$E \rightarrow i\hbar \frac{\partial}{\partial t}, \quad \mathbf{p} \rightarrow -i\hbar \mathbf{grad}$$

and operating on a wave function  $\psi(\mathbf{r}, t)$  to yield the Schrödinger equation,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2\mu} \nabla^2 \psi + V(\mathbf{r}, t)\psi \quad (1)$$

More generally,

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \quad (2)$$

where  $H$  is the Hamiltonian of the system with  $\mathbf{p}$  replaced by  $-i\hbar \mathbf{grad}$ . The wave function is normalized if  $\int \bar{\psi}\psi d\tau = \int |\psi|^2 d\tau = 1$ , where the integral is over all space ( $d\tau = dx dy dz$ ), and  $\bar{\psi}$  is the complex conjugate of  $\psi$ .

The probability density  $P$  and the probability current density  $\mathbf{S}$  are

$$P(\mathbf{r}, t) = |\psi(\mathbf{r}, t)|^2, \quad \mathbf{S}(\mathbf{r}, t) = \frac{\hbar}{2i\mu} (\bar{\psi} \mathbf{grad} \psi - \psi \mathbf{grad} \bar{\psi}) \quad (3)$$

and obey the continuity equation

$$\frac{\partial P}{\partial t} + \operatorname{div} \mathbf{S} = 0 \tag{4}$$

If  $F$  is a function or an operator expressed in terms of  $\mathbf{r}$  and  $t$ , its average or expectation value for the state  $\psi$  is

$$\langle F \rangle = \int \bar{\psi} F \psi \, d\tau \tag{5}$$

The uncertainty  $\Delta x$  can be defined as the root-mean-square deviation of  $x$  from its expectation value,

$$(\Delta x)^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 \tag{6}$$

in which case a typical uncertainty relation becomes

$$\Delta x \cdot \Delta p_x \geq \frac{1}{2} \hbar \tag{7}$$

For the minimum value of uncertainty product, the wave packet  $\psi$  has the instantaneous  $x$  dependence

$$\psi(x) = [2\pi(\Delta x)^2]^{-1/4} \exp \left[ -\frac{(x - \langle x \rangle)^2}{4(\Delta x)^2} + \frac{ix \langle p_x \rangle}{\hbar} \right] \tag{8}$$

Ehrenfest's theorem states that the expectation values computed for a wave packet that satisfies the Schrödinger equation, obey the classical equations of motion; for example,

$$\frac{d}{dt} \langle \mathbf{r} \rangle = \frac{1}{\mu} \langle \mathbf{p} \rangle, \quad \frac{d}{dt} \langle \mathbf{p} \rangle = \langle -\mathbf{grad} V \rangle \tag{9}$$

The Fourier transform of  $\psi(\mathbf{r}, t)$  can be used to specify the momentum probability density, which is so defined that  $P(\mathbf{k}, t) \, dk_x \, dk_y \, dk_z$  is the probability that the momentum components lie between  $\hbar k_x$  and  $\hbar(k_x + dk_x)$ , etc. Here  $(d\tau_k = dk_x \, dk_y \, dk_z)$ :

$$\left. \begin{aligned} \psi(\mathbf{r}, t) &= (8\pi^3)^{-1/2} \int \phi(\mathbf{k}, t) e^{i\mathbf{k} \cdot \mathbf{r}} d\tau_k \\ \phi(\mathbf{k}, t) &= (8\pi^3)^{-1/2} \int \psi(\mathbf{r}, t) e^{-i\mathbf{k} \cdot \mathbf{r}} d\tau \\ P(\mathbf{k}, t) &= |\phi(\mathbf{k}, t)|^2 \end{aligned} \right\} \tag{10}$$

An operator  $\Omega$  has the eigenfunction  $u_n$  corresponding to the eigenvalue  $\omega_n$  if

$$\Omega u_n = \omega_n u_n \tag{11}$$

The numbers  $\omega_n$  are then the only possible results of precise measurement of the dynamical variable represented by the operator  $\Omega$ .

Energy eigenfunctions exist if  $V$  is independent of  $t$ .

$$\psi(\mathbf{r}, t) = u(\mathbf{r})e^{-iEt/\hbar}, \quad -\frac{\hbar^2}{2\mu}\nabla^2 u + Vu = Eu \quad (12)$$

Wherever  $V$  is finite (whether or not continuous),  $u$  and  $\mathbf{grad} u$  must be finite and continuous;  $u$  must remain finite or vanish as  $r \rightarrow \infty$ . If  $V \rightarrow \infty$  as  $r \rightarrow \infty$ , well-behaved solutions exist only for discrete values of  $E$ . If  $V \rightarrow V_0$  as  $r \rightarrow \infty$ , well-behaved solutions exist for all values of  $E$  greater than  $V_0$ ; if they exist for  $E < V_0$  it is only for discrete values of  $E$ . Energy eigenfunctions that correspond to different energy eigenvalues are orthogonal.

$$\int \bar{u}_E(\mathbf{r})u_{E'}(\mathbf{r})d\tau = 0, \quad \text{if } E \neq E' \quad (13)$$

Whenever  $V(\mathbf{r})$  is unchanged by reflection of  $x, y, z$  in the origin [so that  $V(-\mathbf{r}) = V(\mathbf{r})$ ], linear combinations of the energy eigenfunctions can be found that have a definite parity; that is, either  $u(-\mathbf{r}) = u(\mathbf{r})$  (even parity), or  $u(-\mathbf{r}) = -u(\mathbf{r})$  (odd parity). If an energy level is nondegenerate (only one linearly independent eigenfunction), then that function is either even or odd.

Discrete energy eigenfunctions are normalized by setting  $\int |u_E(\mathbf{r})|^2 d\tau = 1$ , since  $u_E$  falls off rapidly as  $r \rightarrow \infty$ , and we have a localized or bound state. Continuous energy eigenfunctions ( $E > V_0$ ) cannot be normalized in this way since  $|u_E| \rightarrow \text{constant}$  as  $r \rightarrow \infty$  and the integral is infinite. We can normalize in a large cubical box of volume  $L^3$  by imposing periodic boundary conditions at the walls, in which case the continuous energy levels become discrete with very close spacing. For example, the box-normalized momentum eigenfunctions are

$$u_{\mathbf{k}}(\mathbf{r}) = L^{-3/2} \exp(i\mathbf{k} \cdot \mathbf{r}), \quad \text{where } k_x = 2\pi n_x/L, \text{ etc.}$$

and  $n_x, n_y, n_z$  are positive or negative integers or zero. Then

$$\int \bar{u}_{\mathbf{k}}(\mathbf{r})u_{\mathbf{l}}(\mathbf{r})d\tau = \delta_{k_x l_x} \delta_{k_y l_y} \delta_{k_z l_z} \quad (14)$$

where  $\delta_{nm} = 1$  if  $n = m$  and zero otherwise (Kronecker  $\delta$  symbol.) Alternatively, we can normalize in an infinite region by using the Dirac  $\delta$  function, defined by

$$\delta(x) = 0 \quad \text{if } x \neq 0, \quad \int_{-\infty}^{\infty} \delta(x)dx = 1 \quad (15)$$

or by

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} dk \quad (16)$$

Then  $u_{\mathbf{k}}(\mathbf{r}) = (8\pi^3)^{-1/2} \exp(i\mathbf{k} \cdot \mathbf{r})$ , and

$$\int \tilde{u}_{\mathbf{k}}(\mathbf{r}) u_{\mathbf{l}}(\mathbf{r}') d\tau = \delta(k_x - l_x) \delta(k_y - l_y) \delta(k_z - l_z) \quad (17)$$

For both normalizations, the momentum eigenfunctions have the closure property

$$\sum_{\mathbf{k}} \tilde{u}_{\mathbf{k}}(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r}') = \delta(x - x') \delta(y - y') \delta(z - z') \quad \left. \vphantom{\sum_{\mathbf{k}}} \right\} \begin{array}{l} \text{(box normalization)} \\ \end{array} \quad (18)$$

$$\int \tilde{u}_{\mathbf{k}}(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r}') d\tau_{\mathbf{k}} = \delta(x - x') \delta(y - y') \delta(z - z') \quad \left. \vphantom{\int} \right\} \begin{array}{l} \text{(\delta function normalization)} \\ \end{array} \quad (19)$$

Complete sets of eigenfunctions of other operators have properties analogous to the above properties of the momentum eigenfunctions.

The  $\delta$  function has the additional properties

$$\left. \begin{array}{l} \delta(x) = \delta(-x), \quad \delta'(x) = -\delta'(-x), \quad x\delta(x) = 0, \quad x\delta'(x) = -\delta(x) \\ \delta(ax) = a^{-1}\delta(x), \quad (a > 0) \\ \delta(x^2 - a^2) = (2a)^{-1}[\delta(x - a) + \delta(x + a)], \quad (a > 0) \\ \int \delta(a - x)\delta(x - b)dx = \delta(a - b) \\ f(x)\delta(x - a) = f(a)\delta(x - a) \end{array} \right\} \quad (20)$$

In each case, a subsequent integration over the argument of the  $\delta$  functions is implied; a prime denotes differentiation with respect to the argument.

**1.4. Special solutions of the Schrödinger equation for bound states.** The linear harmonic oscillator is described by the equation

$$-\frac{\hbar^2}{2\mu} \frac{d^2u}{dx^2} + \frac{1}{2}kx^2u = Eu \quad (1)$$

and has all discrete energy eigenvalues since  $V \rightarrow \infty$  as  $x \rightarrow \pm \infty$ . The energy levels are  $E_n = (n + \frac{1}{2})\hbar\omega$ , where  $\omega = (k/\mu)^{1/2}$  is the angular frequency of the corresponding classical oscillator. The normalized wave functions are

$$u_n(x) = \left( \frac{\alpha}{\pi^{1/2} 2^n n!} \right)^{1/2} H_n(\alpha x) e^{-\alpha^2 x^2/2}, \quad \alpha = \left( \frac{\mu k}{\hbar^2} \right)^{1/4} \quad (2)$$

$H_n$  is a Hermite polynomial (§ 12.1 of Chapter 1).

In three dimensions, the spherical coordinates of a point are related to the rectangular coordinates of that point by  $x = r \sin \theta \cos \phi$ ,  $y = r \sin \theta \sin \phi$ ,

$z = r \cos \theta$ . Whenever the potential energy  $V(r)$  is spherically symmetric, the angular dependence of the wave function can be separated out.

$$\begin{aligned}
 & -\frac{\hbar^2}{2\mu} \nabla^2 u + V(r)u = Eu \\
 & u(r, \theta, \phi) = R_l(r) Y_{lm}(\theta, \phi) \\
 & l = 0, 1, 2, \dots, \quad m = -l, -l+1, \dots, l-1, l \\
 & Y_{lm}(\theta, \phi) = \left[ \frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos \theta) e^{im\phi} \quad (3)
 \end{aligned}$$

$P_l^{|m|}(\cos \theta)$  is an associated Legendre function (§ 8.11 of Chapter 1). Here  $Y_{lm}(\theta, \phi)$  is a tesseral harmonic, and is the normalized angular momentum eigenfunction.

The angular momentum operator is

$$\left. \begin{aligned}
 \mathbf{M} &= \mathbf{r} \times \mathbf{p} = -i\hbar \mathbf{r} \times \mathbf{grad} \\
 M_x &= yp_z - zp_y = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\
 &= i\hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \\
 M_y &= zp_x - xp_z = -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\
 &= i\hbar \left( -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \\
 M_z &= xp_y - yp_x = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = -i\hbar \frac{\partial}{\partial \phi} \\
 \mathbf{M}^2 &= M_x^2 + M_y^2 + M_z^2 \\
 &= -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]
 \end{aligned} \right\} (4)$$

The functions  $Y_{lm}(\theta, \phi)$  satisfy the equations

$$\left. \begin{aligned}
 \mathbf{M}^2 Y_{lm}(\theta, \phi) &= \hbar^2 l(l+1) Y_{lm}(\theta, \phi) \\
 M_z Y_{lm}(\theta, \phi) &= \hbar m Y_{lm}(\theta, \phi) \\
 \int_0^\pi \int_0^{2\pi} \bar{Y}_{lm}(\theta, \phi) Y_{l'm'}(\theta, \phi) \sin \theta \, d\theta \, d\phi &= \delta_{ll'} \delta_{mm'}
 \end{aligned} \right\} (5)$$

so that they form an orthonormal (orthogonal and normalized) set of eigenfunctions of  $\mathbf{M}^2$  and  $M_z$ . Here  $l$  is the azimuthal or orbital angular momentum quantum number, and  $m$  is the magnetic quantum number.

The radial function satisfies the equation

$$-\frac{\hbar^2}{2\mu} \cdot \frac{1}{r^2} \cdot \frac{d}{dr} \left( r^2 \frac{dR_l}{dr} \right) + \left[ V(r) + \frac{\hbar^2 l(l+1)}{2mr^2} \right] R_l = ER_l \quad (6)$$

and may have discrete negative energy eigenvalues that correspond to bound states.

For  $V(r)$  in the form of a square well,

$$V(r) = -V_0 < 0 \quad \text{for } r < a, \quad V(r) = 0 \quad \text{for } r > a \quad (7)$$

there is at least one bound state if  $V_0 a^2 > \pi^2 \hbar^2 / 8\mu$ , and none otherwise. The radial functions can be expressed in terms of Bessel functions of order  $\pm(l + \frac{1}{2})$ . (See Sec. 9 of Chapter 1.) For  $r < a$ ,

$$R_l(r) = A j_l(\alpha r), \quad \frac{\hbar^2 \alpha^2}{2\mu} = V_0 + E, \quad j_l(\rho) = \left( \frac{\pi}{2\rho} \right)^{1/2} J_{l+1/2}(\rho) \quad (8)$$

For  $r > a$  and  $E < 0$ ,

$$\left. \begin{aligned} R_l(r) &= B h_l^{(1)}(i\beta r), \quad \frac{\hbar^2 \beta^2}{2\mu} = -E \\ h_l^{(1)}(\rho) &= j_l(\rho) + i n_l(\rho), \quad h_l^{(2)}(\rho) = j_l(\rho) - i n_l(\rho) \\ n_l(\rho) &= (-1)^{l+1} \left( \frac{\pi}{2\rho} \right)^{1/2} J_{-l-1/2}(\rho) \end{aligned} \right\} \quad (9)$$

The constants  $A$  and  $B$  and the energy level  $E$  are determined by the requirements that  $R_l$  and  $dR_l/dr$  be continuous at  $r = a$ , and by the normalization requirement

$$\int_0^\infty R_l^2 r^2 dr = 1$$

For an attractive Coulomb potential  $V(r) = -Ze^2/r$ , the radial equation has an infinite number of discrete energy eigenvalues.

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2}, \quad (n = 1, 2, 3, \dots) \quad (10)$$

With  $Z = 1$ , this is the Bohr formula for the energy levels of the hydrogen atom, obtained from the old quantum theory. For each value of the total quantum number  $n$  there are linearly independent solutions with the same energy for  $l = 0, 1, \dots, n-1$ ; since for each value of  $l$  the magnetic quantum number can lie between  $-l$  and  $+l$ , there are altogether  $n^2$  linearly independent solutions with the same energy  $E_n$ . The  $n$ th level is said to be  $n^2$ -fold degenerate. The normalized energy eigenfunctions are

$$\left. \begin{aligned} u_{nlm}(r, \theta, \phi) &= R_{nl}(r) Y_{lm}(\theta, \phi) \\ R_{nl}(r) &= \left( \frac{2Z}{na_0} \right)^{3/2} \left\{ \frac{(n-l-1)!}{2n[(n+l)!]^{3/2}} \right\}^{1/2} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho) \end{aligned} \right\} \quad (11)$$

where  $a_0 = \hbar^2/\mu e^2$ ,  $\rho = 2Zr/na_0$ , and  $L$  is an associated Laguerre polynomial (§ 11.5 of Chapter 1). The Coulomb wave functions can also be expressed in terms of parabolic coordinates  $\xi = r(1 - \cos \theta)$ ,  $\eta = r(1 + \cos \theta)$ ,  $\phi = \phi$ . The unnormalized energy eigenfunctions are

$$u_{n_1 n_2 m}(\xi, \eta, \phi) = e^{-\alpha(\xi+\eta)/2} (\xi\eta)^{|m|/2} L_{n_1+|m|}^{|m|}(\alpha\xi) L_{n_2+|m|}^{|m|}(\alpha\eta) e^{im\phi} \quad (12)$$

$$\alpha = \frac{\mu Z e^2}{\hbar^2(n_1 + n_2 + |m| + 1)} \quad (13)$$

where the  $L$ 's are again associated Laguerre polynomials and the total quantum number (which determines the energy) is  $n = n_1 + n_2 + |m| + 1$ .

If the particle of mass  $\mu$  does not move in a stationary (infinitely massive) force field, but in the field of another particle of finite mass  $M$ , we must replace  $\mu$  by the reduced mass  $\mu M/(\mu + M)$  in all equations of this section and the last.

### 1.5. Solutions of the Schrödinger equation for collision problems.

Let a group of  $n$  stationary particles of mass  $m_2$  be bombarded with a parallel flux of  $N$  particles of mass  $m_1$  per unit area and time; then the number of  $m_1$  particles that are scattered per unit time into a small solid angle  $\Delta\omega_0$  about a direction that makes polar angles  $\theta_0, \phi_0$  with respect to the bombarding direction is  $nN\sigma_0(\theta_0, \phi_0)\Delta\omega_0$ , where  $\sigma_0(\theta_0, \phi_0)$  is the differential scattering cross section in the laboratory system. Its integral over all angles is the total cross section  $\sigma_0$  in the laboratory system. In the center-of-mass coordinate system, in which the center of mass of the colliding particles is at rest, the differential and total cross sections are  $\sigma(\theta, \phi)$  and  $\sigma$ , respectively. The relations between the two coordinate systems are

$$\left. \begin{aligned} \tan \theta_0 &= \frac{\sin \theta}{\gamma + \cos \theta}, \quad \phi_0 = \phi, \quad \gamma = \frac{m_1}{m_2} \\ \sigma_0(\theta_0, \phi_0) &= \frac{(1 + \gamma^2 + 2\gamma \cos \theta)^{3/2}}{|1 + \gamma \cos \theta|} \sigma(\theta, \phi) \\ \sigma_0 &= \sigma \end{aligned} \right\} \quad (1)$$

If  $\gamma > 1$ ,  $\theta_0$  cannot exceed that angle less than  $90^\circ$  whose sine is equal to  $1/\gamma$ .

If the kinetic energy of particle  $m_1$  in the laboratory system is  $E_0 = \frac{1}{2}m_1v^2$ , the energy associated with the relative motion in the center-of-mass system is  $E = m_2E_0/(m_1 + m_2)$ , and the energy associated with the motion of the center of mass is  $m_1E_0/(m_1 + m_2)$ . Here  $v$  is the speed of  $m_1$  in the laboratory system, and is also the relative speed of  $m_1$  with respect to  $m_2$  in the center-of-mass system. If the collision process is a reaction in which particles of masses  $m_3$  and  $m_4$  emerge ( $m_1 + m_2 = m_3 + m_4$ ), an energy  $Q$  is released (so that the relative energy in the center-of-mass system after the reaction is  $E + Q$ ), and the particle  $m_3$  is observed, then the relations between laboratory and center-of-mass coordinate systems are as given above except that now

$$\gamma = + \{ (m_1 m_3 / m_2 m_4) [E / (E + Q)] \}^{1/2}.$$

The differential cross section in the center-of-mass system can be expressed in terms of phase shifts  $\delta_l$  when the potential is spherically symmetric. The reduced mass is  $\mu = m_1 m_2 / (m_1 + m_2)$ , and  $E = \frac{1}{2}\mu v^2 > 0$ ; then for  $r$  so large that  $V(r)$  can be neglected, the radial wave function can be written

$$R_l(r) = A_l [\cos \delta_l j_l(kr) - \sin \delta_l n_l(kr)], \quad \frac{\hbar^2 k^2}{2\mu} = E \quad (2)$$

and asymptotically

$$R_l(r) \xrightarrow{r \rightarrow \infty} (kr)^{-1} A_l \sin(kr - \frac{1}{2}l\pi + \delta_l) \quad (3)$$

The complete wave function has the asymptotic form

$$\left. \begin{aligned} u(r, \theta) &\xrightarrow{r \rightarrow \infty} A \left( e^{ikr \cos \theta} + f(\theta) \frac{e^{ikr}}{r} \right) \\ f(\theta) &= k^{-1} \sum_{l=0}^{\infty} (2l + 1) e^{i\delta_l} \sin \delta_l P_l(\cos \theta) \end{aligned} \right\} \quad (4)$$

and the differential and total cross sections are

$$\left. \begin{aligned} \sigma(\theta) &= |f(\theta)|^2 = \frac{1}{k^2} \left| \sum_{l=0}^{\infty} (2l + 1) e^{i\delta_l} \sin \delta_l P_l(\cos \theta) \right|^2 \\ \sigma &= \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l + 1) \sin^2 \delta_l \end{aligned} \right\} \quad (5)$$

Because of the spherical symmetry of  $V$ ,  $\sigma(\theta)$  and the scattered amplitude  $f(\theta)$  do not depend on  $\phi$ .

For a perfectly rigid sphere of radius  $a$  [ $V(r) = +\infty$  for  $r < a$ ,  $V(r) = 0$  for  $r > a$ ], the scattering for very low energies ( $ka \ll 1$ ) is spherically symmetric with  $\sigma = 4\pi a^2$ . For very high energies ( $ka \gg 1$ ), half of the scattering is spherically symmetric and the other half is concentrated in a sharp forward maximum whose angular width is of order  $1/ka$  radians (diffraction peak); each contributes  $\pi a^2$  to the total cross section, so that  $\sigma = 2\pi a^2$ .

In the collision of particles of charges  $ze$  and  $Ze$ , the interaction is the Coulomb potential energy  $V(r) = zZe^2/r$ . The scattered amplitude and differential cross section in the center-of-mass coordinate system are

$$\left. \begin{aligned} f_c(\theta) &= \frac{n}{2k} \operatorname{cosec}^2 \frac{1}{2}\theta e^{-in \ln (\sin^2 \theta/2) + i\pi + 2i\eta_0} \\ \sigma_c(\theta) &= |f_c(\theta)|^2 = \left( \frac{zZe^2}{2\mu v^2} \right)^2 \operatorname{cosec}^4 \frac{1}{2}\theta, \quad n = \frac{zZe^2}{\hbar v} \end{aligned} \right\} \quad (6)$$

where  $\eta_0 = \arg \Gamma(1 + in)$  (see 13 of Chapter 1). Here  $\sigma_c(\theta)$  is just the Rutherford formula derived from classical dynamics. The total cross section is infinite. If  $V(r)$  deviates from the Coulomb form only for short distances, the asymptotic form of the radial wave function can be written

$$R_l(r) \xrightarrow{r \rightarrow \infty} (kr)^{-1} A_l \sin(kr - \frac{1}{2}l\pi - n \ln 2kr + \eta_l + \delta_l) \quad (7)$$

where  $n_l = \arg \Gamma(l + 1 + in)$ . The scattered amplitude is then

$$f(\theta) = f_c(\theta) + k^{-1} \sum_{l=0}^{\infty} (2l + 1) e^{i\delta_l} \sin \delta_l P_l(\cos \theta) \quad (8)$$

and the differential cross section is  $\sigma(\theta) = |f(\theta)|^2$ . Here  $\sigma$  is again infinite.

**1.6. Perturbation methods.** If the Hamiltonian  $H$  is independent of the time, the Schrödinger wave equation  $i\hbar(\partial\psi/\partial t) = H\psi$  has stationary solutions  $\psi = u \exp(-iEt/\hbar)$ , where  $u$  is independent of time and satisfies the equation  $Hu = Eu$ . Suppose that this equation cannot be solved, but that the corresponding equation with  $H_0$  can be solved, where  $H = H_0 + H'$ :  $H_0 u_n = E_n u_n$ . Then if  $H'$  is small compared with  $H_0$ , an approximate (perturbation) solution can be obtained that expresses  $u$  and  $E$  in terms of the normalized  $u_n$ ,  $E_n$  and  $H'$ . Define the matrix element

other states may be degenerate) the perturbed energy level and state lying close to  $E_m$  and  $u_m$  are given, through terms of second order in  $H'$ , by

$$\left. \begin{aligned} E &\cong E_m + H'_{mm} + \sum'_n \frac{|H'_{nm}|^2}{E_m - E_n} \\ u &\cong u_m + \sum'_n \frac{H'_{nm}u_n}{E_m - E_n} + \sum'_n \left\{ -\frac{1}{2} \cdot \frac{|H'_{nm}|^2 u_m}{(E_m - E_n)^2} \right. \\ &\quad \left. + \left[ -\frac{H'_{nm}H'_{mm}}{(E_m - E_n)^2} + \sum'_k \frac{H'_{nk}H'_{km}}{(E_m - E_n)(E_m - E_k)} \right] u_n \right\} \end{aligned} \right\} \quad (2)$$

The prime on the summation over  $n$  or  $k$  means that the term  $n = m$  or  $k = m$  is to be omitted from the sum; if some of the states are continuously distributed, the sums are to be replaced by integrals over those states. If the unperturbed state  $m$  is degenerate, the calculation is more complicated, and involves first finding linear combinations of the unperturbed degenerate states that are approximate eigenfunctions of the complete Hamiltonian  $H$  with unequal eigenvalues.

The Born approximation is an application of perturbation theory to a collision problem, in which the unperturbed states are continuously distributed in energy and degenerate. Let  $H = -(\hbar^2/2\mu)\nabla^2 + V(\mathbf{r})$ , where  $V$  is not necessarily spherically symmetric, and regard  $V$  as the perturbation. Then an approximate expression for the scattered amplitude, valid to first order in  $V$ , is

$$\left. \begin{aligned} f(\theta, \phi) &\cong -\frac{\mu}{2\pi\hbar} \int V(\mathbf{r})e^{i\mathbf{K}\cdot\mathbf{r}}d\tau \\ \mathbf{K} &= \mathbf{k}_0 - \mathbf{k} \end{aligned} \right\} \quad (3)$$

where  $\mathbf{k}_0$  is a vector along the bombarding direction, and  $\mathbf{k}$  a vector along the direction of observation, both of magnitude  $k = (2\mu E/\hbar^2)^{1/2}$ ;  $\theta$  and  $\phi$  are the polar angles of  $\mathbf{k}$  with respect to  $\mathbf{k}_0$ . If  $V$  is spherically symmetric,  $f$  depends only on  $\theta$ , and

$$f(\theta) \cong -\frac{2\mu}{\hbar^2 K} \int_0^\infty r \sin Kr V(r)dr, \quad K = 2k \sin \frac{1}{2}\theta \quad (4)$$

In both cases, the differential scattering cross section is  $|f|^2$ . The phase

A convenient criterion for the validity of the Born approximation is

$$\frac{\mu}{2\pi\hbar^2} \left| \int \frac{1}{r} e^{i(kr+\mathbf{k}_0 \cdot \mathbf{r})} V(\mathbf{r}) d\tau \right| \ll 1 \quad (6)$$

If  $V$  is spherically symmetric, this validity criterion becomes

$$\frac{\mu}{\hbar^2 k} \left| \int_0^\infty (e^{2ikr} - 1) V(r) dr \right| \ll 1 \quad (7)$$

Perturbation theory may also be used to calculate the probability for a transition between stationary states  $u_n$  of an unperturbed Hamiltonian  $H_0$  ( $H_0 u_n = E_n u_n$ ), that are caused by a time-dependent perturbation  $H'$ . If  $H'$  is a transient disturbance, the first-order probability that the system has made a transition from any state  $m$  to any state  $n$  after a long time is

$$\frac{1}{\hbar^2} \left| \int_{-\infty}^\infty H'_{nm} e^{i(E_n - E_m)t/\hbar} dt \right|^2 \quad (8)$$

If  $H'$  is independent of time except for being turned on at some instant, the first-order probability per unit time that the system will make a transition from any state  $m$  to a state  $n$  that has the same energy is

$$w = \frac{2\pi}{\hbar} \rho(n) |H'_{nm}|^2 \quad (9)$$

where  $\rho(n)dE_n$  is the number of final states with energies between  $E_n$  and  $E_n + dE_n$ . In this latter case, if  $H'_{nm} = 0$ , it may be replaced in the formula by the second-order matrix element

$$\sum_k \frac{H'_{nk} H'_{km}}{E_m - E_k} \quad (10)$$

If any of the states  $k$  are continuously distributed, the sum is to be replaced by an integral over those states.

**1.7. Other approximation methods.** Let  $E_0$  be the smallest energy eigenvalue of a Hamiltonian  $H$  ( $Hu_0 = E_0u_0$ ). Then

$$E_0 \leq E \equiv \frac{\int \bar{u} H u d\tau}{\int |u|^2 d\tau} \quad (1)$$

for any function  $u$ . The equal sign holds if and only if  $u = u_0$ . This is the variation method, and  $u$  is the trial function, which usually contains parameters that can be varied to minimize the variational energy  $E$ . If  $u$  differs from  $u_0$  by a first-order infinitesimal, then  $E$  exceeds  $E_0$  only by a second-order infinitesimal. If the trial function is chosen in the form

$$u = \frac{u_0 \int \bar{u}_0 u d\tau}{\int |u_0|^2 d\tau} \quad (2)$$

the variational energy will provide an upper limit on the next to the smallest energy eigenvalue.

The WKB (Wentzel-Kramers-Brillouin) approximation can be used to obtain approximate solutions of the one-dimensional time-independent wave equation

$$\frac{d^2u}{dx^2} + k^2(x)u = 0, \quad k^2 = \frac{2\mu}{\hbar^2} [E - V(x)] \quad (3)$$

when the potential changes slowly enough so that  $dk/dx \ll k^2$ . If  $k$  is real ( $V < E$ ), the two linearly independent solutions are

$$A_1 k^{-1/2} \exp \left[ i \int_{a_1}^x k(x) dx \right], \quad A_2 k^{-1/2} \exp \left[ -i \int_{a_2}^x k(x) dx \right] \quad (4)$$

If  $\kappa = ik$  is real ( $V > E$ ), the solutions are

$$B_1 \kappa^{-1/2} \exp \left[ \int_{b_1}^x \kappa(x) dx \right], \quad B_2 \kappa^{-1/2} \exp \left[ - \int_{b_2}^x \kappa(x) dx \right] \quad (5)$$

Near the turning points of the corresponding classical motion (where  $V = E$ ),  $dk/dx \gg k^2$ , and the above approximate solutions are not valid. They can be connected to each other across a turning point (taken to be at  $x = 0$  with  $V > E$  for  $x < 0$  and  $V < E$  for  $x > 0$ ) by means of the following formulas.

$$\left. \begin{aligned} \frac{1}{2} \kappa^{-1/2} \exp \left( - \int_x^0 \kappa dx \right) &\rightarrow k^{-1/2} \cos \left( \int_0^x k dx - \frac{1}{4} \pi \right) \\ \sin \eta \kappa^{-1/2} \exp \left( \int_x^0 \kappa dx \right) &\leftarrow k^{-1/2} \cos \left( \int_0^x k dx - \frac{1}{4} \pi + \eta \right) \end{aligned} \right\} \quad (6)$$

where  $\eta$  is appreciably different from zero or an integer multiple of  $\pi$ . Without more careful consideration, the connections can be made only in the directions indicated by the arrows; for example, in the first formula, the expression on the left goes into that on the right, but the reverse is not necessarily true.

If  $x_1$  and  $x_2$  are two turning points of a potential well, so that  $V < E$  for  $x_1 < x < x_2$ , the WKB approximation states that the energy levels are given by the formula

$$\int_{x_1}^{x_2} k(x) dx = \left( n + \frac{1}{2} \right) \pi, \quad (n = 0, 1, 2, \dots) \quad (7)$$

This is the same as the Bohr-Wilson-Sommerfeld quantization rule (see § 1.1) except that  $n$  is now replaced by  $n + \frac{1}{2}$ .

The time-dependent Schrödinger wave equation

$$i\hbar \frac{\partial \psi}{\partial t} = H(t)\psi \quad (8)$$

can be solved approximately if  $H$  depends on  $t$ , provided it has a simple enough form and changes slowly enough with time. The adiabatic approximation shows that the system stays in a particular state  $u_m(t)$  for a long time, where

$$H(t)u_m(t) = E_m(t)u_m(t) \quad (9)$$

provided that

$$\hbar \frac{\partial H}{\partial t} \ll (E_n - E_m)^2 \quad (10)$$

for all other states  $n$ .

On the other hand, if  $H(t)$  changes very rapidly from one constant form to another, the wave function  $\psi$  is approximately the same just before and just after the change in  $H$ . The sudden approximation shows that if the change in  $H$  takes place in a short time  $\tau$ , the wave function is unchanged if  $\hbar/\tau$  is large in comparison with the energy differences between the initial state of the original Hamiltonian and those final states of the altered Hamiltonian that are most prominent in the expansion of  $\psi$ .

**1.8. Matrices in quantum mechanics.** Hermitian and unitary matrices (see § 7.11 of Chapter 1), often with infinite numbers of rows and columns, play an important role in quantum mechanics. Every dynamical variable can be represented by an operator, or by an infinite number of Hermitian matrices, one for every complete orthonormal set of eigenfunctions of that or any other operator. For example, suppose that we have two dynamical variables represented by operators  $\Omega$  and  $\Omega'$ , with orthonormal eigenfunction sets  $u_n$  and  $v_s$ ,

$$\Omega u_n = \omega_n u_n, \quad \Omega' v_s = \omega'_s v_s$$

Then four matrices that have the following elements can be calculated.

$$\left. \begin{aligned} \int \bar{u}_m \Omega u_n d\tau &= \omega_n \delta_{mn}, & \int \bar{u}_m \Omega' u_n d\tau &= \Omega'_{mn} \\ \int \bar{v}_r \Omega v_s d\tau &= \Omega_{rs}, & \int \bar{v}_r \Omega' v_s d\tau &= \omega'_s \delta_{rs} \end{aligned} \right\} \quad (1)$$

The first and third of these are different representations of  $\Omega$ , and the second and fourth are different representations of  $\Omega'$ . The first and fourth are diagonal matrix representations, in which case the diagonal elements are the eigenvalues of the operators. If these eigenvalues are real, as they are for physically meaningful variables, the operators and matrices (whether or

not diagonal) are Hermitian. A matrix element  $\Omega_{rs}$  is sometimes written ( $r | \Omega | s$ ).

A transformation from the nondiagonal to the diagonal representation of  $\Omega$  can be effected by means of the unitary matrix  $U_{mr} = \int \bar{u}_m v_r d\tau$ .

$$\sum_r \sum_s U_{mr} \Omega_{rs} (U^{-1})_{sn} = \omega_n \delta_{mn} \quad (2)$$

The unitary property of  $U$  means that

$$(U^{-1})_{sn} = (\bar{U})_{sn} = \bar{U}_{ns} \quad (3)$$

where  $U^{-1}$  is the reciprocal of  $U$ ,  $\bar{U}$  is the Hermitian conjugate of  $U$ ,  $\bar{U}_{ns}$  is the complex conjugate of the matrix element  $U_{ns}$ .

Heisenberg's form of the equations of motion of quantum mechanics expresses the change in dynamical variables with time without explicit use of wave functions, and hence are valid in any matrix representation. If  $H$  is the Hamiltonian, the equation of motion for any dynamical variable  $\Omega$  is

$$\frac{d\Omega}{dt} = \frac{\partial\Omega}{\partial t} + \frac{1}{i\hbar} (\Omega H - H\Omega) \quad (4)$$

Here the term  $d\Omega/dt$  indicates the time derivative of a typical matrix element of  $\Omega$ , the term  $\partial\Omega/\partial t$  indicates the corresponding matrix element of the partial derivative of  $\Omega$  with respect to  $t$  (which is zero if  $\Omega$  does not depend explicitly on the time), and the parenthesis is calculated according to the rules for matrix multiplication. If  $\Omega$  does not depend explicitly on the time, and if it commutes with the Hamiltonian ( $\Omega H = H\Omega$ ), then  $d\Omega/dt = 0$  and  $\Omega$  is a constant of the motion.

In general, to quantize a classical system replace Poisson brackets (see § 1.6 of Chapter 2) by commutator brackets in the following way.

$$\{A, B\} \equiv \sum_i \left( \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial q_i} \frac{\partial A}{\partial p_i} \right) \rightarrow \frac{1}{i\hbar} [A, B] = \frac{1}{i\hbar} (AB - BA)$$

Thus for canonical coordinates and momenta  $q_i, p_i$ , we get the quantum conditions

$$[q_i, p_j] = i\hbar \delta_{ij}, \quad [q_i, q_j] = 0, \quad [p_i, p_j] = 0 \quad (5)$$

A particular representation for these quantum conditions is that used in (1.3) to write down the Schrödinger wave equation

$$q_i = q_i, \quad p_i = -i\hbar \frac{\partial}{\partial q_i} \quad (6)$$

**1.9. Many-particle systems.** The Schrödinger wave function for many particles depends on the coordinates of all the particles, and the Hamiltonian is the sum of their kinetic, potential, and interaction energies. If the particles are identical, the wave function must be either symmetrical or antisymmetrical with respect to an interchange of all the coordinates of any two particles (including in the interchange both space and spin coordinates). Particles that obey Einstein-Bose statistics are described by symmetrical wave functions, and particles that obey Fermi-Dirac statistics, or (equivalently) the Pauli exclusion principle, are described by antisymmetrical wave functions.

In the special case in which the particle interaction energies can be neglected, the wave function can be written as a sum of products of one-particle wave functions like

$$v_\alpha(1)v_\beta(2) \dots v_\nu(n) \quad (1)$$

where  $v_\alpha(1)$  denotes that particle 1 is in the state  $\alpha$  with energy  $E_\alpha$ . The total energy is then  $E_\alpha + E_\beta + \dots + E_\nu$ . A symmetrical wave function is the sum of all distinct terms that arise from permuting the numbers 1, ...,  $n$  among the functions. An antisymmetrical wave function can be written as a determinant

$$\begin{vmatrix} v_\alpha(1) & v_\alpha(2) & \dots & v_\alpha(n) \\ v_\beta(1) & v_\beta(2) & \dots & v_\beta(n) \\ \dots & \dots & \dots & \dots \\ v_\nu(1) & v_\nu(2) & \dots & v_\nu(n) \end{vmatrix} \quad (2)$$

and vanishes if any two of the states  $\alpha, \beta, \dots, \nu$  are the same.

**1.10. Spin angular momentum.** A particle, like an electron, proton, or neutron, that has spin angular momentum  $\frac{1}{2}\hbar$ , can be described non-relativistically by a two-component wave function. The spin angular momentum operator  $\mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\sigma}$  operates on these two-component functions, and can be expressed in terms of the two-row, two-column Pauli spin matrices.

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (1)$$

The two spin states may be chosen to be eigenfunctions of  $S_z$  as well as of  $\mathbf{S}^2$ , in which case they may be written

$$u_{1/2}(\mathbf{r}) = \begin{pmatrix} 1 \\ 0 \end{pmatrix} w(\mathbf{r}), \quad u_{-1/2}(\mathbf{r}) = \begin{pmatrix} 0 \\ 1 \end{pmatrix} w(\mathbf{r}) \quad (2)$$

It then follows that

$$\left. \begin{aligned} S_z u_{1/2} &= \frac{1}{2} \hbar u_{1/2}, & S_z u_{-1/2} &= -\frac{1}{2} \hbar u_{-1/2} \\ S^2 u_{1/2} &= \frac{3}{4} \hbar^2 u_{1/2}, & S^2 u_{-1/2} &= \frac{3}{4} \hbar^2 u_{-1/2} \end{aligned} \right\} \quad (3)$$

For a particle of spin  $s$ , which can be one of the numbers  $0, \frac{1}{2}, 1, \frac{3}{2}, \dots$ , the spin matrix has  $2s + 1$  rows and columns, and the wave functions have  $2s + 1$  components. These wave functions may be chosen to be eigenfunctions of  $S_z$  with eigenvalues  $s\hbar, (s - 1)\hbar, \dots -s\hbar$ , and all are eigenfunctions of  $S^2$  with eigenvalue  $s(s + 1)\hbar^2$ .

If  $s = 0, 1, 2, \dots$ , the particles obey Einstein-Bose statistics; if  $s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ , they obey Fermi-Dirac statistics. In both cases the differential scattering cross section for a collision of two identical particles in the center-of-mass coordinate system may be written in terms of the scattered amplitude  $f(\theta)$  as

$$\sigma(\theta) = |f(\theta)|^2 + |f(\pi - \theta)|^2 + \frac{(-1)^{2s}}{2s + 1} 2\text{Re}[f(\theta)f(\pi - \theta)] \quad (4)$$

where  $\text{Re}$  denotes the real part of what follows.

**1.11. Some radiation formulas.** Interaction of a particle of charge  $e$  with radiation may be taken into account by replacing  $\mathbf{p}$  or  $-i\hbar \mathbf{grad}$  with  $\mathbf{p} - (e/c)\mathbf{A}$  or  $-i\hbar \mathbf{grad} - (e/c)\mathbf{A}$  in the Schrödinger equation, where  $\mathbf{A}$  is the radiation vector potential (see § 3.3 of Chapter 10).

When a one-electron atom in state  $n$  is irradiated by electromagnetic waves that are continuously distributed in frequency (with random phases) in the neighborhood of the angular frequency  $|E_n - E_k|/\hbar = \omega$ , transitions will be induced from the state  $n$  to the state  $k$  (corresponding to either absorption or emission of energy) at the rate

$$\frac{4\pi^2 e^2}{m^2 c \omega^2} I(\omega) \left| \int \bar{u}_k e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{grad}_{\text{pol}} u_n d\tau \right|^2 \quad (1)$$

per unit time. Here  $e$  and  $m$  are the charge and mass of the electron,  $I(\omega)$  is the intensity of the incident radiation per unit angular frequency range,  $\mathbf{k}$  is the propagation vector of the incident radiation, and the component of the gradient along the polarization vector of the incident radiation is taken.

For allowed or electric-dipole transitions, this formula becomes

$$\frac{4\pi^2 e^2}{3\hbar^2 c} I(\omega) \left| (\mathbf{r})_{kn} \right|^2 \quad (2)$$

where the last factor is equal to the sum of the squares of the magnitudes

of the matrix elements of  $x$ ,  $y$ , and  $z$ . The rate of spontaneous radiative electric-dipole transitions per unit time is

$$\frac{4e^2\omega^3}{3\hbar c^3} |(\mathbf{r})_{kn}|^2 \quad (3)$$

Forbidden transitions (electric quadrupole, magnetic dipole, etc.) generally have a rate smaller than allowed transitions by a factor of order  $(ka)^2$  or less, where  $a$  is a typical linear dimension of the atomic system.

In simple cases, the intensity radiated per unit frequency range is proportional to

$$[(\omega - \omega_0)^2 + \frac{1}{4}\omega^2]^{-1} \quad (4)$$

where  $\omega_0$  is the center of the emitted line and the line breadth is proportional to  $\omega$ , the spontaneous transition probability per unit time.

**1.12. Relativistic wave equations.** A scalar particle (spin 0) of mass  $m$  is described relativistically by the Schrödinger relativistic wave equation

$$E^2\psi = c^2\mathbf{p}^2\psi + m^2c^4\psi \quad (1)$$

or

$$-\hbar^2 \frac{\partial^2 \psi}{\partial t^2} = -\hbar^2 c^2 \nabla^2 \psi + m^2 c^2 \psi \quad (2)$$

If the particle has charge  $e$ , the electric charge and current densities are

$$\left. \begin{aligned} P &= \frac{ie\hbar}{2mc^2} \left( \bar{\psi} \frac{\partial \psi}{\partial t} - \psi \frac{\partial \bar{\psi}}{\partial t} \right) \\ \mathbf{S} &= \frac{e\hbar}{2im} (\bar{\psi} \mathbf{grad} \psi - \psi \mathbf{grad} \bar{\psi}) \end{aligned} \right\} \quad (3)$$

and satisfy the conservation law

$$\frac{\partial P}{\partial t} + \text{div } \mathbf{S} = 0 \quad (4)$$

When electromagnetic fields described by the potentials  $A$ ,  $\phi$  (see § 3.3 of Chapter 10) are present, the substitutions  $E \rightarrow E - e\phi$  and  $\mathbf{p} \rightarrow \mathbf{p} - (e/c)\mathbf{A}$  can be made in the wave equation above. The energy levels in a Coulomb field ( $\mathbf{A} = 0$ ,  $e\phi = -Ze^2/r$ ), including the rest energy  $mc^2$ , are given by

$$\left. \begin{aligned} E &= mc^2 \left[ 1 + \frac{\alpha^2}{\left\{ n - l - \frac{1}{2} + \left[ \left( l + \frac{1}{2} \right)^2 - \alpha^2 \right]^{1/2} \right\}^2} \right]^{-1/2}, \quad \alpha = \frac{Ze^2}{\hbar c} \\ &\quad (l = 0, 1, \dots, n - 1; \quad n = 1, 2, 3, \dots) \end{aligned} \right\} \quad (5)$$

This formula disagrees with the Sommerfeld fine-structure formula, derived on the basis of the old quantum theory, and also disagrees with experiment.

An electron (spin  $\frac{1}{2}\hbar$ ) is described relativistically by Dirac's relativistic wave equation

$$E\psi + c(\boldsymbol{\alpha} \cdot \mathbf{p})\psi + mc^2\beta\psi = 0 \tag{6}$$

or

$$i\hbar \frac{\partial\psi}{\partial t} - i\hbar c\boldsymbol{\alpha} \cdot \mathbf{grad} \psi + mc^2\beta\psi = 0 \tag{7}$$

where

$$\left. \begin{aligned} \alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1 \\ \alpha_x\alpha_y + \alpha_y\alpha_x = \alpha_y\alpha_z + \alpha_z\alpha_y = \alpha_z\alpha_x + \alpha_x\alpha_z = 0 \\ \alpha_x\beta + \beta\alpha_x = \alpha_y\beta + \beta\alpha_y = \alpha_z\beta + \beta\alpha_z = 0 \end{aligned} \right\} \tag{8}$$

Here  $\beta$  and  $\boldsymbol{\alpha}$  can be expressed as four-row, four-column matrices

$$\left. \begin{aligned} \beta = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} & \quad \alpha_x = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \\ \alpha_y = \begin{bmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{bmatrix} & \quad \alpha_z = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{bmatrix} \end{aligned} \right\} \tag{9}$$

The wave function has four components.

$$\psi(\mathbf{r}, t) = \begin{bmatrix} \psi_1(\mathbf{r}, t) \\ \psi_2(\mathbf{r}, t) \\ \psi_3(\mathbf{r}, t) \\ \psi_4(\mathbf{r}, t) \end{bmatrix} \tag{10}$$

The electric charge and current densities are

$$P = e\bar{\psi}\psi, \quad S = -ce\bar{\psi}\boldsymbol{\alpha}\psi \tag{11}$$

where  $\bar{\psi}$  is the Hermitian conjugate matrix to  $\psi$ ;  $P$  and  $S$  satisfy the usual conservation law.

Electromagnetic fields can be included by making the substitutions  $E \rightarrow E - e\phi$  and  $\mathbf{p} \rightarrow \mathbf{p} - (e/c)\mathbf{A}$ . In the nonrelativistic limit with  $\phi = 0$  and  $\mathbf{A}$  constant in time, the Schrödinger wave equation is obtained with an extra term in the Hamiltonian  $-(e\hbar/2mc)\boldsymbol{\sigma} \cdot \mathbf{H}$ ; this is the energy of the electron's magnetic moment of magnitude  $e\hbar/2mc$  in a magnetic field  $\mathbf{H}$ . In this limit, the  $\boldsymbol{\sigma}$ 's are the Pauli spin matrices, and the wave function has two components.

In a central field [ $A = 0$ ,  $e\phi = V(r)$ ], the nonrelativistic limit gives the Schrödinger wave equation with an extra term that is the spin-orbit energy

$$\frac{1}{2mc^2r} \cdot \frac{dV}{dr} \mathbf{S} \cdot \mathbf{M} \quad (12)$$

added to the Hamiltonian. Here the wave function has two components,  $\mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\sigma}$  is the spin angular momentum, and  $\mathbf{M} = \mathbf{r} \times \mathbf{p}$  is the orbital angular momentum.

The relativistic energy levels in a Coulomb field ( $A = 0$ ,  $e\phi = -Ze^2/r$ ), including the rest energy  $mc^2$ , are given by

$$E = mc^2 \left\{ 1 + \frac{\alpha^2}{[n - k + (k^2 - \alpha^2)^{1/2}]^2} \right\}^{-1/2}, \quad \begin{array}{l} (k = 1, 2, \dots, n) \\ (n = 1, 2, \dots) \end{array} \quad (13)$$

where  $\alpha = Ze^2/\hbar c$ . This formula is the same as the Sommerfeld fine-structure formula, and is in good agreement with experiment.

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## Chapter 22

### NUCLEAR THEORY

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Nuclear physics is still in a state of rapid change, and with the passage of time new developments and shifts of emphasis are inevitable. The material selected for presentation in this chapter was chosen so as to provide a comprehensive survey of the field. However, the choice of material is also conditioned by the criteria that the formal aspect of the topics treated be fairly well-developed and of reasonable expectation value of relative permanence at the time of writing. The omission of some subject matter in the field of nuclear physics may be understood in this light.

#### 1. Table of Symbols

The numbers in **boldface** in parentheses preceding the various groups of symbols that follow indicate the section where particular symbols are introduced. (*Bold-face italic* type is used for vectors and vector operators.)

(2.1)

$N$  = number of neutrons in nucleus.

$Z$  = number of protons in nucleus.

$A = N + Z$ , mass number.

$M_Z^A$  = mass of neutral atom.

${}_Z M^A$  = mass of nucleus;  ${}_1 M^1 \equiv M_p$ ,  ${}_0 M^1 = M_n$ , proton and neutron masses, respectively.

$m$  = (rest) mass of electron.

$\Delta_Z^A = M_Z^A - A$ , mass excess.

$\mathcal{P}_Z^A = (M_Z^A - A)/A$ , packing-fraction.

$\epsilon_Z^A$  = binding energy.

$e$  = proton charge (in esu).

$R$  = nuclear radius.

$\beta_+$ , ( $\beta_-$ ) refers to positive (negative) electrons emitted by nucleus.

$\epsilon_e$  = binding energy of orbital electron.

$c$  = vacuum velocity of light.

### (2.2)

$\sigma_k^{(j)}$  =  $k$ th component of the Pauli spin vector for the  $j$ th nucleon.

$s^{(j)}$  =  $\frac{1}{2}\sigma^{(j)}$ ,  $\hbar s^{(j)}$  is the spin operator for the  $j$ th nucleon.

$\hbar$  = Dirac action constant.

$S = \sum_j s^j$ ; eigenvalue of  $S^2 \equiv S(S+1)$ .

$L$  = orbital angular momentum operator divided by  $\hbar$  [Eq. (2.3)]; eigenvalues of  $L^2 = L(L+1)$ ,  $L = 0, 1, 2, \dots$

$\nabla_j$  = gradient operator in configuration space of  $j$ th nucleon.

$J$  = total angular momentum operator divided by  $\hbar$  [Eq. (2.4)]; eigenvalues of  $J^2 = J(J+1)$ .

$m_J$  = eigenvalue of  $J_3$ .

$\Psi$  = nuclear wave function (sometimes written with appropriate quantum numbers as index).

$H$  = nuclear Hamiltonian, eigenvalue  $E = -\epsilon_Z^A$ , ( $E = 0$  for nucleons at rest and at infinite separation).

$\nabla_j^2$  = Laplacian operator in space of  $j$ th nucleon.

$\mathcal{U}$  = nuclear interaction operator.

$\langle O \rangle = (\Psi, O\Psi)$ , expectation value of the operator  $O$  where the inner product is taken in configuration and spin space of all the nucleons and  $(\Psi, \Psi) = 1$ .

$\mu_0 = e\hbar/2M_p c$ , nuclear magneton.

$\mu_n$  = neutron magnetic moment in units  $\mu_0$ ,  $\mu_n = -1.9135$ .

$\mu_p$  = proton magnetic moment in units  $\mu_0$ ,  $\mu_p = 2.7926$ .

### (2.3)

$P_K$  = exchange operator in two-nucleon interactions,  $K = M, H, B$ .

$m_s^{(j)}$  = eigenvalue of  $s_3^{(j)}$ .

$\tau^j$  = isotopic spin (matrix) vector for  $j$ th nucleon.

$m_\tau^{(j)}$  = eigenvalue of  $\tau_3^{(j)}$ .

$r$  = distance between two nucleons.

$V^0$  = scale parameter in two nucleon interactions determining strength of interaction.

$b$  = range parameter in two-nucleon interaction.

(2.4)

$$\eta = \sqrt{M\epsilon}/\hbar.$$

$$\Psi'_S = {}^3S_1 \text{ part of deuteron wave function, } S^2\Psi'_S = 2\Psi'_S, \quad L^2\Psi'_S = 0, \\ J^2\Psi'_S = 2\Psi'_S.$$

$$\Psi'_D = {}^3D_1 \text{ part of deuteron wave function, } S^2\Psi'_D = 2\Psi'_D, \quad L^2\Psi'_D = 6\Psi'_D, \\ J^2\Psi'_D = 2\Psi'_D.$$

$\hbar\omega$  = energy of electromagnetic radiation.

$\sigma_e, \sigma_m$  = total cross sections for photoelectric and photomagnetic disintegration of deuteron, respectively.

$\sigma_e(\vartheta), \sigma_m(\vartheta)$  = cross sections per unit solid angle for disintegration with angle  $\vartheta$  between photon and relative direction of motion of nucleons.

$\epsilon'$  = negative binding energy of  ${}^1S$  state of deuteron,  $\epsilon' \cong 75$  kev.

(2.5)

A particle of mass  $M_1$  is scattered by a target nucleus of mass  $M_2$ .

**Laboratory ( $L$ ) system :**

$\bar{E}_n, \bar{E}'_n$  kinetic energy of  $M_n$  before and after scattering.

$\Theta$ , scattering angle of  $M_1$ , azimuth  $\phi$ .

$$d\Omega_\Theta = \sin \Theta \, d\Theta \, d\phi.$$

$\sigma_0(\Theta)$  = scattering cross section per unit solid angle.

**Center of mass ( $C$ ) system :**

$E$  = sum of kinetic energies of both particles.

$\theta$  = scattering angle of  $M_1$ , azimuth  $\varphi$ .

$$d\Omega = \sin \theta \, d\theta \, d\varphi.$$

$M_r = M_1M_2/(M_1 + M_2)$ , reduced mass.

$k = \sqrt{2M_rE}/\hbar$ , wave number at  $r = \infty$ .

$v$  = relative velocity at  $r = \infty$ .

$\delta_l$  = nuclear phase shift of partial wave with orbital angular momentum  $l\hbar$ .

$P_l$  = Legendre polynomial (argument  $\cos \theta$ ).

$\delta_r$  = real part of  $s$ -phase shift ( $l = 0$ ).

$\frac{1}{2}\Delta$  = imaginary part of  $s$ -phase shift.

$Z_1, Z_2$  = atomic numbers for scattered and target nuclei.

$$\alpha = e^2/\hbar v.$$

(2.6)

$\bar{E}_n, E_n$  = energy of particle of mass  $M_n$  in  $L, C$  systems, respectively.

$Q = (M_1 + M_2 - M_3 - M_4)c^2$  is energy release in transmutation, ( $Q$ -value).

$\Theta_n$ ,  $\theta_n$  angle between outgoing direction of  $M_n$  and incident beam, in ( $L$ ), ( $C$ ) systems, respectively.

$H_{l+\frac{1}{2}}^{(1,2)}(x)$  = Hankel functions of first, second kind and order  $l + \frac{1}{2}$ .

$\kappa = Z_P Z_A \alpha$  or  $Z_Q Z_B \alpha$ ;  $Z_P$  or  $Z_Q = 0$  for neutrons and photons.

$\zeta_i(r) = kr - \frac{1}{2}l\pi - \kappa \ln kr + \arg [(l + i\kappa)!]$ .

$J_{\pm(l+1/2)}(x)$  = Bessel function of order  $\pm (l + \frac{1}{2})$ .

### (2.7)

$W$  = electron (or positron) energy (including rest energy) in units  $mc^2$ .

$p = \sqrt{W^2 - 1}$ ,  $\beta$ -particle momentum in units  $mc$ .

$W_0 = (\Delta M)_{\pm}/m$ , maximum  $W$ .

$G_F$  = Fermi coupling constant for  $\beta$ -decay,  $G^2 \sim 10^{-2} \text{ sec}^{-1}$ .

$d\Omega_\nu$  = differential solid angle for neutrino.

$\Psi_e$  = wave function of  $\beta_{\pm}$ -particle.

$\Psi_\nu$  = wave function of neutrino.

$\Psi_f, \Psi_i$  = nuclear wave functions for final and initial states, respectively.

$y = e^2 ZW/\hbar c p$ .

$\gamma = (1 - e^4 Z^2/\hbar^2 c^2)^{1/2}$ .

## 2. Nuclear Theory

**2.1. Nuclear masses and stability.** a. *Energy relations.* Neglecting the binding of the orbital electrons

$${}_Z M^A = M_Z^A - Zm \quad (1)$$

Numerical values are defined by  $M_8^{16} \equiv 16.0$  and 1 mass unit = 931 Mev =  $10^3$  mmu. The binding energy of the nucleus is

$$\left. \begin{aligned} \epsilon_Z^A &= ZM_1^1 + NM_0^1 - M_Z^A = Z\Delta_1^1 + N\Delta_0^1 - \Delta_Z^A \\ &\approx A[\frac{1}{2}(P_1^1 + P_0^1) - P_Z^A] \end{aligned} \right\} \quad (2)$$

Semi-empirical formula for binding energy (incompressible nucleus) \*

$$\epsilon_Z^A = u_v A - u_s A^{2/3} - u_\tau \frac{(N - Z)^2}{A} - \frac{3}{5} u_c \frac{Z(Z - 1)}{A^{1/3}} \quad (3)$$

\* WEIZSACKER, C. V., *Z. Physik*, **96**, 431 (1935); BETHE, H. A. and BACHER, R., *Revs. Modern Phys.*, **8**, 82 (1936). FEENBERG, E., *Revs. Modern Phys.*, **19**, 239 (1947) gives the small correction arising from nuclear compressibility.

where

$$u_p = 15.1 \text{ mmu} = 14.1 \text{ Mev}, \quad u_s = 14.1 \text{ mmu} = 13.1 \text{ Mev},$$

$$u_\tau = 19.4 \text{ mmu} = 18.1 \text{ Mev}, \quad u_e = e^2/r_0 = 0.157 \text{ mmu} = 0.146 \text{ Mev}.$$

The result [Eq. (3)] corresponds to a nuclear radius  $R$  given (in cm) by

$$R = r_0 A^{1/3} = 1.47 \times 10^{-13} A^{1/3} \quad (4)$$

b. *Stability conditions.* A necessary and sufficient condition for stability against nuclear particle emission is

$$M_A^Z < \Sigma M_{A'}^{Z'} \quad (5)$$

where the sum is taken over all possible combinations for which

$$\Sigma A' = A, \quad \Sigma Z' = Z \quad (6)$$

Therefore Eq. (5) includes the condition  $\epsilon_Z^A > 0$ .

For  $\beta_\pm$  decay and capture of orbital electrons the stability conditions are (assuming zero neutrino rest mass)

$$(\Delta M)_- = M_Z^A - M_{Z+1}^A < 0, \quad (\text{for } \beta_- \text{ decay}) \quad (7)$$

$$(\Delta M)_+ = M_Z^A - M_{Z-1}^A - 2m < 0, \quad (\text{for } \beta_+ \text{ decay}) \quad (8)$$

$$(\Delta M)_\nu = M_Z^A - M_{Z-1}^A - \epsilon_e/c^2 < 0, \quad (\text{for orbital electron capture}) \quad (9)$$

Only the very small difference of electronic binding energies of the parent and daughter nuclei is neglected. When these conditions are not fulfilled  $(\Delta M)_\pm c^2$  is the total energy (including rest energy of the  $\beta_\pm$  particle) liberated in the decay process and  $(\Delta M)_\nu c^2$  is the neutrino energy.

The decay constant  $\lambda$  for a disintegration process is defined by

$$\lambda = -d \ln N/dt \quad (10)$$

where  $N$  is the number of decaying nuclei at time  $t$ . The mean life and half-life are, respectively,

$$T = 1/\lambda, \quad T_{1/2} = (\ln 2)/\lambda \quad (11)$$

**2.2. Stationary state properties.** The spin properties of particles with spin  $\frac{1}{2}\hbar$  (nucleons) are described in terms of the Pauli spin matrices. In the spin space of each nucleon the matrix-vector  $\sigma$  has components

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (1)$$

The spin operator  $\hbar s = \frac{1}{2}\hbar\boldsymbol{\sigma}$ . For a complex nucleus  $s$  is replaced by

$$S = \frac{1}{2} \sum_{j=1}^A \boldsymbol{\sigma}^{(j)} \quad (2)$$

where  $\boldsymbol{\sigma}^{(j)}$  refers to the  $j$ th nucleon and a direct product with unit matrices in the space of the other nucleons is implied in each term of Eq. (2). The spin quantum number  $S = n/2$ ,  $n \leq A$  and  $n$  even (odd) for  $A$  even (odd). For a single nucleon  $S = s = \frac{1}{2}$ .

The orbital angular momentum operator is  $\hbar L$

$$L = -i \sum_{j=1}^A (\mathbf{r}_j \times \nabla_j) \quad (3)$$

where the summand is a direct product of  $A$  unit matrices.

The total angular momentum operator is  $\hbar J$

$$J = S + L \quad (4)$$

For any nuclear state  $J^2$  is diagonal, with eigenvalues  $J(J+1)$ , and  $J = n/2$ ,  $(-)^n = (-)^A$ . Along the quantization axis the component of total angular momentum is  $m_j \hbar$

$$m_j = -J, -J+1, \dots, J-1, J \quad (5)$$

A nuclear wave function  $\Psi_{J, m_j}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_A)$  is a simultaneous eigenfunction of  $J^2$ ,  $J_z$  with the eigenvalues  $J(J+1)$  and  $m_j$ , and of a Hamiltonian operator with eigenvalue  $E$ .

$$H\Psi = \left( - \sum_{j=1}^A \frac{\hbar^2}{2M_j} \nabla_j^2 + \mathcal{U} \right) \Psi = E\Psi \quad (6)$$

where  $\mathcal{U}$  is the total interaction operator (§ 2.3);  $\Psi$  is also an eigenfunction of the *parity* operator (inversion through the origin, center of mass)

$$\Psi(-\mathbf{r}_1, -\mathbf{r}_2, \dots, -\mathbf{r}_A) = \pm \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_A) \quad (7)$$

the  $+$  and  $-$  sign belonging to states of even and odd *parity*, respectively. For interacting nucleons  $H$ ,  $J^2$ ,  $J_z$ , and parity are conserved (diagonal) but in general  $S^2$  and  $L^2$  are not. In special case where the latter are conserved the quantum numbers  $S$  and  $L$  are introduced.

The magnetic dipole moment (neglecting small contributions from exchange currents) is

$$\boldsymbol{\mu} = \mu_0 \left\langle \sum_{j=1}^Z \left[ \mu_p \boldsymbol{\sigma}_3^{(j)} - i \left( x_j \frac{\partial}{\partial y_j} - y_j \frac{\partial}{\partial x_j} \right) \right] + \mu_n \sum_{j=Z+1}^A \boldsymbol{\sigma}_3^{(j)} \right\rangle_{m_J=J} \quad (8)$$

The electric quadrupole moment is

$$q = \left\langle \sum_{j=1}^Z (3z_j^2 - r_j^2) \right\rangle_{m_J=J} \quad (9)$$

where the sum is over protons only. For  $J < 1$ ,  $q = 0$ .

**2.3. Nuclear interactions.\*** *Restriction:* only velocity-independent interactions are considered; interactions are in the two-particle system (neglect difference in mass of neutron and proton).

a. *Central interactions.* Aside from the Coulomb interaction between protons  $\mathcal{U}(\mathbf{r})$  is, in general, a linear combination of the following four fundamental interactions: (1)  $V_W(r)$  ordinary (or Wigner) interaction, (2)  $V_M(r)P_M$  space exchange (or Majorana) interaction, (3)  $V_H(r)P_H$  space-spin exchange (or Heisenberg) interaction, (4)  $V_B(r)P_B$  spin exchange (or Bartlett) interaction. If  $\Psi(\mathbf{r}_1, m_s^{(1)}; \mathbf{r}_2, m_s^{(2)})$  is the two-nucleon wave function, the exchange operators are defined by

$$\left. \begin{aligned} P_M \Psi[\mathbf{r}_1, m_s^{(1)}; \mathbf{r}_2, m_s^{(2)}] &= \Psi[\mathbf{r}_2, m_s^{(1)}; \mathbf{r}_1, m_s^{(2)}] \\ P_H \Psi[\mathbf{r}_1, m_s^{(1)}; \mathbf{r}_2, m_s^{(2)}] &= \Psi[\mathbf{r}_2, m_s^{(2)}; \mathbf{r}_1, m_s^{(1)}] \\ P_B \Psi[\mathbf{r}_1, m_s^{(1)}; \mathbf{r}_2, m_s^{(2)}] &= \Psi[\mathbf{r}_1, m_s^{(2)}; \mathbf{r}_2, m_s^{(1)}] \end{aligned} \right\} \quad (1)$$

The  $P$ -operators commute, and any one is the product of the other pair. For these interactions  $L^2$  and  $S^2$  are conserved. Then  $S = 0, 1$ ,

$$P_M \Psi = (-)^L \Psi; \quad P_B \Psi = (-)^{S+1} \Psi \quad (2)$$

and for identical particles  $S + L$  is an even integer.

*Isotopic spin formalism.* All nucleons are treated as (charge) substates of a single particle (Fermion). The isotopic spin matrices  $\tau_1^{(j)}, \tau_2^{(j)}, \tau_3^{(j)}$  are introduced (one matrix vector for each nucleon) just as in Eq. (1) of § 2.2 except that  $\tau_i^{(j)}$  operates on the isotopic spin coordinate  $m_\tau^{(j)} (= \pm 1)$  which is adjoined to  $\mathbf{r}^{(j)}$  and  $m_s^{(j)}$  as arguments in  $\Psi$ ;  $m_\tau = 1$  (neutron),  $m_\tau = -1$  (proton). (Exclusion principle for two particles.)

$$\Psi(\mathbf{r}_1, m_s^{(1)}, m_\tau^{(1)}; \mathbf{r}_2, m_s^{(2)}, m_\tau^{(2)}) = -\Psi(\mathbf{r}_2, m_s^{(2)}, m_\tau^{(2)}; \mathbf{r}_1, m_s^{(1)}, m_\tau^{(1)}) \quad (3)$$

\* ROSENFELD, L., *Nuclear Forces*, 2 vols., Interscience Publishers, Inc., New York, 1948.

Requirement of invariance under the rotation-reflection group in spin, isotopic-spin and configurational space admits the following central operators :  $1$ ,  $\boldsymbol{\tau}^{(1)} \cdot \boldsymbol{\tau}^{(2)}$ ,  $\boldsymbol{\sigma}^{(1)} \cdot \boldsymbol{\sigma}^{(2)}$ ,  $\boldsymbol{\tau}^{(1)} \cdot \boldsymbol{\tau}^{(2)} \boldsymbol{\sigma}^{(1)} \cdot \boldsymbol{\sigma}^{(2)}$  which are related to the foregoing operators by

$$\left. \begin{aligned} \frac{1}{2}(1 + \boldsymbol{\sigma}^{(1)} \cdot \boldsymbol{\sigma}^{(2)}) &= P_B \\ \frac{1}{2}(1 + \boldsymbol{\tau}^{(1)} \cdot \boldsymbol{\tau}^{(2)}) &= -P_E \end{aligned} \right\} \quad (4)$$

b. *Noncentral interaction.* Invariance requirements admit the additional (tensor) operator

$$S_{12} = \frac{3(\boldsymbol{\sigma}^{(1)} \cdot \mathbf{r})(\boldsymbol{\sigma}^{(2)} \cdot \mathbf{r})}{r^2} - \boldsymbol{\sigma}^{(1)} \cdot \boldsymbol{\sigma}^{(2)} \quad (5)$$

and the product  $\boldsymbol{\tau}^{(1)} \cdot \boldsymbol{\tau}^{(2)} S_{12}$ . The following interaction models have been used\* :

$$\text{I. } \mathcal{U} = \boldsymbol{\tau}^{(1)} \cdot \boldsymbol{\tau}^{(2)} [V_0(r) + V_1(r) \boldsymbol{\sigma}^{(1)} \cdot \boldsymbol{\sigma}^{(2)} + V_2(r) S_{12}] \quad (6)$$

$$\text{II. } \mathcal{U} = \frac{1}{2}(1 + \boldsymbol{\tau}^{(1)} \cdot \boldsymbol{\tau}^{(2)}) [V'_0(r) + V'_1(r) \boldsymbol{\sigma}^{(1)} \cdot \boldsymbol{\sigma}^{(2)} + V'_2(r) S_{12}] \quad (7)$$

$$\text{III. } \mathcal{U} = V''_0(r) + V''_1(r) \boldsymbol{\sigma}^{(1)} \cdot \boldsymbol{\sigma}^{(2)} + V''_2(r) S_{12} \quad (8)$$

which are sometimes referred to as “symmetrical,” “charged,” and “neutral” (meson field theories) interactions, respectively. If  $\mathcal{U}_0$  and  $\mathcal{U}_e$  refer to the (neutron-proton) interactions in the states of odd and even  $L$ , respectively,

$$\mathcal{U}_0 = -3^{1-2S} \mathcal{U}_e, \quad (\text{for I}) \quad (9)$$

$$\mathcal{U}_0 = -\mathcal{U}_e \quad (\text{for II}) \quad (10)$$

$$\mathcal{U}_0 = \mathcal{U}_e \quad (\text{for III}) \quad (11)$$

with  $S = 0, 1 : [\boldsymbol{\sigma}^{(1)} \cdot \boldsymbol{\sigma}^{(2)} = 2S(S+1) - 3]$ .

For interactions in nuclei with more than two constituents the restriction to two-body interactions is customarily made so that

$$\mathcal{U} = \sum_{i > j} \left[ \mathcal{U}_{ij} + \frac{1}{4} \cdot \frac{e^2}{|r_i - r_j|} (1 - \tau_3^{(i)}) (1 - \tau_3^{(j)}) \right] \quad (12)$$

where  $\mathcal{U}_{ij}$  is the specific nuclear interaction between nucleons  $i$  and  $j$  described above.

\* RARITA, W. and SCHWINGER, J., *Phys. Rev.*, **59**, 436, 556 (1941).

In all cases the functions  $V_0$ ,  $V_1$ , etc. are defined in terms of two parameters: a depth parameter  $V^0$  which fixes the scale of the interaction, and a range  $b$  such that for  $r > b$ ,  $V \ll V^0$ . For example,

$$V = -V^0 g(r/b); \quad V^0 > 0 \quad (13)$$

Square well,  $g_S(x) = 1$  for  $x < 1$ ,  $g = 0$  for  $x > 1$ ; Yukawa well,  $g_Y(x) = e^{-x}/x$ ; exponential well,  $g_E(x) = e^{-x}$ ; Gaussian well,  $g_G(x) = e^{-x^2}$ .

**2.4. Properties of the deuteron.** a. *Ground state properties.* Fundamental data are:  $J = 1$ ,  $\mu/\mu_0 = 0.85761$ ,  $q = 2.766 \times 10^{-27}$  cm<sup>2</sup>, and  $\epsilon_1^2 \equiv \epsilon = 2.228$  Mev, parity even. (For central interactions  $L = 0$ ,  $S = 1$ .) Take  $M_p = M_n = M$ . For each well shape the assigned value of  $\epsilon$  fixes a relation between  $V^0$  and  $b$ . For a square well [ $\mathcal{U} = -V^0 g_S(r/b)$ ],

$$\sqrt{\frac{M}{\hbar^2} (V - \epsilon)} \cot b \sqrt{\frac{M}{\hbar^2} (V^0 - \epsilon)} = -\eta \equiv -\sqrt{\frac{M\epsilon}{\hbar^2}} \quad (1)$$

With tensor forces,  $L^2$  is not conserved but  $S^2$  is. For the ground state ( $S = 1$ ),

$$\Psi = \Psi_S + \Psi_D \quad (2)$$

b. *Interaction with electromagnetic radiation* (No tensor forces considered). For photon wavelengths  $\gg b$  the total cross section for *photoelectric disintegration* of the deuteron is [with neglect of nuclear force in the final ( ${}^3P$ ) state]

$$\sigma_e = \frac{8\pi}{3} \cdot \frac{e^2 \hbar}{Mc} \cdot \frac{\epsilon^{1/2} (\hbar\omega - \epsilon)^{3/2}}{(1 - \eta\rho) (\hbar\omega)^3} \quad (3)$$

and  $\rho$  is an effective range,

$$\rho = 2 \int_0^\infty [e^{-2\eta r} - u^2(r)] dr \quad (4)$$

$u = r\Psi_S$  normalized to  $e^{-\eta r}$  at  $r = \infty$ . The angular distribution is given by

$$\sigma_e(\vartheta) = \frac{3}{8\pi} \sigma_e \sin^2 \vartheta \quad (5)$$

The *photomagnetic disintegration* cross section is

$$\sigma_m = \frac{2\pi}{3} \frac{(\mu_p - \mu_n)^2}{1 - \eta\rho} \frac{e^2 \hbar}{M^2 c^3} \cdot \frac{\sqrt{|\epsilon'|} |(\hbar\omega - \epsilon)| (\sqrt{\epsilon} + \sqrt{|\epsilon'|})^2}{\hbar\omega(\hbar\omega - \epsilon + |\epsilon'|)} \quad (6)$$

The angular distribution is isotropic

$$\sigma_m(\vartheta) = \sigma_m/4\pi \quad (7)$$

The total photodisintegrations cross section is then

$$\sigma = \sigma_m + \sigma_e \quad (8)$$

and for the angular distribution

$$\sigma(\vartheta) = \frac{\sigma_e}{4\pi} \left( \frac{\sigma_m}{\sigma_e} + \frac{3}{2} \sin^2 \vartheta \right) \quad (9)$$

The cross section for capture of neutrons of energy  $\bar{E}_1$  by protons ( $^1S \rightarrow ^3S$  transition) is

$$\sigma_e = \pi \frac{(\mu_p - \mu_n)^2}{1 - \eta\rho} \cdot \frac{e^2 \hbar}{M^3 c^5} \sqrt{\frac{2\epsilon}{\bar{E}_1}} \frac{(\sqrt{\epsilon} + \sqrt{|\epsilon'|})^2 (\epsilon + \frac{1}{2}\bar{E}_1)}{|\epsilon'| + \frac{1}{2}\bar{E}_1} \quad (10)$$

**2.5. Potential scattering.** a. *Transformation between laboratory (L) and center of mass (C) reference systems*

$$E = \frac{M_2}{M_1 + M_2} \bar{E}_1 \quad (1)$$

$$\tan \Theta = \frac{M_2 \sin \theta}{M_1 + M_2 \cos \theta}, \quad \phi = \varphi \quad (2)$$

For  $M_1 \geq M_2$ ,  $\Theta \leq \arcsin M_2/M_1 \leq \pi/2$ . (See also § 2.6a.)

$$d\Omega_\Theta = d\Omega M_2^2 \frac{M_2 + M_1 \cos \theta}{(M_2^2 + M_1^2 + 2M_1 M_2 \cos \theta)^{3/2}} \quad (3)$$

$$\bar{E}'_1 = \frac{\bar{E}_1}{(M_1 + M_2)^2} (M_2^2 + M_1^2 + 2M_1 M_2 \cos \theta) \quad (4)$$

$$\bar{E}'_2 = \frac{2\bar{E}_1 M_1 M_2}{(M_1 + M_2)^2} (1 - \cos \theta) \quad (5)$$

b. *Method of phase shifts.* In the following only central interactions will be considered. Therefore  $L^2$  and  $S^2$  are conserved. In the  $C$  system, the scattering cross section per unit solid angle (for target and scattered nuclei not identical) is

$$\sigma(\theta, \varphi) = |f(\theta, \varphi)|^2 = \sigma_0(\Theta, \phi) d\Omega_\Theta / d\Omega \quad (6)$$

where the scattering amplitude  $f(\theta, \varphi)$  is defined by the asymptotic ( $r \rightarrow \infty$ ) form of the solution of the wave equation

$$\left[ \nabla^2 + \frac{2M_r}{\hbar^2} (E - \mathcal{U}) \right] \Psi = 0 \quad (7)$$

which is

$$\Psi_\infty = e^{ikz} + f(\theta, \varphi) \frac{e^{ikr}}{r} \quad (8)$$

Here the  $z$  axis has been taken along the direction of the incident beam, and the scattered particle is observed without regard to its spin state. When there is no preferred direction in the plane normal to the incident beam (scattering of unpolarized particles)  $\partial |f|/\partial\varphi = 0$ .

The solution of Eq. (7) which has the required asymptotic form is a sum of partial waves each one of which is an eigenfunction of  $L^2$  with eigenvalue  $l(l+1)$ .

$$\Psi = \sum_{l=0}^{\infty} e^{i(\delta_l + l\pi/2)} (2l+1) \frac{F_l(kr)}{kr} P_l(\cos\theta) \quad (9)$$

where  $F_l$  is the solution of

$$\frac{d^2 F_l}{dr^2} + \left( k^2 - \frac{2M_r}{\hbar^2} \mathcal{V} - \frac{l(l+1)}{r^2} \right) F = 0 \quad (10)$$

normalized to

$$F_l(\infty) = \sin\left( kr - \frac{l\pi}{2} + \delta_l \right) \quad (11)$$

Then

$$f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) (e^{2i\delta_l} - 1) P_l(\cos\theta) \quad (12)$$

The total cross section (in either reference frame) is

$$\sigma = \sigma_0 = \int |f(\theta)|^2 d\Omega = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l \quad (13)$$

*For s-scattering of neutrons.* For  $kR \ll 1$ ,  $\delta_l \sim (kR)^{l+1}$  and  $f(\theta) \cong \delta_0/k$ ,

$$\sigma = \frac{4\pi}{k^2} \sin^2 \delta_0, \quad \sigma(\theta) = \frac{\sigma}{4\pi} \quad (14)$$

For scattering with absorption the phase  $\delta_0$  is complex

$$2\delta_0 = 2\delta_r + i\Delta, \quad (\delta_r, \Delta \text{ real}) \quad (15)$$

The  $s$ -scattering and absorption cross sections are then

$$\sigma_{sc} = \frac{\pi}{k^2} [(1 - e^{-\Delta})^2 + 4e^{-\Delta} \sin^2 \delta_r] \quad (16)$$

$$\sigma_a = \frac{\pi}{k^2} (1 - e^{-2\Delta}) \quad (17)$$

and the total cross section is

$$\sigma_t = \sigma_{sc} + \sigma_a = \frac{2\pi}{k^2} [2e^{-\Delta} \sin^2 \delta_r + 1 - e^{-\Delta}] \quad (18)$$

For very fast neutrons ( $kR \gg 1$ ) all phase shifts  $\delta_l(l \lesssim kR)$  contribute and  $\sigma_t$ , the total cross section, is given by

$$\frac{1}{2}\sigma_t = \sigma_{sc} = \sigma_a = \pi R^2 \quad (19)$$

c. *Scattering length.* For zero energy neutrons  $r\Psi$  is a linear function of  $r$  outside the range of the nuclear forces. The extrapolation of this linear function  $r\Psi_{\text{ext}}$  gives the scattering length  $a$  according to

$$\Psi_{\text{ext}}(a) = 0, \quad (a \geq 0) \quad (20)$$

For incident  $s$ -neutrons scattered by a nucleus of total angular momentum (spin)  $= I\hbar$ , the value of  $a$  will depend on the relative spin orientation of neutron and nucleus, i.e., on the total angular momentum  $J = I \pm \frac{1}{2}$  of the combined system. There will be two scattering lengths  $a_{I \pm \frac{1}{2}}$  in this case. In general the phase shifts may be expressed as a power series in  $k$  by means of the following \*

$$k \cot \delta_J = -\frac{1}{a_J} + \frac{1}{2}k^2 r_e(J) + \dots \quad (21)$$

where  $r_e(J)$  is the effective range,

$$r_e(J) = 2 \int_0^\infty \left[ \left( 1 - \frac{r}{a_J} \right)^2 - u_0^2 \right] dr \quad (22)$$

and  $u_0 = r\Psi$  (for  $E = 0$ ) normalized to  $u_0 = 1 - r/a_J$  at  $r = \infty$ . In terms of  $a_J$  the scattering cross section for slow neutrons is to zeroth order in  $k$ ,

$$\sigma = 4\pi \left( \frac{I+1}{2I+1} a_{I+\frac{1}{2}}^2 + \frac{I}{2I+1} a_{I-\frac{1}{2}}^2 \right) \quad (23)$$

When neutrons are scattered by a crystal the total scattering is composed of two parts, coherent and incoherent scattering

$$\sigma_{\text{coh}} = 4\pi \left( \frac{I+1}{2I+1} a_{I+\frac{1}{2}} + \frac{I}{2I+1} a_{I-\frac{1}{2}} \right)^2 \quad (24)$$

$$\sigma_{\text{inc}} = 4\pi \frac{I(I+1)}{(2I+1)^2} (a_{I+\frac{1}{2}} - a_{I-\frac{1}{2}})^2 \quad (25)$$

For neutron-proton scattering ( $I = \frac{1}{2}$ ),

$$\sigma_{n-p} = \frac{\pi\hbar^2}{M} \left( \frac{3}{\epsilon + \frac{1}{2}\bar{E}_1} + \frac{1}{|\epsilon'| + \frac{1}{2}\bar{E}_1} \right) \quad (26)$$

\* BETHE, H. A., *Phys. Rev.*, **76**, 38 (1949). BLATT, J. M. and JACKSON, J. D., *Phys. Rev.*, **76**, 18 (1949).

which is independent of the well shape to a high degree of approximation. Equation (26) is applicable for  $E_0 < \text{about } 10 \text{ Mev}$ , but below about 1 ev molecular binding and crystal diffraction effects have to be considered. Also in neutron diffraction the scattering lengths  $a_j$  in Eqs. (24) and (25) must be multiplied by the Debye-Waller temperature factor and by a factor  $1 + M_n/M_Z^A$ .

d. *Scattering of charged particles.* If the two particles participating in the collision are not identical the results of Eqs. (6) and (12) are used with  $\delta_l$  replaced by

$$\bar{\delta}_l = \delta_l + \arg \left[ \left( l + \frac{ie^2 Z_1 Z_2}{\hbar v} \right)! \right] \quad (27)$$

where  $\delta_l$  are the nuclear phase shifts, and the additional term is the phase shift due to the Coulomb interaction.

For the collision of (unpolarized) identical particles of spin  $I\hbar$

$$\sigma(\theta) = \frac{I}{2I+1} |f(\theta) \pm f(\pi-\theta)|^2 + \frac{I+1}{2I+1} |f(\theta) \mp f(\pi-\theta)|^2 \quad (28)$$

where the upper signs apply for Fermi statistics and the lower for Bose statistics and Eq. (12) together with (27) is to be used. For proton-proton scattering only  $s$ -wave nuclear scattering is important, and only the first term of Eq. (28) contributes to the nuclear part of the scattering. In the ( $L$ ) system

$$\sigma_0(\Theta) = \left. \begin{aligned} & \frac{e^4}{E_1^2} \cos \Theta \left[ \frac{1}{\sin^4 \Theta} + \frac{1}{\cos^4 \Theta} - \frac{\cos \alpha \ln \tan^2 \Theta}{\sin^2 \Theta \cos^2 \Theta} \right. \\ & \left. - \frac{2}{\alpha} \sin \delta_0 \left( \frac{\cos(\delta_0 + \alpha \ln \sin^2 \Theta)}{\sin^2 \Theta} + \frac{\cos(\delta_0 + \alpha \ln \cos^2 \Theta)}{\cos^2 \Theta} \right) \right. \\ & \left. + \frac{4}{\alpha^2} \sin^2 \delta_0 \right] \end{aligned} \right\} \quad (29)$$

For the scattering of  $\alpha$ -particles in  $\text{He}^4$  in the ( $L$ ) system

$$\sigma_0(\Theta) = \left. \begin{aligned} & \left( \frac{4e^2}{E_1} \right)^2 \cos \Theta \left[ \frac{e^{-4i\alpha \ln \sin^2 \Theta}}{\sin^2 \Theta} + \frac{e^{-4i\alpha \ln \cos^2 \Theta}}{\cos^2 \Theta} \right. \\ & \left. + \frac{i}{2\alpha} \sum_{l \text{ even}} (2l+1) (e^{2i\delta_l} - 1) \frac{(1+4i\alpha)^2 \dots (l+4i\alpha)^2}{(1+16\alpha^2) \dots (l^2+16\alpha^2)} \right. \\ & \left. \times P_l(\cos 2\Theta) \right]^2 \end{aligned} \right\} \quad (30)$$

and, in general, only  $l \lesssim kR$  need be considered.

**2.6. Resonance reactions.\*** a. *Energy relations for the reaction*

$$M_1 + M_2 \rightarrow M_3 + M_4, \quad (\bar{E}_2 = 0)$$

$$E_3 = \frac{Q + M_2 \bar{E}_1 / (M_1 + M_2)}{1 + M_3 / M_4} = \frac{M_4}{M_3} E_4 \quad (1)$$

$$(\bar{E}_1)_t = - \left( Q + \frac{M_1}{M_2} \right), \quad (\text{threshold energy}) \quad (2)$$

$$\tan \Theta_3 = \frac{\tan \theta_3}{1 + \sqrt{(M_1 M_3 / M_2 M_4) \{ \bar{E}_1 / [\bar{E}_1 - (\bar{E}_1)_t] \}} \sec \theta_3} \quad (3)$$

$$\sin(\theta_3 - \Theta_3) = \sqrt{\frac{M_1 M_3}{M_2 M_4} \frac{\bar{E}_1}{\bar{E}_1 - (\bar{E}_1)_t}} \sin \Theta_3 \quad (4)$$

$$\left. \begin{aligned} \bar{E}_3 &= \frac{1}{(M_3 + M_4)^2} \\ &\left\{ \sqrt{M_1 M_3 \bar{E}_1} \xi_3 + \sqrt{\bar{E}_1 M_1 M_3} \xi_3^2 + (M_3 + M_4) [Q M_4 + (M_4 - M_1) \bar{E}_1] \right\}^2 \end{aligned} \right\} \quad (5)$$

where  $\xi_3 = \cos \theta_3$ . A corresponding result holds for  $\bar{E}_4$  by interchanging indexes 3, 4. Alternatively

$$\bar{E}_4 = \bar{E}_1 - \bar{E}_3 + Q \quad (6)$$

For photon emission no distinction need be made between *C* and *L* systems in practical cases ( $\hbar\omega \ll M_n c^2$ ).

b. *Scattering and reaction cross sections.* Consider the nuclear transmutation symbolized by



where *P* is the projectile nucleus, *A* the target nucleus, *C* the compound nucleus, *B* the residual nucleus, and *Q* the observed outgoing particle; *P* and/or *Q* may also refer to photons. The total angular momenta (units  $\hbar$ ) are *s*, *I*, *J*, *I'*, *s'*, respectively. The orbital angular momenta for the *P* - *A* and *B* - *Q* relative motion are *l* and *l'* (units  $\hbar$ ), respectively.

$$\mathfrak{S} = I + s, \quad \mathfrak{S}' = I' + s' \quad (8)$$

\* BETHE, H. A., *Revs. Modern Phys.*, **9**, 69 (1937); LIVINGSTON, M. S. and BETHE, H. A., *Revs. Modern Phys.*, **9**, 245 (1937); BLATT, J. M. and WEISSKOPF, V. F., "The Theory of Nuclear Reactions," *ONR Technical Report 42*.

are referred to as total intrinsic spins for the breakup of the compound state into particle with the specified angular momenta  $I, s$  and  $I', s'$ , respectively. All particles are considered to be unpolarized. The mean life of a specified compound state ( $n$ ) for breakup into  $P + A$  or  $B + Q$  is

$$\left. \begin{aligned} T_{P,l,\mathfrak{E}}^{(n)} &= \frac{\hbar}{\Gamma_{P,l,\mathfrak{E}}^{(n)}} \\ T_{Q,l',\mathfrak{E}'}^{(n)} &= \frac{\hbar}{\Gamma_{Q,l',\mathfrak{E}'}^{(n)}} \end{aligned} \right\} \quad (9)$$

where  $\Gamma_{P,l,\mathfrak{E}}$  etc. are partial widths of the specified state ( $n$ ). The total width of this state of the compound nucleus is

$$\Gamma^{(n)} = \sum_{P,l,\mathfrak{E}} \Gamma_{P,l,\mathfrak{E}}^{(n)} \quad (10)$$

and  $E_n$  is the resonance energy of the state.

The resonance elastic scattering cross section for  $P$  scattered by  $A$ , with  $C$ -system energy  $E$  ( $= \hbar ck$  for photons), is approximately [see Eqs. (15) and (16)]

$$\sigma_{sc}^{(J)} = \frac{\pi}{k^2} \cdot \frac{2J+1}{(2I+1)(2s+1)} S \left| \frac{\Gamma_{P,l,\mathfrak{E}}^{(n)}}{E - E_n + (i/2)\Gamma^{(n)}} + \mathcal{A}_l \right|^2 \quad (11)$$

where

$$S = \sum_{\mathfrak{E}=|I-s|}^{I+s} \sum_{l=|J-\mathfrak{E}|}^{J+\mathfrak{E}} \quad (12)$$

Here  $l$  is even (odd) if the parity of ( $n$ ) is even (odd);  $\mathcal{A}_l$  gives the contribution of the potential scattering. For neutrons

$$\mathcal{A}_l = - \frac{H_{l+\frac{1}{2}}^{(1)}(kR)}{H_{l+\frac{1}{2}}^{(2)}(kR)} - 1 \approx \frac{2i(2l+1)(kR)^{2l+1}}{[1 \cdot 3 \cdot 5 \dots (2l+1)]^2} \quad (13)$$

The last result applies for  $kR \ll 1$ . For charged particles

$$\left. \begin{aligned} \mathcal{A}_l &\approx \mathcal{A}_0 \frac{(2kR)^{2l}}{(2l)!(2l+1)!} \prod_{\nu=1}^l (\nu^2 + \kappa^2) \\ \mathcal{A}_0 &\approx 2ikR \frac{2\pi\kappa}{e^{2\pi\kappa} - 1} \end{aligned} \right\} \quad (14)$$

and again  $kR \ll 1$ . In addition to Eq. (11) there is a contribution (usually

small) to  $\sigma_{sc}^{(J)}$  in which the orbital angular momentum and/or the total intrinsic spin changes. This is

$$\delta\sigma_{sc}^{(J)} = \frac{\pi}{k^2} \frac{2J+1}{(2I+1)(2s+1)} \cdot \mathcal{S}\mathcal{S}' \frac{\Gamma_{Pl\mathcal{E}}^{(n)} \Gamma_{Pl'\mathcal{E}'}^{(n)} (1 - \delta_{ll'} \delta_{\mathcal{E}\mathcal{E}'})}{(E - E_n)^2 + [\frac{1}{2} \Gamma^{(n)}]^2} \quad (15)$$

$$\mathcal{S}' \equiv \sum_{\mathcal{E}'=|I'-s'|}^{I'+s'} \sum_{\nu=|J-\mathcal{E}'|}^{J+\mathcal{E}'}$$

except that for  $l = l' = 0$  only  $\mathcal{E} = \mathcal{E}'$  is allowed. The other states of the compound nucleus contribute a background (nonresonance) scattering so that the total elastic cross section is

$$\sigma_{sc} = \sum_{J, \text{parity}} (\sigma_{sc}^{(J)} + \delta\sigma_{sc}^{(J)}) \quad (16)$$

The absorption cross section (including inelastic scattering of  $P$ ) is, *near resonance*,

$$\sigma_a = \frac{\pi}{k^2} \frac{2J+1}{(2I+1)(2s+1)} \cdot \frac{\Gamma_P^{(n)} \Gamma_Q^{(n)}}{(E - E_n)^2 + [\frac{1}{2} \Gamma^{(n)}]^2} \quad (17)$$

$$\Gamma_P^{(n)} = \mathcal{S} \Gamma_{Pl\mathcal{E}}^{(n)}, \quad \Gamma_Q^{(n)} = \mathcal{S}' \Gamma_{Ql'\mathcal{E}'}^{(n)} \quad (18)$$

and the selection rules are

$$\left. \begin{aligned} (-)^l &= (-)^{l'} && \text{(if parity of } A = \text{parity of } B) \\ (-)^l &= (-)^{l'+1}, && \text{(if parity of } A \neq \text{parity of } B) \end{aligned} \right\} \quad (19)$$

For photon absorption (or emission)  $2s + 1$  (or  $2s' + 1$ ) = 2.

*Selection rules for photon emission.* The entries below give the type of multipole field emitted with greatest intensity. Multipole fields of higher order can always be neglected. Here  $I'\hbar$  is the angular momentum of the final state in the transition and  $\mathcal{L} = |J - I'|$ .

Parity	Even	Odd
changes	electric $2\mathcal{L}$ pole magnetic $2\mathcal{L}+1$ pole	electric $2\mathcal{L}+1$ pole magnetic $2\mathcal{L}$ pole
does not change	electric $2\mathcal{L}+1$ pole magnetic $2\mathcal{L}$ pole	electric $2\mathcal{L}$ pole magnetic $2\mathcal{L}+1$ pole

and  $J = 0, I' = 0$  is absolutely forbidden for single quantum emission. \*

\* Internal conversion coefficients are given conveniently only in numerical form, see *Phys. Rev.*, **83**, 79 (1951).

The energy and  $l$ -dependence of the partial widths is given by

$$\Gamma^{(n)} = \chi_l(E) \Gamma_0^{(n)} \cong \chi_l(E) \sqrt{\frac{E}{E_n}} \Gamma_0^{(n)}(E_n) \quad (20)$$

where superfluous indices have been suppressed. The barrier penetrability  $\chi_l$  is

$$\chi_l = \frac{1}{F_l^2(R) + G_l^2(R)} \quad (21)$$

where  $F_l$  and  $G_l$  are the real solutions of Eq. (10) *without specific nuclear interactions* and with the normalization at  $r = \infty$

$$G_l(\infty) + iF_l(\infty) = e^{i\zeta_l(r)} \quad (22)$$

For neutrons \* ( $Z_0 = 0, \kappa = 0$ )

$$\left. \begin{aligned} G_l(R) &= \sqrt{\frac{\pi kR}{2}} J_{-l+\frac{1}{2}}(kR) \\ F_l(R) &= \sqrt{\frac{\pi kR}{2}} J_{l+\frac{1}{2}}(kR) \end{aligned} \right\} \quad (23)$$

and for  $kR \ll 1, G_l \gg F_l$  and

$$\chi_l = \frac{(kR)^{2l}}{[1 \cdot 3 \cdot 5 \dots (2l-1)]^2} \quad (24)$$

For charged particles + and  $kR \ll 1$

$$\left. \begin{aligned} \chi_l &\approx \chi_0 \frac{2^{2l}}{(2l)!^2} (kR)^{2l} \prod_{\nu=1}^l (\nu^2 + \kappa^2) \\ \chi_0 &\approx [2\pi\kappa / (e^{2\pi\kappa} - 1)] e^{4\sqrt{2}\kappa R} \end{aligned} \right\} \quad (25)$$

**2.7. Beta decay.** The probability per unit time for the emission of a  $\beta$  particle with energy between  $W$  and  $W + dW$  is  $\times$

$$P_\beta(W)dW = \frac{1}{2\pi^3} \langle |H_\beta|^2 \rangle_{\text{av}} pW(W_0 - W)^2 dW \quad (1)$$

where  $H_\beta$  is the Hamiltonian for  $\beta$  decay

$$\langle |H_\beta|^2 \rangle_{\text{av}} = \frac{G_F^2}{2p^2} \int d\Omega_\nu \sum_e \left| \int dv_N \sum_j H_j \right|^2 \quad (2)$$

\* Cf. WIGNER, E. P. and EISENBUD, L., *Phys. Rev.*, **72**, 29 (1947).

+ Cf. YOST, F. L., WHEELER, J. A. and BREIT, G., *Phys. Rev.*, **49**, 174 (1935).

$\times$  KONOPINSKI, E. J., *Revs. Modern Phys.*, **15**, 209 (1943).

In Eq. (2)  $\sum_e$  is a sum over all eigenvalues of diagonal operators specifying the angular momentum direction of motion of the  $\beta$  particle,  $\int dv_N$  implies an integration over the space and spin coordinates of all nucleons, and  $\sum_i$  is sum over neutrons (protons) for  $\beta_- (\beta_+)$  emission. The relativistic invariant  $H_j$  is formed by contractions of five possible covariants. In the spin space of the light particles ( $\beta$  particle and neutrino) and each of the nucleons the following 4 by 4 matrices are defined

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (3)$$

$$\bar{\sigma} = -\frac{i}{2} (\alpha \times \alpha), \quad \gamma_5 = i\alpha_1\alpha_2\alpha_3 \quad (4)$$

wherein each element in Eq. (3) is a 2 by 2 matrix [see Eq. (2) of § 2.2]. Then  $H_j$  is, in general, a linear combination of the five invariants

$$H_S = (\Psi_f^* \beta \tau_1^{(j)} \Psi_i) (\psi_e^* \beta \psi_\nu) \quad (5)$$

$$H_V = (\Psi_f^* \tau_1^{(j)} \Psi_i) (\psi_e^* \psi_\nu) - (\Psi_f^* \alpha \tau_1^{(j)} \Psi_i) \cdot (\psi_e^* \alpha \psi_\nu) \quad (6)$$

$$H_T = (\Psi_f^* \beta \bar{\sigma} \tau_1^{(j)} \Psi_i) \cdot (\psi_e^* \beta \bar{\sigma} \psi_\nu) + (\Psi_f^* \beta \alpha \tau_1^{(j)} \Psi_i) \cdot (\psi_e^* \beta \alpha \psi_\nu) \quad (7)$$

$$H_A = (\Psi_f^* \bar{\sigma} \tau_1^{(j)} \Psi_i) \cdot (\psi_e^* \bar{\sigma} \psi_\nu) - (\Psi_f^* \gamma_5 \tau_1^{(j)} \Psi_i) (\psi_e^* \gamma_5 \psi_\nu) \quad (8)$$

$$H_P = (\Psi_f^* \beta \gamma_5 \tau_1^{(j)} \Psi_i) (\psi_e^* \beta \gamma_5 \psi_\nu) \quad (9)$$

The index  $S, V, T, A, P$  indicate that the invariants have been formed by contraction of scalar, polar vector, tensor, axial vector, and pseudoscalar covariants. All quantities in  $H_j$  are evaluated at the position of the  $j$ th nucleon.

*Allowed transition.* The selection rules are \*

	Nuclear spin change	Parity
Scalar	0	no change
Polar vector	0	no change
Tensor	0, $\pm 1$ (no $0 \rightarrow 0$ )	no change
Axial vector	0, $\pm 1$ (no $0 \rightarrow 0$ )	no change
Pseudoscalar	0	change

\* See GREULING, E., *Phys. Rev.*, **61**, 568 (1942) for forbidden transitions.

The decay constant is

$$\lambda_\beta = \int_1^{W_0} P(W) dW \quad (10)$$

For each of the five interactions [Eqs. (5), (6), (7), (8), (9)] the spectrum shape is the same.

$$P_{\beta^\pm}(W) = \frac{G_F^2}{2\pi^3} |\mathcal{M}|^2 p W (W_0 - W)^2 F(\mp Z, W) dW \quad (11)$$

The constant  $\mathcal{M}$  is

$$\mathcal{M} = \int dv_N \sum_j \Psi_j^* \mathcal{O} \tau_1^{(j)} \Psi_i$$

where  $\mathcal{O} = \beta, 1, \beta\bar{\sigma}, \bar{\sigma}$  and  $\beta\gamma_5$  acting on the nucleon spin for the five invariants (5, 6, 7, 8, 9) respectively. The effect of the (unscreened) Coulomb field acting on the electron is represented by the Fermi function

$$F(Z, W) = \frac{2(1 + \gamma) (2pR)^{2\gamma-2} |(\gamma - 1 + iy)!|^2 e^{\pi y}}{(2\gamma)!^2} \quad (12)$$

where  $Z$  and  $R$  refer to the final nucleus. The probability per unit energy interval for a decay process with angle  $\vartheta$  between  $\beta$  particle and neutrino is

$$P_{\beta^\pm} \left( 1 + \frac{np}{W} \cos \vartheta \right) \quad (13)$$

with  $n = -1$  for  $S$  and  $P$ ,  $n = 1$  (for  $V$ ),  $n = \frac{1}{3}$  (for  $T$ ) and  $n = -\frac{1}{3}$  (for  $A$ ).

The decay constant for capture of  $K$ -shell electrons is

$$\lambda_K = \frac{G_F^2}{\pi^2} |\mathcal{M}|^2 (2R)^{2\gamma-2} \left( \frac{e^2 Z}{\hbar c} \right)^{2\gamma+1} \frac{1 + \gamma}{(2\gamma)!} (W_0 + 1 - \epsilon_K)^2 \quad (14)$$

and  $\epsilon_K \cong 1 - \gamma$  is the  $K$ -shell electron binding energy in units  $mc^2$ .

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## Chapter 23

# COSMIC RAYS AND HIGH-ENERGY PHENOMENA

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The following formulas have been chosen because they represent the reliable tools of the worker in high-energy physics. While the results of calculations based on meson theories have had a great heuristic value, they are not quantitatively reliable and are being continuously revised. The present chapter is therefore restricted to the "classical" and presumably nearly permanent aspects of high-energy physics. The formulas have been chosen to guide the student of the subject as well as to provide useful information for the advanced research worker.

### 1. Electromagnetic Interactions

#### 1.1. Definitions and some natural constants.

$\sigma(E, \Theta)$  = the cross section in  $\text{cm}^2$  of an *atom* for an interaction involving a final energy  $< E$  and a final zenith angle  $< \Theta$  (all processes considered have azimuthal symmetry). Thus  $(\partial\sigma/\partial E)dE$  is the cross section for a process involving a final energy between  $E$  and  $E + dE$ ;  $(\partial\sigma/\partial\omega)d\omega$  is the cross section for a process whose final state involves a particle lying in the solid angle  $d\omega$  at the angle  $\Theta$ , where  $\omega = 2\pi(1 - \cos \Theta)$ .

$E$  = kinetic energy.  $E = mc^2\sqrt{1 - \beta^2} - mc^2$

$m$  = rest mass

$U$  = total energy.  $U = E + mc^2$

$p$  = momentum.  $(pc)^2 + (mc^2)^2 = U^2$ ;  $p = mv/\sqrt{1 - \beta^2}$

$\beta$  = velocity relative to the velocity of light.  $\beta = |pc|/U$

$m_e c^2$  = rest energy of the electron, 0.51098 Mev

$m_p c^2$  = rest energy of the proton, 938.2 Mev

$m_\pi c^2$  = rest energy of the  $\pi$  meson, 139.4 Mev for  $\pi^\pm$ , 135 Mev for  $\pi^0$

$m_\mu c^2$  = rest energy of the  $\mu$ -meson, 105.7 Mev

$\alpha$  = Fine-structure constant,  $e^2/\hbar c = 1/137.038$ .

$r_e$  = classical radius of the electron,  $e^2/m_e c^2 = 2.8178 \times 10^{-13}$  cm

$Z, A$  = atomic number and atomic weight of the material in which the interactions take place

$z$  = atomic number of the bombarding particle

$N, e, c, \hbar$  have their usual significance (Avogadro number, electronic charge, velocity of light, Planck's constant). Values may be found in Chapter 4.

Note that  $e$  always represents a positive magnitude

$x$  = thickness of matter in g cm<sup>-2</sup>, given by  $l\rho$ , the product of distance and density. The probability for the occurrence of a process with cross section  $\sigma$  in thickness  $dx$  is  $(\sigma N/A)dx$

$X_0$  = the radiation length (§ 1.7) expressed in g cm<sup>-2</sup>

$t$  = thickness of matter in radiation lengths,  $t = x/X_0$

The sign of the charge of electrons is distinguished, where necessary, by the terms positon and negaton.

**1.2. Cross sections for the collision of charged particles with atomic electrons, considered as free (knock-on probabilities).** Let  $E$  be the energy of the bombarding particle of mass  $m$ ; let  $E'$  be the energy acquired by an atomic electron. If

$$\left. \begin{aligned} E' \ll E'_{\max} &= \frac{2m_e p^2 c^4}{m_e^2 c^4 + m^2 c^4 + 2m_e c^2 (p^2 c^2 + m^2 c^4)^{1/2}} \\ \text{then } \frac{\partial \sigma_{\text{col}}}{\partial E'} dE' &= \frac{2Zz^2 \pi r_e^2}{\beta^2} \cdot \frac{m_e c^2 dE'}{(E')^2} \end{aligned} \right\} (1)$$

is valid for all particles (Rutherford formula).

At larger  $E'$ , spin of bombarding particle becomes important and we have

*Particles of mass  $m$  and spin 0 :*

$$\frac{\partial \sigma}{\partial E'} = \left( \frac{\partial \sigma}{\partial E'} \right)_{\text{Rutherford}} \left( 1 - \beta^2 \frac{E'}{E'_{\max}} \right) \quad (2)$$

*Particles (not electrons) of mass  $m$ , spin 1/2 :*

$$\frac{\partial \sigma}{\partial E'} = \left( \frac{\partial \sigma}{\partial E'} \right)_{\text{Rutherford}} \left[ 1 - \beta^2 \frac{E'}{E'_{\max}} + \frac{1}{2} \left( \frac{E'}{E + mc^2} \right)^2 \right] \quad (3)$$

*Positons with  $E \gg m_e c^2$  :*

$$\frac{\partial \sigma}{\partial E'} = \left( \frac{\partial \sigma}{\partial E'} \right)_{\text{Rutherford}} \left[ 1 - \frac{E'}{E} + \left( \frac{E'}{E} \right)^2 \right]^2 \quad (4)$$

Negatons (negative electrons) with  $E \gg m_e c^2$ :

$$\frac{\partial \sigma}{\partial E'} = \left( \frac{\partial \sigma}{\partial E'} \right)_{\text{Rutherford}} \frac{E^2}{(E - E')^2} \left[ 1 - \frac{E'}{E} + \left( \frac{E'}{E} \right)^2 \right]^2 \quad (5)$$

This is the cross section for leaving *either* negaton in the energy state  $E'$ , so that  $E' \leq E/2$ .

### 1.3. Energy loss by collision with atomic electrons (ionization loss).

Let  $k_{\text{col}}(E) = - (dE/dx)_{\text{col}}$  be the energy lost per g cm<sup>-2</sup> in collisions with atomic electrons (the effect of atomic binding is included, but the particle's velocity is assumed to be large compared with that of the  $K$  electrons).

Heavy particles ( $m > m_e$ ):

$$k_{\text{col}}(E) = \frac{4Nz^2(Z/A)\pi r_e^2 m_e c^2}{\beta^2} \left[ \ln \frac{2m_e c^2 \beta^2}{(1 - \beta^2)I(Z)} - \beta^2 \right] \quad (1)$$

Electrons with  $\beta \approx 1$ :

$$k_{\text{col}} = 4N \frac{Z}{A} \pi r_e^2 m_e c^2 \left[ \ln \frac{\pi m_e c^2}{(1 - \beta^2)^{3/4} I(Z)} - \frac{a}{2} \right] \quad (2)$$

where  $a = 2.9$  for negatons, 3.6 for positons. The average ionization potential,  $I(Z)$ , may be approximated by  $I(Z) = (12.5Z)$  ev.

The energy loss considering only collisions in which the energy transferred is less than  $\eta$  is

$$k_{\text{col}(<\eta)}(E) = \frac{2Nz^2(Z/A)\pi r_e^2 m_e c^2}{\beta^2} \left[ \ln \frac{2m_e c^2 \beta^2 \eta}{(1 - \beta^2)I^2(Z)} - \beta^2 \right] \quad (3)$$

This formula holds for both electrons and heavy particles if  $\eta$  is not too large ( $\sim 10^5$  ev for electrons).

The actual collision loss, in condensed materials, of particles with  $\beta \approx 1$  will be reduced somewhat by the "density effect," which has not been formulated concisely. Calculations for certain materials will be found in Refs. 5 and 29.

**1.4. Range of heavy particles.** When collision loss (§ 1.3) represents the only important type of energy loss, all similar heavy particles of a given energy travel approximately the same distance in matter before being stopped. This distance is the range (or mean range)

$$R(E) = \int_{E_{\text{exp}}}^E \frac{dE'}{k_{\text{col}}(E')} + R_{\text{exp}}$$

where  $R_{\text{exp}}$  is the observed range for a known energy  $E_{\text{exp}}$ .

Since for a given material  $k_{\text{col}} = z^2 f(\beta)$ , and  $\beta = g(E/m)$ , we have

$$R = \frac{m}{z^2} F_1 \left( \frac{E}{m} \right) = \frac{m}{z^2} F_2 \left( \frac{p}{m} \right) \quad (1)$$

Numerical values for  $z^2 R/m$  as functions of  $E/m$  or  $p/m$  are given, for example, in Refs. 24 and 29. A useful approximation for  $E < mc^2$  (it is high by 15 per cent at  $E = mc^2$ ) is

$$R = 43 \left( \frac{mc^2}{100 \text{ Mev}} \right) \left( \frac{E}{mc^2} \right)^{1.75}, \quad (\text{g cm}^{-2} \text{ in air}) \quad (2)$$

$$R = 80 \left( \frac{mc^2}{100 \text{ Mev}} \right) \left( \frac{E}{mc^2} \right)^{1.75}, \quad (\text{g cm}^{-2} \text{ in lead}) \quad (3)$$

**1.5. Specific ionization.** The total number of ion pairs produced in matter per  $\text{g cm}^{-2}$  by a charged particle and its secondaries is the *total specific ionization*,  $j_T(E)$ . For a given material it is found experimentally (at least for gases) that  $j_T(E)$  is proportional to  $k_{\text{col}}(E)$ ; that is,  $j(E) = k_{\text{col}}(E)/V_0$ . For air,  $V_0$  has the value 35 ev/ion pair. Its value for other substances may be found in Ref. 23.

The *primary specific ionization*,  $j_p$ , is the average number of collisions per  $\text{g cm}^{-2}$  that result in the ejection of an electron from an atom. It is given by Bethe (Ref. 1) as

$$j_p = \frac{2Nz^2(Z/A)\pi r_e^2 m_e c^2}{\beta^2} \cdot \frac{r}{I_0} \left[ \ln \frac{2m_e c^2 \beta^2}{(1-\beta^2)I_0} + s - \beta^2 \right] \quad (1)$$

where for hydrogen  $r = 0.285$ ,  $s = 3.04$ , and  $I_0$  is the Rydberg energy. Calculations are not available for other gases, but experimentally  $j_p$  is usually about one-third of  $j_T$ .

### 1.6. Cross sections for emission of radiation by charged particles.

a. *Electrons.* We consider the cross section for emission of a photon of energy  $E'$  when an electron of kinetic energy  $E$ , total energy  $U$  collides with an atom. The result depends on the degree to which the atomic electrons screen the electrostatic field of the nucleus. The parameter

$$\gamma = 100 \frac{m_e c^2}{U} \cdot \frac{E'/U}{1 - E'/U} Z^{-1/3}$$

determines the magnitude of this effect; if  $\gamma \gg 1$ , screening can be neglected; if  $\gamma \ll 1$ , screening may be considered "complete." For  $U \gg 137 m_e c^2 Z^{-1/3}$  the latter may be considered always to be the case.

Write the cross section, assuming  $U \gg m_e c^2$ , as

$$\frac{\partial \sigma_{\text{rad}}}{\partial E'} dE' = 4\alpha Z(Z+1)r_e^2 \frac{dE'}{E'} F(U, v) \quad (1)$$

where  $v = E'/U$ , and  $F(U, v)$  is given by :

For no screening,  $\gamma \gg 1$ ,

$$F(U, v) = \left[ 1 + (1-v)^2 - \frac{2}{3}(1-v) \right] \left[ \ln \left( \frac{2U}{m_e c^2} \cdot \frac{1-v}{v} \right) - \frac{1}{2} \right] \quad (2)$$

For complete screening,  $\gamma \approx 0$ ,

$$F(U, v) = \left\{ \left[ 1 + (1-v)^2 - \frac{2}{3}(1-v) \right] \ln(183Z^{-1/3}) + \frac{1}{9}(1-v) \right\} \quad (3)$$

Expressions for the intermediate cases may be found in Ref. 20.

The factor  $Z(Z+1)$  (instead of the conventional  $Z^2$ ) takes account of radiative transitions of the atomic electrons in an approximate way; no satisfactory calculation is available.

These cross sections are calculated in the Born approximation; experiments at 62 Mev show that they are too large for high  $Z$  materials, about 10 per cent for lead. For simplicity we shall use the same correction term as that which has been accurately determined in the case of pair production,  $[1 + 0.12(Z/82)^2]$ . These cross sections should therefore be *divided* by  $[1 + 0.12(Z/82)^2]$ .

The divergence of the cross section as  $E' \rightarrow 0$  correspond physically to the fact that an infinite number of extremely low-energy quanta are emitted in every collision. The energy loss remains finite (§ 1.7).

The root mean square of the angle  $\Theta$  at which the photon of energy  $E'$  is emitted is approximately

$$\sqrt{\langle \Theta^2 \rangle_{\text{av}}} \sim 0.65 \frac{m_e c^2}{U} \ln \frac{U}{m_e c^2}$$

b. *Heavy particles.* We give the result for mass  $m$ , spin  $\frac{1}{2}$ , and normal magnetic moment. (Other cases are considered in Ref. 20.)

$$\frac{\partial \sigma_{\text{rad}}}{\partial E'} dE' = 4\alpha Z^2 r_e^2 \left( \frac{m_e}{m} \right)^2 \frac{dE'}{E'} F(U, v) \quad (4)$$

where

$$F(U, v) = \left[ 1 + (1-v)^2 - \frac{2}{3}(1-v) \right] \left[ \ln \left( \frac{2U}{mc^2} \cdot \frac{\hbar}{mc(0.49r_e A^{1/3})} \cdot \frac{1-v}{v} \right) - \frac{1}{2} \right]$$

The effect of the nuclear radius has been included; the effect of the atomic electrons has not.

**1.7. Energy loss of electrons by radiation.** The average radiation loss of electrons per  $g\text{ cm}^{-2}$  is

$$-\left(\frac{dE}{dx}\right)_{\text{rad}} = k_{\text{rad}}(E) = \int_0^E E' \frac{N}{A} \frac{\partial \sigma_{\text{rad}}}{\partial E'} dE' \quad (1)$$

(The amount of energy transferred to the nucleus can be neglected). When  $E \gg 137m_e c^2 Z^{-1/3}$  (complete screening) we have

$$k_{\text{rad}}(E) = 4\alpha Z(Z+1) \frac{N}{A} r_e^2 E \left[ \ln(183Z^{-1/3}) + \frac{1}{18} \right] \left[ 1 + 0.12 \left( \frac{Z}{82} \right)^2 \right]^{-1} \quad (2)$$

Radiation loss increases with energy in a linear fashion (even slightly faster in the region of incomplete screening) and exceeds collision loss at approximately the *critical energy*,  $\epsilon$ , of shower theory (§ 2.1).

In dealing with radiation phenomena it is convenient to measure thickness in terms of the *radiation length*,  $X_0\text{ g cm}^{-2}$ , defined by

$$\frac{1}{X_0} = 4\alpha Z(Z+1) \frac{N}{A} r_e^2 [\ln(183Z^{-1/3})] \left[ 1 + 0.12 \left( \frac{Z}{82} \right)^2 \right]^{-1} \quad (3)$$

Table 1 gives some numerical values for  $X_0$  and  $\epsilon$ .

TABLE 1

VALUES FOR THE RADIATION LENGTH  $X_0$ , AND CRITICAL ENERGY,  $\epsilon$ , FOR VARIOUS SUBSTANCES

Substance	Z	A	$X_0\text{ g cm}^{-2}$	$\epsilon\text{ Mev}$	
				Formula of Sect. 1.3	With density effect correction
Carbon	6	12	44.6	102	76
Nitrogen	7	14	39.4	88.7	
Oxygen	8	16	35.3	77.7	
Aluminium	13	27	24.5	48.8	
Argon	18	39.9	19.8	35.2	21
Iron	26	55.84	14.1	24.3	
Copper	29	63.57	13.1	21.8	
Lead	82	207.2	6.5	7.8	7.6
Air	7.37	14.78	37.7	84.2	65
Water	7.23	14.3	37.1	83.8	

The probability of radiating in a thickness  $dt$  radiation lengths

$$(t = x/X_0) \text{ is } \frac{N}{A} \cdot \frac{\partial \sigma_{\text{rad}}}{\partial E'} dE' X_0 dt$$

and does not depend strongly on atomic number. In the limit of  $E \gg 137m_e c^2 Z^{-1/3}$  it is independent of atomic number. A crude high-energy approximation often used for this probability is  $(dE'/E')dt$ . Similarly, the fractional energy loss per radiation length,

$$-\frac{1}{E} \left( \frac{dE}{dt} \right)_{\text{rad}} = \frac{1}{E} k_{\text{rad}}(E) X_0 \quad (4)$$

is nearly independent of  $Z$ , and at high energies becomes

$$-\frac{1}{E} \left( \frac{dE}{dt} \right)_{\text{rad}} = 1 + b$$

where without appreciable error we may take  $b = 0.014$  for all elements.

Radiation is not an important source of energy loss of particles heavier than electrons, with the exception of  $\mu$ -mesons of  $E > 10^{11}$  ev.

Fluctuations in the radiation loss of electrons are very large. Neglecting collision loss, the probability that an electron of total energy  $U_0$  will have energy  $U$  in  $dU$  after  $t$  radiation lengths is approximately

$$w(U_0, U, t) dU = \frac{dU}{U_0} \left[ \ln \frac{U_0}{U} \right]^{(t/\ln 2) - 1} \left[ \Gamma \left( \frac{t}{\ln 2} \right) \right]^{-1} \quad (5)$$

(for  $\Gamma$  see § 13.1 of Chapter 1).

**1.8. Cross sections for scattering of charged particles.** Classically the nonrelativistic cross section for scattering of a particle of charge  $ze$  by a fixed point charge  $Ze$  is

$$\frac{\partial \sigma}{\partial \omega} d\omega = \frac{1}{4} z^2 Z^2 r_e^2 \left( \frac{m_e c}{\beta p} \right)^2 \frac{d\omega}{\sin^4(\Theta/2)} \quad (1)$$

the *Rutherford scattering law*. Quantum mechanics gives the same result: (1) exactly for the nonrelativistic region ( $\beta^2 \ll 1$ , spin effects unimportant); (2) in the Born approximation ( $Z\alpha/\beta \ll 1$ ) for (relativistic) *particles of spin 0*.

For *particles of spin  $\frac{1}{2}$*  and normal magnetic moment,

$$\frac{\partial \sigma}{\partial \omega} = \left( \frac{\partial \sigma}{\partial \omega} \right)_{\text{Rutherford}} \left[ 1 - \beta^2 \sin^2 \frac{\Theta}{2} + Z\pi\alpha\beta \sin \frac{\Theta}{2} \left( 1 - \sin \frac{\Theta}{2} \right) + \dots \right] \quad (2)$$

The third term in the square brackets is a correction to the Born approximation. Still higher corrections are needed for  $Z \gtrsim 50$  (see Ref. 12).

The correction for radiative effects is usually less than 5 per cent, even for electrons (Ref. 25).

The cross section for scattering by real atoms is reduced in the limits of small and large angles : at small angles the screening by atomic electrons becomes important at  $\Theta \sim \Theta_1 = \alpha Z^{1/3}(m_e c/p)$  and the angular dependence of the cross section is

$$\sim \frac{d\omega}{[(\Theta/2)^2 + (\Theta_1/2)^2]^2}$$

For an accurate treatment see Ref. 14. At large angles the nuclear size becomes important for

$$\Theta \sim \Theta_2 = 280A^{-1/3} \frac{m_e c}{p} \tag{3}$$

**1.9. Scattering of charged particles in matter.** The probability that a particle be scattered through an angle  $\Theta$  in traversing a thickness of material  $x$  can be found (in numerical form) in Refs. 26 and 15; the latter is more accurate for high- $Z$  materials because of corrections to the Born approximation.

A convenient approximation is given by Williams' (Ref. 30) calculation of small-angle multiple scattering, neglecting single processes in which a large angular deflection occurs. For a thickness  $x$  small enough so that energy loss can be neglected, the mean square angle of scattering can be expressed as

$$\langle \Theta^2 \rangle_{av} = \left( \frac{E_s}{\beta c p} \right)^2 \frac{x}{X_0} \tag{1}$$

where  $E_s = (4\pi/\alpha)^{1/2} m_e c^2 = 21 \times 10^6$  ev.

For the projected angle  $\vartheta$  made by the projection of the particle's track on a plane containing the initial trajectory one has, for small angles,

$$\langle \vartheta^2 \rangle_{av} = \frac{1}{2} \langle \Theta^2 \rangle_{av} \tag{2}$$

The distribution in  $\vartheta$  can be approximated by a Gaussian,

$$P(\vartheta) d\vartheta = \frac{1}{\sqrt{2\pi \langle \vartheta^2 \rangle_{av}}} e^{-\vartheta^2/2 \langle \vartheta^2 \rangle_{av}} d\vartheta \tag{3}$$

for small  $\vartheta$ . At larger angles, the probability that the deflection occur in a single collision will be larger than the value of this Gaussian, and one can estimate  $P(\vartheta)$  from the probability for *single* scattering alone, obtained from the space-angle cross section of § 1.8.

An accurate expression for the *mean* absolute projected angle of scattering in a thickness  $x$ , neglecting energy loss but considering the complete scatter-

ring probability function and using corrected cross sections (i.e., not merely Born approximation) is (Ref. 4)

$$\langle \vartheta \rangle_{\text{av}} = 2z \left( Z^2 \frac{N}{A} r_e^2 \alpha \right)^{1/2} \left( \frac{m_e c}{\beta \rho} \right) \cdot \left[ 1.45 + 0.8 \sqrt{\ln \left( 0.2 \pi Z^{-2/3} \frac{N}{A} r_e^2 \frac{x}{\alpha^2} \frac{1}{(1 + 0.3 \beta^2 / \alpha^2 z^2 Z^2)} \right)} \right] \quad (4)$$

**1.10. Compton effect.** A photon of energy  $E$  scattered through an angle  $\Theta$  by a free electron initially at rest will have an energy

$$E' = \frac{E}{1 + (E/m_e c^2)(1 - \cos \Theta)}$$

The cross section for this process is the *Klein-Nishina* formula (Ref. 10)

$$\frac{\partial \sigma_{\text{Comp}}}{\partial E'} dE' = Z \pi r_e^2 \frac{m_e c^2}{E} \cdot \frac{dE'}{E'} \left[ 1 + \left( \frac{E'}{E} \right)^2 - \frac{E'}{E} \sin^2 \Theta \right] \quad (1)$$

As usual we have written the cross section *per atom*;  $\sin \Theta$  is written in place of the explicit function of  $E'$  and  $E$  for algebraic simplicity; the term containing it is negligible when  $E \gg m_e c^2$ .

The effect of the binding of the atomic electrons is unimportant when the recoil energy of the electron is large compared to its binding energy; this is nearly always the case if  $E > m_e c^2$ .

**1.11. Pair production.** The materialization of a photon of energy  $E$  as a pair of electrons of energies  $E'$  (positron) and  $E''$  (negaton) occurs with very little energy transfer to the nucleus, so that to good approximation

$$E' + E'' + 2m_e c^2 = E \quad (1)$$

Letting  $v = (E' + m_e c^2)/E$  be the fractional energy of the positron (or negaton—the formulas are symmetrical for  $E \gg m_e c^2$ ) we have

$$\gamma = 100 \frac{m_e c^2}{E} \cdot \frac{1}{v(1-v)} Z^{-1/3} \quad (2)$$

as the quantity which determines the influence of screening by the atomic electrons.

Write the cross section, assuming  $E \gg m_e c^2$ , as

$$\frac{\partial \sigma_{\text{pair}}}{\partial E'} dE' = 4\alpha Z(Z+1) r_e^2 \frac{dE'}{E} G(E, v) \quad (3)$$

where  $G(E, v)$  is given in the two limiting cases by :

For no screening,  $\gamma \gg 1$ ,

$$C(E, v) = \left[ v^2 + (1 - v)^2 + \frac{2}{3} v(1 - v) \right] \left[ \ln \left( \frac{2E}{m_e c^2} v(1 - v) \right) - \frac{1}{2} \right]$$

For complete screening,  $\gamma \approx 0$ ,

$$G(E, v) = [v^2 + (1 - v)^2 + \frac{2}{3} v(1 - v)] \ln (183Z^{-1/3}) - \frac{1}{3} v(1 - v)$$

Expressions for the intermediate cases may be found in Ref. 20.

As in § 1.6, the factor  $Z(Z + 1)$  instead of the conventional  $Z^2$  must be considered merely as an improved approximation.

Again as in § 1.6, experiments show these cross sections to be too high for high- $Z$  materials; they should be *divided* by the empirical correction term  $[1 + 0.12(Z/82)^2]$ .

The total cross section for pair production in the high-energy limit

$$\sigma_{\text{pair}} = 4\alpha Z(Z + 1)r_e^2 \left[ \frac{7}{9} \ln (183Z^{-1/3}) - \frac{1}{54} \right] \quad (4)$$

The probability for pair production in a thickness  $dt$  radiation lengths does not depend strongly on atomic number. In the high-energy limit  $E \gg 137m_e c^2 Z^{-1/3}$  it becomes

$$\frac{N}{A} \sigma_{\text{pair}} X_0 dt = \left( \frac{7}{9} - \frac{b}{3} \right) dt \quad (5)$$

where without appreciable error we may take  $b = 0.014$ .

The root-mean-square angle between the direction of one of the electrons with energy  $E'$  and the original direction of the photon is approximately

$$\sqrt{\langle \Theta^2 \rangle_{\text{av}}} \approx 0.47 \frac{m_e c^2}{E'} \ln \frac{E}{m_e c^2}$$

## 2. Shower Theory

### 2.1. Definitions

$X_0$  is the radiation length (§ 1.6 and Table 1).

$t$  specifies distance into the material, measured in radiation lengths.

$\pi^{(e)}(E_0, E, t)dE$ , called a differential spectrum, is the average number of *electrons* with energy in  $dE$  at  $E$  that cross a plane at distance  $t$  beyond the start of a shower initiated by an *electron* of energy  $E_0$ . No distinction is made between positons and negatons.

$\pi^{(\gamma)}(E_0, E, t)dE$  is the same quantity for a shower initiated by a *photon* of energy  $E_0$ .

$\gamma^{(e)}(E_0, E, t)dE$  is, analogously, the average number of *photons* in a shower initiated by an *electron* of energy  $E_0$ .

$\gamma^{(\nu)}(E_0, E, t)dE$  is the same quantity for a shower initiated by a *photon* of energy  $E_0$ .

The integral spectra are designated by capital letters :

$$\Pi^{(\nu)}(E_0, E, t) = \int_E^\infty \pi(E_0, E', t)dE', \quad \text{etc.}$$

$P_0(E_0, E) = \int_0^\infty \Pi(E_0, E, t)dt$  is the integral electron track length, essentially an energy spectrum averaged over the shower.

$G_0(E_0, E) = \int_0^\infty \Gamma(E_0, E, t)dt$  is the integral photon track length.

$\epsilon$ , the critical energy, is defined by the equation  $\epsilon = k_{\text{col}(<\eta)}(\epsilon)X_0$  (§ 1.3 and § 1.7). Table 1 contains some numerical values calculated for  $\eta = 5 \times 10^6$  ev, which is the limiting energy below which electrons are considered "lost." It is at approximately the critical energy that energy loss by radiation (for electrons) becomes predominant.

$E_s = 21$  Mev is the scattering energy (§ 1.9).

## 2.2. Track lengths

Tamm and Belenky solution

$$P_0^{(\nu)}(E_0, E) = \frac{E_0}{\epsilon} e^x \left[ e^{-x} + xE_i(-x) - \frac{x}{x_0} e^{-x_0} - xE_i(-x_0) \right] \quad (1)$$

where  $x = (1/0.437)(E/\epsilon)$ ,  $x_0 = (1/0.437)(E_0/\epsilon)$ , and

$$E_i(-x) = - \int_x^\infty (e^{-s}/s)ds$$

is the exponential integral tabulated, for example, in Ref. 8. This expression is derived under the following assumptions ("Approximation B" of Rossi and Greisen, Ref. 20): asymptotic (complete screening) cross sections (§ 1.6 and § 1.11), continuous collision loss with  $k_{\text{col}}(E) = \epsilon/X_0$ , and neglect of Compton effect. However, exact numerical calculations (Refs. 18 and 21) have indicated that it is quite accurate (less than 10 per cent error) at least for low-atomic-number materials and  $E > \frac{1}{10}\epsilon$ ; and  $P_0^{(\nu)}(E_0, E)$  differs significantly from  $P_0^{(\pi)}(E_0, E)$  only when  $E \sim E_0$ .

Numerical results on  $G_0(E_0, E)$  can be found in Ref. 18.

If the restriction  $E \gg \epsilon$  is made, collision loss may be neglected entirely ("Approximation A" of Ref. 20), and with the further restriction  $E \ll E_0$ , the integral track lengths become

$$\left. \begin{aligned} P_0^{(\pi)}(E_0, E) &= P_0^{(\nu)}(E_0, E) = 0.437 \frac{E_0}{E} \\ \Gamma_0^{(\pi)}(E_0, E) &= \Gamma_0^{(\nu)}(E_0, E) = 0.572 \frac{E_0}{E} \end{aligned} \right\} \quad (2)$$

**2.3. Integral spectrum.** With the assumption of asymptotic cross sections and neglect of collision loss and Compton effect ("Approximation A"), solutions for the spectra valid for  $\epsilon \ll E \ll E_0$  and  $t \gg 1$  are given in Ref. 20. An approximate analytic expression for this range of validity has been given by Heisenberg (Ref. 6).

$$\left. \begin{aligned} \Pi_{A^{(\pi)}}(E_0, E, t) = \Pi_{A^{(\gamma)}}(E_0, E, t) = & \left[ \frac{\ln E_0/E - 0.56}{t(t - 1.4)} \right]^{1/2} \\ & \cdot \exp \left\{ -t + 2 \left[ (t - 1.4) \left( \ln \frac{E_0}{E} - 0.56 \right) \right]^{1/2} \right\} \end{aligned} \right\} \quad (1)$$

Inclusion of a continuous collision loss as in (§ 2.2) allows an approximate solution for the "total" number of electrons in the shower. (Only electrons arising from pair production are counted—the knock-on electrons are lumped with the collision loss.) We write it as a factor times the Approximation A solution with  $E = \epsilon$ .

$$\Pi^{(\pi)}(E_0, 0, t) = K \left( \frac{E_0}{\epsilon}, t \right) \Pi_{A^{(\pi)}}(E_0, \epsilon, t) \quad (2)$$

The factor  $K$  is given in Ref. 20. It has the value 2.3 at the shower maximum, and may be expressed in rough approximation by

$$K = 1 + 1.3 \left( t / \ln \frac{E_0}{\epsilon} \right)^{1/2} \quad (3)$$

**2.4. Properties of the shower maxima.** If  $T$  is the value of  $t$  for which the functions  $\Pi$ , etc., have a maximum for a fixed value of  $E$ , then in the range  $\epsilon \ll E \ll E_0$  we have

$$T(E_0, E) = 1.01 \left( \ln \frac{E_0}{E} - n \right) \quad (1)$$

$$\left. \frac{\pi_{\max}(E_0, E) dE}{\gamma_{\max}(E_0, E) dE} \right\} = \frac{l}{[\ln(E_0/E) - m]^{1/2}} \cdot \frac{E_0}{E^2} dE \quad (2)$$

$$\Pi_{\max}(E_0, E) = \frac{l}{[\ln(E_0/E) - m]^{1/2}} \cdot \frac{E_0}{E} \quad (3)$$

where  $l$ ,  $m$ , and  $n$  are given in Table 2.

For  $E \sim 0$ , we have  $T(E_0, 0) = T(E_0, \epsilon)$  (see above) and

$$\Pi_{\max}^{(\pi)}(E_0, 0, T) = \frac{0.31}{[\ln(E_0/E) - 0.18]^{1/2}} \cdot \frac{E_0}{\epsilon}$$

TABLE 2

Function \ Primary particle	Electron			Photon		
	$l$	$m$	$n$	$l$	$m$	$n$
$\pi$	0.137	0	0	0.137	-0.18	-0.5
$\gamma$	0.180	0.18	0.5	0.180	0	0
$\Pi$	0.137	0.37	1	0.137	0.18	0.5

**2.5. Stationary solutions.** If at  $t=0$  a beam of electrons and/or photons is incident with an energy distribution in the form of a power law,  $dN = \text{const}(dE_0/E_0^{s+1})$ , this distribution in energy will retain its form as long as  $E \gg \epsilon$ , yielding solutions of the form  $\pi(E,t)dE$  or

$$\gamma(E,t)dE = [a(s)e^{\lambda_1(s)t} + b(s)e^{\lambda_2(s)t}] \frac{dE}{E^{s+1}}$$

For large  $t$  the total number of particles decreases exponentially with  $t$  if  $s > 1$ , increases if  $s < 1$ . Details will be found in Ref. 20.

**2.6. Lateral and angular spread of showers.** The only explicit calculation of lateral and angular distribution of shower particles is due to Moliere (Ref. 13), where results are given in graphical form. The lateral distribution function gives the fraction  $dF$  of all shower particles which are at distances between  $r$  and  $r + dr$  from the shower axis, averaged over the shower. An analytic approximation for Moliere's calculation of this fraction, adequate for  $r/r_1 \lesssim 1$ , is

$$dF = 2.85 \left(1 + 4 \frac{r}{r_1}\right) \exp \left[ -4 \left(\frac{r}{r_1}\right)^{2/3} \right] \frac{dr}{r_1} \quad (1)$$

where  $r_1 = (E_s/\epsilon)X_0$ , and  $E_s = 21$  Mev (see § 1.9).

The mean-square lateral spread and mean-square angular spread for shower particles, averaged over the shower, are given for all energies in Ref. 19. Their values for particles of energy  $E \gg \epsilon$  are

	<i>electrons</i>	<i>photons</i>
$\langle r^2 \rangle_{\text{av}}$	$0.64 \left(\frac{E_s}{E}\right)^2 X_0^2$	$1.13 \left(\frac{E_s}{E}\right)^2 X_0^2$
$\langle \Theta^2 \rangle_{\text{av}}$	$0.55 \left(\frac{E_s}{E}\right)^2$	$0.18 \left(\frac{E_s}{E}\right)^2$

These results are valid only for  $E \ll E_0$ ; they therefore apply equally to showers initiated by either electrons or photons.

### 3. Nuclear Interactions

**3.1. Nuclear radius and transparency.** The geometrical cross section of a nucleus of mass number  $A$  is

$$\sigma_g = \pi r_n^2 = \pi r_0^2 A^{2/3}, \quad (r_0 \approx 1.38 \times 10^{-13} \text{ cm}) \quad (1)$$

If the average cross section for a nucleon-nucleon interaction of a given type is  $\bar{\sigma}$ , the assumption that the particles in the nucleus are independent leads to the following cross section for this type of collision of the particle with a nucleus, if  $\sqrt{\bar{\sigma}/\pi}$  is small compared with  $r_n$

$$\sigma_i = \left[ 1 - t \left( \frac{l_c}{r_n} \right) \right] \pi r_n^2 \quad (2)$$

where  $l_c = \frac{4}{3}(\pi r_n^3 / A \bar{\sigma})$ , and the transparency

$$t \left( \frac{l_c}{r_n} \right) = \frac{l_c^2}{2r_n^2} \left[ 1 - e^{-2r_n/l_c} - 2 \frac{r_n}{l_c} e^{-2r_n/l_c} \right] \quad (3)$$

**3.2. Altitude variation of nuclear interactions: Gross transformation.** An isotropic flux of particles of intensity per unit solid angle  $J_0$  is incident on a semi-infinite slab (e.g., the atmosphere). If the particles are absorbed exponentially with a mean free path  $L$ , the intensity at a depth  $x$ , integrated over angle, is

$$\int_0^{\pi/2} J(x, \vartheta) d\omega = 2\pi \frac{x}{L} J_0 \left[ e^{-x/L} + \frac{x}{L} E_i \left( -\frac{x}{L} \right) \right] \quad (1)$$

see § 2.2 for  $E_i(-t)$ .

### 4. Meson Production

**4.1. Threshold energies.** A nucleus (or other system) of mass  $M_i$ , initially at rest, is bombarded by a particle of mass  $m$ . All masses are "rest masses" (§ 1.1). In order to create a new particle of mass  $\mu$ , the bombarding particle must have at least a kinetic energy

$$E = \frac{[(\mu + \Sigma M_f)^2 - (m + M_i)^2]c^2}{2M_i} \quad (1)$$

where  $\Sigma M_f$  is the sum of all masses present (except  $\mu$ ) after the collision.

**4.2. Relativity transformations.** The maximum energy in the center-of-mass system, when a particle of energy  $E$  bombards a particle initially at rest, is the quantity  $\mu c^2$  in the equation of (§ 4.1) (it is assumed that the projectile and target particles are left at rest in the center-of-mass system).

The velocity of the center of mass, in this collision, is

$$\beta_c c = \frac{c\sqrt{E^2 + 2mc^2E}}{E + (m + M_i)c^2} \quad (2)$$

Let  $\Theta$  be the angle between this velocity and the trajectory of an ejected meson in the laboratory system,  $\Theta^*$  and  $\beta^*c$  the corresponding angle and the velocity of the meson in the center-of-mass system; then

$$\tan \Theta = \frac{\sin \Theta^*}{\cos \Theta^* + \beta_c/\beta^*} \cdot \sqrt{1 - \beta_c^2} \quad (3)$$

In the extreme relativistic approximation  $\sqrt{1 - \beta_c^2} \ll 1$  and  $\sqrt{1 - \beta^{*2}} \ll 1$  this becomes

$$\tan \Theta = \sqrt{1 - \beta_c^2} \tan \frac{\Theta^*}{2} \quad (4)$$

If the angular distribution of mesons in the center-of-mass system is  $F(\Theta^*)d\omega^*$ , the corresponding angular distribution in the laboratory system (with the additional restriction  $\Theta \ll 1$ ) is

$$G(\Theta)d\omega = F[\Theta^*(\Theta)] \frac{4(1 - \beta_c^2)}{(1 - \beta_c^2 + \Theta^2)^2} d\omega \quad (5)$$

General formulas for the transformation of both angular and energy distributions are given in Ref. 3.

## 5. Meson Decay

**5.1. Distance of flight.** If  $\tau$  is the mean life of the meson at rest, the mean distance traversed before decay, when the meson has constant momentum  $p$ , is  $L = p\tau/m$ .

In a real medium  $p$  is a function of the thickness traversed,  $x$  g cm<sup>-2</sup>. The density of the material,  $\rho$ , may be a function of  $x$  (e.g.,  $x/\rho = \text{constant}$  in an isothermal static atmosphere). The probability that the meson has not decayed before reaching  $x_2$ , if it existed at  $x_1$ , is

$$w(x_1, x_2) = \exp \left[ - \int_{x_1}^{x_2} \frac{m dx}{\tau \rho(x) p(x)} \right] \quad (1)$$

**5.2. Energy distribution of decay products.** Let a particle of mass  $m_1$  disintegrate into particles of masses  $m_2$  and  $m_3$ . Then the total energy of one of the products,  $U_2^*$  (the star designates the center-of-mass system) is

$$U_2^* = \left( \frac{m_1^2 + m_2^2 - m_3^2}{2m_1} \right) c^2 \tag{1}$$

If the original particle had total energy  $U_1$  and momentum of magnitude  $p_1$  (as seen from the laboratory system) the differential energy distribution of a product particle has the constant value

$$F(U_2)dU_2 = \frac{1}{2} \frac{m_1}{p_1 p_2^*} dU_2 \tag{2}$$

for

$$\frac{U_1 U_2^*}{m_1 c^2} - \frac{p_1 p_2^*}{m_1} < U_2 < \frac{U_1 U_2^*}{m_1 c^2} + \frac{p_1 p_2^*}{m_1}$$

and is zero otherwise.

If the original particle disintegrates into more than two particles, and  $U_2^*$  designates the total energy of one of them in the center-of-mass system, then

$$U_{2_{\max}}^* = \left( \frac{m_1^2 + m_2^2 - (m_3 + m_4 + \dots)^2}{2m_1} \right) c^2 \tag{3}$$

and

$$\langle U_2 \rangle_{\text{av}} = \frac{U_1}{m_1 c^2} \langle U_2^* \rangle_{\text{av}} \tag{4}$$

**5.3. Angular distribution in two-photon decay.** The equations of § 5.2 may be applied to a simple case of physical interest, the neutral  $\pi$ -meson (mass  $m_1$ ) which decays into two gamma rays. If (in the laboratory system) the gamma rays have energies  $E_2$  and  $E_3$ , and the angle included between their trajectories is  $\phi$ , then  $\sin(\phi/2) = m_1 c^2 / 2\sqrt{E_2 E_3}$ . The distribution in the angle  $\phi$ , in terms of  $U_1 = E_2 + E_3$ , and  $p_1$ , is

$$f(\phi)d\phi = \frac{m_1 c}{p_1} \frac{\cos(\phi/2)d\phi}{[4 \sin^2(\phi/2)] [(U_1/m_1 c^2)^2 \sin^2(\phi/2) - 1]^{1/2}} \tag{1}$$

The distribution function goes to infinity at the minimum angle,

$$\phi_{\min} = 2 \sin^{-1}(m_1 c^2 / U_1)$$

## 6. Geomagnetic Effects

**6.1. Motion in static magnetic fields.** The equation of motion in a static magnetic field for a particle of charge  $ze$ , mass  $m$  is  $(dp/dt) = (ze/c)v \times B$ ,

where  $\mathbf{p} = m\mathbf{v}/\sqrt{1 - \beta^2}$  is the momentum of the particle, sometimes called the kinetic momentum to distinguish it from the variable  $[mv_x/\sqrt{1 - \beta^2} + (ze/c)A_x]$  which is canonically conjugate to the coordinate  $x$ . Since  $ds/dt$ , the magnitude of  $\mathbf{v}$ , is constant, we have as the equation for the trajectory

$$\frac{d\mathbf{t}}{ds} = \frac{ze}{pc} \mathbf{t} \times \mathbf{B} \quad (1)$$

where  $\mathbf{t}$  is the unit tangent vector defined in § 6.9 of Chapter 1.

If  $\mathbf{B}$  is uniform, the path is a helix, the angle  $\alpha$  between  $\mathbf{p}$  and  $\mathbf{B}$  is constant, and the radius of the projection of the path on a plane perpendicular to  $\mathbf{B}$  is  $R = (pc \sin \alpha/zeB)$ . If  $B$  is measured in gaussses,  $R$  in cm, and  $pc/ze$  in volts,  $(pc \sin \alpha/ze) = 300 BR$ . The quantity  $pc/ze$  is called the magnetic rigidity of the particle; for  $z = 1$  it is numerically equal, when expressed in volts, to the momentum in units of  $ev/c$ .

**6.2. Flux of particles in static magnetic fields.** Let the directional intensity of a flux of noninteracting charged particles be  $I(\mathbf{r}, \mathbf{p}) d\mathbf{p} d\omega d\sigma =$  the number of particles, observed at point  $\mathbf{r}$ , having momentum  $\mathbf{p}$  in  $d\mathbf{p} d\omega$ , crossing area  $d\sigma$  perpendicular to  $\mathbf{p}$ . Then  $I(\mathbf{r}, \mathbf{p})$  is constant along any particle trajectory. If one assumes that the flux of particles at great distances from the earth is isotropic, the problem of the influence of the earth's magnetic field on cosmic-ray intensities at the earth's surface is therefore reduced to the investigation of classes of allowed trajectories.

**6.3. Limiting momenta on the earth's surface.** Let the earth's magnetic field be represented by a dipole of moment  $M$ , the earth's radius by  $r_0$ , and an observation point on the earth's surface by the geomagnetic latitude  $\lambda$ . A particle of rigidity  $pc/ze$  can arrive (from outer space) at any point, in any direction, if  $pc/ze > M/r_0^2 \approx 60 \times 10^9$  volts. The particle cannot arrive at all, at a particular point, if

$$\frac{pc}{ze} < \frac{M}{r_0^2} \cdot \frac{\cos^4 \lambda}{[(1 + \cos^3 \lambda)^{1/2} + 1]^2}$$

Let the angle between the direction of arrival of the particle and the tangent to the circle of latitude be  $\vartheta$ , and let  $\vartheta = 0$  correspond to arrival from the west for positive particles. (Then for negative particles  $\vartheta$  must be redefined so that  $\vartheta = 0$  corresponds to arrival from the east. Note that  $z$  and  $e$  are positive magnitudes, so that no question of sign arises in the equations).

If we observe in the direction  $\vartheta$ , at latitude  $\lambda$ , no particle can arrive from outer space if

$$\frac{pc}{ze} < \frac{M}{r_0^2} \cdot \frac{\cos^4 \lambda}{[(1 + \cos \vartheta \cos^3 \lambda)^{1/2} + 1]^2}$$

Thus more positive particles will come from the west than from the east.

The cone of semivertex angle  $\vartheta$ , for a fixed  $pc/ze$ , is called the Störmer cone. The equation is correct for any dipole field if  $r_0$  is the distance to the point of observation.

Not all momenta above the limit set by this equation are allowed, when one considers observations on the real earth. For a certain range of momenta above this lower limit the trajectories are so tortuous that certain classes of them intersect the earth (at some other point) before arriving at the observation point. This "shadow effect" of the earth is unimportant at higher latitudes (say,  $|\lambda| > 40^\circ$ ), except for some nearly horizontal directions of approach. Near the equator the shadow effect is very small in the vertical direction, and raises the lower limit, at  $45^\circ$  zenith angle, by a few per cent for east and west azimuths, and perhaps 15 per cent for north and south azimuths. Intermediate latitudes are particularly complex; details and further references will be found in Ref. 28.

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## Chapter 24

# PARTICLE ACCELERATORS

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### 1. General Description and Classification of High-Energy Particle Accelerators

**1.1. General description.** High-energy particle accelerators are devices employed to accelerate atomic or subatomic particles (electrons, protons, deuterons, alpha particles, etc.) to high energies. "High energies" is generally interpreted to mean energies greater than a few hundred kilovolts. Existing accelerators of various types are adapted to accelerate particles to energies in the range from a few hundred kilovolts to about 400 million volts, but higher energy accelerators are under construction. The high-energy particles produced are employed principally to study the properties of nuclei of atoms and nuclear transformations or reactions, and also to study the properties of the fundamental particles themselves. They are also used in medical applications.

**1.2. Classification according to particle accelerated.** Accelerators may be first classified according to the type of particle they have been designed to accelerate. The two principal types according to this classification are electron accelerators employed to accelerate electrons, and which, by allowing the electrons to strike a target, can also be used as a source of high-energy x rays; and heavy-particle accelerators employed to accelerate protons, deuterons, alpha particles, and in some cases nuclei of heavier atoms. Because of the great difference in mass between the electron and the heavier particles, there are (except in the case of electrostatic accelerators) great differences in the problems to be met in the two cases; consequently electron accelerators differ considerably from heavy-particle accelerators both in design and often in principle of operation. Usually the same principle of operation can be used for the acceleration of protons, deuterons, and

alpha particles, and some machines can easily be adapted to accelerate any of these particles.

The principal types of electron accelerators employed at present are Cockcroft-Walton machines, electrostatic generators, linear electron accelerators, betatrons, and synchrotrons. The principal types of heavy-particle accelerators employed at present are Cockcroft-Walton machines, electrostatic generators, linear accelerators for heavy particles, cyclotrons, and synchrocyclotrons. Under construction at the present time are heavy-particle accelerators for the very high-energy range employing combinations of the cyclotron, betatron, and synchrotron principles. The principal differences in design and principle of operation of electron and heavy-particle accelerators stem from the fact that the electron mass varies greatly during the acceleration process because of relativistic effects, while the mass of heavy particles varies only by a relatively small amount during acceleration in present-day machines.

**1.3. Classification according to particle trajectories.** Accelerators may also be classified according to the spatial region occupied by the trajectories of the particles being accelerated. Two broad classifications occur: linear accelerators in which the trajectories are essentially straight lines, and circular accelerators in which the trajectories are confined to a circular region. To the first class belong Cockcroft-Walton machines, electrostatic generators, and number of different types of so-called linear accelerators. Circular accelerators may further be divided into accelerators in which the trajectories are essentially spirals extending from the center to the edge of a circular region (of which cyclotrons and synchrocyclotrons are examples), and accelerators in which the trajectories are confined to an annular region of relatively small radial breadth (of which the betatron and synchrotron are the principal examples).

**1.4. Designation of accelerators.** Accelerators are usually designated by the maximum energy to which they are designed to accelerate particles. In the case of cyclotrons and synchrocyclotrons, which can be used for different heavy particles and for which the maximum energies depend on the particle being accelerated, the machine is often designated in terms of the diameter of the pole piece of the magnet employed to confine the particle trajectories in the acceleration region.

**1.5. Basic components.** Almost all high-energy accelerators have certain basic features and components in common although the physical form

of these may vary greatly from one type of accelerator to another. These basic components are :

a. An acceleration chamber within which the trajectories of the accelerated particles are confined. In linear accelerators, the chamber defines a linear region along which the particles travel in essentially straight lines. In circular accelerators the chamber defines a disk-shaped or annular region depending on whether the trajectories are essentially spirals or circles. In all accelerators the acceleration chamber must be evacuated to a high vacuum in order to prevent undue scattering of the accelerated particles by molecules of gas.

b. In a circular accelerator a magnetic field must be employed to cause the accelerated particles to move in circles. In some accelerators the magnetic guide field is a static field, in others it varies with time.

c. A means of supplying energy to the particles in order to accelerate them must be provided. In all machines the acceleration is performed by electric fields, but the manner in which the electric fields are provided varies greatly. It may consist of an electrostatic or quasi-electrostatic field (Cockcroft-Walton machines and electrostatic generators), an electric field produced by magnetic induction (betatron), the electric field in a standing or traveling electromagnetic wave (linear accelerators), or the acceleration may occur by having the particle pass at appropriate times through a gap across which an alternating voltage is established (cyclotron, synchrocyclotron, and synchrotron). In some machines (Cockcroft-Walton, electrostatic generator, betatron, and traveling wave linear accelerators) the particles may be continuously accelerated; in others (cyclotron, synchrocyclotron, synchrotron, and standing wave linear accelerators) the acceleration process may take place in steps by a series of impulses.

d. In some machines, some "focusing" of the beam of accelerated particles must be provided in order that motion of the particles along the desired trajectories shall be stable. In circular machines some focusing can easily be provided by an appropriate radial variation of the magnetic guiding field. In linear accelerators the problem of providing focusing may be much more critical.

e. Other components generally required, but which we shall not discuss, are electron guns or ion sources to supply the particles to be accelerated, vacuum pumps and associated equipment, electronic equipment to provide the radio frequency accelerating fields where these are necessary, etc.

## 2. Dynamic Relations for Accelerated Particles

**2.1. Fundamental relativistic relations.** If the mass of a particle at rest is  $m_0$  and if  $c$  represents the velocity of light, then when the particle is moving with a velocity  $v$

$$\text{Momentum :} \quad p = m_0 v / (1 - v^2/c^2)^{1/2} \quad (1)$$

$$\text{Total energy :} \quad E = m_0 c^2 / (1 - v^2/c^2)^{1/2} \quad (2)$$

$$\text{Kinetic energy :} \quad T = E - m_0 c^2 \quad (3)$$

$$\text{Relativistic mass :} \quad m = m_0 / (1 - v^2/c^2)^{1/2} \quad (4)$$

$$\text{Rest energy :} \quad E_0 = m_0 c^2 \quad (5)$$

**2.2. Derived relations.** The relations in 2.1 lead to the following derived relations.

$$E = mc^2 = (m_0^2 c^4 + c^2 p^2)^{1/2} \quad (1)$$

$$p = [(E/c)^2 - m_0^2 c^2]^{1/2} \quad (2)$$

$$v = c^2 p / E = c [1 - (m_0 c^2 / E)^2]^{1/2} = p / [m_0^2 + (p/c)^2]^{1/2} \quad (3)$$

$$m = E / c^2 = [m_0^2 + (p/c)^2]^{1/2} \quad (4)$$

**2.3. Nonrelativistic relations.** When  $v \ll c$  or  $p \ll m_0 c$ , the relations in 2.1 and 2.2 take the forms

$$p = m_0 v \quad (1)$$

$$E = m_0 c^2 + \frac{1}{2} m_0 v^2 = m_0 c^2 + p^2 / 2m_0 \quad (2)$$

$$T = \frac{1}{2} m_0 v^2 = p^2 / 2m_0 \quad (3)$$

**2.4. Units.** The above equations hold when all quantities are measured in absolute units (e.g.,  $m_0$  and  $m$  in grams,  $E$  and  $T$  in ergs,  $v$  and  $c$  in cm/sec,  $p$  in gm-cm/sec). The velocity of light  $c = 2.998 \times 10^{10}$  cm/sec.

The energies of accelerated particles are often expressed in "million-electron-volts" (Mev). The energy unit 1 Mev is defined as the energy gained by a particle bearing one elementary charge ( $e = 4.802 \times 10^{-10}$  esu) in falling through a potential difference of one million volts.

$$(1 \text{ Mev} = 1.602 \times 10^{-6} \text{ erg})$$

In all the equations which follow, the quantity  $e$  is presumed to be measured in electrostatic units. Furthermore, all electric field strengths and potential differences are to be measured in absolute electrostatic units and all magnetic field strengths in absolute electromagnetic units (gausses or oersteds).

### 3. Magnetic Guiding Fields

**3.1. Specification of magnetic guiding fields.** Magnetic guiding fields, whether static or time-dependent, generally have cylindrical symmetry, so that polar coordinates  $(r, \vartheta, z)$  are used to specify the field with the  $z$  axis chosen along the axis of symmetry. Ideally, in the regions in which the accelerated particles move, the fields have the following properties.

a. There exists a median plane normal to the axis of the field in which the magnetic field has only a  $z$  component. In this median plane which is generally taken to be the plane  $z = 0$ ,  $H_z$  is a function only of  $r$  and possibly of the time  $t$ .

b. The magnetic field has no azimuthal component  $H_\vartheta$ .

c. The magnetic field is symmetrical about the median plane.

$$H_z(r, z; t) = H_z(r, -z; t), \quad H_r(r, z; t) = -H_r(r, -z; t) \quad (1)$$

d. If the active region of the field includes points on the axis ( $r = 0$ ), then  $H_z$  can be written as a power series.

$$H_z(r, z; t) = H_0 \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} h_{lm} r^l z^{2m} = H_0 (1 + h_{01} z^2 + h_{20} r^2 + h_{21} r^2 z^2 + \dots) \quad (2)$$

From Maxwell's equations it follows that  $H_r$  can be written as

$$\left. \begin{aligned} H_r(r, z; t) &= -H_0 \sum_{l=0}^{\infty} \sum_{m=1}^{\infty} \frac{2m h_{lm}}{l+2} r^{l+1} z^{2m-1} \\ &= -H_0 (h_{01} r z + \frac{1}{2} h_{21} r^3 z + \dots) \end{aligned} \right\} \quad (3)$$

The following relations hold among the coefficients.

$$h_{00} = 1, \quad h_{1m} = 0 \quad (4)$$

While in the general case the coefficients  $h_{lm}$  may be time-dependent, usually they are essentially constant, and only  $H_0$  is a function of the time.

e. The field described by the equations in (d.) can be derived from a vector potential  $A$  ( $H = \text{curl } A$ ) having only an azimuthal component ( $A_r = A_z = 0$ ) given by

$$A_\vartheta = H_0 \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \frac{h_{lm}}{l+z} r^{l+1} z^{2m} \quad (5)$$

f. The *field exponent*  $n(r;t)$  is defined by the equation

$$n(r;t) = \frac{r}{H_z(r,0;t)} \frac{\partial H_z(r,0;t)}{\partial r} = \frac{\partial \ln H_z(r,0;t)}{\partial \ln r} \quad (6)$$

and plays an important role in determining the stability of particle motion (see below).

It is often convenient, especially when the active region of the magnetic field does not include points on the axis (annular field) to specify the variation of the field in the median plane over a small annular region about a radius  $r_0$  in the form

$$H_z(r,0;t) = H_z(r_0,0;t) \left( \frac{r}{r_0} \right)^{n(r_0;t)} \quad (7)$$

For the field specified in (d.), the field exponent is given by the expression

$$n(r;t) = \frac{\sum_{l=2}^{\infty} l h_{l0} r^l}{\sum_{l=0}^{\infty} h_{l0} r^l} = \frac{2h_{20}r^2 + 3h_{30}r^3 + \dots}{h_{00} + h_{20}r + h_{30}r^3 + \dots} \quad (8)$$

**3.2. Force on a charged particle in a magnetic field.** A charged particle with charge  $Ze$  moving with a velocity  $v$  in a static magnetic field  $H$  is subjected to a force at right angles to both the field and the direction of motion given by

$$\mathbf{F} = \frac{Ze}{c} \mathbf{v} \times \mathbf{H} \quad (1)$$

If the magnetic field is changing with time, the associated induced electric field will give rise to an additional force having a component in the direction of motion of the particle.

The radius of curvature  $\rho$  of the orbit of a charged particle of momentum  $p$  moving perpendicularly to a magnetic field is given by

$$\rho = \frac{cp}{|Z|eH} \quad (2)$$

**3.3. Equations of motion of a charged particle in a magnetic guiding field.** If  $r$ ,  $\vartheta$ , and  $z$  represent the cylindrical coordinates of a particle of charge  $Ze$  moving in a magnetic guiding field of the type described in Sec. 3.1 and  $A_\vartheta(r,z;t)$  represents the vector potential from which the

magnetic field is derived, then the equations of motion of the particle are given by

$$\frac{d}{dt} \left[ \frac{m_0 \dot{r}}{\sqrt{1 - v^2/c^2}} \right] + Ze \dot{\vartheta} A_\vartheta(r, z; t) + \frac{Zer \dot{\vartheta} \partial A_\vartheta(r, z; t)}{\partial r} = f_r \quad (1)$$

$$\frac{d}{dt} \left[ \frac{m_0 r^2 \dot{\vartheta}}{\sqrt{1 - v^2/c^2}} - Zer A_\vartheta(r, z; t) \right] = f_\vartheta \quad (2)$$

$$\frac{d}{dt} \left[ \frac{m_0 \dot{z}}{\sqrt{1 - v^2/c^2}} \right] + \frac{Zer \dot{\vartheta} \partial A_\vartheta(r, z; t)}{\partial z} = f_z \quad (3)$$

where dots denote time differentiation,  $f_r$ ,  $f_\vartheta$ , and  $f_z$  represent the radial, azimuthal, and vertical components of any forces acting on the particle other than those due to the field  $A_\vartheta$ , and

$$v^2 = \dot{r}^2 + r^2 \dot{\vartheta}^2 + \dot{z}^2 \quad (4)$$

**3.4. Equilibrium orbit.** A charged particle (charge  $Ze$ ) with momentum  $p$  and energy  $E$  moving in a static cylindrical guide field of the type described in § 3.1 has as a possible orbit, a motion in a circle concentric with the axis of the field and lying in the median plane. The radius of this circular orbit is determined by the solution for  $r_e$  of the following equation.

$$cp = |Z| e r_e H_z(r_e, 0) \quad (1)$$

This orbit is called the *equilibrium orbit* for the particle, and the radius  $r_e$  is called the *equilibrium radius*.

The angular frequency of revolution of the particle in its equilibrium orbit (the so-called “*cyclotron frequency*”) is given by

$$\omega_e = \frac{|Z| e H_e}{mc} = \frac{|Z| ec H_e}{E} \quad (2)$$

where  $H_e = H_z(r_e, 0)$ .

The period of revolution in this orbit is therefore given by

$$T_e = \frac{2\pi E}{|Z| ec H_e}$$

If the momentum of the particle and the magnetic field vary sufficiently slowly with time (adiabatically), the equilibrium orbit radius and cyclotron frequency are defined at each instant by the above equations and may be considered also to vary adiabatically with the time. The physical importance of the equilibrium orbit lies in the fact that in all circular accelerators, the

acceleration process involves an approximately adiabatic variation of the parameters, defining the equilibrium orbit, and the general motion of an accelerated particle can be described in terms of oscillations about an adiabatically varying equilibrium orbit.

**3.5. Stability of motion in the equilibrium orbit.** Motion of a particle in its equilibrium orbit is stable against small disturbances of this motion if and only if

$$0 < n(r_e, t) < 1 \quad (1)$$

where  $n(r_e)$  is the field exponent defined in (§ 3.1f) evaluated at the equilibrium radius.

**3.6. Oscillations about the equilibrium orbit.** Small disturbances of the motion of a particle in its equilibrium orbit, or a small non-adiabatic variation of the parameters defining this orbit, will give rise to small vertical ( $z$ ) and radial ( $r$ ) oscillations of the particle about the equilibrium orbit. The angular frequency of free oscillations of this character are given by the equations

$$\omega_r = [1 - n(r_e; t)]^{1/2} \omega_e \quad (1)$$

$$\omega_z = [n(r_e, t)]^{1/2} \omega_e \quad (2)$$

**3.7. Coupling of oscillations about the equilibrium orbit.** The presence of high-order nonlinear terms in the equations of motion describing radial and vertical oscillations leads to coupling of these oscillations with each other and with the rotational motion. For certain values of the field exponent  $n$ , leading to commensurability of harmonics of the frequencies of oscillation and of the frequency of rotation (cyclotron frequency), resonance may occur between oscillations, leading to increases in the amplitude of a mode of oscillation to a degree where the particles may strike the walls of the accelerating chamber. The principal case where such resonance may occur (corresponding to  $n$  values which are generally to be avoided) are :

(a) If  $\sqrt{n/(1-n)}$  or  $\sqrt{(1-n)/n}$  is an integer  $N$  (or lies close to an integer), resonance between radial and vertical oscillations may take place.

(b) If  $1/\sqrt{n}$  or  $1/\sqrt{1-n}$  is an integer  $N$ , resonance between rotational motion and radial and vertical oscillations, respectively, may take place. This can be especially serious if the acceleration process takes place impulsively with a frequency which is a harmonic of the rotation frequency (as is often actually the case) or if azimuthal inhomogeneities are present in the magnetic guide field.

If  $n$  varies with time, the seriousness of these resonances will depend on  $N$  and on how long a time  $n$  spends in the neighborhood of a critical value defined in (a) and (b) alone. Resonances are more serious, the smaller the value of  $N$ .

**3.8. Damping of radial and vertical oscillations.** If the parameters defining the equilibrium orbit are varied adiabatically, the amplitude of the free radial and vertical oscillations about the equilibrium orbit will be damped (either positively or negatively). The principle of adiabatic invariance of the action applied to these oscillations leads to the result that the amplitude of free vertical oscillations will vary as  $\omega_z^{-1/2}$  as  $\omega_e$  varies adiabatically, and the amplitude of free radial oscillations will vary as  $\omega_r^{-1/2}$  as  $W_e$  varies adiabatically. In case  $n$  does not vary with time, the amplitudes of both oscillations will vary as  $(E/H_e)^{1/2}$ .

#### 4. Particle Acceleration

The agency for accelerating particles in all types of accelerators consists of properly applied electric fields. The electric fields employed may be either static, quasi-static, or time-varying. Acceleration processes may be divided into two classes according to whether the particle is continuously accelerated or whether the accelerating takes place in discrete steps of an impulsive character. The former is employed in linear accelerators of the Cockcroft-Walton, Van de Graaff, and traveling-wave types, and in the betatron, while the latter is employed in the cyclotron, synchrocyclotron, synchrotron, and their variants, as well as in linear accelerators employing drift tubes.

**4.1. Electrostatic and quasi-electrostatic acceleration.** In the Van de Graaff accelerator, the charged particles are accelerated by falling through an electrostatic potential difference of magnitude corresponding to the final energy of the particles. This method requires the establishment over some linear region of very high potential differences. The same type of acceleration process is used in Cockcroft-Walton machines except that the potential difference is an alternating one of such low frequency that the particles undergo the complete acceleration process before the potential has changed sign. The practical difficulties of establishing and maintaining large potential differences limits present application of these methods to energies up to about 5 Mev.

**4.2. Induction acceleration.** In this type of acceleration, which is used in the betatron, the electric fields are azimuthal and are produced by

electromagnetic induction by varying the magnetic flux through the area spanned by the orbit of the accelerated particles. If the particle orbit is a circle, the gain in energy of the particle per revolution (in electron volts) is given by the electromotive force about the particle orbit. The particles make many revolutions during the acceleration cycle, so that the electromotive force around the orbit is generally a small fraction of the final energy of the accelerated particles. Hence while the acceleration process is continuous the electromotive forces present at any instant of time are much smaller than the corresponding potential differences in electrostatic acceleration to the same final energy. The energy gain of the accelerated particle per revolution in a betatron is given by

$$\Delta E = 2\pi r_e \left| Z \right| e dF_e/dt$$

where  $F_e$  is the magnetic flux through a circle of radius  $r_e$  concentric with the field and lying in the median plane.

**4.3. Traveling wave acceleration.** In this type of acceleration, the electric field employed for acceleration consists of the longitudinal electric field of an electromagnetic wave traveling through a wave guide. Acceleration takes place by having the particles travel in groups down the wave guide with a velocity closely equal to that of the wave. By having the groups of particles enter the wave guide at the proper phase of the electromagnetic field, the particles will be continuously accelerated down the guide by the co-moving electric field. Since the particle velocity is always less than that of light and increases during the accelerating process, it is necessary to “load” the wave guide with irises or other structures to reduce the phase velocity of the electromagnetic field to a value smaller than the velocity of light. By variation of the loading along the guide, the phase velocity of the wave may be varied to keep pace with the change in velocity of the particles.

Since at any instant, both accelerating and decelerating regions of the traveling electromagnetic field are accessible to the particles being accelerated, it is necessary that certain “phase stability” conditions be met in order that the particles be eventually accelerated to high energies, or the acceleration process must be terminated before the particles enter decelerating phases. The phase stability conditions require that if a particle finds itself in a region of phase unfavorable to its continued acceleration, its subsequent acceleration or deceleration be such as to return it to a favorable phase relative to the electromagnetic field.

**4.4. Impulsive acceleration.** When acceleration of particles is obtained by allowing them to pass once or repeatedly through one or more

regions in which alternating electric fields are established, one has a process of impulsive acceleration. This type of acceleration is used both in circular accelerators and in linear accelerators. As in traveling wave acceleration, it is possible for the particles to pass through the alternating fields at such times as to be decelerated rather than accelerated. Again certain conditions of "phase stability" must be met in order that particles be eventually accelerated to high energies, or the acceleration process must be terminated before the particles reach decelerating phases. In general, all employed types of impulsive acceleration can, to a good approximation for theoretical study of the phase stability problem, be replaced by an equivalent traveling wave acceleration in which the successive impulsive accelerations are smoothed out into an equivalent continuous acceleration.

## 5. Phase Stability and Phase Oscillations

**5.1. Phase stability.** As mentioned in the previous section, the successful operation of accelerators employing traveling-wave or impulsive acceleration requires a condition of phase stability to be met. The exact formulation of this condition depends generally on the detailed construction of the accelerator concerned, but provided certain quantities are appropriately defined in each case, the pertinent equations may be made to take analogous forms.

The first of these quantities is the phase of the particle relative to alternating electric field. In all cases we shall define the phase  $\phi$  as the phase of the electric field at the time which the particle traverses it relative to the last time that the electric field has passed through the value zero from a *decelerating* to an *accelerating* value at that point.

The second quantity is the effective amplitude  $\mathcal{E}$  of the accelerating electric field. For a traveling wave accelerator we shall define it as the amplitude of the electric field component in the direction of motion of the particle of the traveling electromagnetic wave. For impulsive acceleration, we shall define it as the corresponding amplitude of the equivalent traveling wave, where the equivalent traveling wave is one leading to the same average acceleration of the particle over several impulsive accelerations.

It is further helpful to define what is meant by *synchronous motion* of the particle. In a circular accelerator, this is defined to be motion in which the angular velocity of the particle is effectively at each instant equal to the angular frequency of the accelerating alternating electric field. In a linear accelerator, this is defined to be a motion in which the linear velocity of the particle is effectively at each point equal to the phase velocity of the

accelerating traveling wave or the phase velocity of the equivalent accelerating traveling wave at that point.

**5.2. Phase oscillations in circular accelerators.** When alternating electric fields are employed in circular accelerators, the motion of an accelerated particle may be most easily described in terms of the deviation of its motion from a special synchronous motion in which the frequency of revolution of the particle is at each instant equal to the frequency of the applied electric fields. Let

$$\omega_s(t) = \text{the angular frequency of the applied electric fields at time } t \quad (1)$$

$$r_s(t) = \left. \begin{array}{l} \text{the value of the equilibrium radius } r_e(t) \text{ for which } \omega_e(t) = \omega_s(t) \\ \text{at each instant } t \end{array} \right\} \quad (2)$$

$$H_s(t) = H_z(r_s, 0; t) \quad (3)$$

$$E_s(t) = |Z| e c H_s / \omega_s \quad (4)$$

$$\vartheta_s(t) = \int_0^t \omega_s(t) dt \quad (5)$$

$$\Delta E_s = \frac{2\pi}{\omega_s} \cdot \frac{dE_s}{dt} \quad (6)$$

$$\mathcal{E} = V / 2\pi r_s \quad (7)$$

$$L_s = \left. \begin{array}{l} = \frac{4\pi}{3} \frac{|Z|^2 e^2}{r_s^2} \left( \frac{E_s}{m_0 c^2} \right)^4 = \text{energy loss of particle per revolution} \\ \text{due to radiation} \end{array} \right\} \quad (8)$$

$$\epsilon_s = \left. \begin{array}{l} = \text{tangential component of induced electric field at the syn-} \\ \text{chronous radius } r_s(t) \text{ due to changing magnetic flux} \end{array} \right\} \quad (9)$$

Then the synchronous phase  $\phi_s(t)$  is defined by the equation

$$|Z| e V \sin \phi_s = \Delta E_s + L_s - 2\pi r_s |Z| e \epsilon_s \quad (10)$$

When the accelerating particle is not following the synchronous orbit, (but follows an adiabatically varying equilibrium orbit) let its energy at time  $t$  be  $E_e(t)$  and the corresponding equilibrium radius be  $r_e(t)$ ; also let

$$H_e(t) = H_z(r_e, 0; t) \quad (11)$$

$$\omega_e(t) = |Z| e c H_e / E_e \quad (12)$$

If the azimuth of the particle at time  $t$  is  $\vartheta_e(t)$ , then

$$\omega_e(t) = d\vartheta_e/dt \tag{13}$$

The phase  $\phi(t)$  of the particle is then defined by

$$\phi = \vartheta_e - \vartheta_s + \alpha \tag{14}$$

where  $\alpha$  is a constant. The constant  $\alpha$  may always be so chosen that the energy gain per revolution of the particle due to the alternating electric fields can be written as

$$|Z| eV \sin \phi \tag{15}$$

where  $|Z| eV$  is the maximum energy gain per revolution.

Then the following relations hold.

$$\frac{d\phi}{dt} = \omega_e - \omega_s \tag{16}$$

$$\frac{d}{dt} \left[ \frac{E_s}{\omega_s^2 K_s} \frac{d\phi}{dt} \right] + \frac{L'_s c^2}{2\pi(1 - n_s) r_s \omega_s^3} \frac{d\phi}{dt} + \frac{|Z| eV}{2\pi} \sin \phi = \frac{|Z| eV}{2\pi} \sin \phi_s \tag{17}$$

where

$$L'_s = \partial L_s / \partial r_s, \quad n_s = n(r_s; t), \quad K_s = 1 + \frac{n_s}{1 - n_s} \cdot \frac{c^2}{r_s^2 \omega_s^2} \tag{18}$$

Equation (17) is the fundamental equation governing the variation of the phase of the particle with time. Once the phase of the particle is known, its equilibrium angular frequency is determined by Eq. (16); its equilibrium energy is given by

$$E_e(t) = E_s(t) \left[ 1 - \frac{1}{K_s \omega_s} \frac{d\phi}{dt} \right] \tag{19}$$

and its equilibrium radius can then be determined from Eq. (12).

A first integral of Eq. (17) can be easily obtained when the slow variation of  $E_s/\omega_s^2 K_s$ ,  $\phi_s$ , and possibly  $V$  with time is neglected together with the radiation loss term. The first integral is then

$$\left( \frac{d\phi}{dt} \right)^2 = \frac{|Z| eV \omega_s^2 K_s}{\pi E_s} [U(\phi_m) - U(\phi)] \tag{20}$$

where

$$U(\phi) = -[\cos \phi + \phi \sin \phi_s]$$

and  $\phi_m$  is a constant of integration determined by the initial conditions for the motion and representing the maximum value of the phase of the particle.

The condition for phase-stable motion (motion in which the phase of the particle performs stable oscillations about the synchronous phase, the equi-

librium energy of the particle performs stable oscillations about the synchronous energy, and the equilibrium radius performs stable oscillations about the synchronous radius) is

$$\phi_s \leq \phi_m < \pi - \phi_s \quad (21)$$

The corresponding initial conditions are that the initial phase  $\phi_0$  and the initial  $(d\phi/dt)_0$  lie within closed curve in the  $(\phi, d\phi/dt)$  plane obtained by plotting Eq. (20) with  $\phi_m$  equal to  $\pi - \phi_s$ .

The frequency of small phase oscillations about the synchronous orbit is given by

$$\omega_\phi = \left[ \frac{|Z| e V K_s \cos \phi_s}{2\pi E_s} \right]^{1/2} \omega_s \quad (22)$$

When  $E_s$ ,  $\omega_s$ ,  $V$ , and  $K_s$  vary adiabatically, the corresponding variations in the amplitude of small oscillation of  $\phi$ ,  $E_e$ , and  $r_e$  are given by

$$(\phi - \phi_s)_{\max} \propto [K_s \omega_s^2 / V E_s \cos \phi_s]^{1/4} \quad (23)$$

$$(E_e - E_s)_{\max} \propto [V E_s \omega_s^2 \cos \phi_s / K_s]^{1/4} \quad (24)$$

$$(r_e - r_s)_{\max} \propto \left[ \frac{1}{\omega_s r_s (1 - n_s)} (V \cos \phi_s / E_s^3 K_s \omega_s^2) \right]^{1/4} \quad (25)$$

Radiation losses by the accelerated particle can lead to further damping of the oscillations.

**5.3. Phase motion in linear accelerators.** The motion of an accelerated particle in a linear accelerator employing traveling wave acceleration or its equivalent is most easily described in terms of the deviation of the motion from a special synchronous motion in which the velocity of the particle is at each point equal to the phase velocity of the traveling wave at that point. Let

$$v_s(x) = \left. \begin{array}{l} \text{phase velocity of the traveling wave at a distance } x \text{ along} \\ \text{the accelerator} \end{array} \right\} \quad (1)$$

$$\omega = \text{angular frequency of the traveling wave} \quad (2)$$

$$t_s(x) = \int_0^x dx / v_s(x) \quad (3)$$

$$E_s(x) = m_0 c^2 [1 - v_s^2/c^2]^{-1/2} \quad (4)$$

$$\text{and define } \phi_s \text{ by } |Z| e \mathcal{E} \sin \phi_s = dE_s/dx \quad (5)$$

For an accelerating particle not following the synchronous motion, let

$$t(x) = \text{time at which particle reaches the point } x \quad (6)$$

$$v(x) = 1/[dt(x)/dx] \quad (7)$$

$$E(x) = m_0 c^2 [1 - v^2/c^2]^{-1/2} \quad (8)$$

$$\phi(x) = \omega[t(x) - t_s(x)] + \alpha \quad (9)$$

where the constant  $\alpha$  can always be chosen so that

$$dE/dx = |Z| e \mathcal{E} \sin \phi \quad (10)$$

with  $\mathcal{E}$  = electric field amplitude of the (equivalent) traveling wave. Then

$$\frac{d\phi}{dx} = \omega \left[ \frac{1}{v} - \frac{1}{v_s} \right] \quad (11)$$

$$\text{and} \quad E(x) = m_0 \left[ 1 - \left( \frac{c}{v_s} + \frac{c}{\omega} \frac{d\phi}{dx} \right)^{-2} \right]^{-1/2} \quad (12)$$

The fundamental equation governing the motion of the phase is

$$\left. \begin{aligned} \frac{d}{dx} \left\{ m_0 c^2 \left[ 1 - \left( \frac{c}{v_s} + \frac{c}{\omega} \frac{d\phi}{dx} \right)^{-2} \right]^{-1/2} - m_0 c^2 \left( 1 - \frac{v_s^2}{c^2} \right)^{-1/2} \right\} \\ = |Z| e \mathcal{E} \sin \phi - |Z| e \mathcal{E} \sin \phi_s \end{aligned} \right\} \quad (13)$$

### Special cases

*Case I.*  $v_s \ll c$  (heavy-particle accelerators). In this case the phase equation reduces to

$$\frac{d}{dx} \left[ \left( \frac{v_s}{c} \right)^3 \left( \frac{E_s}{m_0 c} \right)^2 \frac{c E_s}{\omega} \cdot \frac{d\phi}{dx} \right] + |Z| e \mathcal{E} \sin \phi = |Z| e \mathcal{E} \sin \phi_s \quad (14)$$

In case the slow variation of  $v_s$ ,  $E_s$ , and (possibly)  $\mathcal{E}$  with  $x$  is neglected, a first integral of this equation is

$$\left( \frac{d\phi}{dx} \right)^2 = \frac{2 |Z| e \mathcal{E} \omega}{c E_s (v_s/c)^3 (E_s/m_0 c^2)^2} [U(\phi_m) - U(\phi)] \quad (15)$$

where  $U$  and  $\phi_m$  have the same meaning as in § 5.2.

The condition for phase-stable motion is again

$$\phi_s \leq \phi_m < \pi - \phi_s \quad (16)$$

and the corresponding initial conditions are the same again as in § 5.2. The frequency of small phase oscillations about the synchronous orbit is given by

$$\omega_\phi = \left[ \frac{c^2 |Z| e \mathcal{E} \cos \phi_s}{\omega E_s v_s (E_s/m_0 c^2)^2} \right]^{1/2} \omega \quad (17)$$

When  $v_s$ ,  $E_s$ , and  $\mathcal{E}$  vary adiabatically, the corresponding variation in the amplitude of oscillation of  $\phi$  is given by

$$(\phi - \phi_s)_{\max} \propto (v_s^2 E_s^3 \mathcal{E} \cos \phi_s)^{-1/4} \quad (18)$$

*Case II.*  $v_s = c$ ,  $(c - v) \ll c$ . In this case  $\phi_s = 0$  and the phase equation reduces to

$$m_0 c^2 \left( \frac{\omega}{2c} \right)^{1/2} \left( \frac{d\phi}{dx} \right)^{-3/2} \frac{d^2\phi}{dx^2} + 2 |Z| e \mathcal{E} \sin \phi = 0 \quad (19)$$

If  $\mathcal{E}$  does not vary along the accelerator, a first integral of this equation is

$$m_0 c^2 \left( \frac{\omega}{2c} \right)^{1/2} \left[ \left( \frac{d\phi}{dx} \right)^{1/2} - \left( \frac{d\phi}{dx} \right)_0^{1/2} \right] = |Z| e \mathcal{E} (\cos \phi - \cos \phi_0) \quad (20)$$

where  $(d\phi/dx)_0$  and  $\phi_0$  are the initial values of  $d\phi/dx$  and  $\phi$ , respectively.

Expressed in terms of energies the first integral is

$$E = E_0 \left[ 1 + \frac{2 |Z| c \mathcal{E} E_0}{m_0^2 c^3 \omega} (\cos \phi - \cos \phi_0) \right]^{-1} \quad (21)$$

where  $E_0$  is the initial energy.

## 6. Injection and Focusing

The considerations involved in providing appropriate particle injection and adequate focusing vary so greatly among different types of accelerators that no adequate summary in a brief space is possible. Reference should be made to the literature for information on these questions.

## 7. Additional Remarks about Special Accelerators

**7.1. The conventional cyclotron.** This is a circular accelerator for heavy particles with spiral particle trajectories, employing a time constant magnetic field and impulsive acceleration at constant frequency. The phase-stability principle is not employed but the acceleration process is terminated before decelerating phases are reached. This limits attainable energies except by the use of excessive accelerating voltages. The starting phase of the particles is effectively  $90^\circ$ . The output is practically continuous.

**7.2. The betatron.** This is a circular accelerator for electrons with particle trajectories confined to an annular region and employing induction acceleration only. The same time-varying magnetic field is commonly employed to provide both the magnetic guiding field and the induction

acceleration. To maintain the equilibrium radius constant, the following well-known “*two-to-one*” condition must be met.

$$\frac{dF_e}{dt} = 2\pi r_e^2 \frac{dH_e}{dt} \quad (1)$$

where  $F_e$  is the magnetic flux through the equilibrium orbit and  $H_e$  is the magnetic field at the equilibrium radius  $r_e$ . The attainable energies are limited by energy loss of the accelerating electrons due to radiation. The betatron is most commonly used to produce a pulsed output of x rays.

**7.3. The synchrotron.** This is a circular accelerator, at present employed for accelerating electrons (although construction of proton synchrotrons is underway) with particle trajectories confined to an annular region and employing a combination of induction and impulsive electric acceleration. A time-varying magnetic field is used, together with constant or time-varying radio frequency accelerating electric fields. The principle of phase stability is employed, allowing very high energies to be attained, although the ultimate attainable electron energies will probably be limited by inability to compensate radiation losses. The synchrotron is at present mainly used for the production of a pulsed output of high energy x rays.

**7.4. The synchrocyclotron or frequency modulated cyclotron.** This is a circular accelerator for heavy particles with spiral (synchronous) particle trajectories employing varying frequency impulsive electric acceleration in a time constant magnetic guide field. The principle of phase stability is employed to attain high energies limited at present only by practical considerations. The output is pulsed and has an average value considerably smaller than that of a conventional cyclotron. The accelerated particles are also much more difficult to remove from the machine than in the conventional cyclotron.

**7.5. Linear accelerators.** Linear accelerators employing impulsive electric or traveling-wave acceleration are employed for accelerating both electrons and heavy particles. Individual designs vary considerably. Present attainable energies for linear heavy particle accelerators are limited by electric defocusing or by the devices (grids) employed to avoid the defocusing.

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## Chapter 25

### SOLID STATE

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#### Introduction

This chapter attempts to cover the fields that are of most interest in connection with contemporary basic research in solid-state physics, omitting, however, fields such as electron emission, optics, and ferromagnetism, which fall naturally in the domain of other chapters of the book. Since a major part of our theoretical knowledge of solid state physics is based on approximate models, the choice of formulas for inclusion had to be based on the author's guesses of the durability of present concepts and of their utility to research workers while they last. Such considerations, for example, prompted omission of much of the detailed lore of the electron theory of metals, but inclusion of similar material relating to semiconductors. The sections are arranged as follows: Section 1 introduces some mathematical concepts that are used in a number of places later in the chapter; Sections 2 through 5 deal with formulas in which a solid is treated as a continuum; Sections 6 through 8 deal with formulas involving the atomic but not the electronic structure of solids; Sections 9 and 10 deal with free electrons; Section 11 contains miscellaneous isolated formulas from all these areas. Most of the subsections contain references to publications where derivations and more detailed expositions of the formulas can be found; these of course do not usually represent the original source of the formulas, but have been selected as sources most likely to be accessible and convenient for the reader. The formulas presented here are not always identical with those in the references, however, since it sometimes seemed expedient to introduce minor generalizations and refinements.

#### 1. Crystal Mathematics

**1.1. Translations.** In any crystal there exists a set of translations  $\mathbf{t}_i$  such that the environment of any point  $\mathbf{r}$  in the crystal is identical with that

of the point  $\mathbf{r} + \mathbf{t}_i$ . These translations form an additive group of infinite order called the *translation group* of the crystal. There always exists a set of three translation vectors  $\mathbf{t}_1, \mathbf{t}_2, \mathbf{t}_3$  (not necessarily unique, however) such that for any  $\mathbf{t}_i$

$$\mathbf{t}_i = l_i \mathbf{t}_1 + m_i \mathbf{t}_2 + n_i \mathbf{t}_3, \quad (l_i, m_i, n_i \text{ integers})$$

These are called *fundamental translations*.

**1.2. The unit cell and the  $s$  sphere.** A *unit cell* is defined as any region of space  $R$  with the two properties :

a. Region  $R$  does not overlap any of the regions resulting from displacement of it by a translation vector  $\mathbf{t}_i$ .

b. Region  $R$  and these translated regions fill all space. There are many possible shapes for a unit cell; one of the most convenient ways of constructing a unit cell is to let  $R$  consist of all the points reachable from the origin without crossing any of the planes which are perpendicular bisectors of the various  $\mathbf{t}_i$ . The volume  $\Omega$  of a unit cell is always that of the parallelepiped formed by any three fundamental translations.

$$\Omega = \mathbf{t}_1 \cdot \mathbf{t}_2 \times \mathbf{t}_3 \quad (1)$$

For crystals whose atoms all occupy equivalent positions a concept useful in some types of theoretical work is that of the  $s$ -sphere, defined as a sphere centered on an atom and having a volume equal to the volume per atom of the crystal.

The following table gives, for some of the commoner crystal structures, values of the volume  $\Omega$  of the unit cell, the number  $S$  of atoms per unit cell, the radius  $r_s$  of the  $s$ -sphere, and the half-distance  $r_{\min}$  between nearest neighbor atoms.

Lattice type	Parameters	$\Omega$	$S$	$r_s$	$r_{\min}$
Body-centered cubic	Cube-side $d$	$d^3/2$	1	$\sqrt[3]{(3/8\pi)d}$ $= 0.49237d$	$(\sqrt{3}/4)d$ $= 0.43301d$
Face-centered cubic	Cube-side $d$	$d^3/4$	1	$\sqrt[3]{(3/16\pi)d}$ $= 0.39080d$	$(\sqrt{2}/4)d$ $= 0.35355d$
Diamond type	Cube-side $d$	$d^3/4$	2	$\sqrt[3]{(3/32\pi)d}$ $= 0.31017d$	$(\sqrt{3}/8)d$ $= 0.21651d$
Close-packed hexagonal	Fundamental translations $a$ in basal plane, $c$ along hexagonal axis	$\frac{1}{2}\sqrt{3} ca^2$	2	$\sqrt[3]{(3^{3/2}/16\pi)\sqrt{ca^2}}$ $= 0.46932a\sqrt[3]{c/a}$	$a/2$ if $c/a > \sqrt{8/3}$ , $\frac{1}{2}\sqrt{a^2/3 + c^2/4}$ if $c/a < \sqrt{8/3}$
Ideal case of close-packed hexagonal	Same with $c/a = \sqrt{8/3}$	$\sqrt{2}a^3$	2	$\sqrt[3]{(3/2^{5/2}\pi)a}$ $= 0.55267a$	$a/2$

**1.3. The reciprocal lattice.** If  $\mathbf{t}_1, \mathbf{t}_2, \mathbf{t}_3$  are any three fundamental translation vectors of a given crystal lattice, the vectors  $\mathbf{g}_1, \mathbf{g}_2, \mathbf{g}_3$  defined by

$$\mathbf{g}_1 = \frac{\mathbf{t}_2 \times \mathbf{t}_3}{\mathbf{t}_1 \cdot \mathbf{t}_2 \times \mathbf{t}_3}, \quad \mathbf{g}_2 = \frac{\mathbf{t}_3 \times \mathbf{t}_1}{\mathbf{t}_1 \cdot \mathbf{t}_2 \times \mathbf{t}_3}, \quad \mathbf{g}_3 = \frac{\mathbf{t}_1 \times \mathbf{t}_2}{\mathbf{t}_1 \cdot \mathbf{t}_2 \times \mathbf{t}_3} \quad (1)$$

are called fundamental translations of the corresponding *reciprocal lattice*, and the reciprocal lattice itself is defined as the set of all vectors of the form

$$\mathbf{g}_j = l_j \mathbf{g}_1 + m_j \mathbf{g}_2 + n_j \mathbf{g}_3, \quad (l_j, m_j, n_j \text{ integers}) \quad (2)$$

If  $\mathbf{t}_i$  is any translation vector of the original lattice,  $\mathbf{t}_i \cdot \mathbf{g}_j$  is an integer for any  $\mathbf{g}_j$ .

Any function of position which has the same periodicity properties as the original lattice can be written in the form of a Fourier series

$$\sum_j a_j \exp(2\pi i \mathbf{g}_j \cdot \mathbf{r})$$

and conversely any such series has the periodicity of the original lattice.

The unit cell contained within the perpendicular bisectors of the vectors  $2\pi \mathbf{g}_j$  is called the *first Brillouin zone* (see also § 10.7).

**1.4. Periodic boundary conditions.** In problems involving wave motion, potentials, vibrations, etc., in crystals, the size of the region which must be studied is sometimes reduced to finite dimensions by imposition of periodic boundary conditions, a device which avoids the introduction of boundary surfaces where physical conditions differ from those in the rest of the crystal. This device consists in requiring that in an infinite crystal all physical properties be trebly periodic with the periods  $G_1 \mathbf{t}_1, G_2 \mathbf{t}_2, G_3 \mathbf{t}_3$ , where  $\mathbf{t}_1, \mathbf{t}_2, \mathbf{t}_3$  are fundamental translations of the crystal lattice, and  $G_1, G_2, G_3$  are three very large integers. Thus specification of physical conditions over the volume  $v$  of the parallelepiped formed by  $G_1 \mathbf{t}_1, G_2 \mathbf{t}_2, G_3 \mathbf{t}_3$ —called the *fundamental volume*—specifies conditions throughout all space.

Any function of position satisfying the periodic boundary conditions can be expanded into a Fourier series of the form  $\sum_{\nu} A_{\nu} \exp(i \mathbf{k}_{\nu} \cdot \mathbf{r})$ , where the vectors  $\mathbf{k}_{\nu}$  run over a closely spaced lattice of points in the space of the reciprocal lattice, the allowed values of the  $\mathbf{k}_{\nu}$  being simply  $2\pi$  times the vectors of the lattice reciprocal to that of  $G_1 \mathbf{t}_1, G_2 \mathbf{t}_2, G_3 \mathbf{t}_3$ . The number of  $\mathbf{k}_{\nu}$  per unit volume  $\Delta k_x \Delta k_y \Delta k_z$  of  $k$ -space is

$$\rho = \frac{v}{8\pi^3} \quad (1)$$

and the number lying within the first Brillouin zone (see § 1.3) is  $N = v/\Omega$ , the number of unit cells in the fundamental volume.

## 2. Elastic Constants

**2.1. Stress and strain components.** The components of the stress-tensor  $p_{\mu\nu}$  and the symmetrical part of the strain-tensor  $u_{\mu\nu}$  can each be designated by a single suffix running from 1 to 6, thus :

$$p_1 = p_{xx}, p_2 = p_{yy}, p_3 = p_{zz}, p_4 = p_{yz} = p_{zy}, p_5 = p_{xz} = p_{zx}, p_6 = p_{xy} = p_{yx};$$

$$u_1 = u_{xx}, u_2 = u_{yy}, u_3 = u_{zz}, u_4 = u_{yz} + u_{zy}, u_5 = u_{xz} + u_{zx}, u_6 = u_{xy} + u_{yx}$$

We shall use the sign convention that  $p_{xx}$  is positive for a tensile stress.

Since relations involving the  $p$ 's and  $u$ 's depend on the orientation of the coordinate axes relative to the crystal lattice, it is customary in elasticity and piezoelectricity to use "natural" crystallographic axes, conventions for which have been laid down by the Piezoelectric Crystals Committee of the IRE (Ref. 11). According to these conventions, the  $x$ ,  $y$ , and  $z$  axes always form a right-handed system. For crystals of the cubic system these axes are to be chosen parallel to axes of fourfold symmetry, or if such are lacking, to axes of twofold symmetry. For crystals of the trigonal and hexagonal systems the  $z$  axis is to be chosen along the three- or sixfold axis, the  $x$  axis along a twofold axis or perpendicular to a plane of symmetry if either exists; when the latter criterion does not suffice to locate the  $x$  direction uniquely in any  $60^\circ$  sector, it is to be chosen in the direction of one of the shortest fundamental translations. For crystals of lower symmetry, Ref. 11 should be consulted.

**2.2. Elastic constants and moduli.** The *elastic constants*  $c_{ij}$  are defined by

$$p_i = \sum_{j=1}^6 c_{ij} u_j \quad (1)$$

in any elastic deformation. The numerical values of the  $c_{ij}$  may depend on the nature of the auxiliary constraints under which the elastic deformation is carried out (e.g., adiabatic or isothermal conditions, etc.). Energetic considerations require the matrix  $c_{ij}$  to be symmetrical ( $= c_{ji}$ ) and positive definite (see § 2.5 for analytical expressions of this criterion).

The *elastic moduli* or *compliance coefficients*  $s_{ij}$  are the components of the matrix reciprocal to that of the elastic constants, so that

$$u_i = \sum_{j=1}^6 s_{ij} p_j \quad (2)$$

The matrix  $s_{ij}$  is also symmetrical and positive definite.

**2.3. Forms of  $c_{ij}$  or  $s_{ij}$  for some common crystal classes** (Refs. 14 and 27). With the “natural” crystallographic axes described in § 2.1, the restrictions imposed by crystal symmetry enable the values of  $c_{ij}$  for arbitrary indexes,  $i$  and  $j$  to be expressed in terms of a small number of independent components, thus :

<i>Cubic system</i>						<i>Hexagonal system</i>					
<i>ij</i>						<i>ij</i>					
$c_{11}$	$c_{12}$	$c_{12}$	0	0	0	$c_{11}$	$c_{12}$	$c_{13}$	0	0	0
	$c_{11}$	$c_{12}$	0	0	0		$c_{11}$	$c_{13}$	0	0	0
		$c_{11}$	0	0	0			$c_{33}$	0	0	0
			$c_{44}$	0	0				$c_{44}$	0	0
				$c_{44}$	0					$c_{44}$	0
					$c_{44}$						$\frac{1}{2}(c_{11} - c_{12})$

<i>Isotropic body</i>					
<i>ij</i>					
	$\lambda + 2\mu$	$\lambda$	$\lambda$	0	0
		$\lambda + 2\mu$	$\lambda$	0	0
			$\lambda + 2\mu$	0	0
				$\mu$	0
				$\mu$	0
					$\mu$

For the corresponding matrices for crystals of lower symmetry see Refs. 14 and 27. The corresponding matrices of the elastic moduli for cubic and hexagonal crystals are obtained by simply substituting  $s$ 's for  $c$ 's in the above, except that the coefficient of  $(s_{11} - s_{12})$  in the 66 position for hexagonal crystals is 2 instead of  $\frac{1}{2}$ .

**2.4. Relation of elastic constants and moduli.** For cubic crystals

$$c_{11} = \frac{s_{11} + s_{12}}{(s_{11} - s_{12})(s_{11} + 2s_{12})}, \quad c_{12} = \frac{-s_{12}}{(s_{11} - s_{12})(s_{11} + 2s_{12})}, \quad c_{44} = \frac{1}{s_{44}} \quad (1)$$

For hexagonal crystals, with  $D = (s_{11} + s_{12})s_{33} - 2s_{13}^2$ ,

$$\left. \begin{aligned} c_{11} &= \frac{s_{11}s_{33} - s_{13}^2}{D(s_{11} - s_{12})}, & c_{12} &= \frac{s_{13}^2 - s_{12}s_{33}}{D(s_{11} - s_{12})} \\ c_{13} &= \frac{-s_{13}}{D}, & c_{33} &= \frac{s_{11} + s_{12}}{D}, & c_{44} &= \frac{1}{s_{44}} \end{aligned} \right\} \quad (2)$$

All these equations remain valid if  $s$ 's and  $c$ 's are interchanged.

**2.5. Forms taken by the condition of positive definiteness, for some common crystal classes.** For cubic crystals,

$$c_{44} > 0, \quad c_{11} > |c_{12}|, \quad c_{11} + 2c_{12} > 0$$

For hexagonal crystals,

$$c_{44} > 0, \quad c_{11} > |c_{12}|, \quad (c_{11} + c_{12})c_{33} > 2c_{13}^2$$

The elastic moduli  $s_{ij}$  satisfy identical inequalities.

**2.6. Relation of  $c_{ij}$  and  $s_{ij}$  to other elastic constants** (Ref. 14). The volume compressibility  $\kappa$ , is given by

$$\kappa = \sum_{ij=1}^3 s_{ij} \quad (1)$$

For a specimen of a cubic substance whose long axis has direction cosines  $\alpha, \beta, \gamma$ , with respect to the crystal axes, Young's modulus  $E$  is given by

$$E = (s_{11} - 2s\Gamma)^{-1} \quad (2)$$

where  $s = s_{11} - s_{12} - \frac{1}{2}s_{44}$ ,  $\Gamma = \alpha^2\beta^2 + \alpha^2\gamma^2 + \beta^2\gamma^2$

The longitudinal linear compressibility is

$$\kappa^{(l)} = s_{11} + 2s_{12} = \kappa/3 \quad (3)$$

If such a specimen has a circular cross section, the mean shear modulus, as measured for example in simple torsion, is

$$G = (s_{44} + 4s\Gamma)^{-1} \quad (4)$$

For a specimen of a hexagonal substance whose long axis makes an angle  $\theta$  with the hexagonal axis, Young's modulus is

$$E = [s_{11} \sin^4 \theta + s_{33} \cos^4 \theta + (2s_{13} + s_{44}) \cos^2 \theta \sin^2 \theta]^{-1} \quad (5)$$

and the longitudinal linear compressibility is

$$\kappa^{(l)} = s_{11} + s_{12} + s_{13} - (s_{11} - s_{33} + s_{12} - s_{13}) \cos^2 \theta \quad (6)$$

If the cross section is circular, the mean shear modulus is

$$G = \left. \begin{aligned} & [s_{44} + (s_{11} - s_{12} - \frac{1}{2}s_{44}) \sin^2 \theta \\ & + 2(s_{11} + s_{33} - 2s_{13} - s_{44}) \cos^2 \theta \sin^2 \theta]^{-1} \end{aligned} \right\} \quad (7)$$

**2.7. Thermodynamic relations** (Refs. 16 and 27). Let the superscripts  $ad$  and  $is$  denote, respectively, adiabatic and isothermal coefficients, let  $T$  be the absolute temperature, let  $u_i (i = 1 \text{ to } 6)$  be the strain components

as defined in § 2.1, and let  $\alpha_i = \partial u_i / \partial T$  at zero stress be a generalized expansion coefficient. Then

$$c_{ij}^{(ad)} = c_{ij}^{(is)} + \sum_{r,s=1}^6 \frac{c_{ir}^{(is)} c_{js}^{(is)} \alpha_r \alpha_s T v}{C_v}, \quad s_{ij}^{(ad)} = s_{ij}^{(is)} - \frac{\alpha_i \alpha_j T}{C_p} \quad (1)$$

where  $v$  is the volume and  $C_v$  and  $C_p$  the constant volume and constant pressure heat capacities, respectively, of a standard amount of the crystalline material (e.g., 1 mole). For cubic crystals the adiabatic and isothermal shear constants are identical, while the volume compressibilities  $\kappa$  satisfy

$$\kappa^{(ad)} = \kappa^{(is)} - \frac{9v\alpha^2 T}{C_p} \quad (2)$$

where  $\alpha = \alpha_1$  is the linear expansion coefficient.

### 3. Dielectrics and Piezoelectricity

**3.1. Piezoelectric constants** (Refs. 5 and 16). Let  $p_i, u_i (i = 1$  to 6) be, respectively, the stress and strain components as defined in § 2.1. Let  $E_\alpha, P_\alpha (\alpha = 1$  to 3) be the components of electric field and electric polarization, respectively. The *piezoelectric constants* or *stress coefficients*  $e_{\alpha i}$  and the *piezoelectric moduli* or *strain coefficients*  $d_{\alpha i}$  are defined by

$$e_{\alpha i} = \left( \frac{\partial P_\alpha}{\partial u_i} \right)_E = - \left( \frac{\partial p_i}{\partial E_\alpha} \right)_{u,s} \quad (1)$$

$$d_{\alpha i} = \left( \frac{\partial P_\alpha}{\partial p_i} \right)_E = \left( \frac{\partial u_i}{\partial E_\alpha} \right)_{p,s} \quad (2)$$

If the temperature is held constant in the differentiations just written, these equations define the *isothermal* constants and moduli; if the entropy is kept constant, they define the *adiabatic* quantities. In either case

$$d_{\alpha i} = \sum_{j=1}^6 s_{ji} e_{\alpha j}, \quad e_{\alpha j} = \sum_{i=1}^6 c_{ij} d_{\alpha i} \quad (3)$$

where  $c_{ij}, s_{ji}$  are the elastic constants and moduli, respectively (see § 2.2), defined for the case  $E = 0$ , and isothermal or adiabatic according to whether the piezoelectric quantities are isothermal or adiabatic, respectively.

The equalities of the partial derivatives used in the above definitions of  $e_{\alpha i}$  and  $d_{\alpha i}$  are exact when the initial state of the crystal is one with  $P = E = 0$ , as is normally the case in work with crystals without a permanent polarization; for this case the stresses  $p_i$  represent simply the stresses imposed

on the crystal by external tractions or inertial reactions. When the derivatives are evaluated for states with finite fields, as is the case for crystals with a permanent moment, the equations as written are not exactly correct, although usually only a negligible error is involved in using them, with the  $p_i$  interpreted in the manner just mentioned. The equations can be made exactly correct for this case by replacing  $(\partial P_\alpha / \partial u_i)_E$  and  $(\partial P_\alpha / \partial p_i)_E$  by  $(1/v)[\partial(vP_\alpha) / \partial u_i]_E$  and  $(1/v)[\partial(vP_\alpha) / \partial p_i]_E$ , respectively, where  $v$  is the volume of the crystal, and interpreting the stresses  $p_i$  as the set whose surface tractions and body forces equal the difference of the mechanically imposed forces and the tractions and body forces due to the Maxwellian field-stress tensor

$$p_{\alpha\beta}^{(f)} = \frac{E_\alpha D_\beta}{4\pi} - \frac{E^2 \delta_{\alpha\beta}}{8\pi} \quad (4)$$

Many other equally valid sets of definitions and formulas can of course be given.

**3.2. Dielectric constants** (Refs. 5 and 16). The *dielectric constant tensor*  $\epsilon_{\alpha\beta}$  and the *susceptibility tensor*  $\eta_{\alpha\beta}$  are ordinarily defined as

$$\eta_{\alpha\beta} = \frac{\partial P_\alpha}{\partial E_\beta} \quad (1)$$

$$\epsilon_{\alpha\beta} = \delta_{\alpha\beta} + 4\pi\eta_{\alpha\beta} = \frac{\partial D_\alpha}{\partial E_\beta} \quad (2)$$

For piezoelectric crystals different susceptibilities and dielectric constants result according to whether the derivatives are evaluated at constant strain (clamped crystal) or at constant stress (free crystal), and for pyroelectric crystals the isothermal and adiabatic values are different (see § 3.5). These different kinds of susceptibilities and dielectric constants will be denoted by superscripts designating which of the quantities  $u$  (strain) and  $p$  (stress) are to be kept constant, and *ad* or *is* for adiabatic or isothermal conditions.

Relations exactly valid for crystals without a permanent polarization (derivatives evaluated at  $E = P = 0$ ) and approximately valid even for those with a permanent moment are

$$\begin{aligned} \epsilon_{\alpha\beta} &= \epsilon_{\beta\alpha}, \quad \eta_{\alpha\beta} = \eta_{\beta\alpha}, \quad (\text{for any set of conditions}) \\ \epsilon_{\alpha\beta}^{(p)} &= \epsilon_{\alpha\beta}^{(u)} + 4\pi \sum_{i=1}^6 e_{\alpha i} d_{\beta i} \end{aligned} \quad (3)$$

the last equation being valid when either isothermal or adiabatic quantities are used throughout.

For crystals with a permanent polarization  $\eta_{\alpha\beta}^{(p)}$  is not in general exactly equal to  $\eta_{\beta\alpha}^{(p)}$ , though the difference is usually small. However, if we define

$$\eta'_{\alpha\beta}{}^{(p)} = \frac{1}{v} \left[ \frac{\partial(vP_\alpha)}{\partial E_\beta} \right]_{p',s} \quad (4)$$

we have

$$\eta'_{\alpha\beta}{}^{(p)} = \eta_{\beta\alpha}{}^{(p)} = \eta_{\alpha\beta}^{(u)} + \sum_{i=1}^6 e_{\alpha i} d_{\beta i} \quad (5)$$

exactly.

**3.3. Pyroelectricity and the electrocaloric effect** (Ref. 5). The temperature derivatives  $(\partial P_\alpha/\partial T)_{E,p',s}$  of the components of the polarization vector  $P$  at constant (usually zero) field and stress are called *pyroelectric coefficients*. They are related to the *electrocaloric effect*: adiabatic application of an electric field  $E$  causes the temperature of a pyroelectric crystal to change by an amount measured by

$$\left( \frac{\partial T}{\partial E_\alpha} \right)_{S,p',s} = - \frac{T[\partial(v_m P_\alpha)/\partial T]_{E,p',s}}{C_p^{(E)}} \approx - \frac{T v_m (\partial P_\alpha/\partial T)_{E,p',s}}{C_p^{(E)}} \quad (1)$$

where  $v_m$  is the volume of a standard amount of material (e.g., a gram or a mole) and  $C_p^{(E)}$  is the specific heat associated with the same amount of material, at constant stress and constant field  $E$ . Here as in § 3.1 the stresses  $p_i$  are for all practical purposes to be identified with the stresses applied by purely mechanical external forces, although rigorously they differ from these by small terms due to the Maxwell stresses.

**3.4. Elastic constants of piezoelectric crystals** (Ref. 5). The elastic constants  $c_{ij}$  and moduli  $s_{ij}$  of a piezoelectric crystal are defined, just as for ordinary crystals (see § 2.2), by

$$c_{ij} = \left( \frac{\partial p_i}{\partial u_j} \right) = c_{ji}, \quad s_{ij} = \left( \frac{\partial u_i}{\partial p_j} \right) = s_{ji} \quad (1)$$

where  $p_i, u_j$  represent respectively the stress and strain components as defined in § 2.1. This definition leads to several different elastic constants according to whether the differentiation is carried out under isothermal or adiabatic conditions and according to which of the electric field quantities  $E, D, P$  is held constant. These different elastic constants will be denoted by attaching as superscripts the symbols of the quantities to be held constant.

The relation of isothermal to adiabatic constants is as given in § 3.5. For either isothermal or adiabatic constants we have the relations, exactly true

for materials without permanent polarization, and usually true to within a negligible error for permanently polarized substances,

$$\left. \begin{aligned} c_{ij}^{(D)} &= c_{ij}^{(E)} + 4\pi \sum_{\alpha, \beta=1}^3 e_{\beta i}(\epsilon^{-1})_{\beta\alpha} e_{\alpha j} \\ s_{ij}^{(D)} &= s_{ij}^{(E)} - 4\pi \sum_{\alpha, \beta=1}^3 d_{\beta i}(\epsilon^{-1})_{\beta\alpha} d_{\alpha j} \\ c_{ij}^{(P)} &= c_{ij}^{(E)} + \sum_{\alpha, \beta=1}^3 e_{\beta i}(\eta^{-1})_{\beta\alpha} e_{\alpha j} \\ s_{ij}^{(P)} &= s_{ij}^{(E)} - \sum_{\alpha, \beta=1}^3 d_{\beta i}(\eta^{-1})_{\beta\alpha} d_{\alpha j} \end{aligned} \right\} \quad (2)$$

where  $(\epsilon^{-1})_{\beta\alpha}$ ,  $(\eta^{-1})_{\beta\alpha}$  are the matrices reciprocal, respectively, to those of the dielectric constant  $\epsilon_{\alpha\beta}$ , and the susceptibilities  $\eta_{\alpha\beta}$ , and  $e_{\alpha j}$ ,  $d_{\beta i}$  are the piezoelectric constants and moduli as defined in § 3.1. The small errors in these equations for permanently polarized media are of the same order as the ambiguities introduced into the definitions of the elastic constants by the Maxwell stresses, i.e., by forces of electrostatic origin.

**3.5. Relations of adiabatic and isothermal piezoelectric and dielectric constants** (Ref. 16). For pyroelectric crystals there is a difference between the adiabatic and isothermal values of the piezoelectric and dielectric constants, as defined in § 3.1 and § 3.2, respectively. Using the superscripts *ad* and *is* to denote, respectively, adiabatic (constant entropy) and isothermal quantities, we have

$$d_{\alpha i}^{(ad)} = d_{\alpha i}^{(is)} - \left[ \frac{\partial(v_m P_\alpha)}{\partial T} \right]_{E, v', s} \cdot \frac{T(\partial u_i / \partial T)_{E, v', s}}{C_p^{(E)}} \quad (1)$$

where  $v_m$  is the volume of a standard amount of material (e.g., a gram or a mole),  $C_p^{(E)}$  is the specific heat associated with the same amount of material at constant stress and field,  $u_i$  is a strain component as defined in § 2.1, so that  $(\partial u_i / \partial T)_{E, v', s}$  is a generalized expansion coefficient, and the quantity in square brackets can usually be closely approximated by  $v_m$  times the pyroelectric coefficient  $(\partial P_\alpha / \partial T)_{E, v', s}$ . For the dielectric constants the relation

$$\epsilon_{\alpha\beta}^{(p, ad)} = \epsilon_{\alpha\beta}^{(p, is)} - \frac{4\pi T v_m}{C_p^{(E)}} \left( \frac{\partial P_\alpha}{\partial T} \right)_{E, v', s} \left( \frac{\partial P_\beta}{\partial T} \right)_{E, v', s} \quad (2)$$

is ordinarily a very close approximation to the truth.

#### 4. Conduction and Thermoelectricity

**4.1. Conductivity tensor of a crystal.** When Ohm's law is obeyed, the electric field  $\mathbf{E}$  and current density  $\mathbf{j}$  in a homogeneous crystal at constant temperature are related by

$$j_{\alpha} = \sum_{\beta} \sigma_{\alpha\beta} E_{\beta} \quad (1)$$

Similarly the heat flux  $\mathbf{q}$  and the gradient of temperature  $T$  are related, in the absence of electric currents, by

$$q_{\alpha} = \sum_{\beta} \kappa_{\alpha\beta} \frac{\partial T}{\partial x_{\beta}} \quad (2)$$

The conductivity tensors have the symmetry of the crystal, and in the absence of magnetic fields Onsager's principle of microscopic reversibility requires that they satisfy in addition (Ref. 6)

$$\sigma_{\alpha\beta} = \sigma_{\beta\alpha}, \quad \kappa_{\alpha\beta} = \kappa_{\beta\alpha} \quad (3)$$

**4.2. Matthiessen's rule.** The presence of any sort of impurities or lattice imperfections usually increases the resistivity  $\rho$  of a metal above the value  $\rho^{(0)}$  characteristic of a perfect crystal. In most cases it is found that over a considerable temperature range

$$\rho - \rho^{(0)} = \text{constant independent of temperature} \quad (1)$$

This is called *Matthiessen's rule*.

**4.3. Thomson effect.** When a current of density  $\mathbf{j}$  (in direction of equivalent flows of positive charge) flows in homogeneous material in the presence of a temperature gradient, the rate  $q$  at which heat is developed per unit volume contains a term linear in  $\mathbf{j}$  and  $\nabla T$ .

$$q = \rho j^2 - \tau \mathbf{j} \cdot \nabla T \quad (1)$$

where  $\rho$  is the resistivity and  $\tau$  is called the *Thomson coefficient*. For crystals of lower than cubic symmetry,  $\tau$ , like  $\rho$ , must be replaced by a tensor.

**4.4. Seebeck effect.** The *absolute thermoelectric power*  $\epsilon$  of any electronic conductor measures the emf set up by the presence of a temperature gradient in a homogeneous material, when the current density  $\mathbf{j}$  vanishes. Explicitly, for a cubic or isotropic substance (Ref. 10),

$$e\epsilon = \left( \frac{d\bar{\mu}}{dT} \right)_{j=0} \quad (1)$$

where  $e$  is the magnitude of the electronic charge and  $\bar{\mu}$  is the electrochemical potential or partial molar free energy per electron, which for metals (as opposed to semiconductors) is for all practical purposes a constant minus  $e\Phi$ , where  $\Phi$  is the electrostatic potential. For metals the quantity  $\epsilon$  obeys the thermodynamic relation (Refs. 7 and 10)

$$\epsilon = \int_0^T \frac{\tau}{T'} dT' \quad (2)$$

where  $\tau$  is the Thomson coefficient (see § 4.3). In metals of lower than cubic symmetry this integral may be used as a definition of  $\epsilon$ , with  $\epsilon$  and  $\tau$  replaced by tensors. For non-cubic semiconductors the  $\epsilon$ -tensor is best defined by (1) and (2) of § 4.6

A thermocouple made of two electronic conductors  $A$ ,  $B$ , with junctions at temperatures  $T_1$ ,  $T_2$ , develops an emf (*Seebeck effect*)

$$\text{emf} = \int_{T_1}^{T_2} (\epsilon_A - \epsilon_B) dT' \quad (3)$$

If either conductor is of lower than cubic symmetry, the thermoelectric emf is in general dependent on the shape and orientation of the conductor; for a filamentary shape the expression just written can be used if each  $\epsilon$  is interpreted as  $\epsilon_{\alpha\alpha}$ , where the  $\alpha$  direction is along the filament.

**4.5. Peltier effect.** The *Peltier coefficient*  $\Pi_{AB} = -\Pi_{BA}$  between two electronic conductors  $A$ ,  $B$ , is defined as the heat developed at the junction of  $A$  and  $B$  per unit current (positive charge) flowing from  $B$  to  $A$ . It is given by (Ref. 7)

$$\Pi_{AB} = T(\epsilon_B - \epsilon_A) \quad (1)$$

where  $T$  is the absolute temperature of the junction and the  $\epsilon$ 's are thermoelectric powers as defined in § 4.4. In crystals of lower than cubic symmetry the  $\epsilon$ 's are of course tensors, and the heat developed per unit area is

$$T \sum_{\alpha, \beta=1}^3 [(\epsilon_B)_{\alpha\beta} (j_B)_\alpha - (\epsilon_A)_{\alpha\beta} (j_A)_\alpha] n_\beta \quad (2)$$

where  $j_A$ ,  $j_B$  are the current densities in the two conductors, and  $n$  is the unit normal to the surface.

**4.6. Entropy flow and Bridgman effect** (Refs. 4 and 10). If  $\epsilon_{\alpha\beta}$  is the absolute thermoelectric power tensor (see § 4.4) and  $j$  the electric current density (equivalent current of positive charge) in any conductor, the flow of current is accompanied by a reversible flux of entropy whose direction and

magnitude (entropy per unit area per unit time) are given by the vector with components

$$\eta_\alpha = \sum_{\beta=1}^3 \epsilon_{\beta\alpha} \dot{j}_\beta \quad (1)$$

In an isothermal specimen

$$\eta = \frac{1}{T} \left( W + \frac{\bar{\mu} \mathbf{j}}{e} \right) \quad (2)$$

where  $W$  is the energy flux vector,  $\bar{\mu}$  the electrochemical potential per electron, and  $e$  the magnitude of the electronic charge. Thus when the direction of  $\mathbf{j}$  changes during passage of current through a crystal of lower than cubic symmetry, a heating or cooling analogous to the Peltier effect occurs, and is called the *Bridgman effect*.

**4.7. Galvanomagnetic and thermomagnetic effects.** Let  $\mathbf{j}$ ,  $\mathbf{q}$  be the vector densities of electric current and heat current, respectively, and let  $\mathbf{H}$  be the magnetic field strength. Let  $\mathbf{E}_t$ ,  $\nabla_t T$  be the projections of the electric field vector and the temperature gradient, respectively, on the plane normal to  $\mathbf{j}$  or  $\mathbf{q}$ , whichever is nonvanishing. Then the Hall coefficient  $R$ , the Nernst coefficient  $Q$ , the Ettingshausen coefficient  $P$ , and the Righi-Leduc coefficient  $S$  are defined, respectively, by

$$\text{Hall: } \mathbf{E}_t = -R \mathbf{j} \times \mathbf{H}$$

$$\text{Nernst: } \mathbf{E}_t = Q \nabla T \times \mathbf{H} \text{ under condition } \mathbf{j} = 0$$

$$\text{Ettingshausen: } \nabla_t T = P \mathbf{j} \times \mathbf{H} \text{ under condition } \mathbf{j} \cdot \nabla T = 0, \mathbf{q} = 0$$

$$\text{Righi-Leduc: } \nabla_t T = S \mathbf{H} \times \nabla T \text{ under condition } \mathbf{j} = 0$$

These definitions may be used for large  $\mathbf{H}$  or for substances of lower than cubic symmetry if  $\mathbf{E}_t$ ,  $\nabla_t T$  are interpreted as the parts of these quantities which are odd in the magnetic field. For such cases  $R$ ,  $Q$ ,  $P$ ,  $S$  are in general functions of the directions of  $\mathbf{H}$  and  $\mathbf{j}$  or  $\mathbf{q}$ . Thermodynamics requires (Ref. 4

$$P = TQ/\kappa \quad (1)$$

where  $\kappa$  is the thermal conductivity.

## 5. Superconductivity

**5.1. The London equations** (Ref. 13). According to F. and H. London the charge density  $\rho$  and current density  $\mathbf{j}$  in superconducting matter can each be written as a sum of a "normal part (superscript  $n$ ) and a "superconducting" part (superscript  $s$ ), in such a way that

$$\frac{\partial \rho^{(n)}}{\partial t} + \nabla \cdot \mathbf{j}^{(n)} = 0, \quad \frac{\partial \rho^{(s)}}{\partial t} + \nabla \cdot \mathbf{j}^{(s)} = 0 \quad (1)$$

and at the same time

$$\mathbf{j}^{(n)} = \sigma \mathbf{E}, \quad \frac{\partial(\Lambda \mathbf{j}^{(s)})}{\partial t} = \mathbf{E}, \quad \nabla \times (\Lambda \mathbf{j}^{(s)}) = -\frac{\mathbf{B}}{c} \quad (2)$$

where  $\mathbf{E}$ ,  $\mathbf{B}$  are, respectively, the electric field in esu and the magnetic induction in emu,  $c$  is the velocity of light,  $\Lambda$  is a temperature-dependent constant of the material with dimensions (time)<sup>2</sup>, and  $\sigma$  is a conductivity which is finite at all temperatures. In addition we have the Maxwell equations (see also Chapter 13),

$$\left. \begin{aligned} \nabla \times \mathbf{E} &= -\frac{1}{c} \cdot \frac{\partial \mathbf{B}}{\partial t}, & \nabla \times \mathbf{H} &= \frac{1}{c} \cdot \frac{\partial \mathbf{D}}{\partial t} + \frac{4\pi(\mathbf{j}^{(s)} + \mathbf{j}^{(n)})}{c} \\ \nabla \cdot \mathbf{D} &= 4\pi\rho, & \nabla \cdot \mathbf{B} &= 0 \end{aligned} \right\} \quad (3)$$

It is customary to assume further that  $\mathbf{D} = \epsilon \mathbf{E}$ ,  $\mathbf{B} = \mu \mathbf{H}$ , where  $\epsilon$  and  $\mu$  are practically unity.

**5.2. Field distribution in a steady state** (Ref. 13). When all field quantities are independent of time, the equations of § 5.1 lead to

$$\mathbf{E} = 0, \quad \rho = \rho^{(n)} + \rho^{(s)} = 0 \quad (1)$$

When in addition the superconducting matter is homogeneous, so that  $\Lambda$  is constant, the vectors  $\mathbf{B}$ ,  $\mathbf{H}$ , and  $\mathbf{j} = \mathbf{j}^{(s)}$  all obey the differential equation

$$\nabla^2 \mathbf{F} = \mathbf{F}/\lambda^2 \quad (2)$$

where  $\lambda = c\sqrt{\Lambda/4\pi}$  is a temperature-dependent length known as the *penetration depth*. In a superconducting specimen of dimensions  $\gg \lambda$  all these field quantities become practically zero in the deep interior, and near the surface are of the form

$$\mathbf{F} = \text{tangential vector} \times e^{-z/\lambda}$$

where  $z$  is the depth beneath the surface.

Any steady-state solution of the equations of § 5.1 is uniquely determined within a superconducting body by the values, over the surface of the body, of the tangential component of  $\mathbf{H}$  or of the tangential component of  $\mathbf{j}$ .

**5.3. The energy equation** (Ref. 13). In any isothermal process taking place in a superconductor we have, in the notation of § 5.1,

$$\frac{\partial}{\partial t} \left[ \frac{\mathbf{E} \cdot \mathbf{D} + \mathbf{H} \cdot \mathbf{B}}{8\pi} + \frac{\Lambda \mathbf{j}^{(s)2}}{2} \right] + \sigma E^2 + \frac{c}{4\pi} \nabla \cdot (\mathbf{E} \times \mathbf{H}) = 0 \quad (1)$$

The quantity in square brackets thus plays the role of a free-energy density.

**5.4. Critical field and its relation to entropy and specific heat** (Ref. 13). At any absolute temperature  $T$  there exists a critical value  $H_c$  of the magnetic field strength  $H$ , such that any region of a specimen of dimensions  $\gg$  the penetration depth  $\lambda$  of § 5.2 loses its superconductivity when the value of  $H$  at the boundary of this region exceeds  $H_c$ . The value of  $H_c \rightarrow 0$  as  $T \rightarrow T_c$ , the temperature above which superconductivity disappears in the absence of a field, while as  $T \rightarrow 0$ ,  $dH_c/dT \rightarrow 0$ .

At any temperature  $T < T_c$ , the transition from the superconducting to the normal state in the presence of a magnetic field  $H_c(T)$  has a latent heat given by

$$Q = T(S^{(n)} - S^{(s)}) = \frac{-Tv}{4\pi} H_c \frac{dH_c}{dT} \tag{1}$$

where  $S^{(n)}$ ,  $S^{(s)}$  are the entropies in the normal and superconducting phases, respectively, of any standard amount of the material, e.g., a mole, and  $v$  is the volume of this same amount. As in § 5.1, the field  $H_c$  is supposed measured in absolute electromagnetic units. The specific heats of the two phases, referred to this same amount of material, differ by

$$C^{(n)} - C^{(s)} = \frac{-vT}{4\pi} \left[ \left( \frac{dH_c}{dT} \right)^2 + H_c \frac{d^2H_c}{dT^2} \right] \tag{2}$$

We have also

$$Q = \frac{v}{8\pi} H_c^2 \int_T^{T_c} (C^{(n)} - C^{(s)}) dT' \tag{3}$$

**5.5. Equilibrium of normal and superconducting phases for systems of small dimensions** (Ref. 13). The condition  $H = H_c$  was given in § 5.4 for equilibrium of a large-scale superconducting region with a neighboring nonsuperconducting region. This is a special case of a more general condition which, for regions separated by a plane boundary but not necessarily thick compared with the penetration depth  $\lambda$  of § 5.2, takes the form

$$\frac{\Lambda}{2} j_t^{(s)2} = \frac{H_c^2}{8\pi} \tag{1}$$

where  $\Lambda$  is the fundamental constant of § 5.1, related to the penetration depth in § 5.2, and  $j_t^{(s)}$  is the component of superconducting current density tangential to the interface between normal and superconducting regions. If the boundary between the two regions is not plane, a term roughly of the form  $\gamma_{ns}(C_1 + C_2)$  must be added to this equation, where  $\gamma_{ns}$  is the surface tension of the interface between the two phases, and  $C_1$ ,  $C_2$  are the two principal curvatures of the interface.

For a thin film of thickness  $d$  in a tangential field the completely non-superconducting state is thermodynamically more stable than the superconducting state when

$$H > H_c \sqrt{\frac{1 + \Delta\bar{\gamma} \cdot 16\pi/H_c^2 d}{1 - (2\lambda/d) \tanh(d/2\lambda)}}$$

where  $\lambda$  is the penetration depth of § 5.2 and  $\Delta\bar{\gamma}$  is the average, over top and bottom faces of the film, of the specific surface free energy of the normal phase minus that of the superconducting phase.

**5.6. Multiply connected superconductors** (Ref. 13). Let  $C$  be any closed curve lying entirely within superconducting matter,  $S$  any finite surface bounded by  $C$ , and  $\mathbf{n}$  the local unit normal to  $S$ . With the convention that the direction of integration around  $C$  be related by the right-hand rule to the direction of  $\mathbf{n}$ , and with the notation of § 5.1, the quantity

$$\Phi_C = \iint_S \mathbf{n} \cdot \mathbf{B} dS + c \oint_C \Lambda \mathbf{j}^{(s)} \cdot d\mathbf{s} \quad (1)$$

is called the *fluxoid* through  $C$ ; it has the properties

a.  $d\Phi_C/dt = 0$  in any thermal or electromagnetic change of the system, as long as the neighborhood of  $C$  remains at all times superconducting.

b.  $\Phi_C = \Phi_{C'}$  for any two curves which can be deformed continuously into each other without passing out of superconducting matter. Thus in a simply connected superconductor every  $\Phi_C = 0$ , but in multiply connected ones a finite number of nonzero values are possible.

For a multiply connected superconductor whose dimensions (including the dimensions of the holes) are  $\gg$  the penetration depth  $\lambda$  of § 5.2, the magnetic flux through any hole is, to a good approximation, constant in time during any thermal or electromagnetic changes, i.e.,

$$\frac{d}{dt} \iint_S \mathbf{n} \cdot \mathbf{B} dS \approx 0 \quad (2)$$

where  $S$  is any surface lying in the nonsuperconducting region and bounded by the hole in question.

Under steady-state conditions the distribution of current and field in and around any multiply connected superconductor is uniquely determined by (1) the distribution of external currents and (2) either the fluxoids  $\Phi_1, \dots, \Phi_p$  for the different classes of closed curves within the superconductor, or the currents  $i_1, \dots, i_p$  in the  $p$  circuits of which the multiply connected superconductor is composed.

**5.7. General properties of time-dependent disturbances in superconductors** (Ref. 13). Let  $\mathbf{q}$  represent any of the quantities  $\mathbf{B}$ ,  $\mathbf{E}$ ,  $\mathbf{j}^{(s)}$ , or  $\mathbf{j}^{(n)}$ , in the notation of § 5.1. Within any homogeneous superconducting region all these quantities obey the differential equation

$$c^2 \nabla^2 \mathbf{q} = \frac{4\pi}{\Lambda} \mathbf{q} + 4\pi\sigma \frac{\partial \mathbf{q}}{\partial t} + \frac{\partial^2 \mathbf{q}}{\partial t^2} \quad (1)$$

In actual superconducting metals the last term on the right, which represents the effect of displacement current, is negligible compared to the others at all frequencies at which the theory is usable; the second term on the right is usually sizable only at frequencies in the microwave range and above.

In the absence of charges mechanically introduced from the outside, the volume density  $\rho$  of electric charge vanishes at all times in a superconductor.

**5.8. A-c resistance of superconductors** (Ref. 13). Let a superconducting body of dimensions  $\gg$  the penetration depth  $\lambda$  of § 5.2 be subjected to an alternating field containing the time factor  $e^{i\omega t}$ . Let  $R_c$  be the resistance, at the same frequency, of a normal conductor of the same geometry and having a conductivity  $\sigma_c$  large enough to make the skin depth  $\ll$  the dimensions of the specimen. Then the resistance of the superconducting specimen is

$$R = R_c \left( \frac{\sigma_c}{\sigma} \right)^{1/2} \frac{\lambda}{\delta} \left[ \frac{\sqrt{1 + (\lambda/\delta)^4} - 1}{1 + (\lambda/\delta)^4} \right]^{1/2} \quad (1)$$

where  $\sigma$  is the actual conductivity of the superconducting material as defined in § 5.1 and  $\delta = c/(4\pi\sigma\omega)^{1/2}$  is the skin depth which one would compute for a normal conductor of this conductivity. In the superconductor the field and current vary with depth  $z$  beneath the surface according to  $e^{-Kz}$ , where

$$K = \frac{1}{\lambda} \left[ 1 + i \left( \frac{\lambda}{\delta} \right)^2 \right]^{1/2} \quad (2)$$

These relations are based on the assumption of a homogeneous conductivity  $\sigma$ , and do not take account of the fact that even in normal conductors the effective conductivity is altered when the skin depth becomes comparable with or less than the mean free path of the conduction electrons.

**5.9. Optical constants of superconductors.** For wavelengths sufficiently far in the infrared one may reasonably expect the equation of § 5.7 to predict the optical constants correctly. The optical constants,  $n$ ,  $k$  are

defined so that a plane wave of angular frequency  $\omega$  progressing in the  $z$  direction has an amplitude proportional to

$$\exp \left( i\omega t - \frac{i\omega n z}{c} - \frac{k\omega z}{c} \right)$$

The values given by the equation of § 5.7 are, with neglect of the displacement current term,

$$n = \frac{1}{\omega} \left( \frac{2\pi}{\Lambda} \right)^{1/2} \left[ -1 + \sqrt{1 + (\omega\sigma\Lambda)^2} \right]^{1/2} \quad (1)$$

$$k = \frac{1}{\omega} \left( \frac{2\pi}{\Lambda} \right)^{1/2} \left[ 1 + \sqrt{1 + (\omega\sigma\Lambda)^2} \right]^{1/2} \quad (2)$$

where  $\Lambda$ ,  $\sigma$ , have the meanings defined in § 5.1. If  $\omega\sigma\Lambda \gg 1$  these reduce to the expressions characterizing a normal conductor (see § 10.12).

## 6. Electrostatics of Ionic Lattices

**6.1. Potential at a general point of space, by the method of Ewald** (Ref. 3). Consider first the potential due to a continuous distribution of charge whose density  $\rho(\mathbf{r})$  is arbitrary except for the requirement of over-all electrical neutrality and the periodicity condition  $\rho(\mathbf{r} + \mathbf{t}) = \rho(\mathbf{r})$  where  $\mathbf{t}$  is any translation of the crystal lattice (see § 1.1). The potential  $V(\mathbf{r})$  which satisfies Poisson's equation and the periodicity condition and has mean value zero is given by

$$V(\mathbf{r}) = V'(\mathbf{r}, \epsilon) + V''(\mathbf{r}, \epsilon) \quad (1)$$

where  $\epsilon$  is a positive number with the dimensions of reciprocal length, which may be chosen at will anywhere in the range  $0 < \epsilon < \infty$ , and where  $V'$  and  $V''$  are, respectively, a sum over the points of the reciprocal lattice of the crystal, and an integral over ordinary space. Explicitly, if  $\mathbf{K}$  is  $2\pi$  times a general vector of the reciprocal lattice (see § 1.3) and if the Fourier coefficients  $\rho_{\mathbf{K}}$  are defined by

$$\rho(\mathbf{r}) = \sum_{\mathbf{K}} \rho_{\mathbf{K}} e^{i\mathbf{K} \cdot \mathbf{r}}$$

we have

$$V'(\mathbf{r}, \epsilon) = 4\pi \sum_{\mathbf{K} \neq 0} \frac{\rho_{\mathbf{K}}}{K^2} \exp \left( -\frac{K^2}{4\epsilon^2} + i\mathbf{K} \cdot \mathbf{r} \right) \quad (2)$$

$$V''(\mathbf{r}, \epsilon) = \int_{\text{all space}} \rho(\mathbf{r}') \left[ \frac{1 - \text{Erf}(\epsilon |\mathbf{r}' - \mathbf{r}|)}{|\mathbf{r}' - \mathbf{r}|} \right] d\tau' \quad (3)$$

where Erf is the error function

$$(2/\sqrt{\pi}) \int_0^x e^{-x^2} dx$$

Since the sum for  $V'$  converges the more rapidly the smaller  $\epsilon$ , while the integral for  $V''$  converges the more rapidly the larger  $\epsilon$ , a choice  $\epsilon \sim (\text{inter-atomic spacing})^{-1}$  or a little more is usually best for computation.

For a lattice whose unit cell consists of  $p$  point charges of magnitudes  $e_i$  at positions  $\mathbf{r}_i$ , with

$$\sum_{i=1}^p e_i = 0$$

the preceding expressions specialize to

$$V'(\mathbf{r}, \epsilon) = \sum_{i=1}^p e_i \psi'(\mathbf{r} - \mathbf{r}_i, \epsilon), \quad V''(\mathbf{r}, \epsilon) = \sum_{i=1}^p e_i \psi''(\mathbf{r} - \mathbf{r}_i, \epsilon) \quad (3)$$

with 
$$\psi'(\mathbf{r}, \epsilon) = \frac{4\pi}{\Omega} \sum_{\mathbf{K} \neq 0} \frac{\exp(-K^2/4\epsilon^2 + i\mathbf{K} \cdot \mathbf{r})}{K^2}$$

$$\psi''(\mathbf{r}, \epsilon) = -\frac{\pi}{\epsilon^2 \Omega} + \sum_{\mathbf{t}} \frac{1 - \text{Erf}(\epsilon |\mathbf{t} - \mathbf{r}|)}{|\mathbf{t} - \mathbf{r}|}$$

where  $\Omega$  is the volume of the unit cell of the crystal (see § 1.2) and where the vector  $\mathbf{t}$  runs over all the translations of the crystal lattice. The function  $\psi(\mathbf{r}) = \psi'(\mathbf{r}, \epsilon) + \psi''(\mathbf{r}, \epsilon)$  represents the potential resulting from a lattice of unit positive point charges combined with an equal amount of negative charge uniformly distributed throughout space; it is therefore sometimes called the *neutralized potential* of the lattice of positive charges.

**6.2. Potential acting on an ion, by the method of Ewald (Ref. 3).**

Consider a crystal lattice whose unit cell contains a point charge  $e_i$  at position  $\mathbf{r}_i$ , plus other charges continuously or discretely distributed, the total charge density being  $\rho(\mathbf{r})$ . The work required to remove a single one of the charges of type  $i$  to a place of zero potential (defined as the space average of the potential in the lattice) is  $-e_i V_i$ , where

$$V_i = \lim_{\mathbf{r} \rightarrow \mathbf{r}_i} [V(\mathbf{r}) - e_i/r] \quad (1)$$

We have  $V_i = V'_i(\epsilon) + V''_i(\epsilon)$  where, in the notation of § 6.1,

$$V'_i(\epsilon) = -\frac{2e_i \epsilon}{\sqrt{\pi}} + 4\pi \sum_{\mathbf{K} \neq 0} \frac{\rho_{\mathbf{K}}}{K^2} \exp\left(-\frac{K^2}{4\epsilon^2} + i\mathbf{K} \cdot \mathbf{r}_i\right) \quad (2)$$

$$V''_i(\epsilon) = \int_{\text{space}} [\rho(\mathbf{r}') - e_i \delta(\mathbf{r}')] \left[ \frac{1 - \text{Erf}(\epsilon |\mathbf{r}' - \mathbf{r}_i|)}{|\mathbf{r}' - \mathbf{r}_i|} \right] d\tau' \quad (3)$$

For the special case where the lattice consists exclusively of point charges, these reduce to

$$V'_i(\epsilon) = -\frac{2e_i\epsilon}{\sqrt{\pi}} + \frac{4\pi}{\Omega} \sum_{\mathbf{K} \neq 0} \sum_{j=1}^p \frac{e_j \exp[-K^2/4\epsilon^2 + i\mathbf{K} \cdot (\mathbf{r}_i - \mathbf{r}_j)]}{K^2} \quad (4)$$

$$V''_i(\epsilon) = \sum_{\mathbf{R} \neq \mathbf{r}_i} \frac{e_{\mathbf{R}}}{|\mathbf{R} - \mathbf{r}_i|} [1 - \text{Erf}(\epsilon |\mathbf{R} - \mathbf{r}_i|)] \quad (5)$$

where  $\mathbf{R} = \mathbf{r}_j + \mathbf{t}$  runs over the position vectors of all ions of the crystal except the one  $j = i$ ,  $t = 0$ , and  $e_{\mathbf{R}} = e_j$  is the charge of the ion at  $\mathbf{R}$ .

**6.3. Potential due to an infinite linear array, by the method of Madelung** (Ref. 3). Let an infinite line array of charges consist of  $p$  kinds of charges  $e_j$ , the  $j$ th kind being located at positions  $x_j, x_j \pm t, x_j \pm 2t$ , etc., along a line, and let the array be neutral, so that

$$\sum_{j=1}^p e_j = 0$$

Then we have for the potential at a point whose coordinate along the line is  $x$  and whose distance from the line is  $r$ ,

$$V(x, r) = \frac{4}{t} \sum_{n=1}^{\infty} \sum_{j=1}^p e_j K_0\left(\frac{2\pi nr}{t}\right) \cos\left[\frac{2\pi n(x - x_j)}{t}\right] \quad (1)$$

where  $K_0(z) = (\pi i/2)H_0^{(1)}(iz)$  is the modified Bessel function of the second kind.

**6.4. Potential acting on an ion in a linear array, by the method of Madelung** (Ref. 2). For the array of § 6.3 the potential produced at the position of one of the charges of type  $i$  by all the other charges is

$$V_i = -\frac{1}{t} \sum_{j \neq i} \left[ \Psi\left(\frac{x_j - x_i}{t}\right) + \Psi\left(\frac{t + x_i - x_j}{t}\right) \right] + 2 \frac{\gamma e_i}{t} \quad (1)$$

where  $\Psi(z) = d \log \Gamma(z)/dz$ , and  $\gamma = 0.5772$  is Euler's constant.

**6.5. Potential due to a plane array, by the method of Madelung** (Ref. 2). Let  $\mathbf{t}_1, \mathbf{t}_2$  be the fundamental translations of a two-dimensional

lattice in the  $x$ - $y$  plane, and let the unit parallelogram of this lattice contain charges  $e_j$  at positions  $\mathbf{r}_j$  ( $j = 1$  to  $p$ ) with

$$\sum_{j=1}^p e_j = 0$$

Then the potential at any point  $\mathbf{r} = (x, y, z)$  is

$$V(x, y, z) = \frac{2\pi}{|\mathbf{t}_1 \times \mathbf{t}_2|} \sum_j \sum_{\mathbf{K} \neq 0} \frac{e_j e^{-K|z|} e^{i\mathbf{K} \cdot (\mathbf{r} - \mathbf{r}_j)}}{K} \quad (1)$$

where  $\mathbf{K}/2\pi$  runs over the lattice of vectors in the  $x$ - $y$  plane reciprocal to that generated by  $\mathbf{t}_1, \mathbf{t}_2$ , i.e.,  $\mathbf{K} \cdot \mathbf{t}_1/2\pi = \text{integer}$ ,  $\mathbf{K} \cdot \mathbf{t}_2/2\pi = \text{integer}$ .

### 7. Thermal Vibrations

**7.1. Normal modes of a crystal** (Ref. 20). Let  $\mathbf{r}^{jl}$  be the position vector of the  $j$ th atom in the  $l$ th unit cell of a crystal in equilibrium, where  $j$  runs from 1 to  $s$ , where  $s$  is the number of atoms per unit cell; let  $\mathbf{u}^{jl}$  be the displacement of this atom from its equilibrium position. If the atoms are bound to each other by harmonic forces and if they are subjected to periodic boundary conditions (see § 1.4) at the edges of the crystal the normal modes of vibration have displacements  $u_\mu^{j'l}$  ( $\mu = 1$  to 3) proportional to

$$u_\mu^{j'l}(\mathbf{k}, n) = \text{Re}\{A_\mu^j(\mathbf{q}, n) \exp [i(\mathbf{q} \cdot \mathbf{r}^{jl} - \omega_{qn}t)]\} \quad (1)$$

where  $\text{Re}$  means “real part of,” the vector  $\mathbf{q}$  and the index  $n$  label the various normal modes,  $\omega_{qn}$  is the angular frequency of the normal mode in question, and the  $3s$  quantities  $A_\mu^j(\mathbf{q}, n)$  are determined to within a constant factor by a secular equation involving the atomic masses and the interatomic force constants. The allowed values of  $\mathbf{q}$  are distributed almost continuously over the first Brillouin zone (see § 1.3) in reciprocal lattice space, with the density  $v/8\pi^3$ , where  $v$  is the volume of the crystal. The index  $n$  takes on  $3s$  values, corresponding to  $3s$  bands or branches of the vibrational spectrum. For three of these, which may be designated by  $n = 1, 2, 3$ , and for any given direction of  $\mathbf{q}$ ,

$$\omega_{qn} \rightarrow \text{constant } \mathbf{q} \text{ as } \mathbf{q} \rightarrow 0, \quad (n = 1 \text{ to } 3) \quad (2)$$

and

$$A_\mu^j(\mathbf{q}, n) \sim A_\mu^i(\mathbf{q}, n), \quad (\text{for all } i, j) \quad (3)$$

These are called the *acoustical branches*. For the other branches  $\omega_{qn} \rightarrow \text{finite limit as } \mathbf{q} \rightarrow 0$  ( $n > 3$ ), and the  $A_\mu^j$  for different  $j$  may remain different; these are often called the *optical branches*.

For small  $q$  the asymptotic frequencies and  $A_\mu^j$  of the acoustical branches can be expressed in terms of the elastic constants of the crystal. The secular equation determining the limiting ratios  $\omega_{qn}/q$  is (Ref. 3)

$$\left| \sum_{\alpha, \beta=1}^3 c_{\mu\alpha\nu\beta} q_\alpha q_\beta - \rho \omega_{qn}^2 \delta_{\mu\nu} \right| = 0 \quad (4)$$

where  $\mu$  and  $\nu$  label the rows and columns of the determinant,  $\rho$  is the density of the crystal, and  $c_{\mu\nu\alpha\beta}$  is the elastic constant tensor defined by the equation

$$\hat{p}_{\mu\alpha} = \sum_{\nu, \beta=1}^3 c_{\mu\alpha\nu\beta} u_{\nu\beta} \quad (5)$$

relating the stress tensor  $\hat{p}_{\mu\alpha}$  to the strain tensor  $u_{\nu\beta}$ . For cubic crystals the only nonvanishing components of  $c_{\mu\alpha\nu\beta}$  are, relative to the "natural" axes of § 2.1,  $c_{\alpha\alpha\alpha\alpha} = c_{11}$ ,  $c_{\alpha\alpha\beta\beta} = c_{12}$ ,  $c_{\alpha\beta\alpha\beta} = c_{\alpha\beta\beta\alpha} = c_{44}$ , where  $\alpha$  and  $\beta$  take on any values from 1 to 3 ( $\alpha \neq \beta$ ) and where the  $c_{ij}$  are the usual elastic constants as defined in § 2.2.

**7.2. Thermodynamic functions, general case** (Ref. 22). At any absolute temperature  $T$  the energy  $U$ , free energy  $F$ , and entropy  $S$  of a crystal whose atoms are bound by harmonic forces can be expressed as sums of terms involving the frequencies  $\omega_{qn}$  of the various normal modes, as follows

$$U = U_0 + \sum_{qn} \frac{\hbar\omega_{qn}}{\exp(\hbar\omega_{qn}/kT) - 1} \quad (1)$$

$$F = U_0 + kT \sum_{qn} \ln [1 - \exp(-\hbar\omega_{qn}/kT)] \quad (2)$$

$$S = k \sum_{qn} \left\{ -\ln [1 - \exp(-\hbar\omega_{qn}/kT)] + \frac{(\hbar\omega_{qn}/kT)}{\exp(\hbar\omega_{qn}/kT) - 1} \right\} \quad (3)$$

where  $\hbar$  is Planck's constant divided by  $2\pi$ ,  $k$  is Boltzmann's constant, and  $U_0$  is the energy of the crystal at the absolute zero, including the zero point energy

$$\frac{1}{2} \sum_{qn} \hbar\omega_{qn}$$

The molar specific heat  $C_v$  is given by

$$C_v = 3sR \left\{ \frac{(\hbar\omega_{qn}/kT)^2 \exp(\hbar\omega_{qn}/kT)}{[\exp(\hbar\omega_{qn}/kT) - 1]^2} \right\}_{\text{av on } q,n} \quad (4)$$

where  $R$  is the gas constant.

**7.3. Thermodynamic functions at high temperatures** (Refs. 9 and 24). If  $kT < \hbar\omega_{\max}/2\pi$ , where  $\omega_{\max}$  is the highest frequency occurring for any of the normal modes, the energy and specific heat of the crystals of § 7.2 can be expanded into convergent series in powers of  $1/T$ . For a crystal containing  $N$  unit cells of  $s$  atoms each, the series for the energy is

$$U = U_0 + 3Ns \left[ kT - \frac{1}{2} \langle \hbar\omega \rangle_{\text{av}} + \sum_{p=1}^{\infty} \frac{B_{2p} \langle (\hbar\omega)^{2p} \rangle_{\text{av}}}{2p!(kT)^{2p-1}} \right] \quad (1)$$

where  $\langle (\hbar\omega)^{2p} \rangle_{\text{av}}$  is the average over all normal modes  $k, n$  of  $(\hbar\omega_{kn})^{2p}$ , and where  $B_{2p}$  are the Bernoulli numbers  $B_2 = \frac{1}{6}$ ,  $B_4 = -\frac{1}{30}$ ,  $B_6 = \frac{1}{42}$ ,  $B_8 = -\frac{1}{30}$ ,  $B_{10} = \frac{5}{66}$ , .... The molar specific heat can be obtained from this by differentiation, since for the case  $Nk = R$ ,  $C_v = \partial U/\partial T$ . The corresponding series for the entropy is

$$S = -k \sum_{q,n} \ln(\hbar\omega_{qn}/kT) + 3Nsk \left[ 1 + \sum_{p=1}^{\infty} \frac{B_{2p} \langle (\hbar\omega)^{2p} \rangle_{\text{av}}}{(2p)^2(2p-2)!(kT)^{2p}} \right] \quad (2)$$

**7.4. Thermodynamic functions at low temperatures** (Ref. 9). At sufficiently low temperatures the only normal modes to be appreciably excited will be those for which  $\omega_{qn}$  is practically proportional to  $q$  and calculable in terms of the elastic constants by means of the secular equation given in § 7.1. In this low frequency region the number of normal modes with angular frequencies in the range  $\omega$  to  $\omega + d\omega$  is

$$f(\omega)d\omega = \frac{3v}{2\pi^2} \left\langle \frac{1}{V^3} \right\rangle_{\text{av}} \omega^2 d\omega = 9Ns \left( \frac{\hbar}{k\Theta} \right)^3 \omega^2 d\omega \quad (1)$$

where  $v$  is the volume of the crystal containing  $N$  unit cells of  $s$  atoms each,  $V$  is the velocity  $\omega_{qn}/q$  of a sound wave, the average being taken over all directions of propagation and over the three states of polarization, and where  $\Theta$  is an effective Debye temperature (see § 7.5) defined by

$$k\Theta = \hbar \left( \frac{6\pi^2}{\left\langle \frac{1}{V^3} \right\rangle_{\text{av}}} \cdot \frac{Ns}{v} \right)^{1/3} \quad (2)$$

In terms of these quantities the asymptotic values of the energy, free energy, entropy, and molar specific heat of the crystal are, respectively

$$U \sim U_0 + \frac{\pi^2}{10} v \left\langle \frac{1}{V^3} \right\rangle_{\text{av}} \frac{(kT)^4}{\hbar^3} = U_0 + \frac{3\pi^4}{5} \left( \frac{T}{\Theta} \right)^4 Nsk\Theta \quad (3)$$

$$F \sim U_0 - \frac{\pi^2}{30} v \left\langle \frac{1}{V^3} \right\rangle_{\text{av}} \frac{(kT)^4}{\hbar^3} = U_0 - \frac{\pi^4}{5} \left( \frac{T}{\Theta} \right)^4 Nsk\Theta \quad (4)$$

$$S \sim \frac{4\pi^4}{5} \left(\frac{T}{\Theta}\right)^3 Nsk, \quad C_v \sim \frac{12\pi^4}{5} \left(\frac{T}{\Theta}\right)^3 sR = 233.8 \left(\frac{T}{\Theta}\right)^3 sR \quad (5)$$

**7.5. Debye approximation** (Refs. 3, 9, and 22). A useful approximation to the distribution of normal modes in frequency is to take for the number of modes in the range  $\omega$  to  $\omega + d\omega$  of angular frequencies

$$\left. \begin{aligned} f(\omega)d\omega &= 9Ns \left(\frac{\hbar}{k\Theta_D}\right)^3 \omega^2 d\omega, \approx (\text{for } \hbar\omega < k\Theta_D) \\ &= 0 \quad (\text{for } \hbar\omega > k\Theta_D) \end{aligned} \right\} (1)$$

where  $N$  is the number of unit cells in the crystal,  $s$  is the number of atoms per cell, and  $\Theta_D$  is a parameter called the *Debye temperature* which is to be chosen empirically. This gives for the energy, free energy, entropy, and molar specific heat, respectively,

$$U = U_0 + 3NskTD \left(\frac{\Theta_D}{T}\right) \quad (2)$$

$$F = U_0 + NskT \left[ 3 \ln(1 - e^{-\Theta_D/T}) - D \left(\frac{\Theta_D}{T}\right) \right] \quad (3)$$

$$S = Nsk \left[ 4D \left(\frac{\Theta_D}{T}\right) - 3 \ln(1 - e^{-\Theta_D/T}) \right] \quad (4)$$

$$C_v = 3sR \left[ 4D \left(\frac{\Theta_D}{T}\right) - \frac{3\Theta_D/T}{e^{\Theta_D/T} - 1} \right] \quad (5)$$

where the function  $D(x)$  is defined by

$$D(x) = \frac{3}{x^3} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1}$$

so that  $D(0) = 1$ ,  $D(\infty) = 0$ .

The asymptotic values of these expressions for  $U$ ,  $F$ ,  $S$ , and  $C_v$  at low temperatures are given by the formulas of § 7.4 with  $\Theta_D$  substituted for  $\Theta$ . At temperatures above  $\Theta_D/2\pi$ ,

$$D \left(\frac{\Theta_D}{T}\right) = 1 - \frac{3}{8} \cdot \frac{\Theta_D}{T} + 3 \sum_{p=1}^{\infty} \frac{B_{2p}}{(2p+3)2p!} \left(\frac{\Theta_D}{T}\right)^{2p} \quad (6)$$

while at any temperature

$$\left. \begin{aligned} D \left(\frac{\Theta_D}{T}\right) &= \frac{\pi^4}{5} \left(\frac{T}{\Theta_D}\right)^3 + 3 \ln(1 - e^{-\Theta_D/T}) \\ &- 9 \sum_{p=1}^{\infty} \frac{[(T/\Theta_D)p^2 + 2(T/\Theta_D)p + 2(T/\Theta_D)^3] e^{-p\Theta_D/T}}{p^4} \end{aligned} \right\} (7)$$

The zero point energy of the normal modes in the present approximation is

$$\frac{1}{2} \sum_{q,n} \hbar \omega_{qn} = \frac{9}{8} N s k \Theta_D \quad (8)$$

**7.6. Equation of state for a crystal** (Ref. 22). If the interatomic forces were strictly harmonic, as has been assumed in the preceding sections, a crystal would show no thermal expansion, and in the equation of state the pressure would be a function of the volume but not of the temperature. The slight departures from harmonicity which actually occur do not, however, necessitate abandoning the formalism of the harmonic approximation; for many purposes they can be taken adequately into account by retaining the preceding expressions for energy, etc., but allowing the frequencies of the normal modes to depend on volume and state of strain. This gives for the pressure corresponding to any volume  $v$ ,

$$p = - \frac{dU_0}{dv} + \frac{1}{v} \sum_{q,n} \frac{\gamma_{qn} \hbar \omega_{qn}}{\exp(\hbar \omega_{qn}/kT) - 1} \quad (1)$$

where, as before,  $U_0$  is the energy in the absence of thermal vibrations but including zero point energy, and

$$\gamma_{qn} = - \frac{d \ln \omega_{qn}}{d \ln v} \quad (2)$$

A common approximation is to assume that  $\gamma_{qn}$  has the same value  $\gamma$  for all normal modes. For this case we have the Mie-Grüneisen equation of state

$$p = - \frac{dU_0}{dv} + \gamma \frac{(U - U_0)}{v} \quad (3)$$

and the linear thermal expansion coefficient is

$$\alpha = \frac{1}{3v} \left( \frac{\partial v}{\partial T} \right)_p = \frac{\kappa \gamma}{3v_m} C_v \quad (4)$$

where  $\kappa$  is the volume compressibility,  $v_m$  the molar volume, and  $C_v$  the molar specific heat at constant volume. If the Debye approximation is used,  $\gamma = - d \ln \Theta / d \ln v$ .

**7.7. Long wavelength optical modes of polar crystals** (Ref. 15).

Consider first a crystal of cubic symmetry containing two ions per unit cell. The normal vibrations of the optical branches (see § 7.1) can then, in the limit of long wavelengths, be characterized as longitudinal (one branch with atomic displacements parallel to the wave vector  $\mathbf{q}$ ) or transverse (two branches with displacements perpendicular to  $\mathbf{q}$ ). As  $\mathbf{q} = 2\pi/\text{wavelength} \rightarrow 0$ ,

let the angular frequency of the longitudinal branch approach  $\omega_l$ , that of the transverse branches  $\omega_t$ . Then if  $\kappa$ ,  $\kappa_0$  represent, respectively, the static dielectric constant and the dielectric constant at frequencies  $\gg \omega_l$  and  $\omega_t$ , but  $\ll$  the frequencies of electronic transitions,

$$\frac{\omega_l^2}{\omega_t^2} = \frac{\kappa}{\kappa_0} \quad (1)$$

Let  $M_1$ ,  $M_2$  be the masses of the two kinds of ions and  $\mu = (1/M_1 + 1/M_2)^{-1}$  the reduced mass. Let  $e_{\text{eff}}$  be the effective charge on an ion, defined by the equation

$$\text{Force} = -e_{\text{eff}}E$$

for the force which would have to be applied to each ion to hold it in its original position in the presence of a uniform macroscopic electric field  $E$ . Then if  $\Omega$  is the volume of the unit cell, i.e., the volume per ion pair

$$\mu\omega_t^2 = \frac{4\pi e_{\text{eff}}^2}{\Omega(\kappa - \kappa_0)} \quad (2)$$

The preceding formulas can be applied to noncubic diatomic crystals if the atomic displacements for the two modes considered lie along a symmetry axis, so that for the longitudinal mode  $q$  lies along this axis, for the transverse mode at right angles to it. For this case  $\kappa$  and  $\kappa_0$  must be interpreted as the dielectric constants in the direction of the atomic displacement.

These formulas can also be applied to those polyatomic binary compounds, e.g., those with the fluorite structure, whose crystal symmetry requires all atoms of each element to have the same displacement in an optical mode of infinite wavelength. In such cases  $M_1$ ,  $M_2$ ,  $e_{\text{eff}}$  are to be replaced by the sums of the masses or effective charges, respectively, of all ions of the same element in a unit cell.

**7.8. Residual rays** (Ref. 8). The reflection coefficient of an ionic crystal for infrared radiation at normal incidence possesses a maximum at a wavelength  $\lambda_R$ , called the residual ray wavelength, somewhat shorter than the wavelength  $\lambda_t = 2\pi c/\omega_t$  which resonates with the transverse optical normal mode defined in § 7.7. If the optical constants in the frequency range under consideration can be represented as arising from slightly damped normal vibrations of the transverse optical branch, we have for diatomic cubic crystals

$$1/\lambda_t^2 = 1/\lambda_R^2 - \frac{N^2 e_{\text{eff}}^2 \rho}{2\pi c^2 A_1 A_2 \kappa_0} \quad (1)$$

where  $N$  is Avogadro's number,  $e_{\text{eff}}$  is the effective charge on an ion as defined in § 7.7,  $\rho$  is the density,  $c$  is the velocity of light,  $A_1$  and  $A_2$  are the atomic weights of the two kinds of ions, and  $\kappa_0$  is the dielectric constant at frequencies  $\gg \omega_i$  but  $\ll$  the frequencies of electronic transitions.

This formula can be applied to noncubic and polyatomic binary crystals under the conditions described in § 7.7; for the polyatomic case  $A_1, A_2, e_{\text{eff}}$  must be replaced by sums of these quantities over all ions of a given element in a unit cell.

## 8. Dislocation Theory

**8.1. Characterization of dislocations** (Ref. 18). A *dislocation* in a crystal lattice is a region of departure from the normal lattice arrangement, localized in the neighborhood of an endless line or curve, called the dislocation line, and with the properties: (1) the atomic arrangement in the regions well away from the dislocation line agrees with that in a perfect crystal lattice except for a small elastic distortion, so that each vector  $\mathbf{t}$  from an atom to one of its near neighbors can be placed in unambiguous correspondence with a vector  $\mathbf{t}^{(0)}$  of the perfect lattice; (2) if we select any sequence of atomic positions lying along a closed path avoiding the neighborhood of the dislocation line but enclosing this line, then for the sum of the vectors associated with successive pairs of neighboring atoms along this path we have

$$\Sigma \mathbf{t} = 0 \quad \text{by definition, but} \quad \Sigma \mathbf{t}^{(0)} = \mathbf{t}' \neq 0$$

where  $\mathbf{t}'$ , a translation vector of the undistorted lattice, is the same for all paths encircling the dislocation line in the same sense (paths encircling it in the opposite direction merely give  $\Sigma \mathbf{t}^{(0)} = -\mathbf{t}'$ ), and is called the *slip vector*, or *Burgers vector*, of the dislocation.

**8.2. Force on a dislocation** (Ref. 17). Consider any dislocation line and let  $\mathbf{t}$ ,  $\nu$  be, respectively, the slip vector of the dislocation and the unit vector along the dislocation line, the directions of these vectors being so specified that, in the notation of § 8.1,  $\Sigma \mathbf{t}^{(0)} = \mathbf{t}$  for circuits taken in the right-hand sense with respect to the direction of  $\nu$ . The force  $dF$  on each element of length of the dislocation is defined by setting the change in elastic energy or free energy, which would accompany any virtual shift of the dislocation line, equal to  $-\int \delta \mathbf{r} \cdot dF$ , where  $\delta \mathbf{r}$  is the arbitrary virtual displacement of any point of the dislocation line and the integration is over all elements  $ds$  along the length of the dislocation line. It is given by

$$dF = \nu \times T^{(t)} | \mathbf{t} | ds \quad (1)$$

where  $T^{(t)}$  is the traction exerted across a plane normal to the slip vector  $\mathbf{t}$  by that portion of the stress field due to sources other than the immediately neighboring parts of the dislocation being considered; explicitly,

$$T_{\alpha}^{(t)} |\mathbf{t}| = \sum_{\beta} t_{\beta} \bar{p}_{\beta\alpha} \quad (2)$$

where if  $\mathbf{r}$  is a vector measured from a point on the dislocation line and  $p_{\beta\alpha}$  is the total stress tensor in the crystal lattice (with the sign convention of § 2.1, which makes tensile stresses positive),

$$\bar{p}_{\beta\alpha} = \lim_{r \rightarrow 0} \frac{1}{2} [p_{\beta\alpha}(\mathbf{r}) + p_{\beta\alpha}(-\mathbf{r})] \quad (3)$$

The limit is independent of the direction of  $\mathbf{r}$  provided  $\mathbf{r}$  is interpreted in the macroscopic sense, i.e.,  $\mathbf{r} \gg$  atomic dimensions, an interpretation which is in fact necessary if the stress is to be treated as a smoothly varying function of position.

### 8.3. Elastic field of a dislocation in an isotropic medium.

Consider a dislocation line lying along the  $z$  axis in an elastically isotropic crystal, and let its slip vector  $\mathbf{t}$  (defined by the equation of 8.1 for a right-hand circuit about the positive  $z$  direction) have components  $t_x, 0, t_z$ . In terms of the shear modulus  $G$  (equals the  $\mu$  of § 2.3) and Poisson's ratio  $\sigma$  the stress tensor (defined as in § 2.1 so that tensions are positive) is, at points sufficiently far from the dislocation line for elasticity theory to be applicable,

$$\left. \begin{aligned} p_{xx} &= \frac{G}{2\pi(1-\sigma)} \frac{t_x y (3x^2 + y^2)}{(x^2 + y^2)^2} \\ p_{yy} &= \frac{G}{2\pi(1-\sigma)} \frac{t_x y (y^2 - x^2)}{(x^2 + y^2)^2} \\ p_{zz} &= 0 \\ p_{yz} &= -\frac{G}{2\pi} \frac{t_z x}{(x^2 + y^2)} \\ p_{zx} &= \frac{G}{2\pi} \frac{t_z y}{(x^2 + y^2)} \\ p_{xy} &= \frac{G}{2\pi(1-\sigma)} \frac{t_x x (y^2 - x^2)}{(x^2 + y^2)^2} \end{aligned} \right\} \quad (1)$$

The elastic displacement  $\mathbf{u}$  of the medium from its unstrained state has the components

$$\left. \begin{aligned} u_x &= -\frac{t_x}{2\pi} \arctan \frac{y}{x} - \frac{t_x}{4\pi(1-\sigma)} \frac{xy}{(x^2+y^2)} \\ u_y &= \frac{(1-2\sigma)t_x}{4\pi(1-\sigma)} \ln(x^2+y^2)^{1/2} + \frac{t_x}{4\pi(1-\sigma)} \frac{x^2}{(x^2+y^2)} \\ u_z &= -\frac{t_z}{2\pi} \arctan \frac{y}{x} \end{aligned} \right\} \quad (2)$$

These are of course multivalued, since  $\mathbf{u}$  must change by  $\mathbf{t}$  in going around the dislocation. The dilatation is

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = \frac{(1-2\sigma)}{2\pi(1-\sigma)} \frac{t_x y}{(x^2+y^2)} \quad (3)$$

## 9. Semiconductors

**9.1. Bands and effective masses.** Let some reference state for a single electron be chosen, e.g., the state of rest outside the crystal, and assigned the energy zero. Relative to this reference state the energy  $\epsilon_c$  of the *bottom of the conduction band* may then be defined for any nonmetallic crystal as the least energy required to take an electron from the reference state and place it in a region of the crystal where there are no lattice imperfections. The energy  $\epsilon_v$  of the *top of the valence band* is similarly defined as the negative of the least energy required to remove an electron from a perfect region of this type and place it in the reference state. The latter process creates an electron deficiency or *hole* in the crystal. In both cases the extra electron or hole with the least possible energy in the crystal always has zero mean velocity. The minimum energy of creation of an electron or hole with a given infinitesimal mean velocity  $\bar{v}$  is, respectively,

$$\epsilon_c + \frac{1}{2}m_e^* \bar{v}^2 + O(\bar{v}^4) \quad \text{or} \quad -\epsilon_v + \frac{1}{2}m_h^* \bar{v}^2 + O(\bar{v}^4)$$

where  $m_e^*$  or  $m_h^*$  is called the *effective mass* of the electron or hole, respectively. The effective mass is usually assumed independent of the direction of motion, but may depend on this direction if the crystal is of lower than cubic symmetry or if the band in question is *degenerate*, i.e., if there exist two or more orthogonal quantum states for the electron or hole having the same energy, the same spin, and zero mean velocity.

**9.2. Density of states** (Refs. 20 and 21). If the conduction band is nondegenerate (see § 9.1) a crystal of volume  $\Omega_N$  contains  $\nu(\epsilon)d\epsilon$  quantum states for an extra or *conduction* electron having energies in the range  $\epsilon_e + \epsilon$  to  $\epsilon_e + \epsilon + d\epsilon$ , where for small  $\epsilon$  the asymptotic form of  $\nu(\epsilon)$  is

$$\left. \begin{aligned} \nu(\epsilon) &= \frac{2^{7/2} \pi m_e^{*3/2} \Omega_N}{h^3} \epsilon^{1/2} \\ \frac{\nu(\epsilon)}{\Omega_N} &= 6.814 \times 10^{21} \left( \frac{m_e^*}{m} \right)^{3/2} \left( \frac{\epsilon}{1\text{eV}} \right)^{1/2} \text{ per cm}^3 \end{aligned} \right\} (1)$$

per electron volt, where  $h$  is Planck's constant and  $m$  the true mass of the electron. Half of these states have one direction of spin, half the other. An analogous expression applies for holes.

**9.3. Traps, donors, and acceptors.** Associated with impurities and other imperfections in the crystal lattice there may be localized discrete energy levels for an electron. If the work  $\epsilon_a$  required to take an electron from the reference state of zero energy and place it at the imperfection satisfies  $\epsilon_v < \epsilon_a < \epsilon_c$ , the imperfection is called an *electron trap*; if the work  $-\epsilon_i$  required to remove an electron from the imperfection into the reference state satisfies  $\epsilon_v < \epsilon_i < \epsilon_c$ , it is called a *hole trap*. Of course, electron trap + electron  $\rightarrow$  hole trap, hole trap + hole  $\rightarrow$  electron trap. A trap which is electrically neutral when it is a hole trap, hence positively charged when it is electron trap, is called a *donor center*; one which is negative when a hole trap and neutral when an electron trap is called an *acceptor center*.

**9.4. The Fermi-Dirac distribution** (Ref. 21). Let  $i$  label the members of a set of quantum states for an electron, and let  $N_i = 0$  or  $1$  be the number of electrons in the  $i$ th state. Suppose first that all combinations of values of the  $N_i$  are statistically possible, and that the dependence of the total energy  $E$  of the system on the  $N_i$  is given by  $E = \text{constant} + \sum N_i \epsilon_i$ , where  $\epsilon_i$  is the energy of the  $i$ th state. Then in thermal equilibrium at absolute temperature  $T$  the fraction of the time that state  $i$  is occupied is

$$\langle N_i \rangle_{\text{av}} = f(\epsilon_i, \epsilon_F) = \frac{1}{\exp [(\epsilon_i - \epsilon_F)/kT] + 1} \quad (1)$$

where  $k$  is Boltzmann's constant and  $\epsilon_F$  is a quantity known as the *Fermi level* and dependent on the mean total number of electrons in the system. The function  $f$  is called the *Fermi-Dirac distribution function*. The quantity  $\epsilon_F$  is in the present case identical with the thermodynamically defined

*electrochemical potential* of the electrons, and must have the same value in any two systems or regions which are in thermal equilibrium with each other. Its value in any large homogeneous region is determined by the requirement that the total number of electrons in all states must be such as to make the region electrically neutral.

The assumptions of the preceding paragraph, though approximately correct for the free electron and hole states enumerated in § 9.2, are not fulfilled by the trap states defined in § 9.3. For example, a donor center of energy  $\epsilon_d$  may correspond to two quantum states with different spin directions, yet if both of these states were occupied the energy would be  $\gg 2\epsilon_d$  because of the electrostatic interaction of the two electrons. To generalize the Fermi distribution to include cases like this let  $g_0$  be the statistical weight of a particular trap  $t$  when the trap is empty, let  $g_1$  be the statistical weight when there is one electron in the trap, and suppose for simplicity that other values of the charge on the trap are so improbable statistically that they can be neglected. Then if  $\epsilon_t$  is the work required to take an electron from the state of zero energy and put it in the initially empty trap, the fraction of the time the trap is occupied under thermal equilibrium conditions is

$$\langle N_t \rangle_{av} = \frac{1}{(g_0/g_1) \exp [(\epsilon_t - \epsilon_F)/kT] + 1} \quad (2)$$

**9.5. Density of mobile charges** (Refs. 20 and 21). When the conduction band is nondegenerate and the density of conduction electrons is sufficiently low so that their mutual interactions can be neglected, the value of this density in thermal equilibrium at any absolute temperature  $T$  can be obtained by integrating § 9.2 over the Fermi-Dirac distribution. If  $\epsilon_F$  is the Fermi level and if  $\epsilon_c - \epsilon_F \gg kT$ , where  $k$  is Boltzmann's constant, this equilibrium density of conduction electrons is well approximated by

$$\left. \begin{aligned} n_e &= \frac{2(2\pi m_e^* kT)^{3/2}}{h^3} \exp\left(-\frac{\epsilon_F - \epsilon_c}{kT}\right) \\ &= 1.4843 \times 10^{20} \left(\frac{m_e^*}{m} \cdot \frac{T}{1000}\right)^{3/2} \exp\left(-\frac{\epsilon_F - \epsilon_c}{kT}\right) \text{ per cm}^3 \end{aligned} \right\} \quad (3)$$

With corresponding assumptions the equilibrium density of holes,  $n_h$ , is given by the same expression with  $m_h^*$  substituted for  $m_e^*$  and  $\epsilon_v - \epsilon_F$  for  $\epsilon_F - \epsilon_c$ .

**9.6. Fermi level and density of mobile charges, intrinsic case** (Ref. 21). If the number of traps per unit volume is  $\ll n_e$  as given by § 9.5 with  $\epsilon_c - \epsilon_F = (\epsilon_c - \epsilon_v)/2$ , the energy  $\epsilon_F$  of the Fermi level and the densities of electrons and holes become independent of the number and nature of the traps and the conduction is called *intrinsic*. Explicitly, for this case and when the other conditions of § 9.5 are fulfilled,

$$\epsilon_F = \frac{\epsilon_c + \epsilon_v}{2} + \frac{3kT}{4} \ln \frac{m_h^*}{m_e^*} \quad (4)$$

$$\left. \begin{aligned} n_e = n_h &= \frac{2(2\pi\sqrt{m_e^* m_h^*} kT)^{3/2}}{h^3} \exp \left[ -\frac{(\epsilon_c - \epsilon_v)}{2kT} \right] \\ &= 1.4843 \times 10^{20} \left( \frac{m_e^*}{m} \cdot \frac{m_h^*}{m} \right)^{3/4} \left( \frac{T}{1000} \right)^{3/2} \exp \left[ -\frac{(\epsilon_c - \epsilon_v)}{2kT} \right] \text{ per cm}^3 \end{aligned} \right\} \quad (5)$$

**9.7. Fermi level and density of mobile charges, extrinsic case.** When the condition of § 9.6 is not fulfilled, the position of the Fermi level depends on the densities of the various kinds of traps present and their energies. In the lower parts of the temperature range either the density of mobile electrons will be many times that of mobile holes or the reverse, and the conduction is called *extrinsic*. If electrons predominate, the material is said to be *n-type*, if holes, *p-type*. In all cases, however, the product  $n_e n_h$  of electron and hole densities equals the square of the expression in § 9.6, provided the conditions of § 9.5 are fulfilled.

While no simple analytical expression can be given for the density of mobile charges in the most general case, there is a case which can be treated fairly simply and which is still sufficiently broad to include many actual semiconductors. For an *n-type* specimen this case is one in which: (1) only a single kind of donor center is present; (2) the acceptor centers, present in smaller concentration, all have energies sufficiently low so that throughout the temperature range of interest the number of holes trapped at the acceptors can be neglected; (3) the conditions of § 9.5 are fulfilled. An exactly similar case of course occurs for a *p-type* specimen when the roles of donors and electrons are interchanged with those of acceptors and holes, respectively.

For an *n-type* specimen satisfying the conditions just mentioned let  $n_a$ ,  $n_d$  and  $\epsilon_d$  be, respectively, the density of acceptor centers, the density of donor centers, and the energy of an electron in a donor center, and let  $g_{0d}/g_{1d}$  be the ratio of the statistical weights of empty and occupied donor centers.

Define

$$\begin{aligned} n_{0e}(T) &= \frac{2(2\pi m_e^* kT)^{3/2}}{h^3} \frac{g_{0d}}{g_{1d}} \exp \left[ -\frac{(\epsilon_c - \epsilon_d)}{kT} \right] \\ &= 1.4843 \times 10^{20} \left( \frac{m_e^*}{m} \cdot \frac{T}{1000} \right)^{3/2} \frac{g_{0d}}{g_{1d}} \exp \left[ -\frac{(\epsilon_c - \epsilon_d)}{kT} \right] \end{aligned}$$

Then the actual density of mobile electrons at any temperature is

$$n_e = \frac{1}{2} \left\{ \left[ 1 + \frac{4n_{0e}(n_d - n_a)}{(n_{0e} + n_a)^2} \right]^{1/2} - 1 \right\} (n_{0e} + n_a) \quad (1)$$

For a *p*-type specimen satisfying the analogous conditions let  $\epsilon_a$  be the energy of an electron in an acceptor level, and let  $g_{0a}/g_{1a}$  be defined as the ratio of the statistical weight of an acceptor center when negatively charged to that when neutral. Define

$$\begin{aligned} n_{0h}(T) &= \frac{2(2\pi m_h^* kT)^{3/2}}{h^3} \cdot \frac{g_{0a}}{g_{1a}} \exp \left[ -\frac{(\epsilon_a - \epsilon_v)}{kT} \right] \\ &= 1.4843 \times 10^{20} \left( \frac{m_h^*}{m} \cdot \frac{T}{1000} \right)^{3/2} \frac{g_{0a}}{g_{1a}} \exp \left[ -\frac{(\epsilon_a - \epsilon_v)}{kT} \right] \end{aligned}$$

Then the density of mobile holes is

$$n_h = \frac{1}{2} \left\{ \left[ 1 + \frac{4n_{0h}(n_a - n_d)}{(n_{0h} + n_d)^2} \right]^{1/2} - 1 \right\} (n_{0h} + n_d) \quad (2)$$

**9.8. Mobility, conductivity, and diffusion** (Ref. 21). In the presence of an electric field  $E$  an electron in the conduction band will migrate with a time average velocity  $\langle v_e \rangle_{av}$  which is to a good approximation proportional to the field if  $E$  is not too large. Holes in the filled band behave similarly, with a drift velocity  $\langle v_h \rangle_{av}$ . The *mobilities* of electrons and holes are designated, respectively, by  $\mu_e$  and  $\mu_h$ , and defined by

$$\langle v_e \rangle_{av} = -\mu_e E, \quad \langle v_h \rangle_{av} = \mu_h E$$

In a cubic crystal  $\mu_e$  and  $\mu_h$  are scalars, but in crystals of lower symmetry the equations just written take the form of linear relations between components of vectors, with the mobilities represented by symmetric tensors. For simplicity, cubic symmetry will be assumed henceforth. The electric conductivity  $\sigma$  or resistivity  $\rho$  of a specimen containing  $n_e$  mobile electrons and  $n_h$  mobile holes per unit volume is given by

$$\sigma = 1/\rho = e(n_e \mu_e + n_h \mu_h) \quad (1)$$

If the  $\mu$ 's are measured in  $\text{cm}^2/\text{volt sec}$  and the  $n$ 's in  $\text{cm}^{-3}$ ,

$$\sigma = 1.6020 \times 10^{-9} \left( \frac{n_e}{10^{16}} \mu_e + \frac{n_h}{10^{16}} \mu_h \right) \text{ ohm}^{-1} \text{ cm}^{-1} \quad (2)$$

The variation of the concentration  $n_e$  of mobile electrons with position and time obeys the generalized diffusion equation

$$\frac{\partial n_e}{\partial t} = \nabla \cdot (D_e \nabla n_e) + \nabla \cdot (n_e \mu_e \mathbf{E}) - s \quad (3)$$

where  $D_e = (kT/e)\mu_e$  is the *diffusion coefficient* for electrons and where  $s$  is the rate of disappearance of electrons from the conduction band, per unit volume, because of recombination or trapping, minus the rate of creation of new free electrons by thermal action, light, etc. An analogous equation applies for holes with  $\mathbf{E}$  replaced by  $-\mathbf{E}$ .

**9.9. Hall effect** (Ref. 21). When no holes are present and when the density of mobile electrons is not too high, the Hall coefficient  $R_e$  (see § 4.7) at any given temperature varies inversely as the electron concentration  $n_e$ , i.e.,  $n_e R_e$  is a function of  $T$  independent of the position of the Fermi level. Similarly the Hall coefficient  $R_h$  for holes when no electrons are present varies inversely as the hole concentration  $n_h$ . When both electrons and holes contribute to the conduction the measured Hall coefficient for a homogeneous specimen is

$$R = \frac{(R_e \sigma_e) \sigma_e + (R_h \sigma_h) \sigma_h}{(\sigma_e + \sigma_h)^2} \quad (1)$$

where  $\sigma_e = en_e \mu_e$  and  $\sigma_h = en_h \mu_h$  are the respective contributions of electrons and holes to the conductivity  $\sigma$ , and where the grouping of factors in the numerator is to emphasize the fact that  $R_e \sigma_e$  and  $R_h \sigma_h$  are independent of  $n_e$  and  $n_h$  at any given temperature. Formulas for these quantities are given in § 9.11; normally  $R_e < 0$ ,  $R_h > 0$ .

**9.10. Thermoelectric effects.** The *thermoelectric power*  $Q$ , defined as  $\epsilon$  in § 4.4, measures the change in height of the Fermi level with temperature in an inhomogeneously heated specimen when no current is flowing :

$$\nabla_{\epsilon_F} = eQ \nabla T, \quad (\mathbf{j} = 0) \quad (1)$$

When both holes and electrons contribute to the conduction,  $Q$  is an average of electron and hole contributions.

$$Q = \frac{Q_e \sigma_e + Q_h \sigma_h}{\sigma_e + \sigma_h} \quad (2)$$

where  $\sigma_e$ ,  $\sigma_h$  are the contributions of electrons and holes, respectively, to the

conductivity, as defined in § 9.9, and  $Q_e, Q_h$  are, respectively, the thermo-electric power which the mobile electrons would have in the absence of holes, and that which the holes would have in the absence of electrons. Formulas for  $Q_e, Q_h$  are given in § 9.11; normally  $Q_e < 0, Q_h > 0$ .

**9.11. Mean free time and mean free path** (Ref. 21). Let it be assumed that over the energy range of interest the effective mass of an electron or hole (see § 9.1) is independent of its direction of motion, and that the scattering processes which act to randomize the velocities of the mobile charges are such that (1) the energy change suffered by a charge in the course of being scattered through a sizable angle is usually only a small part of the original energy  $\epsilon$  relative to the band edge, and (2) the probability  $W(\theta)$  of being scattered in unit time into unit solid angle in a direction making angle  $\theta$  with the initial direction of motion is independent of this original direction. Then quantities such as mobility, Hall coefficient, etc., can be expressed as integrals over energy involving the energy-dependent mean free time  $\tau$ , defined by

$$\frac{1}{\tau(\epsilon)} = \int W(\theta, \epsilon) (1 - \cos \theta) d\omega \tag{1}$$

where  $d\omega$  ranges over all elements of solid angle. If desired,  $\tau$  may be eliminated in terms of the mean free path  $l$ , defined by

$$l(\epsilon) = v(\epsilon)\tau(\epsilon) \tag{2}$$

where  $v(\epsilon) = (2\epsilon/m^*)^{1/2}$  is the speed of an electron or hole of energy  $\epsilon$  relative to the band edge.

Assume the velocity distribution to be Maxwellian (Fermi level well away from allowed band of energies) and let  $f_M(T, \epsilon)d\epsilon$ , be the fraction of the charges whose energies lie in the range  $\epsilon$  to  $\epsilon + d\epsilon$ , with  $\int f_M d\epsilon = 1$ . Denoting the Maxwellian average of any quantity  $F$  by

$$\langle F \rangle = \int_0^\infty F f_M d\epsilon$$

we have at any absolute temperature  $T$

Mobility

$$\left. \begin{aligned} \mu &= e \cdot \frac{\langle v^2 \tau \rangle}{3kT} = \frac{e}{m^*} \bar{\tau}_2 = \frac{4e\bar{l}_1}{3(2\pi m^* kT)^{1/2}} \\ &= 2.4036 \left( \frac{m}{m^*} \right)^{1/2} \left( \frac{100}{T} \right)^{1/2} \frac{\bar{l}_1}{1\text{A}} \text{ cm}^2/\text{volt sec} \end{aligned} \right\} \tag{3}$$

where  $\bar{\tau}_2, \bar{l}_1$  are averages of  $\tau, l$  with weights proportional to  $v^2$  and  $v$ , respect-

ively. Similarly the Hall coefficient, defined as in § 4.7 with  $E$  and  $j$  in absolute electrostatic units,  $H$  in absolute electromagnetic units, is

$$R_{\text{abs}} = \pm \frac{1}{nec} \frac{\langle v^2 \tau^2 \rangle \langle v^2 \rangle}{\langle v^2 \tau \rangle^2} \quad (4)$$

where  $n$  is the number mobile charges per unit volume,  $c$  is the velocity of light, and  $\pm$  is  $+$  for holes,  $-$  for electrons. Also, if  $T$  is high enough,

$$\text{thermoelectric power } Q = \pm \left[ \frac{\Delta \epsilon_F + \langle \epsilon^2 \tau \rangle / \langle \epsilon \tau \rangle}{eT} \right] \quad (5)$$

where  $\Delta \epsilon_F$  is the distance  $\epsilon_F - \epsilon_v$  or  $\epsilon_c - \epsilon_F$  of the Fermi level from the band edge, and where as before  $\pm$  is  $+$  for holes,  $-$  for electrons.

When  $l$  is independent of energy, as is the case for scattering by lattice vibrations of the acoustic branch, the formulas reduce to

$$\left. \begin{aligned} R_{\text{abs}} &= \pm \frac{3\pi}{8nec} \quad \text{or} \quad R = \pm 7.3540 \left( \frac{10^{18} \text{ cm}^{-3}}{n} \right) \text{ cm}^3/\text{coulomb} \\ Q &= \pm \left[ \frac{\Delta \epsilon_F}{eT} + \frac{2k}{e} \right] \end{aligned} \right\} \quad (6)$$

while when  $\tau$  is independent of energy, as is sometimes the case for scattering by lattice vibrations of the optical branch in a polar crystal,

$$\left. \begin{aligned} R_{\text{abs}} &= \pm \frac{1}{nec} \quad \text{or} \quad R = \pm 6.2422 \left( \frac{10^{18} \text{ cm}^{-3}}{n} \right) \text{ cm}^3/\text{coulomb} \\ Q &= \pm \left[ \frac{\Delta \epsilon_F}{eT} + \frac{5k}{2e} \right] \end{aligned} \right\} \quad (7)$$

**9.12. The space charge layer near a surface** (Ref. 25). Both the free surface of a semiconductor and the interface between a semiconductor and a metal usually carry surface-bound charges, which are compensated by a volume distribution of charge in the regions of the semiconductor immediately beneath surface. This volume charge causes the electrostatic potential  $\psi$  to vary with position.

A case of common occurrence is where the following two conditions are fulfilled: (1) the surface charge density  $q$  is negative and the semiconductor is  $n$  type; (2) either practically all donors are ionized and the change in  $e\psi$  between the deep interior and a point just inside the surface is  $\gg kT$ , or the change in  $e\psi$  is  $\gg$  the ionization energy of the donors. A symmetrically related case is one where  $q$  is positive, the semiconductor  $p$  type, and conditions analogous to (1) and (2) are satisfied. For both these cases the volume charge density is nearly constant over the range  $x_0$  of depths  $x$  over which

most of the change of  $\psi$  takes place, at least if the centers are uniformly distributed. We then have, if  $n_d$  is the density of donor centers,  $n_a$  the density of acceptor centers (assumed all occupied),  $\kappa$  the dielectric constant, and the surface is taken as  $x = 0$ ,

$$\psi(x) - \psi(x_0) = -\frac{2\pi e}{\kappa} (n_d - n_a) (x_0 - x)^2 = -V_b \left( \frac{x_0 - x}{x_0} \right)^2 \quad (1)$$

with

$$V_b = 2\pi q^2 / e(n_d - n_a)\kappa,$$

$$x_0 = q/e(n_d - n_a) = \sqrt{\kappa V_b / 2\pi e(n_d - n_a)}$$

$$= 1050 \sqrt{\frac{\kappa V_b \text{ volts}}{(n_d - n_a) / 10^{16} \text{ cm}^{-3}}} \text{ angstroms}$$

These equations apply whether or not an external potential bias has been applied to the contact.

**9.13. Contact rectification** (Ref. 25). A metal-semiconductor contact will show rectification if the change of potential in the space charge layer is in the direction postulated in § 9.12. Let such a contact be assumed plane and the potential a function only of the distance from this plane interface, and let tunneling of charges through the barrier be negligible. Assume that the field  $E$  at the contact ( $= 4\pi q/\kappa$  in the notation of § 9.12) and the mean free path  $l$  of the electrons or holes satisfy either  $|eEl| \gg kT$  (diode case) or  $|eEl| \ll kT$  (diffusion case). Assume finally that the current across the interface region is carried predominantly by majority carriers, i.e., by electrons if the semiconductor is  $n$  type or by holes if it is  $p$  type. Then the relation of current density  $j$  to voltage  $V$  applied across the contact, i.e., across the space charge region, is

$$j = j_0(E)[\exp(eV/kT) - 1] \quad (1)$$

where  $j$  and  $V$  are measured positive in the forward (low resistance) direction and where if  $V$  is in the forward direction it must be restricted to values appreciably below that necessary to wipe out the space charge barrier. Note that  $E$  is in general dependent on  $V$ . The dependence of  $j_0$  on  $E$  is different for the diode case and the diffusion case. For the diode case,

$$j_0(E) = A \frac{m^*}{m} T^2 (1 - \bar{r}) \exp\left(-\frac{e\phi}{kT}\right) \quad (2)$$

where

$$A = \frac{4\pi m k^2 e}{h^3} = 120 \text{ amp/cm}^2 \text{ deg}^2$$

is Richardson's thermionic constant,  $m^*/m$  is the ratio of the effective mass of the carriers (see § 9.1) to the true electron mass,  $\bar{r}$  is the mean reflection coefficient for charges energetically capable of crossing the metal-semiconductor boundary, and  $e\phi$  is the barrier height, defined as the difference between the Fermi level of the metal and the bottom of the conduction band (for  $n$  type material) or top of the filled band (for  $p$  type) at the peak of the space charge barrier. For the diffusion case,

$$j_0(E) \sim \sigma_0 |E| \exp(-e|V_b|/kT) \quad (3)$$

where  $\sigma_0$  is the conductivity of the semiconductor in its deep interior and  $V_b$  is the change in electrostatic potential between the inner boundary of the space region and the peak of the space charge barrier. The formula for the diffusion case is written as an approximation because it is based on the assumption that the energy of the band edge varies linearly with position until it differs from its value at the surface by several times  $kT$ .

In the formula for the diode case the dependence of  $j_0$  on  $E$  occurs only by virtue of the dependence of  $V_b$  on  $E$  due to the Schottky image effect; treating the semiconductor as a continuum of dielectric constant  $\kappa$  gives

$$V_b(E) = V_b(0) - \sqrt{\frac{eE}{\kappa}} = V_b(0) - 3.79 \times 10^{-4} (E_{V/cm}/\kappa)^{1/2} \text{ volts} \quad (4)$$

To make a similar allowance for the image effect in the diffusion case one must abandon the assumed linear variation of band edge energy with depth; however, the principal modification of the formula given above is the replacement of  $V_b$  by the field-dependent value just given.

For some contacts the current across the contact is carried largely by minority carriers, i.e., by holes if the semiconductor is  $n$  type, or by electrons if it is  $p$  type (Ref. 1). For such contacts the preceding formulas do not apply, and in most cases a three-dimensional rather than one-dimensional approach must be used.

#### 9.14. Differential capacity of a metal-semiconductor contact.

When a small alternating potential is applied to a rectifying contact of the sort described in § 9.12 and § 9.13, the contact behaves like a capacitor in parallel with a resistor, the latter being of course derivable from the d-c current-voltage characteristic by differentiation. If the impurity centers are uniformly distributed and if the potential in the semiconductor can be taken to be a function only of distance from an essentially plane metal interface

$$\text{capacity per unit area} = |\rho_b/E| \quad (1)$$

where  $E$  is the electric field strength in the semiconductor just inside the metal boundary and  $\rho_b$  is the charge density in this region. If, as is often the case, the donor centers are all ionized at the boundary and the acceptor centers all filled,  $\rho_b = e(n_d - n_a)$ , where  $n_d, n_a$  are the densities of donor and acceptor centers, respectively.

Alternatively, if the charge density at each point throughout the space charge layer can be assumed unaffected by a small change of potential, then whether or not the charge density is uniform we have, if the one-dimensional treatment is applicable,

$$\text{capacity per unit area} = \kappa/4\pi x_0 \tag{2}$$

where  $\kappa$  is the dielectric constant and  $x_0$  is the thickness of the space charge layer. When in addition the assumptions of § 9.12 are satisfied

$$\left. \begin{aligned} \text{capacity per unit area} &= \sqrt{\frac{\kappa e(n_d - n_a)}{8\pi V_b}} \\ &= 8422\kappa^{1/2} \left(\frac{n_d - n_a}{10^{16} \text{ cm}^{-3}}\right)^{1/2} \left(\frac{1 \text{ v}}{V_b}\right)^{1/2} \mu\mu f/\text{cm}^2 \end{aligned} \right\} \tag{3}$$

where  $V_b$  is the potential change across the space charge layer, equal to the sum of the potential change in equilibrium and the applied bias potential.

**9.15. D-c behavior of  $p$ - $n$  junctions** (Ref. 21). If the relative concentrations of donor and acceptor centers (see § 9.3) vary with position in a semiconducting specimen it is possible for regions of  $n$  and  $p$  type conductivity (see § 9.7) to coexist in it, separated by a region of low conductivity called a *p-n junction*. Such a junction manifests a nonlinear resistance and capacitance similar to those of metal-semiconductor contacts. The following assumptions, often realized in practice, will be made : Let the semiconductor be divisible into an  $n$  region of uniform impurity concentration, a plane-parallel transition region, and a  $p$  region of uniform impurity concentration. At points well away from the junction, let the equilibrium hole density  $n_h(n)$  in the  $n$  region and the equilibrium electron density  $n_e(p)$  in the  $p$  region satisfy

$$n_h(n) \ll n_e(n), \quad n_e(p) \ll n_h(p)$$

Let the quantity  $s$ , introduced in § 9.8 as the difference between the rates of annihilation and creation of mobile charges per unit volume, be describable in terms of so-called *recombination lifetimes*, thus :

$$\left. \begin{aligned} s_h &= \frac{n - n_h(n)}{\tau_h}, & (\text{for holes in the } n \text{ region}) \\ s_e &= \frac{n_e - n_e(p)}{\tau_e}, & (\text{for electrons in the } p \text{ region}) \end{aligned} \right\} (1)$$

Let the thickness of the transition region be  $\ll L_h$  and  $\ll L_e$ , where, if  $D_h, D_e$  are the diffusion coefficients for holes and electrons respectively,

$$L_h = \sqrt{D_h \tau_h}, \quad L_e = \sqrt{D_e \tau_e}$$

are the so-called *diffusion lengths* for holes and electrons, respectively. Assume the transition region to have values of  $s$  comparable with or smaller than those in the  $n$  and  $p$  regions.

Let two planes be given, one on the  $p$  side of the junction and at a distance  $d_p \gg L_e$  from it, the other on the  $n$  side at a distance  $d_n \gg L_h$ , yet neither so far away that the ohmic resistance of  $p$  material of thickness  $d_p$  and  $n$  material of thickness  $d_n$  is comparable with the junction resistance as given below. Let a direct voltage  $V$ , measured positive in the forward direction, be applied between these two planes, and designated as the "voltage across the junction." The resulting current per unit area will then be, to a good approximation

$$\left. \begin{aligned} j &= e \left[ \frac{D_h n_h(n)}{L_h} + \frac{D_e n_e(p)}{L_e} \right] (e^{eV/kT} - 1) \\ &= \frac{b \sigma_i^2}{(1+b)^2} \left( \frac{1}{\sigma_n L_h} + \frac{1}{\sigma_p L_e} \right) \left[ \frac{kT}{e} (e^{eV/kT} - 1) \right] \end{aligned} \right\} (2)$$

where  $b = \mu_e/\mu_h = D_e/D_h$ ,  $\sigma_i$  is the conductivity which the semiconductor would have in the intrinsic state (see § 9.6), and  $\sigma_n$  and  $\sigma_p$  are the conductivities of the  $n$  and  $p$  regions, respectively. The quantity in square brackets is an effective voltage, the quantity multiplying is an effective conductance per unit area.

**9.16. A-c behavior of  $p$ - $n$  junctions.** Let a  $p$ - $n$  junction satisfying the conditions of § 9.15 be subjected to a d-c bias  $V_0$ , measured positive in the forward direction, and to a small alternating voltage  $V_1 e^{i\omega t}$ . The alternating part of the current per unit area will then be  $A V_1 e^{i\omega t}$ , where the complex admittance  $A$  per unit area is given by

$$A = (1 + i\omega\tau_h)^{1/2} G_{h0} e^{eV_0/kT} + (1 + i\omega\tau_e)^{1/2} G_{e0} e^{eV_0/kT} + i\omega C_T \quad (1)$$

where in the notation of § 9.15

$$G_{h0} = \frac{b\sigma_i^2}{(1+b)^2\sigma_n L_h}, \quad G_{e0} = \frac{b\sigma_i^2}{(1+b)^2\sigma_p L_e} \quad (2)$$

and where  $C_T$  is a capacitance associated with the transition region and described below for special cases.

Let  $\kappa$  be the dielectric constant and  $n_i$  the density of holes or electrons in intrinsic material (see § 9.6), and let  $L_D = (\kappa kT/8\pi e^2 n_i)^{1/2}$  be the corresponding Debye length. If most of the change in potential in the transition region occurs in a region within which the densities  $n_d$  of donors and  $n_a$  of acceptors satisfy

$$n_d - n_a = ax$$

where  $x$  is distance normal to the plane of the junction, and if  $a \gg n_i/L_D$ , then

$$C_T \approx \frac{\kappa}{8\pi} \left[ \frac{8\pi ea}{3\kappa(\psi_0 - V_0)} \right]^{1/3} \tag{3}$$

where  $\psi_0$  is a positive quantity equal to the difference in electrostatic potential between the two sides of the junction when no bias is applied. If, on the other hand, most of the change in potential in the transition region occurs in the regions of uniform impurity concentration, as may happen for large reverse bias,

$$C_T \approx \left\{ \frac{\kappa e n_e(n) n_h(p)}{8\pi [n_e(n) + n_h(p)] (\psi_0 - V_0)} \right\}^{1/2} \tag{4}$$

where  $n_e(n)$ ,  $n_h(p)$  are the equilibrium densities of electrons in the  $n$  region and holes in the  $p$  region, respectively.

### 10. Electron Theory of Metals

**10.1. The Fermi-Dirac distribution** (Ref. 20). Let there be  $n$  electrons per unit volume in a metal, and assume that the total energy of the metal can be represented as a constant plus a sum of energies  $\epsilon_i$  of the individual electrons. Then if  $i$  designates any quantum state, i.e., set of orbital and spin quantum numbers, the fraction of the time this state is occupied in thermal equilibrium at temperature  $T$  is the Fermi function  $f(\epsilon_i, \epsilon_F)$  of § 9.4. For metals, as distinguished from semiconductors, the Fermi level  $\epsilon_F$  lies in a region of energies where there is a continuous distribution of quantum states, and usually does not vary much with temperature. If a metal specimen of volume  $\Omega_N$  contains  $n\Omega_N$  electrons and  $\nu(\epsilon)d\epsilon$  quantum states, the Fermi level at temperature  $T$  is

$$\epsilon_F(T) = \epsilon_F(0) - \frac{\pi^2}{6} \left( \frac{d \ln \nu}{d\epsilon} \right)_{\epsilon=\epsilon_F(0)} (kT)^2 + O(T^4) \tag{1}$$

where  $k$  is Boltzmann's constant and  $\epsilon_F(0)$  is determined by

$$\int_{-\infty}^{\epsilon_F(0)} \nu(\epsilon) d\epsilon = n\Omega_N$$

If the energies of the various quantum states are the same as those of free electrons of mass  $m^*$ ,  $\nu(\epsilon)$  is given by the formula of § 9.2. When electrons of both spins are present equally we have, if the atomic volume  $\Omega = (4\pi/3)r_s^3$  contains  $Z$  electrons,

$$\left. \begin{aligned} \epsilon_F(0) &= \frac{\hbar^2}{2m^*} \left( \frac{3n}{8\pi} \right)^{2/3} = 3.6867Z^{2/3} \left( \frac{a_H}{r_s} \right)^2 \left( \frac{m}{m^*} \right) \text{ rydberg units} \\ &= 3.6458 \times 10^{-15} \left( \frac{m}{m^*} \right) (n_{\text{cm}^{-3}})^{2/3} e \text{ volts} \end{aligned} \right\} \quad (2)$$

$$\epsilon_F(T) \sim \epsilon_F(0) - \frac{\pi^2}{12} \cdot \frac{(kT)^2}{\epsilon_F(0)}$$

where  $\hbar$  is Planck's constant,  $m$  the normal electron mass, and  $a_H$  the Bohr radius. For this case the maximum wave vector  $k_m$  (see § 10.5) defined by  $\hbar^2 k_m^2 / 2m^* = \epsilon_F(0)$ , has the value

$$k_m = \left( \frac{3n}{8\pi} \right)^{1/3} = \frac{1.9202Z^{1/3}}{r_s} \quad (3)$$

**10.2. Averages of functions of the energy** (Ref. 23). If  $F(\epsilon)$  is any function of the energy of an electron, the sum of  $F$  over all electrons in the Fermi distribution is, in the notation of § 10.1,

$$\sum_i F(\epsilon_i) \langle N_i \rangle_{av} = \sum_{\epsilon_i < \epsilon_F(0)} F(\epsilon_i) + \frac{\pi^2}{6} \nu_0 \left( \frac{dF}{d\epsilon} \right)_0 (kT)^2 + O(T^4) \quad (1)$$

where the subscript 0 implies that  $\nu$  and  $dF/d\epsilon$  are to be evaluated at  $\epsilon_F(0)$ . Note that  $\nu$ , being the density of quantum states, is, in an unmagnetized metal, twice the density of orbital states.

**10.3. Energy and electronic specific heat** (Ref. 20). For the model described in § 10.1 the electronic contribution to the molar specific heat is

$$C_v^{(e)} = \frac{\pi^2 k^2 T}{3} \nu_m(\epsilon_F) + O(T^3) \quad (1)$$

where  $\nu_m$  is the density in energy of electronic states of both spins, for one mole of material. The term  $O(T^3)$  is negligible if  $kT(d \ln \nu / d\epsilon)_{\epsilon=\epsilon_F} \ll 1$ .

If the energies of the various quantum states are the same as those of free

electrons of mass  $m^*$  and if there are  $Z$  such electrons per atom of a monatomic substance,

$$\left. \begin{aligned}
 C_v^{(e)} &\sim \left(\frac{\pi^2}{2}\right) Z \left(\frac{kT}{\epsilon_F}\right) R \\
 &= 2.317 \times 10^{11} \left(\frac{m^*}{m}\right) \frac{Z}{(n_{\text{cm}^{-3}})^{2/3}} T \quad \text{cal mol}^{-1} \text{ deg}^{-1} \\
 &= 1.694 \times 10^{-5} Z^{1/3} \left(\frac{r_s}{a_H}\right)^2 \left(\frac{m^*}{m}\right) T \quad \text{cal mol}^{-1} \text{ deg}^{-1}
 \end{aligned} \right\} \quad (2)$$

where  $R$  is the gas constant and the other symbols have the meanings explained in § 10.1. For this case of quasi-free electrons the average energy of the occupied levels at the absolute zero is

$$\epsilon_{\text{av}} = \frac{3}{5} \epsilon_F^0(0) \quad (3)$$

**10.4. Spin paramagnetism** (Ref. 20). In the presence of a magnetic field a nonferromagnetic metal will have an equilibrium state in which the numbers of electrons with spins parallel and antiparallel to the field are slightly different. The contribution of these unbalanced spins to the molar magnetic susceptibility is, for the model described in § 10.1,

$$\chi_m^{(s)} = \beta^2 \nu_m(\epsilon_F) + O(T^2) \quad (1)$$

where  $\beta = e\hbar/2mc$  is the Bohr magneton, and  $\nu_m$  is the total number of electronic states of both spins per unit energy range, for one mole of material. The term  $O(T^2)$  is negligible if

$$kT(d \ln \nu/d\epsilon)_{\epsilon=\epsilon_F} \ll 1$$

If the energies of the various quantum states are the same as those of free electrons of mass  $m^*$  and if there are  $Z$  such electrons per atom of a monatomic substance

$$\left. \begin{aligned}
 \chi_m^{(s)} &\sim \frac{3}{2} \cdot \frac{N_0 Z \beta^2}{\epsilon_F} = 1.88 \times 10^{-6} Z^{1/3} \left(\frac{A}{\rho}\right)^{2/3} \left(\frac{m^*}{m}\right) \\
 &= 0.9685 \times 10^{-6} Z^{1/3} \left(\frac{r_s}{a_H}\right)^2 \left(\frac{m^*}{m}\right)
 \end{aligned} \right\} \quad (2)$$

where  $N_0$  is Avogadro's number,  $A$  the atomic weight,  $\rho$  the density,  $a_H$  the Bohr radius, and  $r_s$  the radius of the atomic  $s$ -sphere (see §§ 1.2, 10.1).

For the orbital contribution to the susceptibility see § 10.11.

**10.5. Bloch waves.** Consider the Schrödinger wave equation for a single electron in a potential field possessing the periodicity of a crystal lattice. The solutions satisfying periodic boundary conditions (see § 1.4) may be taken in the form

$$\psi_{\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}) \quad (1)$$

where the function  $u_{\mathbf{k}}$  possesses the periodicity of the lattice, i.e.,  $u_{\mathbf{k}}(\mathbf{r} + \mathbf{t}) = u_{\mathbf{k}}(\mathbf{r})$  for all lattice translations  $\mathbf{t}$ . The wave vector  $\mathbf{k}$  must terminate on one of the closely spaced lattices of points in  $\mathbf{k}$ -space defined in § 1.4; it may, if desired, be specified to lie within the first Brillouin zone (see § 1.3), since if  $\mathbf{g}$  is any vector of the reciprocal lattice (see § 1.3) the quantity  $e^{i\mathbf{k}\cdot\mathbf{r}}$  in the above equation can be replaced by  $e^{i(\mathbf{k}+2\pi\mathbf{g})\cdot\mathbf{r}}$  with substitution of a new periodic function for  $u_{\mathbf{k}}$ . If  $\mathbf{k}$  is thus specified to lie in the first Brillouin zone, it is called the *reduced wave vector* of  $\psi_{\mathbf{k}}$ . The set of energies  $\epsilon_{\mathbf{k}}$  going with a particular reduced wave vector  $\mathbf{k}$  is discrete, but the variation of each of these  $\epsilon_{\mathbf{k}}$ 's with changes in  $\mathbf{k}$  is continuous. Explicitly, if  $\psi_{\mathbf{k}}$  is the only eigenfunction of reduced wave vector  $\mathbf{k}$  and energy  $\epsilon_{\mathbf{k}}$ ,

$$\frac{\partial \epsilon_{\mathbf{k}}}{\partial \mathbf{k}} = -\frac{\hbar^2}{m} \int \psi_{\mathbf{k}}^* \nabla \psi_{\mathbf{k}} d\tau \quad (2)$$

**10.6. Velocity and acceleration.** The mean velocity of an electron in a Bloch wave state  $\psi_{\mathbf{k}}$  of energy  $\epsilon_{\mathbf{k}}$  is, if no other state has the same reduced wave vector and the same energy,

$$\mathbf{v}_{\mathbf{k}} = \frac{1}{\hbar} \cdot \frac{\partial \epsilon_{\mathbf{k}}}{\partial \mathbf{k}} \quad (1)$$

Application of a spatially uniform force  $\mathbf{F}$  to an electron in such a state causes the wave function and energy to change with time, in a manner which for nearly all practical purposes can be described by saying that the wave vector changes uniformly at the rate

$$\frac{d\mathbf{k}}{dt} = \frac{\mathbf{F}}{\hbar} \quad (2)$$

**10.7. Energy levels of almost free electrons** (Ref. 23). For perfectly free electrons  $\epsilon_{\mathbf{k}}^{(0)} = \hbar^2 k^2 / 2m$  varies continuously with  $k$  as  $k$  goes from 0 to  $\infty$ . If the periodic potential field of a crystal is treated as a small perturbation on these free electron levels,  $\epsilon_{\mathbf{k}}$  acquires discontinuities on certain planes in  $\mathbf{k}$ -space, viz., when for any vector  $\mathbf{g}$  of the reciprocal lattice (see § 1.3)

$$\mathbf{g} \cdot (\mathbf{k} - \pi\mathbf{g}) = 0$$

The  $n$ th *Brillouin zone* is defined as that region of  $\mathbf{k}$ -space which can be reached from the origin by crossing  $(n - 1)$  of these planes in the outward

direction. Each point of the first Brillouin zone occurs once and only once among the reduced wave vectors (see § 10.5) of all points in the  $n$ th zone.

If  $\mathbf{k}$  is a point rather closer to the discontinuity plane going with the reciprocal lattice vector  $\mathbf{g}$  than to any other such plane, the value of  $\epsilon_k$  given by the present perturbation treatment is approximately

$$\epsilon_k = \frac{\epsilon_k^{(0)} + \epsilon_{k-2\pi g}^{(0)} \pm \sqrt{(\epsilon_k^{(0)} - \epsilon_{k-2\pi g}^{(0)})^2 + 4 |V_g|^2}}{2} \quad (1)$$

where

$$V_g = \frac{1}{\Omega_N} \int_{\Omega_N} e^{2\pi i \mathbf{g} \cdot \mathbf{r}} V(\mathbf{r}) d\tau$$

is a Fourier coefficient of the potential energy function  $V$ ,  $\Omega_N$  being the volume of the specimen, the “fundamental volume” of § 1.4. Let  $\mathbf{k} = \pi \mathbf{g} + \mathbf{k}_{\parallel} + \mathbf{k}_{\perp}$  where  $\mathbf{k}_{\parallel}$  is parallel to the discontinuity plane,  $\mathbf{k}_{\perp}$  normal to it. Then since  $\epsilon_k^{(0)} = \hbar^2 k^2 / 2m$  we have, if  $k_{\perp} \ll m |V_g| / \pi \hbar^2 g$ ,

$$\epsilon_k \sim \frac{\hbar^2 \pi^2 g^2}{2m} + \frac{\hbar^2}{2m} k_{\parallel}^2 + V_0 \pm |V_g| \pm \frac{\hbar^2}{2m} k_{\perp}^2 \left( \frac{\hbar^2 \pi^2 g^2}{m |V_g|} \pm 1 \right) \quad (2)$$

where  $V_0$  is the space average of the perturbing potential, and where it is customary to use the upper sign if  $\mathbf{k}_{\perp}$  points away from the origin, the lower if toward it. When  $k_{\perp} \gg m |V_g| / \pi \hbar^2 g$ ,

$$\epsilon_k \sim \frac{\hbar^2 k^2}{2m} + V_0 + \frac{m |V_g|^2}{\hbar^2 (2\pi \mathbf{g} \cdot \mathbf{k}_{\perp})} \quad (3)$$

**10.8. Coulomb energy** (Ref. 20). Since a unit cell of a metal is electrically neutral, a convenient step in calculating electrostatic energies is to calculate the energy of a single unit cell by itself. If the unit cell does not differ too much in shape from the  $s$ -sphere (see § 1.2) of equal volume and if the charge of  $Z$  conduction electrons is uniformly distributed over the cell, the electrostatic potential due to this distribution of electrons will be approximately the same as that due to a uniform distribution of electrons over an  $s$ -sphere, viz.,

$$U(r) = -\frac{3Ze}{2r_s} + \frac{Zer^2}{2r_s^3} \quad (1)$$

where  $r_s$  is the radius of the  $s$ -sphere. The contribution to the potential energy of an electron is of course  $-eU$ . The self-energy of this distribution of electrons over an  $s$ -sphere is

$$-\frac{1}{2} Ze \langle U \rangle_{av} = -\frac{3Z^2 e^2}{5r_s} \quad (2)$$

**10.9. Exchange energy** (Ref. 20). Let the ground state wave function for an assembly of  $N$  free electrons be approximated by a determinant of plane wave functions, half with one spin and half with the other. The total energy will then be the sum of the kinetic energies of the various electrons, the energy of interaction of the electrons with whatever positive charges are present, the Coulomb self-energy of the mean charge density of the electrons, and an exchange term given by

$$-\frac{3^{4/3}}{4\pi^{1/3}} e^2 n^{1/3} \cdot N = -\frac{3^{5/3}}{2^{3/3}\pi^{2/3}} \frac{Z^{1/3}e^2}{r_s} \cdot N = -0.458 \frac{Z^{1/3}e^2}{r_s} \cdot N \quad (1)$$

where  $n = N/\Omega_N$  is the number of electrons per unit volume and  $Z$  is the number of electrons in a volume  $4\pi r_s^3/3$ . The change in energy caused by removing an electron from a state with wave vector  $\mathbf{k}$  is, in the present determinantal approximation, equal to the negative of the kinetic and electrostatic energies of this electron, plus the exchange term

$$\left. \begin{aligned} A_{kk} &= \frac{e^2 k_m}{2\pi} \left( 2 + \frac{k_m^2 - k^2}{kk_m} \ln \left| \frac{k + k_m}{k - k_m} \right| \right) \\ &= 1.222 \frac{Z^{1/3}e^2}{r_s} \left[ \frac{1}{2} + \frac{k_m}{4k} \left( 1 - \frac{k^2}{k_m^2} \right) \ln \left| \frac{1 + k/k_m}{1 - k/k_m} \right| \right] \end{aligned} \right\} \quad (2)$$

where  $k_m$  is the maximum  $k$  occurring in the Fermi distribution. The quantity in square brackets has the value 1 at  $k = 0$ ,  $\frac{1}{2}$  at  $k = k_m$ , and 0 at  $k = \infty$ . Its derivative with respect to  $k$  is 0 at  $k = 0$ ,  $-\infty$  at  $k = k_m$ .

**10.10. Electrical and thermal conduction** (Ref. 20). Let the conduction electrons of a metal be assumed to occupy states of the Bloch type (see § 10.5) and to be scattered by lattice vibrations but not by each other. Suppose further that  $T \gg \Theta$ , where  $\Theta$  is the Debye temperature of the lattice (see § 7.5), but that at the same time the electron distribution is highly degenerate, i.e.,  $kT d \ln \nu/d\epsilon \ll 1$ , where  $\nu$  is the number of electronic states per unit energy. Then the electric conductivity  $\sigma$  and the thermal conductivity  $\kappa$  must be related by the *Wiedemann-Franz law*

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \left( \frac{k}{e} \right)^2 = 2.45 \times 10^{-8} \text{ watt-ohm/deg}^2 \quad (1)$$

The Hall constant  $R$ , as defined in § 4.7, can be simply related to the electron density only if some special assumptions are made regarding the variation of energy with wave vector and the angular dependence of the

scattering probability. The simplest case is that where  $\epsilon_k \propto k^2 + \text{constant}$ , degeneracy is complete, and scattering is isotropic; for this case

$$R_{\text{abs}} = -\frac{1}{nec} \quad \text{or} \quad R = -6.2422 \cdot \left( \frac{10^{18} \text{ cm}^{-3}}{n} \right) \text{ cm}^3/\text{coulomb} \quad (2)$$

where  $n$  is the number of electrons per unit volume,  $c$  is the velocity of light, and  $R_{\text{abs}}$  is defined with  $E$  and  $j$  in absolute electrostatic units,  $H$  in absolute electromagnetic units. The same formula applies, with a positive instead of negative sign, to the case where there are  $n$  holes per unit volume in a band and the energies of these empty levels satisfy  $\epsilon_k \propto \text{constant} - (\mathbf{k} - \mathbf{k}_0)^2$ .

**10.11. Orbital diamagnetism** (Ref. 20). When a magnetic field is applied to a metal the conduction electrons not only change their spin distribution but also suffer an alteration of their orbital wave functions. The latter effect causes a contribution  $\chi_m^{(o)}$  to the molar susceptibility, which must be added to the spin contribution  $\chi_m^{(s)}$  of § 10.4. For perfectly free electrons at temperatures approaching the absolute zero

$$\chi_m^{(o)} = -\frac{1}{3}\chi_m^{(s)} \quad (1)$$

A band containing a number  $\Delta n$  per unit volume of electrons or holes with a small effective mass  $m^*$  contributes a rather larger amount to  $\chi_m^{(o)}$ , given approximately by

$$\chi_m^{(o)} = -\frac{1}{3} \chi_m^{(s)} \left( \frac{m}{m^*} \right)^2 = -\frac{4\pi m \beta^2}{3h^2} \left( \frac{3\Delta n}{\pi} \right)^{1/3} \left( \frac{m}{m^*} \right) v_m \quad (2)$$

where  $\beta = e\hbar/2mc$  is the Bohr magneton and  $v_m$  is the molar volume. The second part of this formula may be applied to cases where the effective masses  $m_z^*$  along and  $m_x^*$ ,  $m_y^*$  transverse to the magnetic field are different, by setting  $m^* = (m_x^{*2} m_y^{*2} / m_z^*)^{1/3}$ . All these formulas refer to the susceptibility at zero field; when the magnetic field  $H$  becomes of the order of  $kT/\beta$ , the susceptibility becomes field-dependent.

**10.12. Optical constants** (Ref. 20). In any homogeneous isotropic medium the amplitude of a plane electromagnetic wave of angular frequency  $\omega$  will vary as

$$e^{-k\omega x/c} \begin{pmatrix} \sin \\ \cos \end{pmatrix} \left[ \omega \left( \frac{nx}{c} - t \right) \right]$$

where  $c$  is the velocity of light,  $t$  the time,  $x$  the coordinate in the direction of propagation, and  $k$  and  $n$  are optical constants which are in general functions of  $\omega$ . Consider the case where the medium consists of an assembly

of classical free electrons, of mass  $m$ , charge  $e$ , and density  $n$  per unit volume. Assume the motion of each electron to be damped by a frictional force equal to  $-m\omega_\tau$  times its velocity. For this case

$$n^2 - k^2 = 1 - \frac{\omega_0^2}{\omega^2 + \omega_\tau^2}, \quad nk = \frac{\omega_\tau \omega_0^2}{2\omega(\omega^2 + \omega_\tau^2)} \quad \left. \vphantom{\frac{\omega_0^2}{\omega^2 + \omega_\tau^2}} \right\} (1)$$

where

$$\omega_0^2 = \frac{4\pi ne^2}{m} \quad \text{or} \quad \omega_0 = 1.7841 \times 10^{16} \left( \frac{n}{10^{23} \text{ cm}^{-3}} \right)^{1/2} \text{ sec}^{-1}$$

The quantity  $\omega_\tau$  is related to the d-c conductivity  $\sigma_0$  of this model by

$$\omega_\tau = \frac{ne^2}{m\sigma_0} = 2.8185 \times 10^{13} \left( \frac{n}{10^{23} \text{ cm}^{-3}} \right) \left( \frac{10^6 \text{ ohm}^{-1} \text{ cm}^{-1}}{\sigma_0} \right) \text{sec}^{-1}$$

When this model is used as an approximation to actual metals it turns out that  $\omega_\tau \ll \omega_0$ . When this is fulfilled and  $\omega \ll \omega_\tau$ , the above formulas reduce to

$$n \approx k \approx \left( \frac{2\pi\sigma_0}{\omega} \right)^{1/2} = 54.75 \left( \frac{\lambda}{1\mu} \right)^{1/2} \left( \frac{\sigma_0}{10^6 \text{ ohm}^{-1} \text{ cm}^{-1}} \right)^{1/2} \quad (2)$$

This leads to the *Hagen-Rubens relation* for the reflection coefficient  $R$  of a metal surface in the infrared.

$$R = 1 - 2 \left( \frac{\omega}{2\pi\sigma_0} \right)^{1/2} \quad (3)$$

When  $\omega_\tau \ll \omega$ , on the other hand,  $nk \approx 0$ , so if  $\omega < \omega_0$

$$n \approx 0, \quad k \approx \left( \frac{\omega_0^2}{\omega^2} - 1 \right)^{1/2}$$

and if  $\omega > \omega_0$ ,

$$n \approx \left( 1 - \frac{\omega_0^2}{\omega^2} \right)^{1/2}, \quad k \approx 0 \quad (4)$$

## 11. Miscellaneous

**11.1. Specific heats at constant stress and strain** (Ref. 27). Let  $C_p$  be the heat capacity of some given amount of crystalline material at constant stress  $p$ , and  $C_v$  that at constant volume and state of strain. Let  $v$  be the volume of this same amount of material. Then if  $T$  is the absolute temperature and  $u_i$  ( $i = 1$  to 6) the strain components as defined in § 2.1, so that  $(\partial u_i / \partial T)_p$  are generalized expansion coefficients,

$$C_p - C_v = Tv \sum_{i,j=1}^6 c_{ij} \left( \frac{\partial u_i}{\partial T} \right)_p \left( \frac{\partial u_j}{\partial T} \right)_p \quad (1)$$

where the  $c_{ij}$  are the elastic constants as defined in § 2.2. For cubic or isotropic material this reduces to

$$C_p - C_v = \frac{9Tv\alpha^2}{\kappa} \tag{2}$$

where  $\alpha = (\partial u_1/\partial T)_p$  is the linear expansion coefficient and  $\kappa = -(1/v)(\partial v/\partial p)_T$  is the isothermal volume compressibility.

**11.2. Magnetocaloric effect and magnetic cooling** (Ref. 19). Let  $M$  be the magnetic moment of a specimen of matter subjected to a magnetic field  $H$  due to external sources. If  $H$  is changed in such way that the entropy  $S$  of the specimen remains constant, and if the state of the specimen is always one of thermal equilibrium in the field  $H$ , the absolute temperature  $T$  of the specimen will change according to

$$\left(\frac{\partial T}{\partial H}\right)_S = -\frac{T}{C^{(H)}}\left(\frac{\partial M}{\partial T}\right)_H \tag{1}$$

where  $C^{(H)} = T(\partial S/\partial T)_H$  is the heat capacity of the specimen at constant  $H$ . The equation is valid if all derivatives are taken at constant pressure, or all at constant volume.

**11.3. The Cauchy relations** (Ref. 3). Let the atoms of a crystal be assumed to interact in pairs, with the interaction energy of each pair a function of radial distance only. Let the crystal, initially in equilibrium at zero stress and the absolute zero of temperature, be subjected to an infinitesimal homogeneous strain described by the tensor  $u_{\mu\nu}$ , with resultant stress tensor  $p_{\mu\nu}$  (as used in § 2.1). Let the symmetry of the lattice be such that the displacement of any atom, originally at position  $R^{(i)}$ , is simply

$$\sum_{\nu=1}^3 u_{\mu\nu} R_\nu^{(i)}$$

This condition is satisfied, for example, if each atom is a center of symmetry. Then the elastic constant tensor  $c_{\mu\alpha\nu\beta}$ , defined by

$$p_{\mu\alpha} = \sum_{\nu,\beta=1}^3 c_{\mu\alpha\nu\beta} u_{\nu\beta} \tag{1}$$

(as used in § 7.1), must be symmetrical with respect to all interchanges of the indices  $\mu, \alpha, \nu, \beta$ . The identities which result from this fact go beyond those always required by the symmetry of  $c_{\mu\alpha\nu\beta}$  in  $\mu \rightleftharpoons \alpha, \nu \rightleftharpoons \beta$  and  $\mu, \alpha \rightleftharpoons \nu, \beta$ , and are called the *Cauchy relations*.

In the notation of § 2.2 these are

$$\left. \begin{aligned} c_{23} &= c_{44} & c_{56} &= c_{14} \\ c_{31} &= c_{55} & c_{64} &= c_{25} \\ c_{12} &= c_{66} & c_{45} &= c_{36} \end{aligned} \right\} (2)$$

For cubic crystals these degenerate into the single relation

$$c_{12} = c_{44} \quad (3)$$

**11.4. The Brillouin and Langevin functions** (Ref. 26). Let  $\beta = e\hbar/2mc$  be the Bohr magneton and let  $g$  be the Landé factor for an atom of total angular momentum quantum number  $J$ , so that the eigenvalues of the  $z$  component of magnetic moment run from  $g\beta J$  to  $-g\beta J$ , in steps of  $g\beta$ . When such an atom is in thermal equilibrium at absolute temperature  $T$  in the presence of a magnetic field  $H$ , and in the absence of other orienting influences, its mean magnetic moment is

$$M_{av} = g\beta J B_J \left( \frac{g\beta JH}{kT} \right) \quad (1)$$

where  $k$  is Boltzmann's constant and

$$B_J(y) = \left( \frac{2J+1}{2J} \right) \coth \frac{(2J+1)y}{2J} - \frac{1}{2J} \coth \frac{y}{2J} \quad (2)$$

is called the *Brillouin function*. If  $J$  is  $\gg 1$  but  $g\beta H/kT \ll 1$ ,  $M_{av}$  approaches the value given by the classical statistics, viz., the value obtained by substituting for the function  $B_J$  the *Langevin function*

$$L(y) = \coth y - \frac{1}{y} \quad (3)$$

of the same argument. See also, Chapter 26.

**11.5. Relation of thermal release to capture of mobile charges by traps.** In an insulator or semiconductor let  $\epsilon_c$  be the energy of the bottom of the conduction band (see § 9.1),  $\epsilon_t$  the energy required to take an electron from the state of zero energy and place it in an electron trap (see § 9.3). Assume the energy level at the bottom of the conduction band to be nondegenerate, and let  $m_e^*$  be the effective mass associated with this band (see § 9.1). Let  $\sigma$  be the cross section for capture of a free electron by the trap, averaged over spin orientations and assumed independent of electron energy. Then the mean lifetime  $\tau$  of an electron in the trap, defined by rate of thermal release =  $(1/\tau) \times$  number in traps, is given by

$$\left. \begin{aligned} \tau &= \frac{h^3(g_1/g_0)}{16\pi m_e^*(kT)^2 \sigma} \exp \left( \frac{\epsilon_c - \epsilon_t}{kT} \right) \\ &= 3.332 \times 10^{-12} \left( \frac{m}{m_e^*} \right) \left( \frac{1000}{T} \right)^2 \left( \frac{g_1}{g_0} \right) \left( \frac{10^{-16} \text{ cm}^2}{\sigma} \right) \exp \left( \frac{\epsilon_c - \epsilon_t}{kT} \right) \text{ sec} \end{aligned} \right\} (1)$$

where  $h$  is Planck's constant,  $k$  Boltzmann's constant,  $m$  the normal electron mass,  $T$  the absolute temperature, and  $g_1, g_0$  are the statistical weights of full and empty traps, respectively.

The same formula applies, under analogous assumptions, to release of holes from hole traps (see § 9.3); for this case  $m_e^*$  is replaced by the effective mass  $m_h^*$  of holes,  $g_1$  and  $g_0$  refer to states respectively with and without a trapped hole, and  $\epsilon_c - \epsilon_t$  is replaced by  $\epsilon_t - \epsilon_v$ , the energy required to take an electron from the top of the valence band and place it in a trap which has previously captured a hole.

The same formula can be applied to cases where the capture cross section is inversely proportional to the energy of the mobile charge relative to the band edge, if for  $\sigma$  is set the cross section for an energy  $kT$ . Similarly it can be applied when the capture cross section is inversely proportional to the velocity, if for  $\sigma$  is set the cross section for a charge with the arithmetic mean thermal speed  $v_T = (2^3/2/\pi^{1/2}) (kT/m^*)^{1/2}$ .

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## Chapter 26

# THE THEORY OF MAGNETISM

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The following brief summary comprises some of the major formulas of the atomic theory of magnetism. They have been selected to provide the reader with basic relations and ones most likely to be useful for the research student. It is hoped that the explanatory text will fill in the background necessary for the understanding of the fundamentals. The emphasis is entirely on the atomic or molecular viewpoint, and no attempt is made to include domain theory, or so-called phenomena of "technical magnetization," such as remanence, hysteresis, etc.

### 1. Paramagnetism

**1.1. -Classical theory.** Langevin's formula for the magnetic moment  $M$  per unit volume in a field of arbitrary strength  $H$  is

$$M = N\mu L(\mu H/kT) \quad (1)$$

where  $N$  is the number of atoms or molecules per unit volume,  $\mu$  is the magnetic dipole moment of the atom or molecule, and  $L(x)$  is the Langevin function

$$L(x) = \coth x - 1/x \quad (2)$$

In weak fields (i.e.,  $\mu H/kT \ll 1$ ), the Langevin formula reduces to the following expression for the susceptibility :

$$\chi = M/H = N\mu^2/3kT \quad (3)$$

The proportionality of the paramagnetic susceptibility to the reciprocal of the temperature constitutes Curie's law. The proportionality factor is known as the Curie constant. According to the Langevin formula, the Curie constant is  $N\mu^2/3k$ .

**1.2. Quantum theory.** In quantum mechanics, Curie's law is valid if the matrix elements of the magnetic moment exist only between states whose separation is small compared with  $kT$ , and if there is a permanent magnetic moment  $\mu$ . A permanent magnetic moment signifies that the square of the magnetic moment has the same expectation value for all states that possess an appreciable Boltzmann factor. If in addition matrix elements exist connecting states widely spaced compared with  $kT$ , the susceptibility will contain a term independent of temperature, i.e.,

$$\chi = N\mu^2/3kT + N\alpha$$

If there are matrix elements joining states separated by intervals comparable to  $kT$ , deviations from Curie's law will occur.

a. *Free atoms with multiplets wide compared with  $kT$ .* In a field of arbitrary strength, the moment is

$$M = N J g \beta B_J \left( \frac{J g \beta H}{kT} \right) + N \alpha_J H \quad (1)$$

Here  $J$  is the atom's inner quantum number,  $g$  is the Landé factor,  $\beta$  is the Bohr magneton  $he/4\pi mc = 0.927 \times 10^{-20}$  erg · gauss<sup>-1</sup>, and  $B_J$  is the Brillouin function.

$$B_J(y) = \frac{\sum_{M=-J}^J M e^{M y / J}}{\sum_{M=-J}^J e^{M y / J}} \quad \left. \vphantom{B_J(y)} \right\} \quad (2)$$

$$= \frac{2J+1}{2J} \coth \left( \frac{2Jy+y}{2J} \right) - \frac{1}{2J} \coth \frac{y}{2J}$$

The last member  $N\alpha_J H$  of Eq. (1) is a correction term for the effect of the matrix elements of the magnetic moment which are nondiagonal in  $J$ . It is assumed that the Zeeman separations are small compared with the multiplet intervals  $\hbar\nu(J', J)$ , and that the latter are large compared with  $kT$ . The explicit formula for  $\alpha_J$  is

$$\alpha_J = \frac{\beta^2}{6(2J+1)} \left[ \frac{F(J+1)}{\hbar\nu(J+1, J)} - \frac{F(J)}{\hbar\nu(J, J-1)} \right] \quad (3)$$

where

$$F(J) = \frac{1}{J} [(S+L+1)^2 - J^2] [J^2 - (S-L)^2]$$

In weak fields ( $Jg\beta H \ll kT$ ), the susceptibility is

$$\chi = \frac{Ng^2J(J+1)\beta^2}{3kT} + N\alpha_J \quad (4)$$

The following formulas (5) to (8) are given only for the case of weak fields, i.e., with neglect of saturation effects.

b. *Free atoms with multiplets small compared with  $kT$ .*

$$\chi = \frac{N\beta^2}{3kT} [4S(S+1) + L(L+1)] \quad (5)$$

c. *Free atoms with multiplet separations comparable to  $kT$*

$$\chi = N \frac{\sum_{J=L-S}^{L+S} \left[ \frac{g_J^2 \beta^2 J(J+1)}{3kT} + \alpha_J \right] e^{-E_J/kT}}{\sum e^{-E_J/kT}} \quad (6)$$

Here the  $E_J$  are the energies of the various multiplet components of the atom in the absence of a magnetic field. The subscript  $J$  is attached to the  $g$ -factor to indicate that it depends on  $J$ .

d. *Free molecules.* Practically all free molecules except NO have susceptibilities conforming to the "spin-only" formula

$$\chi = \frac{4N\beta^2 S(S+1)}{3kT} + N\alpha \quad (7)$$

Here  $N\alpha$  is a small correction term, independent of temperature, arising from the orbital magnetic moment, which is highly nondiagonal.

Nitric oxide is the standard example of a molecule that deviates from Curie's law because the multiplets interval  $\Delta\nu$  is comparable with  $kT$ . Here

$$\chi = \frac{4N\beta^2}{3kT} \left[ \frac{1 - e^{-z} + ze^{-z}}{z(1 + e^{-z})} \right] + N\alpha \quad (8)$$

where

$$z = \frac{h\Delta\nu}{kT} = \frac{173}{T}$$

e. *Solids of high magnetic dilution.* In such solutions the paramagnetic ions are widely separated. They are usually highly hydrated salts. Such materials can be treated by means of a one-atom model, based on the idea that an ion is subject to a crystalline potential  $V(x,y,z)$  which represents the effect of the interatomic forces. Let  $E_n$  be the energy of a quantum-mechanical state, including both the Stark energy arising from the crystalline field, and the Zeeman energy caused by the applied magnetic field. The

quantum-mechanical formula for the expectation value of the magnetic moment of an arbitrary state  $n$  is in general,

$$\langle M_n \rangle_{\text{av}} = -\partial E_n / \partial H \quad (9)$$

The magnetic moment per unit volume is thus

$$M = -N \frac{\sum_n (\partial E_n / \partial H) e^{-E_n/kT}}{\sum_n e^{-E_n/kT}} \quad (10)$$

In case the energy  $E_n$  can be developed as a Taylor's series in  $H$ , viz.,

$$E_n = E_n^{(0)} + E_n^{(1)}H + E_n^{(2)}H^2 + \dots$$

the expression for the susceptibility in weak fields is

$$\chi = \frac{N \sum_n [(E_n^{(1)})^2/kT - 2E_n^{(2)}] e^{-E_n^{(0)}/kT}}{\sum_n e^{-E_n^{(0)}/kT}} \quad (11)$$

In salts of the iron group, the crystalline potential largely quenches the orbital moment, and the spin-only formula [Eq. (7) of § 1.2] is often a fairly good approximation. Rare-earth salts at room temperatures can usually be treated as having free atoms [Eq. (4) or (6) of § 1.2].

f. *Magnetically compact solids.* These require inclusion of exchange coupling between atoms and cannot be treated on the basis of the one-atom model. Oftentimes the exchange coupling can be approximately represented by means of a Weiss molecular field [see Eq. (1) of § 2.1].

g. *Nuclear effects.* Nuclear effects on the paramagnetic susceptibility are negligible as long as the hyperfine structure is small compared with  $kT$ .

h. *Spectroscopic stability.* In general any interaction producing a fine structure small compared with  $kT$  does not influence the susceptibility, which is thus the same as if the interaction were completely absent.

## 2. Ferromagnetism

**2.1. Classical theory.** The standard model, semitheoretical, semi-phenomenological, of ferromagnetism in classical theory is that of Weiss, wherein the field in the argument of the Langevin-function involved in Eq. (1) of § 1.1 is taken to be not the applied field, but rather the field augmented by a "Weiss molecular field" proportional to the intensity of magnetization. The total effective field is then

$$H_{\text{eff}} = H + qM \quad (1)$$

and in place of Eq. (1) of § 1.1, one has

$$M = N\mu L \left[ \frac{\mu(H + qM)}{kT} \right] \quad (2)$$

The Curie temperature  $T_c$  is that below which spontaneous magnetization is possible, i.e., below which Eq. (2) admits a solution with  $H = 0$ . It is

$$T_c = N\mu^2q/3k \quad (3)$$

For  $T > T_c$ , the susceptibility, apart from saturation corrections, has the form

$$\chi = N\mu^2/3k(T - T_c) \quad (4)$$

**2.2. Quantum theory.** a. *Heisenberg model.* Heisenberg showed that the origin of the Weiss molecular field is to be found in exchange coupling. In his model each atom contains one or more uncompensated electron spins (Heitler-London model of valence). The exchange effects introduce an interatomic potential of the form

$$V = -2 \sum_i \sum_j \mathcal{J}_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (1)$$

where  $\mathbf{S}_i$  is the spin-vector of atom  $i$ , and  $\mathcal{J}_{ij}$  is the exchange integral joining atoms  $i$  and  $j$ . Usually  $\mathcal{J}_{ij}$  is assumed, for simplicity, to have a nonvanishing value  $\mathcal{J}$  only between adjacent atoms.

Even with this simplification, an exact analytical expression for the moment is obtainable only in the vicinity of the absolute zero, where the so-called Bloch spin waves can be used. In the region, i.e.,  $\mathcal{J}/kT \ll 1$ , one has for the special case  $S = \frac{1}{2}$ ,

$$M = N\beta \left[ 1 - A \left( \frac{kT}{\mathcal{J}} \right)^{3/2} \right] \quad (2)$$

where  $A$  is a constant, which assumes the value 0.1174 for a simple cubic lattice.

At higher temperatures, great simplification follows from the use of the so-called first approximation of the Heisenberg theory, wherein it is assumed that all states of the same resultant spin for the whole crystal have the same energy. This approximation is questionable from a mathematical standpoint but seems to work fairly well and gives results remarkably similar to those of the Weiss theory. In place of Eqs. (2) and (3) of § 2.1 one has

$$M = gNS\beta B_S \left[ \frac{gS\beta(H + qM)}{kT} \right] \quad (3)$$

with  $q = 2z\mathcal{J}/g^2N\beta^2$ .

$$T_c = \frac{2\mathcal{J}zS(S + 1)}{3k} \quad (4)$$

Here  $B_S(y)$  is defined as in Eq. (2) of § 1.2, and  $z$  denotes the number of nearest neighbors possessed by an atom. Eq. (4) of § 2.1 is applicable with

$$\mu^2 = g^2 \beta^2 S(S+1) \quad (5)$$

More accurate analysis gives a somewhat different formula than Eq. (4) for  $T_c$ . An accurate development of the reciprocal of the susceptibility above the Curie point takes the form

$$\frac{1}{\chi} = \frac{3k}{g^2 N \beta^2 S(S+1)} \left( T - \Delta + \frac{a}{T} + \frac{b}{T^2} + \frac{c}{T^3} + \dots \right) \quad (6)$$

The most extensive calculations of the series (6) have been made by Luttinger and Brown, Domb and Sykes, and by Rushbrook and Wood.

b. *Stoner's model of "collective electron ferromagnetism."* The Stoner model is the analogue of the Hund-Mulliken theory of valence, and assumes that electrons wander from atom to atom, instead of being bound to a given atom. Besides the intensity of the exchange coupling or molecular field, the conduction band width enters as a disposable constant.

The free energy  $F$ , specific heat  $C_v$ , and moment  $M$  are computed as follows from a characteristic function  $\Gamma$ .

$$F = NkT - kT\Gamma, \quad C_v = \frac{\partial}{\partial T} \left[ kT^2 \left( \frac{\partial \Gamma}{\partial T} \right)_\eta \right], \quad M = kT \left( \frac{\partial \Gamma}{\partial H} \right)_\eta \quad (7)$$

The Stoner expression for  $\Gamma$  is

$$\left. \begin{aligned} \Gamma &= \int_0^\infty \nu(\epsilon) \ln [1 + e^{\eta - (\epsilon - qM\beta - \beta H)/kT}] d\epsilon \\ &+ \int_0^\infty \nu(\epsilon) \ln [1 + e^{\eta - (\epsilon + qM\beta + \beta H)/kT}] d\epsilon \end{aligned} \right\} \quad (8)$$

Here  $\nu(\epsilon)$  is the number of states in the interval  $\epsilon, \epsilon + d\epsilon$ . The constant  $\eta$  is given in terms of the number of atoms  $N$  per unit volume by the relation

$$N = (\partial \Gamma / \partial \eta)_T \quad (9)$$

**2.3. Anisotropic effects.** These effects, and phenomena such as hysteresis, remanence, etc., are not included in the Heisenberg or Stoner models. Most of these subjects belong to the domain theory of magnetism. The phenomenological energy of anisotropy for a cubic crystal has the form

$$E_{\text{anisotropy}} = K_1(\alpha_1^2 \alpha_2^2 + \alpha_1^2 \alpha_3^2 + \alpha_3^2 \alpha_2^2) + K_2(\alpha_1^2 \alpha_2^2 \alpha_3^2) \quad (1)$$

where  $\alpha_1, \alpha_2, \alpha_3$  are the direction cosines of the intensity of magnetism relative to the principal cubic axes. The anisotropy constants  $K_1, K_2$  have their

origin presumably in spin-orbit interaction, but their theory is at present none too satisfactory.

**2.4. Antiferromagnetics.** For ferromagnetism it is necessary that the exchange integral  $\mathcal{J}$  be positive. If instead it is negative and sufficiently great in magnitude, antiferromagnetism can occur. This is substantially a form of paramagnetism rather than of ferromagnetism, since the susceptibility is relatively small and depends little on field strength. There is a Curie point  $T_c$  at which the susceptibility is a maximum. Below this Curie temperature there is an antiparallel or staggered ordering of the spins, whence the name antiferromagnetism arises. With simple models, the susceptibility at  $T = 0$  is two-thirds of that at the Curie point

$$\chi_{T=0} = \frac{2}{3}\chi_{T=T_c} \quad (1)$$

If approximations analogous to those of the Weiss field are employed, the formula for the susceptibility above the Curie point is

$$\chi = \frac{g^2 N \beta^2 S(S+1)}{3(T + cT_c)} \quad (2)$$

The value of the constant  $c$  is 1 if one includes only coupling between nearest atomic neighbors, but Néel and Anderson showed that with other, more complicated models, which come closer to reality,  $c$  can be as high as 5.

### 3. Diamagnetism and Feeble Paramagnetism

**3.1. Classical theory of diamagnetism.** The Langevin-Pauli formula for the diamagnetic susceptibility of an atom is

$$\chi = -\frac{Ne^2}{6mc^2} \overline{\sum_i r_i^2} \quad (1)$$

where the bars denote the time average and the summation is over all the electrons in the atom.

**3.2. Quantum theory of diamagnetism.** a. *Atoms.* Equation (1) of § 3.1 still holds as long as one is dealing with isolated atoms, e.g., a monatomic gas.

b. *Molecules.* For a nonmonatomic molecule, the expression for the diamagnetic susceptibility is

$$\chi = -\frac{Ne^2}{6mc^2} \sum \overline{r_i^2} + 2N \sum_{n'} \frac{|\mu_z(n;n')|^2}{E_{n'} - E_n} \quad (1)$$

Here  $\mu_z(n;n')$  is an off-diagonal matrix element of the molecule's magnetic moment along the  $z$  axis, which we take as the direction of the applied field.

The summation over  $n'$  in Eq. (1) is over all the excited states of the molecule. We have supposed the ground state to be nondegenerate. If there is degeneracy, Eq. (1) should be averaged over the different states  $n$  associated with the degeneracy.

c. *Free electrons.* Landau's formula for the diamagnetism of free conduction electrons is

$$\chi = -\frac{4m\beta^2}{\hbar^2} \left( \frac{N\pi^2}{9} \right)^{1/3} \quad (2)$$

Classical theory would give instead  $\chi = 0$ .

**3.3. Feeble paramagnetism.** A common kind of magnetic behavior may be termed feeble paramagnetism, wherein the susceptibility is considerably smaller than that given by Langevin's formula and substantially independent of temperature. Feeble paramagnetism can be due to one of three causes.

a. *Atoms or ions with matrix elements of magnetic moment existing between, and only between, states whose separation is large compared with  $kT$ .* This represents simply a preponderance of the second or paramagnetic part of Eq. (1) of § 3.2 compared with the first term, so that the expression is positive.

b. *Inhibition of the alignment of the spin of conduction electrons by the Fermi-Dirac statistics.* According to Boltzmann statistics, free conduction electrons would have a strong paramagnetism because of their spin. Pauli showed that with the actual or Fermi-Dirac statistics, the resulting paramagnetism is, except for sign, three times the expression (2) of § 3.2, i.e.,

$$\chi = \frac{12m\beta^2}{\hbar^2} \left( \frac{N\pi^2}{9} \right)^{1/3} \quad (1)$$

The total susceptibility hence has a value two-thirds as great as that given in Eq. (1).

c. *Antiferromagnetism.* The susceptibility of an antiferromagnetic is small and sensibly independent of  $T$  if  $T_c \gg T$  in Eq. (2) of § 2.4.

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## Chapter 27

### PHYSICAL CHEMISTRY

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#### 1. Chemical Equilibrium

**1.1. Equilibrium constant or "mass action law."** If the chemical reaction



is at equilibrium, then

$$\frac{(P_M)^m(P_N)^n \dots}{(P_A)^a(P_B)^b \dots} = K_p \quad (1)$$

$$\frac{(x_M)^m(x_N)^n \dots}{(x_A)^a(x_B)^b \dots} = K_x \quad (2)$$

$$\frac{(C_M)^m(C_N)^n \dots}{(C_A)^a(C_B)^b \dots} = K_c \quad (3)$$

where  $K_p$  is the equilibrium constant in pressure units;  $P_i$  is the partial pressure of the substance  $i$ , in atmospheres;  $K_x$  is the equilibrium constant in mole fraction units;  $x_i$  is the mole fraction of substance  $i$ ;  $K_c$  is the equilibrium constant in concentration units;  $C_i$  is the concentration of substance  $i$ , in moles per liter. Pressure units are customarily used for equilibrium constants involving gases, though it is possible to use mole fractions or concentrations for gases. Either mole fractions or concentrations may be used for reactions in solution; for reactions in aqueous solution, concentrations are usually used. For a reaction involving both gases and solutions, both pressure units and concentration units may be used in the same equilibrium constant. The concentration of pure solids and pure liquids is taken as unity, and the corresponding factors omitted from the equilibrium constants.

The constants  $K_p$ ,  $K_x$ , and  $K_c$  are approximately independent of concentrations. See also Chapters 10 and 11.

### 1.2. Equilibrium constant from calorimetric data.

$$K = e^{-\Delta F^\circ/RT} = e^{\Delta S^\circ/R} e^{-\Delta H^\circ/RT} \quad (1)$$

where  $\Delta F^\circ$  is the standard free energy change of the reaction, i.e., the free energy change for all reactants at one atmosphere partial pressure (for  $K_p$ ), or unit mole fraction (for  $K_x$ ), or one mole per liter (for  $K_c$ );  $\Delta S^\circ$  is the corresponding standard entropy change;  $\Delta H^\circ$  is the standard enthalpy change. When  $\Delta F^\circ$  is in calories per mole,  $R$  is 1.9865 calories per mole degree.

Since  $\Delta H^\circ$  is the heat absorbed by the reaction at constant pressure, it can be measured calorimetrically. Alternatively,  $\Delta H^\circ$  can be obtained by algebraic addition of heats of combustion of the several reactants, or of their heats of formation from the elements.

Here  $\Delta S^\circ$  can be computed from the tabulated standard entropies of the several reactants,

$$\Delta S^\circ = S_M^\circ + S_N^\circ + \dots - S_A^\circ - S_B^\circ - \dots$$

The individual standard entropies are obtained from

$$S^\circ = \int_0^T C_p d \ln T + \sum \frac{\Delta H_{tr}}{T_{tr}} \quad (2)$$

where  $C_p$  is the heat capacity at constant pressure, and  $\Delta H_{tr}$  is the heat of a phase transition occurring at temperature  $T_{tr}$ .

If the quantities  $\Delta F^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  are known at one temperature and pressure, but required at another temperature or pressure, they can be calculated with the thermodynamic relations,

$$\left. \begin{aligned} \left( \frac{\partial \Delta F}{\partial T} \right)_P &= -\Delta S, & \left( \frac{\partial \Delta F}{\partial P} \right)_T &= \Delta V \\ \left( \frac{\partial \Delta H}{\partial T} \right)_P &= \Delta C_p, & \left( \frac{\partial \Delta H}{\partial P} \right)_T &= \Delta V - T \left( \frac{\partial \Delta V}{\partial T} \right)_P \\ \left( \frac{\partial \Delta S}{\partial T} \right)_P &= \frac{\Delta C_p}{T}, & \left( \frac{\partial \Delta S}{\partial P} \right)_T &= - \left( \frac{\partial \Delta V}{\partial T} \right)_P \end{aligned} \right\} \quad (3)$$

**1.3. Equilibrium constant from electric cell voltages.** The relation between the voltage of a cell and the free energy of the cell reaction is

$$\epsilon = -\frac{\Delta F^0}{n_e \mathcal{F}} - \frac{RT}{n_e \mathcal{F}} \ln \frac{(C_M \gamma_M)^m (C_N \gamma_N)^n \dots}{(C_A \gamma_A)^a (C_B \gamma_B)^b \dots} \quad (1)$$

where  $n_e$  is the number of electrons flowing when the chemical reaction proceeds as written, and  $\mathcal{F}$  is Faraday's constant, 23,059 calories per electron volt. When all reactants are in their standard states, the last term vanishes and

$$\epsilon^0 = -\frac{\Delta F^0}{n_e \mathcal{F}} \quad (2)$$

where  $\epsilon^0$  is the "standard potential" of the cell. The equilibrium constant is given by

$$K = e^{n_e \mathcal{F} \epsilon^0 / RT} \quad (3)$$

At 25° C, this becomes

$$\log K = n_e \epsilon^0 / 0.0591 \quad (4)$$

#### 1.4. Pressure dependence of the equilibrium constant

$$\frac{K_{P_2}}{K_{P_1}} = e^{-\Delta V (P_2 - P_1) / RT} \quad (1)$$

where  $\Delta V$  is the molal volume change of the reaction, not including the volume of any gases consumed or produced. If  $\Delta V$  is in cubic centimeters and  $P_2 - P_1$  is in atmospheres,  $R$  is 82.07 cc atm per deg. Because  $\Delta V$  is usually small, the pressure dependence of most equilibrium constants is small.

#### 1.5. Temperature dependence of the equilibrium constant

$$K = e^{\Delta S^0 / R - \Delta H^0 / RT} \quad (1)$$

Since  $\Delta S^0$  and  $\Delta H^0$  are only slowly varying functions of temperature, they may be treated as constant over a moderate temperature interval. The form

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (2)$$

shows that a graph of  $\ln K$  against  $1/T$  will be almost a straight line. Equivalent expressions are

$$\left. \begin{aligned} \left( \frac{\partial \ln K}{\partial T} \right)_P &= \frac{\Delta H^0}{RT^2} \\ \left( \frac{\partial \ln K}{\partial (1/T)} \right)_P &= -\frac{\Delta H^0}{R} \end{aligned} \right\} \quad (3)$$

If the equilibrium constant is  $K_1$  at  $T_1$  and  $K_2$  at  $T_2$ , then the average values of  $\Delta H^\circ$  and  $\Delta S^\circ$  in this temperature interval are

$$\left. \begin{aligned} \Delta H^\circ &= \frac{4.57T_1T_2 \log(K_2/K_1)}{T_2 - T_1} \\ \Delta S^\circ &= \frac{4.57(T_2 \log K_2 - T_1 \log K_1)}{T_2 - T_1} \end{aligned} \right\} \quad (4)$$

A graph of the left-hand side of the following equation against  $1/T$  gives a perfectly straight line, whose slope is  $\Delta H^\circ_{T_0}/R$ .

$$\ln K - \frac{1}{R} \int_{T_0}^T \Delta C_p d \ln T + \frac{1}{RT} \int_{T_0}^T \Delta C_p dT = \frac{\Delta S^\circ_{T_0}}{R} - \frac{\Delta H^\circ_{T_0}}{RT} \quad (5)$$

## 2. Activity Coefficients

**2.1. The "thermodynamic" equilibrium constant.** The equilibrium constants  $K_p$ ,  $K_x$ , or  $K_c$  actually vary somewhat with concentration. To keep them truly constant, we can use "activities" instead of concentrations, each activity being a concentration multiplied by an "activity coefficient,"  $\gamma$ .

$$\frac{(P_M \gamma_M)^m (P_N \gamma_N)^n \dots}{(P_A \gamma_A)^a (P_B \gamma_B)^b \dots} = K_p \quad (1)$$

$$\frac{(x_M \gamma_M)^m (x_N \gamma_N)^n \dots}{(x_A \gamma_A)^a (x_B \gamma_B)^b \dots} = K_x \quad (2)$$

$$\frac{(C_M \gamma_M)^m (C_N \gamma_N)^n \dots}{(C_A \gamma_A)^a (C_B \gamma_B)^b \dots} = K_c \quad (3)$$

Such equilibrium constants are called "thermodynamic" or "activity" equilibrium constants, and sometimes written  $K_a$ . The  $\gamma$ 's are functions of concentration, which vary so as to keep the  $K_a$ 's exactly constant.

## 2.2. Thermodynamic interpretation of the activity coefficient

$$\gamma = e^{(F_{\text{real}} - F_{\text{ideal}})/RT} = e^{\Delta F^E/RT} \quad (1)$$

The activity coefficient can be calculated from the difference between the free energy of the actual substance and that of an ideal substance at the same concentration. This is sometimes called the "excess" free energy,  $\Delta F^E$ .

**2.3. Activity coefficients of gases.** The ideal gas is taken to be one which obeys the law  $PV = RT$ . The activity coefficient of a real gas is

$$\gamma = e^{\int_0^P \left( \frac{PV}{RT} - 1 \right) \frac{dP}{P}} \quad (1)$$

The integral can be evaluated graphically from the  $P$ - $V$ - $T$  data for a gas. Alternatively, the integral can be evaluated analytically, with the aid of an empirical equation of state for the gas. Some of these are listed below.

a. *van der Waals, 1873* :

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT \quad (1)$$

b. *Dieterici, 1899* :

$$P e^{a/RTV} (V - b) = RT \quad (2)$$

c. *Berthelot, 1907* :

$$\left( P + \frac{a}{TV^2} \right) (V - b) = RT \quad (3)$$

also 
$$\frac{PV}{RT} = 1 + \frac{9}{128} \cdot \frac{PT_c}{P_c T} \left( 1 - 6 \frac{T_c}{T} \right) \quad (4)$$

d. *Kamerlingh Onnes, 1901* :

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \quad (5)$$

or 
$$\left. \begin{aligned} \frac{PV}{RT} = 1 + B \left( \frac{P}{RT} \right) + (C - B^2) \left( \frac{P}{RT} \right)^2 \\ + (D - 3BC + 2B^3) \left( \frac{P}{RT} \right)^3 + \dots \end{aligned} \right\} \quad (6)$$

e. *Keyes, 1917* :

$$\left[ P + \frac{a}{(V-f)^2} \right] (V - b e^{-a/V}) = RT \quad (7)$$

f. *Beattie and Bridgeman, 1927-1928* :

$$P + \frac{A_0}{V^2} \left( 1 - \frac{a}{V} \right) = \frac{RT}{V^2} \left( 1 - \frac{c}{VT^3} \right) \left( V + B - \frac{bB}{V} \right) \quad (8)$$

g. *Benedict, Webb, and Rubin, 1940* :

$$\frac{PV}{RT} = 1 + \frac{V^3}{RT} \left( RTB - A - \frac{C}{T^2} \right) \quad (9)$$

where

$$B = B_0 + \frac{b}{V}$$

$$A = A_0 + \frac{a}{V} - \frac{a\alpha}{V^4}$$

$$C = C_0 - \frac{c}{V} \left( 1 + \frac{\gamma}{V^2} \right) e^{-\gamma/V^2}$$

The activity coefficient calculated from the Kamerlingh Onnes equation of state ("virial equation") is

$$\ln \gamma = \frac{BP}{RT} + \frac{(C - B^2)}{2} \left( \frac{P}{RT} \right)^2 + \frac{(D - 3BC + 2B^3)}{3} \left( \frac{P}{RT} \right)^3 + \dots \quad (10)$$

#### 2.4. Activity coefficient from the "law of corresponding states."

The law of corresponding states, which is obeyed fairly well by most gases, says that  $V/V_c$  is a universal function of  $P/P_c$  and  $T/T_c$ , where  $V_c$ ,  $P_c$ ,  $T_c$  are the critical volume, pressure, and temperature. For gases which obey this law,  $\gamma$  likewise is a universal function of  $P/P_c$  and  $T/T_c$ . Consequently, a single graph can be prepared, giving  $\gamma$  as a function of  $P/P_c$ , for various values of  $T/T_c$  (e.g., Newton, 1935). This is an extremely convenient method for evaluating  $\gamma$  for any gas whose critical constants are known.

**2.5. Activity coefficients of nonelectrolytes in solution.** If the pure liquid is taken as the standard state, an ideal solution is one whose components obey Raoult's law,

$$\frac{P_i}{P_i^0} = x_i \quad (1)$$

where  $P_i$  is the vapor pressure of substance  $i$ ,  $P_i^0$  its vapor pressure when pure, and  $x_i$  its mole fraction. The activity coefficient of component  $i$  in a real solution is given by

$$\frac{P_i}{P_i^0} = \gamma_i x_i \quad (2)$$

The partial pressures  $P$ , and  $P_i^0$  should also be multiplied by the appropriate activity coefficients for the gases, but this is usually a negligible correction.

Sometimes the infinitely dilute solution of component  $i$  is taken as its standard state; in this case, an ideal solution is one which obeys Henry's law,

$$P_i = k_H x_i \quad (3)$$

where  $k_H$  is "Henry's-law constant" for that component. (Henry's law can also be written for various other concentration units.) The activity coefficient is then given by

$$P_i = k_H \gamma_i x_i \quad (4)$$

where

$$k_H = \lim_{x_i \rightarrow 0} (P_i/x_i)$$

**2.6. The Gibbs-Duhem equation.** The activity coefficient of a non-volatile component can be computed, if the activity coefficient of the volatile solvent is known over the whole concentration range, by integrating the relation

$$\sum_j x_j d \ln (\gamma_j x_j) = 0 \quad (1)$$

(Gibbs 1876, Duhem 1886, Margules 1895, Leffelt 1895). For a two-component system this becomes

$$-\ln \gamma_A = \int_0^{x_B} \frac{x_B}{1-x_B} d \ln \gamma_B \quad (2)$$

**2.7. The enthalpy of nonideal solutions.** For an ideal solution, there is no heat of mixing, and  $\Delta H^E$  is zero for all components. For nonideal solutions, the heat of mixing is given approximately by the van Laar (1906), Hildebrand (1927), Scatchard (1931) equation,

$$\Delta H^E = (\delta_2 - \delta_1)^2 (x_1 V_1 + x_2 V_2) \phi_1 \phi_2 \quad (1)$$

where  $\delta$  is a quantity called the "solubility parameter,"  $x$  is the mole fraction,  $V$  the molal volume, and  $\phi$  the volume fraction of the substance in question. The excess enthalpy for an individual component,  $\Delta \bar{H}_1^E$ , is

$$\Delta \bar{H}_1^E = (\delta_2 - \delta_1)^2 V_1 \phi_2^2 \quad (2)$$

and  $\Delta \bar{H}_2^E$  is given by the same equation with subscripts interchanged. For many solutions, called "regular" solutions, the entropy of solution is ideal, and for these the activity coefficient is

$$\gamma_1 = e^{[(\delta_2 - \delta_1)^2 V_1 / RT] \phi_2^2} \quad (3)$$

for component 1, the subscripts being interchanged for component 2.

The solubility parameter,  $\delta$ , for a substance is given by

$$\delta^2 = \Delta E_{\text{vap}}/V \quad (4)$$

where  $\Delta E_{\text{vap}}$  is the energy change of vaporization of the pure liquid at the temperature in question, and  $V$  is the molal volume of the liquid. Solubility parameters for a number of liquids have been tabulated by Hildebrand and Scott (1950).

**2.8. The entropy of nonideal solutions.** For ideal solutions, the entropy change of mixing is

$$-\frac{\Delta S}{R} = x_1 \ln x_1 + x_2 \ln x_2 \quad (1)$$

For solutions of molecules of different molal volume, the entropy change of mixing is given approximately by the Flory (1941), Huggins (1941) equation,

$$-\frac{\Delta S}{R} = x_1 \ln \phi_1 + x_2 \ln \phi_2 \quad (2)$$

For an individual component, the entropy of mixing is

$$-\frac{\Delta \bar{S}_1}{R} = \ln \phi_1 + \phi_2(1 - V_1/V_2) \quad (3)$$

and the excess entropy is

$$-\frac{\Delta \bar{S}_1^E}{R} = \phi_2(1 - V_1/V_2) + \ln [1 - \phi_2(1 - V_1/V_2)] \quad (4)$$

For a solution with no heat of mixing, the activity coefficient is

$$\gamma_1 = [1 - \phi_2(1 - V_1/V_2)]e^{\phi_2(1 - V_1/V_2)} \quad (5)$$

The same equations, with subscripts interchanged, hold for the other component.

These equations were first derived to apply to solutions of high polymers, where the difference in molal volumes of solvent and solute are very great.

If the components have different molal volumes, and there is also a heat of mixing, the Flory-Huggins and the van Laar-Hildebrand-Scatchard equations are combined.

**2.9. The activity coefficients of aqueous electrolytes.** These are usually obtained by applying the Gibbs-Duhem equation (§ 2.6) to the activity coefficient of the water. The latter can be measured through its vapor pressure, or its freezing point or boiling point. To obtain activity coefficients

from freezing points, we first define the “freezing point depression constant,”  $k_F$ , by

$$k_F = \lim_{C \rightarrow 0} (\Delta T/C)$$

where  $\Delta T$  is the freezing point depression and  $C$  the molal concentration of solute. Then the expected freezing point depression for any concentration is  $k_F C$ . We define  $j$  as the fractional amount by which the expected freezing point depression exceeds the actual depression,  $j = (k_F C - \Delta T)/k_F C$ . Then the activity coefficient of the solute is

$$-\ln \gamma = j + \int_0^C j d \ln C \quad (1)$$

The activity coefficient of an electrolyte can also be determined from the voltage of an electrical cell.

$$\epsilon = -\frac{\Delta F^0}{n_e \mathcal{F}} - \frac{RT}{n_e \mathcal{F}} \ln \frac{(C_M \gamma_M)^m (C_N \gamma_N)^n \dots}{(C_A \gamma_A)^a (C_B \gamma_B)^b \dots} \quad (2)$$

Here  $\Delta F^0$  is evaluated by a suitable extrapolation of the cell voltage to infinite dilution, where all  $\gamma$ 's become unity.

The activity coefficient of a single ion cannot be measured; what is actually measured is the “mean activity coefficient” which is often written  $\gamma_{\pm}$  to emphasize this fact.

$$\gamma_{\pm} = \Sigma v_i \gamma_i / \Sigma v_i \quad (3)$$

where  $v_i$  is the number of ions of species  $i$ , whose true activity coefficient is  $\gamma_i$ .

**2.10. The Debye-Hückel equation.** The activity coefficient of a single ion is given approximately by the equation due to Debye and Hückel (1923),

$$-\ln \gamma_i = \left[ \frac{e^3}{(DkT)^{3/2}} \sqrt{\frac{2\pi N}{1000}} \right] z_i^2 \sqrt{\mu} \quad (1)$$

where

$$\mu = \frac{1}{2} \Sigma C_j z_j^2$$

Here  $e$  is the charge of the electron,  $D$  the dielectric constant of water,  $k$  Boltzmann's constant,  $N$  Avogadro's number, and  $z$  the charge of the ion. The quantity  $\mu$  is called the “ionic strength.” At 25°C, the activity coefficient of a single ion is

$$-\log \gamma_i = 0.509 z_i^2 \sqrt{\mu} \quad (2)$$

and the mean activity coefficient is

$$-\log \gamma_{\pm} = 0.509 \frac{\sum v_i z_i^2}{\sum v_i} \sqrt{\mu} \quad (3)$$

The corresponding mean excess free energy, excess enthalpy, and excess entropy of an ion are, at 25° C,

$$\left. \begin{aligned} \Delta \bar{F}_{\pm}^E &= 695 \frac{\sum v_i z_i^2}{\sum v_i} \sqrt{\mu} && \text{calories per mole} \\ \Delta \bar{H}_{\pm}^E &= 359 \frac{\sum v_i z_i^2}{\sum v_i} \sqrt{\mu} && \text{calories per mole} \\ \Delta \bar{S}_{\pm}^E &= -1.12 \frac{\sum v_i z_i^2}{\sum v_i} \sqrt{\mu} && \text{calories per mole degree} \end{aligned} \right\} (4)$$

The Debye-Hückel equation is applicable only to very dilute solutions. An extended equation, good to somewhat higher concentrations, is

$$-\log \gamma_{\pm} = \frac{0.509(\sum v_i z_i^2 / \sum v_i) \sqrt{\mu}}{1 + A \sqrt{\mu}} + B\mu \quad (5)$$

where  $A$  and  $B$  are adjustable parameters.

### 3. Changes of State

**3.1. Phase rule.** If  $p$  is the number of phases in a system at equilibrium,  $c$  the number of components, and  $f$  the number of degrees of freedom, Gibbs' "phase rule" is

$$p + f = c + 2 \quad (1)$$

**3.2. One component, solid-solid and solid-liquid transitions.** Solid phase transitions and melting occur sharply at a temperature  $T_{tr}$ , which can be evaluated from thermal data :

$$T_{tr} = \Delta H_{tr} / \Delta S_{tr} \quad (1)$$

The dependence of the transition temperature on pressure is given by the Clausius-Clapeyron equation,

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S} \quad (2)$$

where  $\Delta V$  is the volume change of the transition, and  $\Delta S$  its entropy change.

**3.3. One component, solid-gas and liquid-gas transitions.** The partial vapor pressure of a pure liquid or solid is

$$P = e^{\Delta S^{\circ}/R - \Delta H^{\circ}/RT} \quad (1)$$

where  $\Delta S^{\circ}$  is the standard entropy change and  $\Delta H^{\circ}$  the standard enthalpy change of the process. Since  $\Delta S^{\circ}$  and  $\Delta H^{\circ}$  are only slowly varying functions of temperature, the vapor pressure is given approximately by

$$\log P = A - \frac{B}{T} \quad (2)$$

and to a somewhat better approximation by

$$\log P = A - \frac{B}{T} + C \log T \quad (3)$$

The partial pressure  $P$  in these equations ought to be multiplied by the activity coefficient of the gas, but this is usually a negligible correction.

The dependence of vapor pressure on total pressure is

$$\frac{P_{\text{at total pressure } P_2}}{P_{\text{at total pressure } P_1}} = e^{(P_2 - P_1)V_{\text{liq}}/RT} \quad (4)$$

where  $V_{\text{liq}}$  is the molal volume of the liquid.

**3.4. Two components, solid-liquid transition.** The general equation for the solubility of a solid in a solution, or, what amounts to the same process, the freezing of one component out of a solution, is

$$x_A \gamma_A = e^{\Delta S_A^{\circ}/R - \Delta H_A^{\circ}/RT} \quad (1)$$

where  $x_A$  is the mole fraction in solution of that substance which is also present as solid,  $\gamma_A$  its activity coefficient in the solution,  $\Delta S_A^{\circ}$  its entropy of fusion and  $\Delta H_A^{\circ}$  its enthalpy of fusion.

For dilute solutions, the freezing-point law takes the approximate form

$$\Delta T = \frac{RT_A^2}{\Delta H_A^{\circ}} x_B \quad \left. \vphantom{\Delta T} \right\} (2)$$

or

$$\Delta T = \frac{RT_A^2 M_A}{\Delta H_A^{\circ} 1000} C_B = k_F C_B$$

where  $T_A$  is the melting point of the solvent,  $\Delta H_A^{\circ}$  its molal heat of fusion, and  $M_A$  its molecular weight;  $x_B$  is the mole fraction of solute, and  $C_B$  the molal concentration of solute.

The eutectic temperature, which is the temperature at which both solids coexist with solution, can be calculated from the general solubility equations for both components, and the additional condition that  $x_A + x_B = 1$ .

The solubility of an electrolyte, which on dissolving gives  $a$  ions A and  $b$  ions B, is given by

$$(C_A)^a(C_B)^b(\gamma_{\pm})^{a+b} = K \quad (3)$$

**3.5. Two components, liquid-vapor transition.** The partial pressure of each component of a solution is given by

$$\frac{P_A}{x_A \gamma_A} = P_A^o = e^{\Delta S_A^o/R - \Delta H_A^o/RT} \quad (1)$$

where  $\gamma_A$  is its activity coefficient in the solution, and  $\Delta S_A^o$  and  $\Delta H_A^o$  its entropy of vaporization and enthalpy of vaporization, respectively.

The boiling point of a solution is the temperature at which  $P_A + P_B = 1$ . The boiling point of a mixture of two mutually insoluble liquids is the temperature at which  $P_A^o + P_B^o = 1$ . The vapor composition at the boiling point is  $x_A = P_A$ ,  $x_B = P_B$ .

If a nonvolatile solute is dissolved in a volatile solvent, the approximate boiling-point elevation in dilute solution is

$$\left. \begin{aligned} \Delta T &= \frac{RT_A^2}{-\Delta H_A^o} x_B \\ \text{or} \quad \Delta T &= \frac{RT_A^2 M_A}{-\Delta H_A^o 1000} C_B = k_B C_B \end{aligned} \right\} \quad (2)$$

where  $T_A$  is the boiling point of the solvent,  $\Delta H_A^o$  its molal heat of vaporization, and  $M_A$  its molecular weight;  $x_B$  is the mole fraction of solute,  $C_B$  its molal concentration.

If  $x$  is the mole fraction of one component in the solution, and  $y$  the mole fraction of that component in the vapor phase, then Rayleigh's equation (1902) for differential distillation is

$$\ln f = \int_{x_0}^x \frac{dx}{y - x} \quad (3)$$

where  $f$  is the fraction of the liquid remaining unvaporized when the solution composition has gone from  $x_0$  to  $x$ .

**3.6. Liquid-liquid transition.** If there are two liquid phases, the general condition for equilibrium is that the activity of any component must be the same in both phases.

$$\left. \begin{aligned} x_A \gamma_A &= x_A' \gamma_A' \\ x_B \gamma_B &= x_B' \gamma_B' \end{aligned} \right\} \quad (1)$$

The temperature at which a binary solution separates into two liquid layers, the "consolute temperature," is given approximately by

$$2RT_c = V(\delta_1 - \delta_2)^2 \quad (2)$$

where  $\delta_1$  and  $\delta_2$  are the solubility parameters of the two pure components (see § 2.7).

**3.7. Osmotic pressure.** The general expression for osmotic pressure is

$$x_1\gamma_1 = e^{-\Pi V_1/RT} \quad (1)$$

where  $\Pi$  is the osmotic pressure,  $x_1$  the mole fraction of solvent in the solution and  $\gamma_1$  its activity coefficient there, and  $V_1$  its molal volume. (The effect of pressure on the molal volume has been disregarded.) If  $\Pi$  is in atmospheres and  $V_1$  in cubic centimeters,  $R$  is 82.07.

For very dilute solutions, the osmotic pressure law takes the approximate form (van't Hoff's law)

$$\Pi V_1 = x_2 RT \quad (2)$$

**3.8. Gibbs-Donnan membrane equilibrium.** Two solutions are separated by a semipermeable membrane; in one of them is a concentration  $C_R$  of an ionic salt AR, the ion R being unable to penetrate the membrane; the solutions also contain a total concentration  $C_B$  of a freely diffusible ionic salt AB. If we denote by  $C_B'$  the concentration of diffusible salt which at equilibrium is in the solution containing AR, and by  $C_B''$  the concentration of diffusible salt in the other solution, the equilibrium condition is

$$\frac{(C_B')(C_B' + C_R)(\gamma_{\pm}')^2}{(C_B'')^2(\gamma_{\pm}'')^2} = 1 \quad (1)$$

For the special case where the activity coefficients are unity, this becomes

$$\frac{C_B''}{C_B'} = \frac{C_B + C_R}{C_B} \quad (2)$$

## 4. Surface Phenomena

**4.1. Surface tension.** The surface tension,  $\gamma$ , is defined as the free energy of formation of unit surface area,

$$dF = \gamma d\sigma \quad (1)$$

It is usually measured in ergs per square centimeter (dynes per centimeter).

## 4.2. Experimental measurement of surface tension

### a. Capillary rise

$$\gamma = \frac{1}{2}gh(\rho - \rho_0)/\cos \theta \quad (1)$$

where  $g$  is the acceleration of gravity,  $h$  the capillary rise,  $\rho$  the liquid density,  $\rho_0$  the density of the vapor above it, and  $\theta$  the contact angle. For a liquid which wets the capillary wall, the contact angle is zero.

b. *Bubble pressure.* The pressure increment across a curved surface, of radius of curvature  $r$ , is

$$\Delta P = 2\gamma/r \quad (2)$$

The maximum pressure sustained by a bubble forming at depth  $h$  in a liquid is

$$\Delta P = 2\gamma/r + gh(\rho - \rho_0) \quad (3)$$

The differential pressure in a "soap bubble," which has two surfaces, is

$$\Delta P = 4\gamma/r \quad (4)$$

### c. Ring tensimeter

$$\gamma = Ff/4\pi r \quad (5)$$

where  $f$  is the force sustained by the ring, whose radius is  $r$ , and  $F$  is a correction factor which lies between 0.75 and 1.02 (Harkins and Jordan, 1930).

### d. Drop weight

$$\gamma = F'mg/4r \quad (6)$$

where  $m$  is the mass of a drop,  $r$  the outer radius of the tube from which it falls, and  $F'$  a correction factor which is approximately unity, but is a function of  $V/r^3$  (Harkins and Brown, 1919).

e. *Hanging drop.* The shape of the drop is measured photographically, and

$$\gamma = g(\rho - \rho_0)(d_e)^2/H \quad (7)$$

where  $d_e$  is the diameter of the drop at its equator, and  $H$  is a factor which is a function only of the ratio of  $d_e$  to the drop diameter at a distance  $d_e$  from its bottom ( $H$  has been tabulated by Andreas, Hauser, and Tucker, 1938).

**4.3. Kelvin equation.** The vapor pressure  $P$  of a drop of liquid of radius  $r$  is

$$\ln \frac{P}{P^0} = \frac{2\gamma}{r} \cdot \frac{V}{RT} \quad (1)$$

where  $P^0$  is the vapor pressure of the liquid in bulk, and  $V$  is its molal volume.

**4.4. Temperature dependence of surface tension.** Since surface tension is a free energy change, it can be expressed in terms of the corresponding enthalpy and entropy changes,

$$\gamma = \Delta h - T \Delta s \quad (1)$$

where  $\Delta h$  is the enthalpy of surface formation per unit area, and  $\Delta s$  the entropy of surface formation per unit area. These are slowly varying functions of temperature, so surface tension is approximately a linear function of temperature.

Empirical equations which reproduce the surface tension over a wide range of temperature include

$$\gamma(V)^{2/3} = 2.12(T_c - T - 6) \quad (2)$$

where  $V$  is the molal volume and  $T_c$  the critical temperature (Eötvös 1886, Ramsay and Shields 1893).

$$\gamma = c(\rho - \rho_0)^4 \quad (3)$$

(McLeod, 1923.)

$$\gamma = \gamma_0(1 - T/T_c)^n \quad (4)$$

where  $n$  is approximately 1.21 and  $\gamma_0$  approximately  $4.4 T_c/V_c^{2/3}$  (Guggenheim, 1945).

**4.5. Insoluble films on liquids.** If the "surface pressure,"  $\pi$ , is  $\gamma_{\text{pure liquid}} - \gamma$ , and the surface area per molecule (i.e., total area divided by number of molecules) is  $\sigma$ , then the equation of state for a very dilute or "gaseous" layer is

$$\pi\sigma = kT \quad (1)$$

where  $k$  is Boltzmann's constant. For a "condensed" layer,

$$\sigma = a - b\pi \quad (2)$$

approximately, where  $a$  and  $b$  are suitable constants.

**4.6. Adsorption on solids.** a. *Langmuir isotherm (1916):*

$$\frac{V}{V_M} = \frac{KP}{1 + KP} \quad (1)$$

where  $V$  is the volume (at standard conditions) of gas adsorbed per unit amount of solid,  $V_M$  the volume adsorbed at saturation,  $P$  the partial pressure of adsorbate, and  $K$  a suitable constant. The Langmuir isotherm can be derived on the assumption that the adsorbed substance occupies a monolayer, and that the surface is energetically uniform.

b. *Brunauer-Emmett-Teller isotherm (1938)* :

$$\frac{V}{V_M} = \frac{KP/P_0}{(1 - P/P_0)(1 - P/P_0 + KP/P_0)} \quad (2)$$

where  $P_0$  is the vapor pressure of the adsorbate in the liquid state. The *B-E-T* isotherm can be derived on the assumption that the adsorbed substance builds up multilayers, the surface being energetically uniform.

c. *Harkins-Jura isotherm (1946)* :

$$1/V^2 = A - B \ln P \quad (3)$$

where  $A$  and  $B$  are suitable constants. The Harkins-Jura isotherm can be derived on the assumption that the adsorbed substance is a "condensed monolayer."

d. *Freundlich isotherm (1909)* :

$$\frac{V}{V_M} = KP^n \quad (4)$$

which has been extended by Sips (1949) :

$$\frac{V}{V_M} = \left( \frac{KP}{1 + KP} \right)^n \quad (5)$$

The Freundlich-Sips isotherm can be derived from the assumption of monolayer adsorption on a nonuniform surface characterized by an exponential distribution of adsorption energies. As written here, these adsorption isotherms apply to the adsorption of gases. Equations of the same form, using concentrations instead of pressures, apply to adsorption from solution.

**4.7. Excess concentration at the surface.** The Gibbs adsorption equation (1878) gives

$$-RT\Gamma_2 = \frac{d\gamma}{d \ln x_2} \quad (1)$$

where  $\Gamma_2$  is the excess concentration of solute at the surface.

**4.8. Surface tension of aqueous electrolytes.** For a one-one electrolyte of molal concentration  $C$  in water at 25° C, the surface tension is approximately

$$\gamma = \gamma_{\text{H}_2\text{O}} + 1.0124C \log \frac{1.467}{C} \quad (1)$$

(Onsager and Samaras, 1934).

**4.9. Surface tension of binary solutions.** According to a theoretical treatment which regards the surface as a monolayer (Schuchowitzky 1944, Belton and Evans 1945, Guggenheim 1945),

$$e^{-\gamma\sigma/kT} = x_1 e^{-\gamma_1\sigma/kT} + x_2 e^{-\gamma_2\sigma/kT} \quad (1)$$

and

$$x_1' = \frac{x_1 e^{-\gamma_1\sigma/kT}}{x_1 e^{-\gamma_1\sigma/kT} + x_2 e^{-\gamma_2\sigma/kT}} \quad (2)$$

where  $x_1$  and  $x_2$  are mole fractions in the bulk solution,  $x_1'$  and  $x_2'$  are surface mole fractions, and  $\gamma_1$  and  $\gamma_2$  are the surface tensions of the pure liquids;  $\sigma$  is the cross-sectional area of a molecule (taken as identical for the two species). All activity coefficients have here been assumed to be unity.

## 5. Reaction Kinetics

**5.1. The rate law of a reaction.** The rate of a chemical reaction, as measured by the rate of disappearance of one of its reactants or appearance of one of its products, is in general proportional to the concentration of one or more of its reactants.

$$-\frac{dC_A}{dt} = k_r C_A C_B C_C \dots \quad (1)$$

This expression is called the "rate law" for the reaction, and  $k_r$  is the "specific rate" or "rate constant." The concentration of a substance may, of course, appear in the rate law to a higher power than the first. The substances whose concentrations appear in the rate law are not, in general, exactly identical with those which appear in the balanced equation for the reaction, so it is necessary to determine the rate law by experiment.

**5.2. Integrated forms of the rate law.** For rate laws involving only a single substance, the integrated forms of some of the simple rate laws are:

Zero order	$-\frac{dC}{dt} = k_0$	$\frac{C}{C_0} = 1 - \frac{k_0 t}{C_0}$
$\frac{1}{2}$ order	$-\frac{dC}{dt} = k_{1/2} C^{1/2}$	$\frac{C}{C_0} = \left(1 - \frac{k_{1/2} t}{2C_0^{1/2}}\right)^2$
First order	$-\frac{dC}{dt} = k_1 C$	$\frac{C}{C_0} = e^{-k_1 t}$
$\frac{3}{2}$ order	$-\frac{dC}{dt} = k_{3/2} C^{3/2}$	$\frac{C}{C_0} = \frac{1}{\left(1 + \frac{C_0^{1/2} k_{3/2} t}{2}\right)^2}$
Second order	$-\frac{dC}{dt} = k_2 C^2$	$\frac{C}{C_0} = \frac{1}{1 + C_0 k_2 t}$

**5.3. Half-lives.** For rate laws involving only a single substance, the time to half reaction is

$$\begin{aligned} \text{Zero order :} & \quad t_{1/2} = C/2k_0 \\ \frac{1}{2} \text{ order :} & \quad t_{1/2} = (2 - 2^{1/2})C_0^{1/2}/k_{1/2} \\ \text{First order :} & \quad t_{1/2} = (\ln 2)/k_1 \\ \frac{3}{2} \text{ order :} & \quad t_{1/2} = (8^{1/2} - 2)/C_0^{1/2}k_{1/2} \\ \text{Second order :} & \quad t_{1/2} = 1/C_0k_2 \end{aligned}$$

**5.4. Integrated form of rate law with several factors.** If the rate law is  $-dC_A/dt = k_r C_A C_B C_C \dots$  and the chemical reaction is such that it consumes  $a$  molecules of A for  $b$  molecules of B for  $c$  molecules of C, etc., we write  $x$  for the fractional extent of reaction of A, and obtain

$$\int_0^x \frac{adx}{(C_{0A} - ax)(C_{0B} - bx)(C_{0C} - cx) \dots} = k_r t \quad (1)$$

where the integral can readily be evaluated by partial fractions.

If the concentration of one substance in a reaction mixture is much smaller than all other concentrations, the others may be taken as constant in integrating the rate law. This is the basis of the experimental technique known as "isolation" or "flooding."

**5.5. Consecutive reactions.** If a reaction proceeds in two successive steps,



the first reaction being kinetically first-order with specific rate  $k_1$  and the second reaction kinetically first-order with specific rate  $k_2$ , and the initial concentration of A is  $C_{0A}$ , the initial concentration of B and C being zero, then the integration of the rate laws gives

$$\left. \begin{aligned} \frac{C_A}{C_{0A}} &= e^{-k_1 t} \\ \frac{C_B}{C_{0A}} &= \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \\ \frac{C_C}{C_{0A}} &= \frac{k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})}{k_2 - k_1} \end{aligned} \right\} (1)$$

If either or both of the reaction steps is kinetically second-order, the rate laws can also be integrated (Chien, 1948).

**5.6. Multiple-hit processes.** The destruction of bacteria by a chemical agent is kinetically first-order ("logarithmic order of death"), but for higher organisms the destruction of more than a single vital spot or cell is supposedly necessary to kill them. If  $N$  hits are necessary, each individual offering just  $N$  targets, then the fraction of individuals surviving at time  $t$  is

$$1 - (1 - e^{-kt})^N \quad (1)$$

If  $N$  hits are necessary, each individual offering an infinite number of targets, the fraction of individuals surviving at time  $t$  is

$$e^{-kt} \left[ 1 + kt + \frac{k^2 t^2}{2!} + \frac{k^3 t^3}{3!} + \dots + \frac{(kt)^{N-1}}{(N-1)!} \right] \quad (2)$$

In these equations  $k$  is the first-order specific rate for a single hit.

**5.7. Reversible reactions.** If the rate of a reaction in one direction is written as  $k_f(C_f)$ , where the notation  $(C_f)$  is understood to indicate the product of concentrations which is the rate law for that reaction, and the rate of the reverse reaction is similarly  $k_b(C_b)$ , then

$$\frac{k_f}{k_b} = K \quad (1)$$

and

$$\frac{(C_f)}{(C_b)} = \frac{1}{(K)} \quad (2)$$

where  $K$  is the numerical value of the equilibrium constant for the reaction, and  $(K)$  is the ratio of concentrations which is the equilibrium constant expression.

**5.8. The specific rate: collision theory** (Arrhenius, 1889). The specific rate for a bimolecular gas reaction is

$$k_r = Z e^{-E/RT} \quad (1)$$

where  $Z$  is the "collision number" or "frequency factor," and  $E$  is the "activation energy." A graph of  $\log k_r$  against  $1/T$  gives a nearly straight line.

From the kinetic theory of gases, the collision number for two molecules of mass  $m$  and diameter  $\sigma$  is

$$Z = \frac{\sigma^2}{NkT} \left( \frac{4\pi}{mkT} \right)^{1/2} 10^{15} \text{ mole liter}^{-1} \text{ sec}^{-1} \text{ atm}^{-2} \quad (2)$$

If the molecules are of diameters  $\sigma_1$  and  $\sigma_2$ ,  $\sigma$  is taken to be  $(\sigma_1 + \sigma_2)/2$ ; if the molecules have masses  $m_1$  and  $m_2$ , the effective mass is

$$m = \left(\frac{1}{2}\right) (1/m_1 + 1/m_2)^{-1}$$

### 5.9. The specific rate : activated complex theory (Eyring, 1935).

The specific rate for any reaction is

$$k_r = \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad (1)$$

where  $k$  is Boltzmann's constant,  $h$  is Planck's constant, and  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  are the standard entropy and enthalpy of forming the "activated complex" from the original reactants. At 25° C, the factor  $kT/h$  is  $6.21 \times 10^{12} \text{ sec}^{-1}$ . The entropy of activation,  $\Delta S^\ddagger$ , can sometimes be computed a priori by the methods of statistical mechanics, and it can often be estimated approximately by analogy with the entropies of known molecules.

For a unimolecular decomposition, the entropy of activation is near zero, so the frequency factor is expected to be of the order of  $10^{13} \text{ sec}^{-1}$ . For a bimolecular gas reaction, the activated complex theory can be shown to lead to just the same equation the collision theory does.

**5.10. Activity coefficients in reaction kinetics.** The relation between the observed specific rate  $k_r$  and the specific rate  $k_r^0$  for an ideal solution is (Brønsted 1922, 1925, Bjerrum 1924)

$$k_r = k_r^0 \frac{\gamma_A \gamma_B \gamma_C \dots}{\gamma^\ddagger} \quad (1)$$

For the reaction of an ion of charge  $z_A$  with another ion of charge  $z_B$ , the Debye-Hückel equation for activity coefficients leads to

$$\log k_r = \log k_r^0 + z_A z_B \sqrt{\mu} \quad (2)$$

at 25° C, for dilute solutions.

If two neutral reactants combine to form an activated complex of radius  $r$  and dipole moment  $\mu^\ddagger$ , a formula of Kirkwood (1934) for the activity coefficient of a dipole in an electrolyte of ionic strength  $\mu$  is

$$-\ln \gamma^\ddagger = \frac{4\pi N e^4}{1000 D^2 k^2 T^2} \cdot \frac{\mu^{\ddagger 2}}{r} \mu \quad (3)$$

For water at 25° C,  $r$  measured in Ångström units and  $\mu^\ddagger$  in Debye units,

$$\log k_r = \log k_r^0 + 0.00238 \frac{\mu^{\ddagger 2}}{r} \mu \quad (4)$$

For the reaction of an ion of charge  $z_A$  with one of charge  $z_B$ , the dependence of the specific rate (extrapolated to zero ionic strength) upon dielectric constant is approximately

$$\ln k_r = \text{constant} - \frac{e^2 z_A z_B}{D r k T} \quad (5)$$

**5.11. Heterogeneous catalysis.** The rate of a surface-catalyzed reaction, per unit surface area, is often described satisfactorily by

a. *A semi-empirical equation of the Freundlich type,*

$$\text{Rate} = k_r(P_A)^\alpha(P_B)^\beta \dots \quad (1)$$

where the exponents  $\alpha$  and  $\beta$  are arbitrarily chosen to fit the data; or

b. *An equation of the Langmuir type,*

$$\text{rate} = \frac{k_r(P_A)(P_B)(P_C) \dots}{1 + K_A(P_A) + K_B(P_B) + \dots} \quad (2)$$

where the product in the numerator includes the concentrations of those substances which make up the activated complex, and the summation in the denominator extends over all those substances which are adsorbed on the surface.

**5.12. Enzymatic reactions.** An enzyme and its substrate often combine to form a relatively stable intermediate ("Michaelis complex," Michaelis and Menten, 1913) previous to the enzymatic reaction itself. The corresponding rate law is

$$-\frac{d(\text{substrate})}{dt} = k_r(\text{enzyme}) \frac{(\text{substrate})}{1 + K_m(\text{substrate})} \quad (1)$$

where  $K_m$  is the equilibrium constant for the formation of the Michaelis complex. Many enzymes can be reversibly denatured into forms which are catalytically inactive; if  $K_d$  is the equilibrium constant for the denaturation reaction,

$$k_r = \frac{k_r^0}{1 + K_d} \quad (2)$$

and the temperature dependence of the rate is given by

$$k_r = \frac{(kT/h)e^{\Delta S^\ddagger/R - \Delta H^\ddagger/RT}}{1 + e^{\Delta S_d^0/R - \Delta H_d^0/RT}} \quad (3)$$

As this equation indicates, the rate of an enzymatic reaction normally increases with temperature at low temperatures, passes through a maximum, and decreases with temperature at high temperatures.

**5.13. Photochemistry.** The law of photochemical equivalence (Stark 1908, Einstein 1912) states that one quantum of active light is absorbed per

molecule of substance which disappears. The rate of the photochemical primary process is, accordingly, proportional to the intensity of light absorbed.

$$\text{rate} = k_1 I_{\text{abs}} \quad (1)$$

The absorption of light can be measured by direct actinometry, or computed from the Lambert-Beer law,

$$I_{\text{abs}} = I_0(1 - e^{-aCx}) \quad (2)$$

**5.14. Photochemistry in intermittent light.** If a reactant is photo-dissociated into two radicals, which can recombine by a bimolecular process to form the original reactant



and it is possible to measure the average concentration of R within a constant factor (e.g. by a chemical reaction of R), the use of intermittent light permits the determination of the mean lifetime of a radical R. Write  $p$  for the ratio of dark period to light period, and  $t$  for the ratio of light period to mean life of R under steady illumination. Then the ratio of the average concentration of R under intermittent illumination to the concentration of R under steady illumination is (Dickinson, 1941)

$$\frac{1}{p+1} \left\{ 1 + \frac{1}{t} \ln \left[ 1 + \frac{pt}{1 + \frac{2(pt + \tanh t)/(pt \tanh t)}{1 + \sqrt{1 + 4/(pt \tanh t) + 4/(p^2 t^2)}}}} \right] \right\} \quad (2)$$

## 6. Transport Phenomena in the Liquid Phase

**6.1. Viscosity: definition and measurement.** The viscosity  $\eta$  is defined as the shear stress per unit shear rate,

$$\eta = \frac{f}{dx/dt} \quad (1)$$

Methods for its measurement include :

### a. Concentric-cylinder viscometer

$$\eta = (L/4\pi\omega h) (1/r_1^2 - 1/r_2^2) \quad (2)$$

where  $L$  is the measured torque,  $\omega$  is the angular velocity of the rotating cylinder,  $h$  the height of the cylinders, and  $r_1$  and  $r_2$  their respective radii.

b. *Capillary flow*

$$\eta = \frac{P\pi r^4}{8lU} \quad (3)$$

where  $U$  is the volume rate of flow of liquid through the capillary,  $l$  its length,  $r$  its radius, and  $P$  the pressure difference (Poiseuille, 1844).

c. *Falling ball*

$$\eta = \frac{2\sigma r^2 \Delta\rho}{9v} \quad (4)$$

where  $v$  is the terminal velocity of the sphere falling through the liquid,  $g$  the acceleration of gravity,  $r$  the radius of the sphere, and  $\Delta\rho$  the difference in density between sphere and liquid (Stokes, 1856).

d. *Fiber method (used for glass)*

$$\eta = \frac{mg}{3\pi r^2 V} \quad (5)$$

where  $V$  is the fractional rate of extension of a fiber, of radius  $r$ , which is loaded by the mass  $m$ .

**6.2. Diffusion : definition and measurement.** The diffusion coefficient  $\mathcal{D}$  is defined as the quantity of solute diffusing across unit area in unit time per unit concentration gradient (Fick, 1855).

$$\mathcal{D} = - \frac{\partial n / \partial t}{A \partial c / \partial x} \quad (1)$$

Methods for its measurement include :

a. *Diaphragm cell method.* Two stirred solutions are separated by a porous diaphragm; the initial concentration difference is  $\Delta C_0$ , and after time  $t$  the concentration difference is  $\Delta C_t$ .

$$\mathcal{D} = - \frac{1}{\alpha t} \ln \frac{\Delta C_t}{\Delta C_0} \quad (2)$$

where  $\alpha$  is a cell factor.

b. *Sheared boundary method.* At zero time, a solution of concentration  $C_1$  and a solution of concentration  $C_0$  are brought into contact along a plane boundary. The differential equation governing the one-dimensional diffusion (Fick's second law) is

$$\frac{\partial C}{\partial t} = \mathcal{D} \frac{\partial^2 C}{\partial x^2} \quad (3)$$

whose approximate solution for the stated boundary conditions is

$$\frac{dC}{dx} = \frac{C_1 - C_0}{2\sqrt{\pi^2 Dt}} e^{-x^2/2Dt} \quad (4)$$

**6.3. Equivalent conductivity : definition and measurement.** The equivalent conductivity of an electrolyte is defined as

$$\Lambda = \frac{\kappa}{c} \quad (1)$$

where  $\kappa$  is the specific conductance in mho per centimeter, and  $c$  is the concentration of electrolyte in equivalents per cubic centimeter. The equivalent conductivity of a salt is the sum of the equivalent conductivities of its individual ions (Kohlrausch's "law of the independent migration of ions"),

$$\Lambda = \Lambda_+ + \Lambda_- \quad (2)$$

The fraction of the current carried by the ions of one kind, the "transference number," is defined as

$$t_+ = \frac{\Lambda_+}{\Lambda} \quad \text{or} \quad t_- = \frac{\Lambda_-}{\Lambda}; \quad t_+ + t_- = 1 \quad (3)$$

Methods for the experimental determination of transference numbers include :

a. *Hittorf method.* After electrolysis, the cathode compartment and the anode compartment are analyzed, and a correction applied for the amount of electrolyte which was consumed by electrolysis. If  $\Delta n_a$  is the excess loss of electrolyte at the anode, due to migration, and  $\Delta n_c$  is the excess loss of electrolyte at the cathode, in equivalents per faraday, then approximately

$$t_+ = \Delta n_a, \quad t_- = \Delta n_c \quad (4)$$

b. *Moving boundary method.* The velocity of travel of one kind of ion permits the computation of its "ionic mobility"  $l$ , the velocity per unit potential gradient in  $\text{cm}^2 \text{sec}^{-1} \text{volt}^{-1}$ . Then

$$\Lambda_+ = \mathcal{F}l_+ \quad \text{or} \quad \Lambda_- = \mathcal{F}l_- \quad (5)$$

where  $\mathcal{F}$  is Faraday's constant, 96,494.

c. *Concentration cell with liquid junction.* This is a cell consisting of two solutions, one of concentration  $C_1$  and the other  $C_2$ , the solutions being in direct contact, and each containing one electrode reversible to (say) the cation. The corresponding concentration cell without liquid junction comprises two

solutions of concentrations  $C_1$  and  $C_2$ , each containing two electrodes—one reversible to the cation and the other to the anion—and connected so their polarities oppose one another. If the voltage of the cell *without* liquid junction is  $\epsilon$ , and the voltage of the cell *with* liquid junction is  $\epsilon_t$ , then

$$t_{\dots} = \frac{\epsilon_t}{\epsilon} \quad (6)$$

The transference number obtained is that for the ion to which the electrode is not reversible.

**6.4. Viscosity of mixtures.** The viscosity of a solution of normal liquids is represented fairly closely by the semi-empirical relation

$$\log \eta = x_1 \log \eta_1 + x_2 \log \eta_2 \quad (1)$$

where  $x_1$  may be mole fraction, weight fraction, or volume fraction (Kendall, 1913).

The viscosity of a dilute suspension of spheres is

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi_2 + \dots \quad (2)$$

where  $\eta_0$  is the viscosity of the pure liquid and  $\phi_2$  is the volume fraction of spheres (Einstein, 1906, 1911).

The viscosity of a solution of linear high polymers is

$$\frac{\eta}{\eta_0} = 1 + KM^\alpha C \quad (3)$$

where  $C$  is the concentration (usually in grams per 100 cc) of polymer,  $M$  its molecular weight,  $K$  a constant characteristic of a given type of polymer, and  $\alpha$  a constant usually falling between 0.6 and 0.8 (Houwink 1940, Flory 1943).

The viscosity of an aqueous electrolyte is given approximately by

$$\frac{\eta}{\eta_0} = 1 + 0.003r^2\sqrt{\mu} \quad (4)$$

where  $\mu$  is the ionic strength and  $r$  is the mean radius of an ion, in Ångström units (approximate form of an equation due to Falkenhagen, 1929). An empirical equation of the form

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{C} + BC \quad (5)$$

holds over a wider range of concentration.

**6.5. Diffusion coefficient of mixtures.** The diffusion coefficient of a liquid solution varies with composition, approximately obeying the law

$$\mathcal{D}\eta = (\mathcal{D}\eta)_{\text{av}} \left[ \frac{d \ln a_1}{d \ln x_1} \right] \quad (1)$$

where  $(\mathcal{D}\eta)_{\text{av}}$  can be the arithmetic mean value, and  $a_1 = x_1\gamma_1$  is the activity of component 1. The quantity in brackets, which can be computed from the activity-coefficient data for the liquid system, corrects for the fact that activity rather than concentration is the driving force for diffusion.

The diffusion coefficient of a number of electrolytes is represented, within the experimental error, by

$$\mathcal{D} = 17.86 \cdot 10^{-10} T \left( \frac{1}{\Lambda_+} + \frac{1}{\Lambda_-} \right) \phi_{\text{H}_2\text{O}} \left[ 1 + \frac{d \ln \gamma_{\pm}}{d \ln C} \right] \frac{\eta_0}{\eta} \quad (2)$$

(Gordon, 1937).

The diffusion coefficient of a large spherical molecule is given by Stokes' law,

$$\mathcal{D}\eta = \frac{kT}{6\pi r}$$

where  $k$  is Boltzmann's constant and  $r$  is the molecular radius. For molecules of the same size as the solvent,

$$\mathcal{D}\eta = \frac{kT}{\lambda} \quad (4)$$

where  $\lambda$  is of the order of a molecular dimension (Eyring, 1936).

**6.6. Dependence of conductivity on concentration.** The conductivity of a partially ionized substance is given approximately by

$$\frac{\Lambda}{\Lambda_0} = \alpha \quad (1)$$

where  $\alpha$  is the degree of dissociation and  $\Lambda_0$  is the conductivity at infinite dilution. More exactly, the relation is

$$\frac{\Lambda}{\Lambda_{(\text{Onsager})}} = \alpha \quad (2)$$

where  $\Lambda_{(\text{Onsager})}$  is the limiting ionic conductivity, corrected approximately for "ionic atmosphere" effects (Onsager and Fuoss, 1932).

At 25° C,  $\Lambda_{(\text{Onsager})}$  for various types of electrolytes is

$$\left. \begin{aligned} 1-1 \quad \Lambda_0 - \sqrt{C}(59.86 + 0.2277\Lambda_0) \\ 2-2 \quad \Lambda_0 - \sqrt{C}(239.4 + 1.822\Lambda_0) \\ 3-3 \quad \Lambda_0 - \sqrt{C}(538.7 + 6.148\Lambda_0) \\ 2-1 \quad \Lambda_0 - \sqrt{C}\left(155.6 + \frac{1.796\Lambda_0}{(1+t_1) + 0.816\sqrt{1+t_1}}\right) \\ 3-1 \quad \Lambda_0 - \sqrt{C}\left(293.3 + \frac{4.280\Lambda_0}{(1+2t_1) + 0.866\sqrt{1+2t_1}}\right) \\ 3-2 \quad \Lambda_0 - \sqrt{C}\left(634.5 + \frac{11.88\Lambda_0}{(1+0.5t_2) + 0.775\sqrt{1+0.5t_2}}\right) \end{aligned} \right\} (3)$$

where  $t_i$  is the transference number of the  $i$ -valent ion.

**6.7. Temperature dependence of viscosity, diffusion, and conductivity.** Approximately,

$$\eta = A_\eta e^{+E_\eta/RT} \quad (1)$$

$$\mathcal{D} = A_{\mathcal{D}} e^{-E_{\mathcal{D}}/RT} \quad (2)$$

$$\Lambda = A_\Lambda e^{-E_\Lambda/RT} \quad (3)$$

where the  $A$ 's and  $E$ 's are suitable constants. A graph of  $\log \eta$  against  $1/T$  gives an almost straight line, and similarly for the other properties.

According to one theory of these phenomena (Eyring, 1936)

$$\eta = \frac{h}{\lambda^3} e^{-\Delta S_\eta^\ddagger/R} e^{\Delta H_\eta^\ddagger/RT} \quad (4)$$

$$\mathcal{D} = \lambda^2 \frac{kT}{h} e^{\Delta S_{\mathcal{D}}^\ddagger/R} e^{-\Delta H_{\mathcal{D}}^\ddagger/RT} \quad (5)$$

$$\Lambda_0 = \frac{\mathcal{F}\lambda^2 z e}{h} e^{\Delta S_\Lambda^\ddagger/R} e^{-\Delta H_\Lambda^\ddagger/RT} \quad (6)$$

where  $\lambda$  is a distance of the order of molecular dimensions,  $h$  is Planck's constant,  $k$  is Boltzmann's constant, and  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  are the entropy of activation and enthalpy of activation for the respective processes. Since the unit processes are not quite identical in the three cases, the values of  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  may be slightly different. For normal liquids,  $\Delta S^\ddagger$  is small and  $\Delta H^\ddagger$  is about one-third or one-fourth the heat of vaporization.

## Chapter 28

### BASIC FORMULAS OF ASTROPHYSICS

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Astrophysics is the borderline field between astronomy and physics. Much of astrophysics is related to the interpretation of atomic spectra. Hence, useful formulas will also appear in Chapters 19, 20, and 21, and the sections on thermodynamics and statistical mechanics also have a relationship to the subject, as has the more specialized chapter on physical chemistry.

#### 1. Formulas Derived from Statistical Mechanics

**1.1. Boltzmann formula** (Ref. 1, Chap. 4). Let there be  $N_n$  atoms in level  $n$  of excitation potential  $\chi_n$  and  $N_{n'}$  atoms in level  $n'$  of excitation potential  $\chi_{n'}$ . Let the statistical weights of level  $n$  and  $n'$  be  $\tilde{\omega}_n$  and  $\tilde{\omega}_{n'}$  respectively. Under conditions of thermal equilibrium

$$\frac{N_n}{N_{n'}} = \frac{\tilde{\omega}_n}{\tilde{\omega}_{n'}} e^{-\chi/kT} \quad (1)$$

where  $\chi = \chi_n - \chi_{n'}$ ,  $T$  is the temperature in absolute degrees, and  $k$  is Boltzmann's constant. If the total number of atoms in all levels of excitation is  $N$ , then

$$\frac{N_n}{N} = \frac{\tilde{\omega}_n}{B(T)} e^{-\chi/kT} \quad (2)$$

where

$$B(T) = \tilde{\omega}_1 + \tilde{\omega}_2 e^{-\chi_2/kT} + \tilde{\omega}_3 e^{-\chi_3/kT} + \dots = \sum_i \tilde{\omega}_i e^{-\chi_i/kT}$$

is called the partition function. Here  $\chi$  is the excitation potential above the ground level.

**1.2. Ionization formula** (Ref. 1, Chap. 4). Let there be  $N_r$ ,  $N_{r+1}$  atoms in the  $r$ th and  $(r+1)$ st stages of ionization per  $\text{cm}^3$ . Let the electron density be  $N_e$  and the temperature be  $T$ . If  $\chi_r$  is the ionization potential from the ground level of the atom in the  $r$ th stage of ionization, then

$$\frac{N_{r+1} N_e}{N_r} = \left( \frac{2\pi m k}{h^2} \right)^{3/2} \frac{2B_{r+1}(T)}{B_r(T)} T^{3/2} e^{-\chi_r/kT} \quad (1)$$

where  $B_r$  and  $B_{r+1}$  represent the partition functions for the  $r$ th and  $(r + 1)$ st stages of ionization. If we use the electron pressure

$$P_e = N_e k T$$

and substitute numerical values we find

$$\log \frac{N_{r+1}}{N_r} P_e = -\frac{5040}{T} \chi_r + \frac{5}{2} \log T + \log \frac{2B_{r+1}(T)}{B_r(T)} - 0.48 \quad (2)$$

where  $P_e$  is expressed in dynes  $\text{cm}^2$  and  $\chi_r$  is expressed in electron volts.

**1.3. Combined ionization and Boltzmann formula** (Ref. 1, Chap. 4). If  $N_{r,s}$  is the number of atoms/ $\text{cm}^3$  in the  $s$ th level of the  $r$ th stage of ionization,  $N_{r,s}$  may be expressed in terms of the number of atoms in the  $(r + 1)$ st stage of ionization, viz.,

$$\log \frac{N_{r+1} P}{N_{r,s}} = -\frac{5040}{T} (\chi_r - \chi_s) + \frac{5}{2} \log T + \log \frac{2B_{r+1}(T)}{\tilde{\omega}_s} - 0.48 \quad (1)$$

where  $\chi_s$  is the excitation potential of the level  $s$  of statistical weight  $\tilde{\omega}_s$  in volts.

**1.4. Dissociation equation for diatomic molecules** (Ref. 1, Chap. 4). Let two elements X and Y combine to form the diatomic molecule XY, viz.,



Then the concentration of the atoms X, Y, and the molecule XY will be governed by an equation of the form

$$\frac{N_X N_Y}{N_{XY}} = \frac{\tilde{\omega}_X \tilde{\omega}_Y}{\tilde{\omega}_{XY}} \left( \frac{2\pi M}{h^2} \right)^{3/2} \frac{h^2}{8\pi^2 I} (kT)^{1/2} (1 - e^{-hW/kT}) e^{-D/kT} \quad (1)$$

Here  $\tilde{\omega}_X$ ,  $\tilde{\omega}_Y$ , and  $\tilde{\omega}_{XY}$  denote the statistical weights of the ground levels of atoms X, Y, and molecule XY.

$$M = \frac{M_X M_Y}{M_X + M_Y} = \text{“reduced mass” expressed in grams.}$$

$$I = M r_0^2 \text{ where } r_0 \text{ is the separation of atoms X and Y in cm}$$

$$W = \text{fundamental vibration frequency of the molecule in units of sec}^{-1}$$

$$D = \text{dissociation energy from lowest vibrational level in cgs units}$$

The right-hand side of the equation corresponds to the dissociation “constant” of ordinary chemical reaction formulas.

## 2. Formulas Connected with Absorption and Emission of Radiation

**2.1. Definitions** (Ref. 1, Chap. 5 and 8). If  $I_\nu(\theta, \phi)$  is the specific intensity of the radiation, the flux through a surface  $S$  is defined by

$$\mathcal{F} = \int_{\theta=a}^{\pi} \int_{\phi=0}^{2\pi} I(\theta, \phi) \cos \theta \sin \theta \, d\theta \, d\phi \quad (1)$$

where  $\theta$  is the angle between the ray direction and the normal to the surface, and  $\phi$  is the azimuthal angle. If  $I$  does not depend on  $\phi$ , and we write  $\mu = \cos \theta$ , then

$$\mathcal{F} = 2\pi \int_{-1}^{+1} I(\mu) \mu \, d\mu \quad (2)$$

The energy density is given by

$$u(T) = \frac{1}{c} \int I(\theta, \phi) \, d\omega \quad (3)$$

where the integration is carried out over all solid angle. For isotropic radiation

$$u(T) = \frac{4\pi}{c} I \quad (4)$$

The radiation pressure is

$$p(T) = \frac{1}{c} \int I(\theta, \phi) \cos^2 \theta \, d\omega \quad (5)$$

For isotropic radiation

$$p(T) = \frac{1}{3} u(T) \quad (6)$$

**2.2. Specific intensity** (Ref. 1, Chaps. 5 and 8). The dependence of intensity upon frequency for blackbody radiation is given by the Planck formula

$$I_\nu(T) = \frac{2h\nu^3}{c^2} \cdot \frac{1}{e^{h\nu/kT} - 1} \quad (1)$$

or in wavelength units

$$I_\lambda = \frac{2hc^2}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda kT} - 1} \quad (2)$$

From these relations are derived Wien's law and Stefan's law (see Chapters 10 and 11).

**2.3. Einstein's coefficients** (Ref. 1, Chaps. 5 and 8). The atomic coefficients of absorption and emission are defined in the following way. If  $N_n$  atoms are maintained in the upper level of a transition of frequency  $\nu(nn')$ , the number of spontaneous downward transitions/cm<sup>3</sup>/sec will be

$$N_n A_{nn'}$$

where  $A_{nn'}$  is the Einstein coefficient of spontaneous emission. If radiation of intensity  $I_\nu$  is present there also will be induced emissions whose number is given by

$$N_n B_{nn'} I_{\nu(nn')}, \text{ per cm}^3/\text{sec}$$

More correctly these induced emissions should be called negative absorptions since the induced quantum is emitted in the same direction as the absorbed quantum. The number of transitions from level  $n'$  to  $n$  produced by the absorption of quanta by the atoms in the lower level is

$$N_{n'} B_{n'n} I_{\nu(nn')}$$

The relations between these coefficients are

$$\tilde{\omega}_n B_{nn'} = \tilde{\omega}_{n'} B_{n'n} \tag{1}$$

$$A_{nn'} = B_{nn'} \frac{2h\nu^3}{c^2} \tag{2}$$

**2.4. Oscillator strength** (Ref. 1, Chaps. 5 and 8). The relation between the Einstein  $A$  coefficient and the oscillator strength or Ladenberg  $f$  is

$$A_{nn'} = \frac{\tilde{\omega}_{n'}}{\tilde{\omega}_n} \frac{8\pi^2 e^2 \nu^2}{mc^3} f_{n'n} \tag{1}$$

or

$$A_{nn'} = 3 \frac{\tilde{\omega}_{n'}}{\tilde{\omega}_n} f_{n'n} \gamma_c \tag{2}$$

where  $\gamma_c$  is the classical damping constant.

**2.5. Absorption coefficients** (Ref. 1, Chaps. 5 and 8). The absorption coefficient for a single atom at rest is

$$\alpha_\nu = \frac{\pi e^2}{mc} f \frac{\Gamma}{4\pi^2} \frac{1}{(\nu - \nu_0)^2 + (\Gamma/4\pi)^2} \tag{1}$$

where  $\Gamma$  is the quantum mechanical damping constant. For pure radiation processes, we can usually write

$$\Gamma = \Gamma_r = \Sigma A_{nn'} \tag{2}$$

where the summation is taken over all lower levels. If collisional broadening also occurs, we can define a

$$\Gamma = \Gamma_r + \Gamma_{\text{col}} \tag{3}$$

where  $\Gamma_{\text{col}}$  represents the effects of collisions.

$$\Gamma_{\text{col}} = 2\pi r_0^2 N_p \nu \tag{4}$$

where  $r_0$  is the effective radius of the perturbing particles which number

$N_p$  per  $\text{cm}^3$ . The relative velocity of the radiating atom and the perturbing atom is  $v$ .

The profiles of all lines are broadened by the Doppler effect. The shape of the absorption coefficient of a line broadened by Doppler effect only is

$$\alpha_\nu = \frac{\pi \epsilon^2}{mc} f \frac{c}{v_0 \nu \sqrt{\pi}} e^{-[c(\nu - \nu_0)/v_0 v_0]^2}$$

Usually both types of broadening operate together and the absorption coefficient given by the integral

$$\alpha_\nu = \alpha_0 \frac{a}{\pi} \int_{-\infty}^{+\infty} \frac{e^{-\chi^2}}{a^2 + (u - \chi)^2} d\chi \quad (6)$$

where

$$\chi = \frac{v}{v_0}, \quad u = \left( \frac{\nu - \nu_0}{\nu_0} \right) \frac{c}{v_0}, \quad a = \frac{c\Gamma}{4\pi v_0 v_0},$$

$$\alpha_0 = \frac{\tilde{\omega}_n}{\tilde{\omega}_{n'}} A \frac{\lambda^3}{8v_0 \pi^{3/2}}$$

Here  $v_0$  is the most probable velocity of the atoms. The integral must be evaluated numerically, and tables have been published by Mitchell and Zemansky, Hjerting, and Daniel Harris. The arguments are usually  $a$  and  $u$  and with the aid of the tables,  $\alpha/\alpha_0$  may be found at once. These formulas do not hold for Stark broadening in hydrogen and helium.

**2.6. Line strengths** (Refs. 4 and 12). The  $A$  or  $f$ -value may be expressed in terms of the "strength" of the line. Thus, for an electric dipole transition between 2 atomic levels  $\gamma SLJ$  and  $\gamma' SL' J'$ ,

$$A_e(\gamma SLJ; \gamma' SL' J') = \frac{1}{2J+1} \frac{64\pi^4 \nu^3}{2hc^3} S_e(\gamma SLJ; \gamma' SL' J') \quad (1)$$

where

$$S_e(\gamma SLJ; \gamma' SL' J') = S(\gamma SLJ; \gamma' SL' J') \sigma^2(nl; n'l')$$

and  $S$  is the relative strength.

$$\sigma = \frac{\epsilon}{\sqrt{4l^2 - 1}} \int_0^r r R(n, l) R(n', l') dr \quad (2)$$

where  $l$  is the azimuthal quantum number;  $R$  is the radial wave function. For magnetic dipole radiation between two levels of the same configuration,

$$A_m(J, J') = 35,320 \left( \frac{\nu}{\nu_R} \right)^3 \frac{S_m(J, J')}{2J+1} \text{sec}^{-1} \quad (3)$$

where  $S_m(J, J')$  is the magnetic dipole strength in atomic units  $\epsilon h^2/16\pi^2 m^2 c^2$ ;  $\nu_R$  = frequency of Lyman limit ( $3.28 \times 10^{15}$  sec $^{-1}$ ). The electric quadrupole transition probability is

$$A_q(J, J') = 2648 \left( \frac{\nu}{\nu_R} \right)^5 \frac{S_q(J, J')}{2J + 1} \text{sec}^{-1} \quad (4)$$

Here  $S_q(J, J')$  is expressed in atomic units  $\epsilon^2 a^4$  ( $a$  = radius of first Bohr orbit) and may be written as

$$S_q(J, J') = C_q(J, J') S_q^2(nl, nl)$$

where

$$S_q = c_e \int_0^r r^2 R^2(nl) dr$$

and  $c_e = 2/5$  for  $p$  electrons. The values of  $C_q(J, J')$  have been tabulated by Shortley and collaborators. If both magnetic dipole and electric quadrupole radiation are permitted for a line

$$A = A_q + A_m \quad (5)$$

### 2.1. Definition of $f$ -values for the continuum (Ref. 7).

$$\alpha_\nu = \frac{\pi \epsilon^2}{mc} \cdot \frac{df}{d\nu} \quad (1)$$

## 3. Relation Between Mass, Luminosity, Radii, and Temperature of Stars

**3.1. Absolute magnitude** (Ref. 10). Relation between absolute magnitude  $M$ , apparent magnitude  $m$ , and distance  $r$  is

$$M = m + 5 - 5 \log r \quad (1)$$

The distance  $r$  is given in parsecs.

$$1 \text{ parsec} = 3.084 \times 10^{18} \text{ cm}$$

which is 206,265 times the distance of the earth from the sun. If the star is dimmed by  $A$  magnitudes due to space absorption,  $m$  must be replaced by  $m - A$ .

**3.2. Color index** (Ref. 1, Chap. 6; Ref. 15, Chap. 6). The difference between the photographic and photovisual magnitudes is called the color index,

$$C = m_{\text{ptg}} - m_{\text{vis}} \quad (1)$$

If the star is undimmed by space absorption, color index and temperature are related by

$$T = \frac{8200}{C + 0.68} \quad (2)$$

The difference between the observed color index and the true color index appropriate to the spectral class and temperature of the star is called the *color excess*.

$$E = C_{\text{obs}} - C \quad (3)$$

In most regions of the Milky Way one can take

$$A_{pg} = 4E \quad (4)$$

If  $M_{\text{vis}}$  = absolute visual magnitude,  $R$  = radius in terms of the sun as 1.0,  $T$  = temperature in absolute degrees,

$$\log R = \frac{5700}{T} - 0.05 - 0.2M_{\text{vis}} \quad (5)$$

For high-temperature stars this formula must be modified, viz.,

$$\log R = \frac{5700}{T} - 0.05 - 0.2M_{\text{vis}} + 0.5 \log [1 - 10^{-14.700/T}] \quad (6)$$

The surface gravity is

$$g = g_0 \frac{M}{R^2}$$

where  $g_0 = 2.74 \times 10^4 \text{ cm/sec}^2$  is the surface gravity of the sun,  $M$  and  $R$  are the mass and radius, respectively, in terms of the corresponding quantities for the sun. For main sequence stars, Russell has given the following empirical formula dependence of surface gravity on temperature.

$$\log_{10} \frac{g}{g_0} = -0.65 + \frac{3250}{T} \quad (8)$$

For the giants

$$\log_{10} \frac{g}{g_0} = +0.76 - \frac{11250}{T} \quad (9)$$

**3.3. Mass-luminosity law** (Ref. 11). The empirical relation between mass  $M$  and luminosity  $L$  (expressed in terms of the corresponding quantities for the sun) is

$$\log M = 0.26 \log L + 0.06 \quad (1)$$

for stars which do not differ greatly in brightness from the sun.

### 3.4. The equation of transfer for gray material (Ref. 2)

$$\mu \frac{dI}{d\tau} = I - J(\tau) \quad (1)$$

where  $I(\mu, \tau)$  is the intensity;  $\mu = \cos \theta$ ;  $\theta$  is the angle between the ray and the outward directed normal. Here  $d\tau = k\rho dx$  where  $dx$  is the element of geometrical depth,  $\rho =$  density,  $k =$  coefficient of continuous absorption.

$$J(\tau) = \frac{1}{2} \int_{-1}^{+1} I(\mu, \tau) d\mu = \frac{1}{2} \int_0^{\infty} E_1(|t - \tau|) J(t) dt \quad (2)$$

where  $E_1(x)$  is the exponential integral

$$E_1(x) = \int_1^{\infty} e^{-yx} \frac{dy}{y}$$

The solution of the equation of transfer is

$$I(0, \mu) = \frac{\sqrt{3}}{4} FH(\mu) \quad (3)$$

where  $I(0, \mu) =$  intensity of emergent ray making an angle  $\theta$  with outward directed normal,  $\pi F$  is the flux, and

$$H(\mu) = 1 + \frac{1}{2}\mu H(\mu) \int_0^1 \frac{H(x)}{\mu + x} dx \quad (4)$$

This equation may be solved by an iteration procedure. For gray material in thermal equilibrium the dependence of temperature in optical depth is given by

$$T^4 = \frac{3}{4} T_e^4 [\tau + q(T)] \quad (5)$$

where  $T_e =$  effective temperature.

Here  $q(T)$  is a monotonic function increasing from  $1/\sqrt{3}$  at  $\tau = 0$  to 0.71045 at  $\tau = \infty$ . In the Eddington approximation the dependence of  $T$  on  $\tau$  was given as

$$T^4 = \frac{3}{4} T_e^4 (\tau + \frac{2}{3}) \quad (6)$$

An approximation of sufficient accuracy for most purposes has been given by D. Labs.

$$T^4 = \frac{3}{4} T_e^4 (\tau + B - Ae^{-\alpha\tau}) \quad (7)$$

where  $A = 0.1331$ ,  $B = 0.7104$ ,  $\alpha = 3.4488$ .

**3.5. Non-gray material** (Ref. 1, Chap. 7). Element of optical depth is defined by

$$d\tau_v = \kappa_v \rho dx \quad (1)$$

where  $\kappa_v$  is continuous absorption coefficient.

For large optical depths the mean absorption coefficient is the Rosseland mean

$$\bar{\kappa} = \frac{\int_0^{\infty} [dB_{\nu}/(\rho dx)] d\nu}{\int_0^{\infty} (1/\kappa_{\nu}) [dB_{\nu}/(\rho dx)] d\nu}$$

where  $B_{\nu}$  is the Planck function. Also,  $\bar{\kappa}$  may be defined by

$$\bar{\kappa} = \frac{1}{F} \int_0^{\infty} \kappa_{\nu} F_{\nu} d\nu$$

where  $\pi F_{\nu}$  is the monochromatic flux. Chandrasekhar suggests that at small optical depths we employ the net monochromatic flux of radiation of frequency  $\nu$  in a gray atmosphere. If

$$\bar{\tau} = \int \bar{\kappa} \rho dx$$

the temperature dependence on  $\bar{\tau}$  is assumed to be the same as in gray atmosphere with  $\tau$  identified with  $\bar{\tau}$ .

**3.6. Model atmosphere in hydrostatic equilibrium** (Ref. 1, Chap. 7; Ref. 13).

$$\frac{dP}{d\tau} = \frac{g}{\kappa} \quad (1)$$

$\kappa(P_e, T)$  can be expressed as  $\kappa(P_g, T)$  when  $P_g$  is known as a function of  $P_e$ ,  $T$ . This depends only on the chemical composition. Here  $g$  = surface gravity.

If the mechanical force exerted by radiation is important, Eq. (1) may be written as

$$\frac{dP_g}{d\tau} = \frac{g}{\kappa} - \frac{\sigma_r}{c} T_e^4$$

where  $P_g$  is the gas pressure and  $\sigma_r$  is the Stefan-Boltzmann constant.

**3.7. Formation of absorption lines** (Ref. 2, p. 321; Ref. 1, Chap. 8). The fundamental equation

$$\cos \theta \frac{dI_{\nu}}{dt_{\nu}} = I_{\nu} - \mathcal{J}_{\nu}(t) \quad (1)$$

where  $dt_{\nu} = (\kappa_{\nu} + l_{\nu}) dx$ ,  $\kappa_{\nu}$  = coefficient of continuous absorption at the line,  $l_{\nu}$  = coefficient of line absorption.

$$\eta_{\nu} = l_{\nu}/\kappa_{\nu}, \quad \lambda_{\nu} = \frac{1 + \epsilon\eta}{1 + \eta} \quad (2)$$

where  $\epsilon$  expresses the role of thermal processes in the line,  $\epsilon = 1$  for line formed by thermal emission and absorption processes,  $\epsilon = 0$  for pure scattering.

$$\mathcal{J}_\nu(t_\nu) = \lambda B_\nu(t_\nu) + (1 - \lambda_\nu) J(t_\nu) \tag{3}$$

Then 
$$I_\nu(0, \mu) = \int_0^\infty \mathcal{J}(t_\nu) e^{-t/\mu} \frac{dt_\nu}{\mu} \tag{4}$$

The intensity in the continuum is

$$I_\nu^c(0, \mu) = \int_0^\infty B_\nu(T_\nu) e^{-\tau_\nu/\mu} \frac{d\tau_\nu}{\mu} \tag{5}$$

The residual intensity in the line

$$r_\nu = \frac{I_\nu(0, \mu)}{I_\nu^c(0, \mu)} \tag{6}$$

For  $\eta = \text{constant}$  and  $B_\nu(t_\nu) = B_0 + B_1 t_\nu$  an exact solution is available. For an arbitrary variation of  $\eta$  and  $B_\nu$ , the equation is solved by a process of iteration (Strömngren) or trial and error (Pannekoek).

**3.8. Curve of growth** (Ref. 1, Chap. 8; Ref. 6; Ref. 14). If  $r_\nu$  is the residual intensity at a point  $\nu$  in a line profile,

$$W_\nu = \int (1 - r_\nu) d\nu \quad \text{and} \quad W_\lambda = \frac{\lambda^2}{c} W_\nu \tag{1}$$

If we regard the lines as being formed in a reversing layer which overlies a photosphere that radiates a continuous spectrum (Schuster-Schwarzschild model, then to a good approximation

$$r_\nu = \frac{1}{1 + N\alpha_\nu} \tag{2}$$

where  $N = \text{number of atoms above the photosphere}$ ,  $\alpha_\nu = \text{atomic absorption coefficient including both collisional, radiative, and Doppler broadening}$ . The relation between  $W_\lambda$  and the number of atoms is given by

$$\frac{W}{\lambda} = \frac{v X_0 \sqrt{\pi}}{c} \left( 1 - \frac{X_0}{\sqrt{2}} + \frac{X_0^2}{\sqrt{3}} - \dots \right) \sim \frac{v X_0 \sqrt{\pi}}{c} \tag{3}$$

when  $N\alpha_\nu < 1$ . Here

$$X_0 = N \frac{\pi \epsilon^2}{mc} f \frac{1}{\sqrt{\pi}} \cdot \frac{c}{v\nu_0} \tag{4}$$

When  $\ln X_0 \gg 1$ ,

$$\frac{W}{\lambda} = 2 \frac{v}{c} (\ln X_0)^{1/2} \left[ 1 - \frac{\pi^2}{24(\ln X_0)^2} - \frac{7\pi^4}{384(\ln X_0)^4} + \dots \right] \tag{5}$$

When  $X_0$  is very large,

$$\frac{W}{\lambda} = \frac{\pi^{1/4}}{2} \left( \frac{v}{c} \right)^{1/2} \left( X_0 \frac{\Gamma}{v} \right)^{1/2} \quad (6)$$

A different set of curves is obtained for each different value of the ratio  $\Gamma/v$ .

**3.9. Equations governing the equilibrium of a star** (Ref. 15, Chaps. 1 and 2; Ref. 3). Let  $M_r$  be mass within a distance  $r$  of the center of the star;  $L_r$  be the total amount of energy developed in a sphere of radius  $r$ . The structure of the star is governed by the following equations.

$$\left. \begin{aligned} P &= \frac{\rho RT}{\mu} + \frac{aT^4}{3}, & (\text{gas + radiation pressure}) \\ \mu &= \mu(\rho, T, \mathcal{A}), & (\text{molecular weight}) \\ \kappa &= \kappa(\rho, T, \mathcal{A}), & (\text{mean absorption coefficient or opacity}) \\ \epsilon &= \epsilon(\rho, T, \mathcal{A}), & (\text{energy generation}) \end{aligned} \right\} \quad (1)$$

Here  $\mathcal{A}$  denotes the relative abundances of the elements or the chemical composition.

$$\left. \begin{aligned} \frac{dP}{dr} &= -G \frac{M_r \rho}{r^2}, & (\text{hydrostatic equilibrium}) \\ M_r &= \int 4\pi r^2 \rho dr \\ \frac{dL_r}{dr} &= 4\pi r^2 \epsilon \rho, & (\text{energy generation}) \end{aligned} \right\} \quad (2)$$

For the domain in radiative equilibrium

$$\frac{d(aT^4)}{dr} = -\frac{3\kappa\rho}{c} \cdot \frac{L}{4\pi r^2} \quad (3)$$

For the domain in adiabatic equilibrium, we neglect radiation pressure and have

$$P = K\rho^\gamma \quad (4)$$

The equations can then be reduced to the form

$$\frac{d}{d\theta} \left( \frac{d\xi}{d\theta} \theta^2 \right) + \theta^2 \xi^n = 0, \quad (\text{Emden's equation}) \quad (5)$$

$$n = \frac{1}{\gamma - 1}, \quad \theta^2 = r^2 \left[ \frac{1}{1+n} \cdot \frac{\mu}{R} 4\pi G \left( \frac{R}{\mu} \cdot \frac{1}{K} \right)^n \right] T_c^{n-1}, \quad T = \xi T_c$$

where  $T_c$  = central temperature, and  $n$  is called the polytropic index.

**3.10. Boundary conditions** (Ref. 15, Chaps. 1 and 2; Ref. 3).

$$\left. \begin{aligned} r = 0, \quad M_r = 0, \quad L_r = 0, & \quad (\text{center of star}) \\ r = R, \quad M_r = M, \quad L_r = L, \quad \rho = 0, \quad T = 0, & \quad (\text{surface of star}) \end{aligned} \right\} \quad (1)$$

**3.11. Theoretical form of mass-luminosity law** (Ref. 15, Chaps. 1 and 2; Ref. 3).

$$L = \text{const} \frac{1}{\kappa_0} \cdot \frac{M^{5+s}}{R^s} (\mu\beta)^{+7+s} \quad (1)$$

where  $\kappa = \kappa_0 \rho T^{-3+s}$ ,  $\beta =$  ratio of gas pressure to total pressure. This equation must be solved in conjunction with the equation governing the energy output.

$$\epsilon = \epsilon_0(\mathcal{A})\rho^m T^n, \quad (\text{energy generation law}) \quad (2)$$

$$L = 4\pi \int_0^R \epsilon_0(\mathcal{A})\rho^{m+1} T^n r^2 dr \quad (3)$$

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## Chapter 29

### CELESTIAL MECHANICS

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The basic equations of celestial mechanics are essentially those of ordinary classical mechanics. In the applications of these equations to the motions of celestial bodies, however, the technique adopted by the astronomer differs somewhat from that ordinarily employed by the physicist who is working on the average problem of classical dynamics. The distinction in general arises from the necessity, for astronomical purposes, of obtaining solutions of the equations of motion that will represent the motions over very long intervals of time with the high accuracy of precise astronomical observations, and in a form adapted to the practical numerical computation of the motion as an explicit function of the time. The emphasis is principally on indefinite integrals. Moreover, necessity demands that a solution which meets the needs of astronomy be obtained regardless of the mathematical difficulty or even impossibility of a general abstract solution in the current state of mathematical knowledge.

These considerations have resulted in the characteristic methods used in celestial mechanics, the more important of which are given in the following summary of formulas for the different types of motion that must be treated.

#### 1. Gravitational Forces \*

At any point external to a body with mass  $M$  and principal moments of inertia  $A, B, C$ , the Newtonian gravitational attraction exerted by the body is  $\text{grad } U$ , where to the *second order* inclusive in the ratio of the linear dimensions of the body to the distance  $r$  of the point from the center of mass, the Newtonian gravitational potential  $U$  is

$$U = k^2 \frac{M}{r} + k^2 \frac{A + B + C - 3I}{2r^3} \quad (1)$$

\* See also Chapter 5.

in which  $I$  is the moment of inertia about  $r$ , and  $k^2$  is the constant of gravitation. In cgs units,  $k^2 = 6.673 \times 10^{-8} \text{ cm}^3 \text{ g}^{-1} \text{ sec}^{-2}$ .

For symmetrical distributions of mass, this expression for  $U$  is accurate to the *third* order. For homogeneous or concentrically homogeneous spherical distributions, the expression reduces to the first term  $k^2 M/r$ , as if the entire mass  $M$  were concentrated in a particle at the center of mass. For any body for which  $A = B$ , e.g., a concentrically homogeneous oblate spheroid of revolution, the value of  $I$  is  $A + (C - A) \sin^2 d$ , where  $d$  is the angle between  $r$  and the plane of the principal axes of  $A$  and  $B$ , and

$$U = k^2 \frac{M}{r} + k^2 \frac{C - A}{2r^3} (1 - 3 \sin^2 d) \quad (2)$$

On every element of mass  $dm$  of another body, the body  $M$  exerts a force for which the force function is  $Udm$ . When  $m$  is a rigid body, the action of this system of forces is the same as if the resultant  $F$  of the forces, which has a force function  $\int_m Udm$ , were applied to a particle of mass  $m$  at the center of mass, and a couple, with a moment equal to the resultant  $G$  of the moments of the forces about the center of mass, were applied to the body. The consequent motion of  $m$  under the action of  $M$  is a translation at velocity  $V$  in which the rate of change of the linear momentum is

$$m \frac{dV}{dt} = F \quad (3)$$

and a rotation around an axis through the center of mass in which the rate of change of the angular momentum  $H$  about the center of mass is

$$\frac{dH}{dt} = G \quad (4)$$

When both  $M$  and  $m$  are homogeneous or concentrically homogeneous spherical bodies, or when the distance  $r$  from  $M$  to  $m$  is so great that higher powers of  $1/r$  may be neglected,

$$\int_m Udm = k^2 \frac{Mm}{r} \quad (5)$$

a function of  $r$  only, and hence the force exerted on  $m$  by  $M$  is

$$F = -k^2 \frac{Mm}{r} \quad (6)$$

directed toward  $M$ ; an equal and oppositely directed force is exerted on  $M$  by  $m$ , and the resultant couples vanish.

Under these conditions, relative to an inertial rectangular coordinate system with arbitrary origin, in which the coordinates of the center of mass of  $m$  are

$x'$ ,  $y'$ ,  $z'$ , and those of  $M$  are  $X'$ ,  $Y'$ ,  $Z'$ , the motion of the center of mass of  $m$  is represented by

$$\frac{d^2x'}{dt^2} = -k^2M \frac{x' - X'}{r^3}, \quad \dots \quad (7)$$

Likewise,  $M$  under the action of  $m$  moves in accordance with the equations

$$\frac{d^2X'}{dt^2} = +k^2m \frac{x' - X'}{r^3}, \quad \dots \quad (8)$$

Consequently, in a rectangular system with *origin at M* and axes in fixed directions in space, in which the position of  $m$  relative to  $M$  is represented by the coordinates  $x = x' - X'$ , ..., the equations of motion are

$$\frac{d^2x}{dt^2} = -k^2(M + m) \frac{x}{r^3}, \quad \dots \quad (9)$$

The integration of this system of equations gives the *motion of m relative to M*; the coordinate system is *noninertial*.

## 2. Undisturbed Motion

Each of two homogeneous or concentrically homogeneous spherical masses,  $M$  and  $m$ , under the action of their mutual Newtonian gravitational attractions, undisturbed by any other forces, moves about their common center of mass in an orbit which has the form of a conic section with one focus at this center of mass. The orbit of either body relative to the other is likewise a conic section with one focus at the center of mass of this other body. This is the general form of Kepler's first law of planetary motion; only for undisturbed motion are Kepler's laws valid.

The form, size, and orientation in space of an undisturbed Newtonian gravitational orbit are fixed by the position and velocity of the body at any one instant, and are invariable. The orbit of  $m$  relative to  $M$  is an ellipse, a parabola, or a hyperbola according as

$$V^2 \begin{cases} \leq \\ > \end{cases} k^2\mu \frac{2}{r}$$

where  $V$  is the linear speed *relative to M* at distance  $r$ , and  $\mu$  is the sum of the masses,  $M + m$ .

The exact form of the orbit is specified by the eccentricity  $e$ , which, for a given initial speed and distance, depends on the initial direction of motion. The size of the orbit is specified by the semimajor axis  $a$  (or, for a parabola, by the minimum value  $q$  of  $r$ ) which, for a given initial direction of motion at

a given distance, depends on the initial speed in accordance with the relation

$$V^2 = k^2\mu \left( \frac{2}{r} - \frac{1}{a} \right) \quad (1)$$

hence  $a \begin{matrix} \geq \\ \leq \\ > \end{matrix} \infty$  according as the orbit is an ellipse, a parabola, or a hyperbola.

The position of the orbital plane in space is determined by the initial position and direction of motion; it is usually specified by its inclination  $i$  to the plane of the ecliptic and the longitude  $\Omega$  of its ascending node on the ecliptic reckoned from the vernal equinox. The orientation of the orbit in this plane is specified by the longitude  $\tilde{\omega}$  of the extremity of the major axis that is the nearer to the central mass  $M$ , defined as the sum of the angle  $\Omega$  along the ecliptic and the arc of the orbit from the node to the apse;  $\tilde{\omega}$  therefore lies in two different planes. The major axis is known as the *line of apsides*.\*

The five constants  $e$ ,  $a$  (or  $q$ ),  $i$ ,  $\Omega$ ,  $\tilde{\omega}$ , fix the orbit of  $m$ ; the position of  $m$  in its orbit is fixed by the position at any one instant, e.g., by the time  $T$  of passage through the apse nearer to  $M$ . These six quantities are called the *elements* of the orbit; their numerical values must be determined from observation, and their determination is equivalent to the evaluation of the constants of integration in the solution of the differential equations of motion.†

The position of  $m$  in its orbit at any instant  $t$  is represented by the radius vector  $r$  from  $M$ , and the angle  $f$  at  $M$  between  $r$  and the line of apsides, reckoned in the direction of motion from the apse nearer  $M$ . This angle  $f$  is known as the *true anomaly*; the value which it would have were  $m$  to move around  $M$  at a uniform angular rate  $n$  equal to the mean value of  $df/dt$  is called the *mean anomaly*  $g$ .

The motion of  $m$  in its orbit is in accordance with the law of areas for the rate at which the radius vector sweeps out the area of a sector in the orbital plane.

$$\frac{1}{2}r^2 \frac{df}{dt} = \frac{1}{2}k\sqrt{\mu p}, \quad (\text{a constant}) \quad (2)$$

(Kepler's second law), where  $p$  is the semilatus rectum of the conic.

\* For applications to the trajectories of projectiles, see *Am. J. Phys.*, 13, 253 (1945) and 19, 52 (1951). On interplanetary trajectories: Astronomical Society of the Pacific, *Leaflets* 168 (1943) and 201 (1945); *Navigation* 2, 259 (1950); *J. Brit. Interplanetary Soc.*, 11, 205 (1952).

† For the integration of the equations of motion, and the expressions for the orbital elements in terms of the constants of integration and the initial conditions, see MOULTON, F. R., *Celestial Mechanics*, 2d ed., The Macmillan Company, New York, 1914, pp. 140-149. For the general principles of the determination of the elements of an undisturbed orbit from observation, see WOOLARD, E. W., *Nat. Math. Mag.*, 14, 1-11 (1940); and for the detailed practical procedures, see HERGET, P., *The Computation of Orbits*, published by the author, 1948. A nomogram for the graphical solution of problems depending upon Kepler's Laws is given in *Skv and Tel.*, 17, 572 (1958).

### 2.1. Elliptic motion

Period of revolution :

$$P = \frac{2\pi a^{3/2}}{k\sqrt{\mu}} \quad (1)$$

Mean motion :

$$n = 2\pi/P = \frac{k\sqrt{\mu}}{a^{3/2}} \quad (2)$$

Kepler's third law :

$$n^2 a^3 = k^2 \mu \quad (\text{a constant}) \quad (3)$$

Kepler's third law is the basis for the definition of the fundamental astronomical unit of length. The *astronomical unit* is the unit of distance in terms of which, in Kepler's third law, the semimajor axis  $a$  of an elliptic orbit must be expressed in order that, with  $n$  in radians, the numerical value of  $k$  may be exactly 0.01720209895 when the unit of mass is the mass of the Sun and the unit of time is the mean solar day. In these units,  $k$  is known as the Gaussian constant; and  $k^2 = 0.00029591221$ . With  $n$  in seconds of arc per mean solar day,  $k = 3548.1876069651$ .

Mean anomaly :  $g = n(t - T)$

or more generally,  $g = g_0 + n(t - t_0)$  where  $g_0$  is the mean anomaly at any arbitrary epoch  $t_0$ . The quantity  $f - g$  is called the *equation of the center*.

*Kepler's equation* : In an elliptic orbit, the angle  $E$  in the usual parametric equations of the ellipse ( $x = a \cos E$ ,  $y = b \sin E$ ) is called the *eccentric anomaly*. It is related to the mean anomaly by Kepler's equation,

$$g = E - e \sin E$$

and its value at any time  $t$  may be found from  $g$  by solving this equation; for practical methods of solution see Herget, P., *op. cit.*, p. 33, and Bauschinger-Stracke, *Tafeln zur theoretischen Astronomie*, 2d ed.

*Position in the orbit*

Finite formulas :

$$\left. \begin{aligned} \tan \frac{1}{2}f &= \sqrt{\frac{1+e}{1-e}} \tan \frac{1}{2}E \\ r &= a(1 - e \cos E) = \frac{a(1 - e^2)}{1 + e \cos f} \\ q &= a(1 - e) \\ r \sin f &= a\sqrt{1 - e^2} \sin E, \quad r \cos f = a(\cos E - e) \end{aligned} \right\} \quad (4)$$

Series developments :

$$\frac{r}{a} = 1 + \frac{1}{2}e^2 - \left[ 2\left(\frac{e}{2}\right) - 3\left(\frac{e}{2}\right)^3 + \dots \right] \cos g \tag{5}$$

$$- \left[ 2\left(\frac{e}{2}\right)^2 - \frac{16}{3}\left(\frac{e}{2}\right)^4 + \dots \right] \cos 2g \tag{6}$$

$$- \left[ 3\left(\frac{e}{2}\right)^3 - \dots \right] \cos 3g \tag{7}$$

$$- \left[ \frac{16}{3}\left(\frac{e}{2}\right)^4 - \dots \right] \cos 4g \tag{8}$$

- ... ..

$$f = g + \left[ 4\left(\frac{e}{2}\right) - 2\left(\frac{e}{2}\right)^3 + \dots \right] \sin g \tag{9}$$

$$+ \left[ 5\left(\frac{e}{2}\right)^2 - \frac{22}{3}\left(\frac{e}{2}\right)^4 + \dots \right] \sin 2g \tag{10}$$

$$+ \left[ \frac{26}{3}\left(\frac{e}{2}\right)^3 - \dots \right] \sin 3g \tag{11}$$

$$+ \left[ \frac{103}{6}\left(\frac{e}{2}\right)^4 - \dots \right] \sin 4g \tag{12}$$

+ ... ..

For tables of elliptic motion, see Bauschinger-Stracke, *op. cit.*, p. 5.\*

The semimajor axis  $a$  is usually called the *mean distance*; but it is the mean value of  $r$  with respect to  $E$ , not with respect to the time

$$a = \frac{1}{2\pi} \int_0^{2\pi} r dE \tag{13}$$

The average in time is  $a(1 + \frac{1}{2}e^2)$ .

\* For the calculation of the heliocentric coordinates of a planet or comet from  $r$ ,  $v$ , and the orbital elements, and the computation of the position on the celestial sphere as seen from the Earth, see Smart, W. M., *Spherical Astronomy*, Cambridge University Press, London, 1931, pp. 122-129; also Moulton, F. R., *op. cit.*, pp. 182-189. On the characteristics of the apparent path on the sphere, see Herget, P., *Popular Astronomy*, June-July, 1939; also Herget, P., *op. cit.*, pp. 37-39.

The quantity  $L = \tilde{\omega} + g$  is called the *mean orbital longitude*; substituting the expression for  $g$  gives the form

$$L = nt + \epsilon$$

where the constant  $\epsilon$  is the mean longitude at the epoch  $t = 0$  from which the time is reckoned, and is often used instead of  $T$  or  $g_0$  as the element which fixes the position of  $m$  in its orbit.

## 2.2. Parabolic motion

$$\tan \frac{1}{2}f + \frac{1}{3} \tan^3 \frac{1}{2}f = \frac{k\sqrt{\mu}(t - T)}{\sqrt{2}q^{3/2}} \quad (1)$$

Solution for  $f$  with auxiliaries  $s$  and  $w$  :

$$\tan s = \frac{2^{3/2}}{3k\sqrt{\mu}} \frac{q^{3/2}}{t - T}, \quad \tan w = \sqrt[3]{\tan \frac{1}{2}s}, \quad \tan \frac{1}{2}f = 2 \cot 2w \quad (2)$$

For solution by successive approximation, see Herget, P., *op. cit.*, p. 32; for tables, see Bauschinger-Stracke, *op. cit.*

$$r = q \sec^2 \frac{1}{2}f$$

**2.3. Hyperbolic and nearly parabolic motion.** See Herget, P., *op. cit.*, pp. 34-37; Bauschinger-Stracke, *op. cit.*

In the cases to which the foregoing equations of undisturbed motion are applied in practice (especially for parabolic and hyperbolic motion),  $M$  is usually unity and  $m$  is commonly neglected, whence  $\mu = 1$ . The unit of time is often taken to be  $1/k$  mean solar days;  $k$  then does not appear explicitly in the equations.

**2.4. Relativity correction.** The only observable effect on the motion of  $m$  from the correction to the Newtonian law of gravitation that is required by the general theory of relativity is a rotation of the orbit within its plane, which causes a variation of  $\tilde{\omega}$ . The rate of rotation, in radians per revolution of  $m$ , is

$$24\pi^3 \frac{a^2}{c^2 P^2 (1 - e^2)} \quad (1)$$

in which  $c$  is the velocity of light.\*

\* See CLEMENCE, G. M., *Revs. Modern Phys.*, **19**, 361 (1947); also DUNCOMBE, R. L., *Astr. J.*, **61**, 174 (1956).

### 3. Disturbed Motion

The actual motion of any celestial body is determined by the gravitational attractions of all the other bodies in the system of which it is a part, and in general conforms only more or less approximately to the foregoing equations of undisturbed motion. In the solar system, the motions of the planets, although dominated by the action of the Sun, are each disturbed by the attractions of the other planets; and the motions of the Moon and many other satellites are appreciably affected by the oblateness of the planets around which they revolve, and by the disturbing attraction of the Sun. The orbits are therefore complex and ever varying curves; however, with few exceptions, the motions do not depart widely from undisturbed elliptic motion, and it is advantageous for many purposes to represent the actual motion mathematically in terms of its departures, or perturbations, from an undisturbed elliptic motion which approximates it.

**3.1. The disturbing function.** When the motion of  $m$  around  $M$  is disturbed by the action of a third mass  $m'$ , the vector difference between the attractions of this disturbing mass on  $m$  and  $M$  produces a motion of  $m$  relative to  $M$  additional to the motion produced by the action of  $M$ , and causes a departure from the elliptic motion that would occur relative to  $M$  under the attraction of  $M$  alone. When all three bodies may be considered as concentrically homogeneous spheres, the force function for this disturbing force on  $m$  that is added to the attraction of  $M$  is

$$R = k^2 m' \left[ \frac{1}{\Delta} - \frac{r}{r'^2} \cos(r, r') \right] \quad (1)$$

where  $\Delta$  is the distance of  $m'$  from  $m$ , and  $r, r'$ , are, respectively, the radii vectores of  $m, m'$ , from  $M$ .

When the central mass  $M$  is not a concentrically homogeneous sphere, a disturbing force likewise acts, equal to the vector difference between the actual attraction and the attraction that a particle of the same mass  $M$  at the center of mass would exert. When  $M$  is an oblate ellipsoid of revolution, with equatorial and polar radii  $a_0$  and  $c_0$  and flattening  $f = (a_0 - c_0)/a_0$ , for which the surface is in equilibrium with gravity (no hypothesis about the interior is then necessary), we have  $C - A = \frac{2}{3} M a_0^2 (f - \frac{1}{2} \kappa)$ , where  $\kappa$  is the ratio of the centripetal acceleration of rotation at the equator to gravity on  $M$ ; and the force function for the disturbing force, to the first order in  $f$  and the second order in  $a_0/r$ , is

$$R' = k^2 M \left( f - \frac{1}{2} \kappa \right) \frac{a_0^2}{r^3} \left( \frac{1}{3} - \sin^2 d \right) \quad (2)$$

in which  $d$  is the angle between  $r$  and the equatorial plane of  $M$ .

In a rectangular coordinate system with origin at  $M$  and axes in fixed directions in space, the equations of motion of  $m$  relative to  $M$  are

$$\frac{d^2x}{dt^2} + k^2(M + m) \frac{x}{r^3} = \frac{\partial \Omega}{\partial x}, \quad \dots \quad (3)$$

where  $\Omega$  is the sum of the disturbing functions  $R$  and  $R'$  for all the bodies acting on  $m$ ; the force function  $\Omega$  is not a potential. When  $\Omega$  consists only of the disturbing function  $R$  for a single mass  $m'$ , the motion of  $m$  is represented by

$$\frac{d^2x}{dt^2} + k^2(M + m) \frac{x}{r^3} = k^2m' \left( \frac{x' - x}{\Delta^3} - \frac{x'}{r'^3} \right), \quad \dots \quad (4)$$

The first term on the right (the principal, or direct, term) represents the attraction of  $m'$  on unit mass of  $m$ , and the second term (indirect term) is the attraction of  $m'$  on unit mass of  $M$ ; their difference imparts to  $m$  the acceleration additional to the acceleration which is imparted by the mutual attractions of  $m$  and  $M$  represented by the second term on the left, and which alone would give undisturbed elliptic motion. *See* note p. 696,

**3.2. Variations of the elements.** Because of the acceleration from the disturbing forces additional to the acceleration from the force that a single particle of mass  $M$  would exert, the variations of the position and velocity of  $m$  from one instant to another are different from the variations that would maintain  $m$  in motion in a fixed ellipse. The position and velocity at any particular instant mathematically determine an elliptic orbit in which, in undisturbed motion around  $M$ , the elliptic position and velocity *at this instant* would be the same as the actual position and velocity, but this orbit is different at different instants, i.e., the orbital elements are variable instead of being constants. The actual motion may be represented as elliptic motion in an orbit which is continually changing form, size, and position in space under the action of the disturbing forces; at each instant, the motion is the resultant of elliptic motion in the instantaneous orbit and the further motion due to the variations of the orbit.\*

Under the action of the total disturbing force, with a disturbing function  $\Omega$ , the rates of variation of the five elements that characterize the orbital curve are

$$\frac{da}{dt} = \frac{2}{k} \sqrt{\frac{a}{\mu}} \frac{\partial \Omega}{\partial \epsilon} \quad (1)$$

\* For simple geometrical derivations of the qualitative effects of the disturbing forces on the orbital elements, see *HERSCHEL*, Sir John, *Outlines of Astronomy*, Chaps. 12-14.

$$\frac{de}{dt} = -\frac{1}{ke} \sqrt{\frac{1-e^2}{\mu a}} \frac{\partial \Omega}{\partial \tilde{\omega}} - \frac{1}{k} \sqrt{\frac{1-e^2}{\mu a}} \cdot \frac{e}{1+\sqrt{1-e^2}} \cdot \frac{\partial \Omega}{\partial \epsilon} \quad (2)$$

$$\frac{di}{dt} = -\frac{1}{k \sin i \sqrt{\mu a(1-e^2)}} \cdot \frac{\partial \Omega}{\partial \zeta} - \frac{1 - \cos i}{k \sin i \sqrt{\mu a(1-e^2)}} \left( \frac{\partial \Omega}{\partial \tilde{\omega}} + \frac{\partial \Omega}{\partial \epsilon} \right) \quad (3)$$

$$\frac{d\zeta}{dt} = \frac{1}{k \sin i \sqrt{\mu a(1-e^2)}} \frac{\partial \Omega}{\partial i} \quad (4)$$

$$\frac{d\tilde{\omega}}{dt} = \frac{1}{ke} \sqrt{\frac{1-e^2}{\mu a}} \cdot \frac{\partial \Omega}{\partial e} + \frac{1 - \cos i}{k \sin i \sqrt{\mu a(1-e^2)}} \cdot \frac{\partial \Omega}{\partial i} \quad (5)$$

The elliptic position in the instantaneous orbit is fixed by the mean orbital longitude  $L = nt + \epsilon$ . The rate of motion *in mean longitude*,

$$\frac{dL}{dt} = n + \left( t \frac{dn}{dt} + \frac{d\epsilon}{dt} \right) \quad (6)$$

is the result partly of the instantaneous elliptic motion *in the orbit* at rate  $n$ , and partly of the addition to this elliptic motion by the *variation* of the orbit, which causes variations of  $n$  and  $\epsilon$ .

$$\left. \begin{aligned} \frac{dL}{dt} = n - \frac{2}{k} \sqrt{\frac{a}{\mu}} \frac{\partial \Omega}{\partial a} + \frac{e}{k\sqrt{\mu a}} \frac{\sqrt{1-e^2}}{1+\sqrt{1-e^2}} \frac{\partial \Omega}{\partial e} \\ + \frac{1 - \cos i}{k \sin i \sqrt{\mu a(1-e^2)}} \frac{\partial \Omega}{\partial i} \end{aligned} \right\} \quad (7)$$

where in the disturbing function  $\Omega$  the quantities  $n$  and  $\epsilon$  appear explicitly only in arguments of sines and cosines in the form  $nt + \epsilon$ , and in the differentiations  $n$  is formally regarded as constant and independent of  $a$ .

In the integral of the right member, since it follows from Kepler's third law and the equation for  $da/dt$  that

$$\frac{dn}{dt} = -\frac{3}{2} \frac{n}{a} \frac{da}{dt} = -\frac{3}{a^2} \frac{\partial \Omega}{\partial \epsilon} \quad (8)$$

we have

$$\int n dt = -3 \iint \frac{1}{a^2} \frac{\partial \Omega}{\partial \epsilon} dt^2 \quad (9)$$

which represents the total amount of motion in the disturbed orbit, and is equal to  $\bar{n}t$  where  $\bar{n}$  is the mean value  $(1/t) \int n dt$  of the continually varying rate of motion in the orbit.

Denote the integral of the remaining terms by  $\epsilon'$ . Then the mean longitude in disturbed motion may be expressed in the form :

$$L = \bar{n}t + \epsilon' \quad (10)$$

instead of in terms of the instantaneous elliptic quantities  $n$  and  $\epsilon$ ; and in  $\Omega$  and its derivatives,  $\bar{n}$  and  $\epsilon'$  may be used in place of  $n$  and  $\epsilon$  in all the preceding equations for the variations of the elements.

**3.3. Perturbations of the coordinates.** In general, the elements have periodic variations about a mean value that itself has a progressive secular change. The coordinates in space or on the celestial sphere at any time may be calculated from the *instantaneous* values of the elements by means of the formulas for undisturbed elliptic motion; or they may be obtained by calculating elliptic coordinates from *arbitrarily adopted* values of the elements, and adding the variations produced in the coordinates by the variations of the elements from these adopted values. In practice, short-period variations of the elements are often represented by equivalent perturbations of the coordinates, while secular and long-period perturbations are left expressed in the form of variations of the orbital elements; the actual position is then represented in terms of its irregularly varying departure from the elliptic position in a slowly changing orbit. See Clemence, G. M., *Astro. J.*, **52**, 89 (1946).

The elliptic orbit to which the actual irregular motion is referred is known as the *mean orbit*, and its elements are called *mean elements*. This mean reference orbit is defined mathematically; it is mathematically arbitrary, and depends on the particular methods adopted for integrating the equations of motion and evaluating the constants of integration from observation. It is often defined differently in different theories; but in defining it for the Moon or for a planet, the semimajor axis is calculated by Kepler's third law from the actually observed mean rate  $\bar{n}$  of the disturbed motion.\*

**3.4. Mean orbit of the Earth.** The *observed* mean motion of the Earth, which in this section will be denoted simply by  $n$ , is the mean value of the disturbed motion of the center of mass of the Earth-Moon system;  $n = 3548''.193$  per mean solar day. The semimajor axis  $a$  of the mean orbit is computed from this mean motion, and the total mass of the system, by Kepler's law

$$k^2 \left[ 1 + E \left( 1 + \frac{M}{E} \right) \right] = n^2 a^3 \quad (1)$$

\* The coordinates may also be obtained directly by numerical integration of the equations of motion, without the intermediary of a mean orbit. See CLEMENCE, G. M. and BROUWER, D., *Sky and Telescope*, **10**, 83-86 (1951); also CLEMENCE, G. M., *Astr. J.*, **63**, 403 (1958) and PORTER, J. G., *Astr. J.*, **63**, 405 (1958).

in which  $E$  is the mass of the Earth and  $M$  the mass of the Moon in terms of the mass of the Sun as the unit.

This mean distance  $a$  is 1.0000 0003 astronomical units. To obtain its equivalent in physical units of length, the value of the solar parallax is required. The mean equatorial horizontal solar parallax  $p$  is the angle subtended by the equatorial radius of the Earth  $a_0$  at a distance of one astronomical unit : 1 a.u. =  $a_0/\sin p$ .

In the expression for  $a$  obtained from Kepler's law, we may put  $k^2E = \rho_1^2G_1$  in which  $\rho_1$  is the radius of the Earth at the latitude  $\varphi_1$  where the gravitational attraction  $G_1$  of the Earth is the same as if the entire mass  $E$  were concentrated at the center;  $\varphi_1$  is very nearly  $\sin^{-1} \sqrt{\frac{1}{3}}$ , and in terms of gravity  $g_1$  at this latitude

$$G_1 = g_1(1 + \kappa_1 \cos \varphi_1) \tag{2}$$

in which  $\kappa_1$  is the ratio of the centripetal acceleration of rotation to gravity. We then have from Kepler's law,

$$\sin p = \frac{a_0}{\rho_1} \left[ \frac{E + M}{1 + (E + M)} \cdot \frac{n^2 \rho_1}{\pi^2 l_1 (1 + \kappa_1 \cos \varphi_1) (1 + M/E)} \right]^{1/3} \tag{3}$$

where  $l_1$  is the length of the seconds pendulum at latitude  $\varphi_1$ , and  $n$  must be expressed in radians/second.

The solar parallax is related to the velocity of light  $c$  by the expression for the length of time  $\tau$  required for light to travel unit distance,

$$\tau = \frac{a_0}{c \sin p} \tag{4}$$

where  $\tau$  is called the equation of light. Hence  $p$  is also related to the aberration of light that is caused by the motion in the mean orbit; in terms of the constant of aberration, which is defined as

$$\alpha = \frac{na}{c\sqrt{1 - e^2}} \tag{5}$$

we have 
$$\sin p = \frac{a_0 n}{\alpha c \sqrt{1 - e^2}} \tag{6}$$

In disturbed motion, the constant part or mean value  $\bar{r}$  of the disturbed radius vector is not equal to the mean distance  $a$ , because of variations of the instantaneous eccentricity and line of apsides which change the average distance without altering  $a$ . In the mean orbit of the Earth

$$\bar{r} = a + 0.0000 0020 \tag{7}$$

**3.5. Mean orbit of the Moon.** The mean distance  $a$  of the Moon from the Earth is defined in terms of the observed mean motion  $n$  of the Moon by Kepler's law.

$$n^2 a^3 = k^2 E(1 + M/E) \quad (1)$$

From the gravitational theory of the motion of the Moon,

$$\frac{1}{a} = \frac{1}{r_0} (1 - 0.0009068) \quad (2)$$

where  $1/r_0$  is the constant term in the expression for the disturbed inverse radius vector. The ratio of the equatorial radius of the Earth  $a_0$  to  $r_0$  is the constant part or mean value of the sine of the equatorial horizontal lunar parallax. At this distance  $r_0$  at which the lunar parallax has its mean value  $P$ , we have, with  $n$  expressed in radians/second,

$$\sin P = 1.0009076 \frac{a_0}{a} \quad (3)$$

$$= 1.0009076 \frac{a_0}{\rho_1} \left[ \frac{1}{1 + M/E} \cdot \frac{n^2 \rho_1}{\pi^2 I_1 (1 + \kappa_1 \cos \varphi_1)} \right]^{1/3} \quad (4)$$

$$= 3422''.54 \sin 1'' \quad (5)$$

where  $P = 57'02''.70$ , and  $r_0 = 60.2665 a_0$ . Both  $r_0$  and  $a$  differ from the average value  $\bar{r}$  of the radius vector.

The solar and lunar parallaxes are related by

$$\sin p = 0.9990932 \sin P \left[ \frac{E + M}{1 + (E + M)} \left( \frac{n_\oplus}{n_\zeta} \right)^2 \right]^{1/3} \quad (6)$$

**3.6. Mass of a planet from the mean orbit of a satellite.** From the observed apparent motion of a satellite relative to the planet around which it revolves, a mean orbit for the satellite may be derived and its secular variations determined. From the elements and their variations, the mass and the flattening of the planet may be found. In particular, in terms of the observed mean motion  $n$  of the satellite, and the semimajor axis  $a$  of its orbit derived from the *directly measured* apparent mean angular distance from the planet, the mass of the planet is

$$m = \left( \frac{n}{n_\oplus} \right)^2 \frac{a^3}{1 + (a_0/a)^2 (f - \frac{1}{2}\kappa)} (1 + E) \quad (1)$$

in which  $a_0$ ,  $f$ , and  $\kappa$  denote, respectively, the equatorial radius, flattening,

and ratio of centripetal acceleration to gravity at the equator, of the planet, and  $a$  is in astronomical units.\*

#### 4. The Rotation of the Earth

The motion of the Earth relative to its center of mass is the resultant of three components. First, it rotates around an axis that always passes through the center of mass. However, this axis does not coincide exactly with the axis of figure. Second, the Earth is continually changing its position slightly in space relative to the axis of rotation by a motion known as the Eulerian nutation, which causes the axis of figure to describe an irregular variable conical surface in space around the axis of rotation while the direction of the axis of rotation remains sensibly constant in space. Hence the axis of rotation lies in successively different positions on a conical surface within the Earth. At the same time, under the gravitational attractions of the Sun and Moon, the axis of rotation possesses a conical motion in space in which the Earth as a whole participates without any change in its position relative to the axis. All three motions are affected by elastic and plastic deformations of the Earth, and by transfers of mass on and within the Earth in geophysical phenomena; in particular the rate of rotation has secular, irregular, and periodic variations.

**4.1. Poisson's equations.** The lunisolar motion of the axis of rotation in space is due to the inequalities of the principal moments of inertia of the Earth. To a high degree of approximation, it is the same as if the Earth were a rigid body.

As a result of the consequent motion of the plane of the equator, the inclination  $\theta$  of the equator to the fixed ecliptic of an adopted epoch is continually varying, and the ecliptic is intersected at a continually different point. Neglecting the departures of the Earth from perfect rigidity, and assuming the equatorial moments of inertia  $A$  and  $B$  to be equal, we find that the variations of  $\theta$  and of the angular distance  $\psi$  of the intersection *westward* from its position at the epoch  $t = 0$ , caused by the action of the mass  $M'$  of the Sun or the Moon at distance  $r$  and declination  $\delta$ , are

$$\frac{d\theta}{dt} = + \frac{1}{C\omega \sin \theta} \frac{\partial V}{\partial \psi}, \quad \frac{d\psi}{dt} = - \frac{1}{C\omega \sin \theta} \frac{\partial V}{\partial \theta} \quad (1)$$

\* On the general theory of disturbed motion, see BROWN, E. W. and SHOOK, C. A., *Planetary Theory*, Cambridge University Press, London (1933); and BROWN, E. W., *Introductory Treatise on the Lunar Theory*, Cambridge University Press, London (1896).

in which  $\omega$  is the angular rate of rotation of the Earth, and

$$V = -k^2 \frac{3M'(C-A)}{2r^3} \sin^2 \delta \quad (2)$$

where  $C$  is the principal moment of inertia with respect to the axis of figure. The variations depend upon  $(C-A)/C$ , called the *dynamical flattening*, not upon the geometric figure of the Earth.\*

The motion is the resultant of a steady progressive secular part, which is called the *lunisolar precession*, and a large number of periodic components that are collectively called the *lunisolar nutation*.

The actual motion of the equinoxes along the ecliptic, and the variation of the obliquity of the ecliptic, are the result of both this lunisolar motion of the equator and a slow secular motion of the ecliptic caused by the secular perturbations of the orbital motion of the Earth. The westward motion of the equinoxes along the ecliptic, called the *general precession* in longitude, results from both the lunisolar precession and the *planetary precession* caused by the motion of the ecliptic.†

**4.2. The Eulerian nutation.** Kinematically, the daily rotational motion of the Earth, instead of being a simple rotation around a fixed diameter, results from a conical surface within the Earth, with vertex at the center of mass and axis along the axis of figure, rolling on another very much smaller conical surface *in space*. The line of contact of the two cones is the instantaneous axis of rotation; it describes the circumference of the small cone each day, and after each circuit it is displaced within the Earth along the circumference of the large cone by the length of the perimeter of the small cone. This motion is a dynamical consequence of the lack of coincidence of the axis of rotation with the axis of figure. It leaves the position of the small cone in space unchanged; and the angular opening of this cone is too small for the daily conical oscillation of the axis of rotation in space to be observable. The Earth as a whole is therefore displaced in space relative to the axis of rotation, while this axis is practically unchanged

\* For the solution explicitly in terms of the masses and the orbital elements of the Sun and Moon, see TISSERAND, F., *Traité de mécanique céleste*, Vol. 2, Gauthier-Villars & Cie., Paris, 1891. See also HILL, G. W., *Collected Mathematical Works*, Vol. 4, Carnegie Institution, Washington, 1907, p. 11.

† The principal term in the nutation is due to the action of the Moon; its coefficient is called the constant of nutation. The coefficient of the principal term in the precession is the constant of precession. The expressions for these constants in terms of the masses and orbital elements of the Earth and the Moon, and the dynamical flattening, are given by HILL, G. W., *loc. cit.*; conversely,  $(C-A)/C$  and  $M/(E+M)$  may be expressed in terms of the constants of precession and nutation.

in space and hence lies in a different position within the Earth; the displacement of the Earth in space causes the axis of figure to describe a cone in space around the axis of rotation.

Unlike the lunisolar precession and nutation, the Eulerian motion is greatly affected by the departures of the Earth from perfect rigidity. Were the Earth an invariable rigid body with  $A = B$ , the axis of rotation would describe a slightly sinuous circular cone within the Earth around the axis of figure, at a nearly uniform rate with a mean period of

$$T = \frac{2\pi}{(C - A)\omega/A} = 303 \text{ days}$$

the sinuosities are due to a daily oscillation with a variable amplitude that may reach  $0''.02$ , which is caused by the lunisolar forces. Actually, because of deformations of the Earth, and the continual disturbances from meteorological and other geophysical processes, the period is lengthened to an average of about 14 months, and the motion is highly irregular and variable, with a superimposed annual component. The consequent irregular motion of the geographic poles over the surface of the Earth is confined within an area about 50 feet in radius, and causes the phenomenon frequently termed "variation of latitude."

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NOTE : When the central mass  $M$  does not attract as if it were a particle, the higher order terms in the potential  $R'$  depend explicitly upon the internal distribution of density. The effects of these terms are important in close binary systems, in the motions of some of the satellites in the solar system and of artificial Earth satellites, and in physical geodesy.

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## Chapter 30

### METEOROLOGY

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Meteorology comprises the branch of geophysics that treats of the earth's atmosphere and its phenomena. However, meteorology, as presently constituted, does not concern itself with the electromagnetic and photochemical phenomena that are important in the upper 1 per cent by mass of the atmosphere. Some of the following formulas are not generally applicable to this upper region.

The basic physical laws of atmospheric behavior derive from other branches of physics. The first section below discusses the four basic equations that govern the large-scale flow patterns in the atmosphere. The second section presents certain auxiliary equations derived from these basic ones.

#### 1. Basic Equations for Large-Scale Flow

**1.1. The hydrodynamic equation of motion.** The hydrodynamic equation of motion is usually written for a frame of reference that is rotating with the earth so that it takes the form

$$\frac{d\mathbf{v}}{dt} = \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -2\boldsymbol{\Omega} \times \mathbf{v} - \frac{1}{\rho} \nabla p - \nabla \Phi + \mathbf{F} \quad (1)$$

The terms on the left-hand side give the accelerations, where  $\mathbf{v}$  is the average velocity (the mode of averaging is discussed below) at a particular location, and  $t$  the time. The first term on the right is the so-called Coriolis force, or deflecting force of the earth's rotation. The vector  $\boldsymbol{\Omega}$  is directed northward, parallel to the axis of rotation of the earth, and has the magnitude  $\omega$ , the angular speed of rotation of the earth. This term arises because the frame of reference is fixed to the earth; it cannot change the speed of an air parcel, but only the direction of its motion relative to the earth. The second term on the right is the pressure-gradient term, where  $\rho$  is the density and

$p$  the pressure. The third term is very nearly the gravitational force, with  $\Phi$  the gravitational potential. (In meteorology, the relatively small centrifugal force due to the earth's rotation is included in this term.) This force has a component in the vertical only, whose magnitude we usually regard as a constant,  $g$ . At the earth's surface, at the poles,

$$g = GM/a^2$$

where  $G$  is the gravitational constant,  $M$  is the mass of the earth, and  $a$  is the earth's polar radius. The value of  $g$  is numerically smaller at the equator than at the poles by about 0.5 percent. The vertical extent of the atmosphere is so small relative to the earth's radius that the vertical variation of  $g$  is generally neglected in meteorology.

The last term on the right side,  $F$ , includes the molecular viscosity and the eddy stresses. These latter are not always clearly defined. They arise because the atmosphere is a turbulent fluid, whose rapidly varying motions we can express only in terms of a time and space average. At any given instant and point in the atmosphere, however,  $\nu$  will ordinarily differ from the average value that is presumed to apply to that given instant and point. The nonlinear terms in the expression  $\nu \cdot \nabla \nu$  then give rise to stresses that depend on the correlations between the velocity components.

A meteorological observation, as usually reported, automatically involves an average that depends on the instrumentation. The scale of the average is typically a few minutes in time and a few hundred meters in space. The stress terms that arise from this scale of averaging are assumed to be negligible for the larger-scale motions and are treated in turbulence theory by a statistical or phenomenological approach.

A second scale of averaging is fixed by the density and frequency of observations. This scale may involve a few hours, or a few hundred kilometers, and the stresses that arise have never been subjected to a consistent study because the relevant observations are not available.

Finally, the analyst may purposely introduce an averaging process on still longer time or distance scales, in which case the consequent stresses must be included in the term  $F$ .

**1.2. Conservation of mass.** Conservation of mass is expressed by the equation of continuity :

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \nu = 0 \quad (1)$$

**1.3. Equation of state.** Air is a mixture of gases, each of which, to a good degree of approximation, obeys the equation of state for an ideal gas.

$$p = \rho \frac{R}{m} T \quad (1)$$

where  $R$  is the universal gas constant,  $m$  the molecular weight of the gas, and  $T$  the absolute temperature. According to Dalton's law, the sum of the partial pressures of gases in a mixture is equal to the total pressure of the mixture. Consequently, the equation of state for air has the same form as for an ideal gas, as long as we define  $m$  in terms of the molecular weights of the individual gases in the air. The appropriate value of  $m$  for air turns out to be 28.97, so that the equation of state is generally used in the form

$$p = \rho R' T \quad (2)$$

where  $R' = R/m = 2.87 \times 10^6 \text{ cm}^2 \text{ sec}^{-2} \text{ deg}^{-1}$

In the strictest sense, this applies to dry air only. Water vapor is always present in air to an extent that varies widely with time and space. To apply the slight correction for the presence of water vapor, replace  $T$  by  $T^*$ , the virtual temperature, defined by

$$T^* = \frac{T}{(1 - 0.379e/p)}$$

where  $e$  is the partial pressure of the water vapor and  $p$  is the total pressure of the dry air and water vapor.

**1.4. First law of thermodynamics.** The first law of thermodynamics for unit mass of an ideal gas is

$$dq = c_p dT - \frac{1}{\rho} dp \quad (1)$$

where  $dq$  is the heat added to or taken from the unit mass, and  $c_p$  is the specific heat of the gas at constant pressure.

## 2. Derived Equations

Section 1 contains a set of four equations, two of hydrodynamic and two of thermodynamic character, which describe the state of the atmosphere. These equations involve five unknowns, namely,  $v$ ,  $p$ ,  $\rho$ ,  $T$ , and  $q$ . In principle, at least, one should be able to specify a fifth equation to define  $q$ , in terms of heat absorbed directly from the sun, heat added to the atmosphere from the earth's surface by conduction or convection, and heat transferred within the atmosphere by phase changes of water. Since we can describe the boundary of the earth's surface and specify the initial state of the atmosphere, the equations are, in theory, soluble. However, in practice, the specification of the heat exchange and the boundary conditions is so extremely complex, and the mathematical difficulties inherent in nonlinear, partial differential

equations are so great, that an exact analytical solution will probably never be possible.

Consequently, meteorological theory tends toward the derivation of other relationships from the four basic equations. One type of derivation has involved the deletion of small terms from the four equations to obtain descriptive formulas. These approximations characteristically ignore terms that, while small in magnitude, are vital for the prediction of changes in the atmosphere. A second type of derived equation transforms the original equations into a form that might be suitable for purposes of prediction or that might lend itself to physical interpretation.

These equations are given here in the coordinate system commonly used in meteorology. This is a Cartesian system, rotating with the earth, with its  $x$ - $y$  plane tangential to the earth at the origin, and the  $z$  axis directed away from the earth. The  $x$  axis is positive toward the east, the  $y$  axis is positive toward the north. To simulate the Coriolis deflection, the  $x$ - $y$  plane is presumed to be rotating around the  $z$  axis with an angular velocity appropriate to the latitude in question. This system achieves some mathematical simplification, but is inappropriate when large areas of the earth's surface are under consideration. In this case, spherical coordinates with their origin at the center of the earth are the natural system to use.

**2.1. Geostrophic wind.** The Coriolis force and the pressure-gradient force are much larger in magnitude than the other terms in the horizontal components of the equation of motion. The eastward speed,  $u$ , and the northward speed,  $v$ , obtained by equating these terms, are

$$\left. \begin{aligned} u &= -\frac{1}{2\rho\omega \sin \varphi} \cdot \frac{\partial p}{\partial y} \\ v &= \frac{1}{2\rho\omega \sin \varphi} \frac{\partial p}{\partial x} \end{aligned} \right\} (1)$$

where  $\varphi$  is the latitude. These so-called "geostrophic" wind components describe the actual wind field in the free atmosphere very accurately. Near the surface, the wind has a sizable component toward low pressure as a result of friction.

**2.2. Hydrostatic equation.** In the vertical component of the equation of motion, the acceleration of gravity is balanced almost entirely by the pressure gradient. Thus

$$\frac{\partial p}{\partial z} = -\rho g$$

With the aid of the equation of state, this gives for the pressure at a distance  $z$  above a reference level with pressure  $p_0$ ,

$$p = p_0 \exp \left( - \int_0^z \frac{g dz}{R'T} \right)$$

This equation gives the vertical distribution of pressure in the atmosphere within the accuracy of observation.

**2.3. Adiabatic lapse rate.** If an air parcel gains or loses no heat, its temperature is related to its pressure by the adiabatic form of the first law of thermodynamics,

$$c_p dT = \frac{1}{\rho} dp \quad (1)$$

In particular, for vertical motion,

$$\frac{\partial T}{\partial z} = \frac{1}{c_p \rho} \cdot \frac{\partial p}{\partial z} = - \frac{g}{c_p} \quad (2)$$

with the help of the hydrostatic equation, and because the density of the parcel is not greatly different from that of its surroundings. This variation of temperature in the vertical is observed in cases where air is heated from below or is thoroughly mixed by turbulence, if the water in the air does not change phase.

In the case where the water does change phase, as in clouds, the latent heat released or used by the water reduces this lapse rate.

**2.4. The circulation theorem.** The circulation  $C$  around a closed curve is defined as the line integral of the velocity component tangential to the curve.

$$C = \oint (u dx + v dy + w dz) \quad (1)$$

With the help of the equation of motion (without the stress terms), this equation reduces to the form common in meteorology, namely,

$$\frac{dC}{dt} = - \oint \frac{dp}{\rho} - 2\omega \frac{dA}{dt} \quad (2)$$

where  $A$  is the projected area of the closed curve on the equatorial plane.

This equation is valuable mainly because of the insight it affords into atmospheric motions. The first term may be interpreted as the increase in circulation caused by the angle between the isosteric (constant specific volume) and isobaric (constant pressure) surfaces. For an autobarotropic atmosphere, i.e., one wherein the spatial distribution of  $\rho$  is always the same function of  $p$  only, this term vanishes. The second term represents the effect of the earth's rotation on the circulation.

**2.5. The vorticity theorem.** As the area of the curve around which the circulation is computed is reduced to zero, the circulation divided by the area approaches the vorticity as a limit. The vorticity is the curl of the velocity.

The "vorticity theorem" as commonly used in meteorology really concerns only the vertical component of the vorticity. This equation is the vertical component of the curl of the equation of motion. For horizontal motion in an auto-barotropic frictionless fluid, the theorem states that

$$\frac{d}{dt}(\zeta + 2\omega \sin \varphi) = -(\zeta + 2\omega \sin \varphi) \left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) \quad (1)$$

where  $\zeta$  is the vertical component of vorticity for the motion of the air parcel relative to the earth. Note that  $2\omega \sin \varphi$  is the vertical component of vorticity resulting from the earth's rotation.

This equation is practically the only one in meteorology that has shown any prognostic value. The past few years have seen numerous attempts to integrate this equation (and variants of it) by numerical methods. These experiments offer significant hope for improvement of weather forecasting.

**2.6. The energy equation.** The scalar product of the equation of motion and the velocity is

$$\frac{d}{dt}(K + W) = -\frac{1}{\rho} \mathbf{v} \cdot \nabla p + \mathbf{v} \cdot \mathbf{F} \quad (1)$$

Here  $K$  is the kinetic energy and  $W$  the potential energy of an air parcel. This combines with the first law of thermodynamics to give the energy equation,

$$\frac{dq}{dt} = \frac{d}{dt}(K + W + I) + \rho \frac{d(1/\rho)}{dt} + \frac{1}{\rho} \mathbf{v} \cdot \nabla p - \mathbf{v} \cdot \mathbf{F} \quad (2)$$

where  $I$  is the internal energy  $c_v T$ .

**2.7. The tendency equation.** To a close approximation, the pressure at a level  $z$  is given by the weight of the overlying air column,

$$p_z = \int_z^\infty g \rho dz \quad (1)$$

Therefore the rate of pressure changes, or pressure "tendency," is

$$\left( \frac{\partial p}{\partial t} \right)_z = - \int_z^\infty g \left( \frac{\partial \rho u}{\partial x} + \frac{\partial \rho v}{\partial y} \right) dz + g(\rho w)_z \quad (2)$$

since  $\rho w$  is assumed to vanish at the upper limit. This is called the tendency equation.

The term under the integral sign, when the indicated differentiation is accomplished, indicates two physical processes that might produce a pressure change. These are advection of air of different density, and velocity divergence. In addition the term outside the integral shows that the pressure at a level may change as a result of a mass transport through the level. These terms are always small in the atmosphere. Note that for horizontal, geostrophic motion, no pressure change would occur. Moreover, the mass divergence in the atmosphere usually changes sign with elevation, so that the net pressure change at the surface represents a slight unbalance among the nearly compensating values of mass divergence at upper levels.

**2.8. Atmospheric turbulence.** Near the surface of the earth, the variation of the wind with elevation depends largely on the term  $\mathbf{F}$  in the equation of motion. If the air flow were laminar,  $\mathbf{F}$  would depend on the molecular viscosity  $\mu$ , and would be given approximately by

$$\mathbf{F} = \frac{1}{\rho} \cdot \frac{\partial}{\partial z} \left( \mu \frac{\partial \mathbf{v}}{\partial z} \right) \quad (1)$$

since the variation of  $\mathbf{v}$  in the horizontal is small.

In the atmosphere, the motion is turbulent and the eddy stresses are far larger than the viscous stresses. These eddy stresses are often represented by a similar formula

$$\mathbf{F} = \frac{1}{\rho} \cdot \frac{\partial}{\partial z} \left( \mu_e \frac{\partial \mathbf{v}}{\partial z} \right) \quad (2)$$

The eddy viscosity,  $\mu_e$ , is a property of the flow and not of the fluid. Its magnitude varies widely, depending principally on distance from the earth's surface, wind speed, and the variation of temperature in the vertical. With a dry adiabatic lapse rate and average wind speed,  $\mu_e$  seems to increase approximately linearly from a value of zero near the ground to a maximum value of about  $10^6$ - $10^7 \mu$  a few hundred meters above the ground. When temperature increases with height and the wind is light,  $\mu_e$  may not exceed  $10^4$ - $10^5 \mu$  at any level.

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\* These books discuss, with varying emphasis, the statics, thermodynamics, kinematics, and dynamics of the atmosphere.

# Chapter 31

## BIOPHYSICS

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### Introduction

Biophysics is the analysis of biological phenomena in physicomathematical terms. It includes all formal theories of the behavior of living organisms and their parts, especially such theories as attempt a reduction of biological to physical (including chemical) concepts. Thus this chapter embraces such topics as enzyme kinetics, a molecular theory of cell forms and cell division, and the mathematical theory of aggregates of cells or of organisms.

### 1. Energy Relations

A living system is a spatially circumscribed phase (or aggregate of such phases) in contact with another phase or set of phases, the environment. It is in constant communication with the environment; both matter and energy pass between the two. Living systems, while they display the characteristics that mark them as living, are never in thermodynamic equilibrium. To describe their energy relations requires a generalization of classical thermodynamics. We divide substances found in living systems into two groups: those that normally do not leave the cell (the "permanent" constituents) and those that circulate between cell and environment. Variables pertaining to the two classes are distinguished by subscripts 1 and 2 respectively.

We define a number of symbols.

$m_a$  = mass density of substance  $a$  in gm cm<sup>-3</sup>

$m$  = total mass density ( $= \sum_a m_a$ )

$V_a$  = velocity of substance  $a$

$C_a$  = concentration of substance  $a$  in moles gm<sup>-1</sup>

$M_a$  = molecular weight of substance  $a$

$R_a$  = chemical reaction rate of substance  $a$  in gm cm<sup>-3</sup> sec<sup>-1</sup>

$\mathcal{P}$  = stress tensor

$F$  = external force

$H$  = total energy per unit volume

$q$  = vector of heat flow

$p$  = hydrostatic pressure

All these quantities except the  $M_a$  are functions of coordinates  $x, y, z$  of points in the cell or its environment relative to any arbitrarily chosen coordinate system, and of the time  $t$ .

We define the mean velocity of the system at a point, relative to the coordinate system, by

$$mV = \sum_a m_a V_a \quad (1)$$

The mean velocity of substances of class 1 is defined by

$$m_1 V_1 = \sum_\alpha m_\alpha V_\alpha, \quad (\alpha \text{ ranges over substances of class 1}) \quad (2)$$

and similarly for  $V_2$ , with  $m_1 = \sum_\alpha m_\alpha$  over class 1, etc.

The diffusion velocity of substance  $a$  is then  $U_a = V_a - V_1$ .

We define

$$R_1 = \sum_\alpha R_\alpha, \quad (\alpha \text{ over class 1})$$

$$R_2 = \sum_i R_i, \quad (i \text{ over class 2})$$

$$J_a = m C_a U_a$$

$$J = mU = \sum_a M_a J_a$$

Here  $M_a$  and  $C_a$  are related by  $m_a = m M_a C_a$ , and  $U = V - V_1$ . The internal energy per gram,  $\epsilon$ , is defined by

$$m\epsilon = H - \frac{1}{2}mV^2 \quad (3)$$

The differential equation corresponding to the first law of thermodynamics is then

$$m \frac{d\epsilon}{dt} = (\mathcal{P} \cdot \nabla) \cdot V - \nabla \cdot q - \sum \nabla \cdot (\mu_a J_a) + \epsilon \nabla \cdot J \quad (4)$$

where  $\mu_a = \partial\epsilon/\partial C_a$  and the operator  $d/dt$  is given by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{V}_1 \cdot \nabla$$

This operator gives the rate of change at a given point in the cell, moving with velocity  $\mathbf{V}_1$ .

Auxiliary equations are the diffusion and continuity equations,

$$\frac{dm}{dt} = -m\nabla \cdot \mathbf{V}_1 - \nabla \cdot \mathbf{J}, \quad m \frac{dC_a}{dt} = \frac{R_a}{M_a} - \nabla \cdot \mathbf{J}_a + C_a \nabla \cdot \mathbf{J} \quad (5)$$

and the hydrodynamic equations

$$m \frac{d\mathbf{V}}{dt} = \nabla \cdot \mathcal{P} + \mathbf{F} - (\mathbf{J} \cdot \nabla) \mathbf{V}, \quad m_1 \frac{d\mathbf{V}_1}{dt} = \nabla \cdot \mathcal{P}_1 + \mathbf{F}_1 - R_1 \mathbf{V}_1 \quad (6)$$

The differential equation corresponding to the second law is

$$m\theta \frac{d\eta}{dt} = (\mathcal{P} \cdot \nabla) \cdot \mathbf{V}_1 + (\mathcal{P} \cdot \nabla) \cdot \mathbf{U} + p\nabla \cdot \mathbf{V}_1 - \sum_a \mu_a \frac{R_a}{M_a} - \nabla \cdot \mathbf{q} \left. \vphantom{\frac{d\eta}{dt}} \right\} (7)$$

$$- \sum_a \mathbf{J}_a \cdot \nabla \mu_a + \left( \epsilon + pv - \sum_a \mu_a C_a \right) \nabla \cdot \mathbf{J}$$

where  $\eta$  is the entropy and  $\theta$  the absolute temperature.

Defining the Gibbs free energy as usual by

$$\psi = \epsilon - \theta\eta$$

we have for this function the equation

$$m \frac{d(\psi/\theta)}{dt} = -\frac{m\epsilon}{\theta^2} \cdot \frac{d\theta}{dt} + \frac{1}{\theta} \left[ -p\nabla \cdot \mathbf{V}_1 + \sum_a \mu_a \frac{R_a}{M_a} - \sum_a \mu_a \nabla \cdot \mathbf{J}_a \right. \left. + \left( \sum_a \mu_a C_a - pv \right) \nabla \cdot \mathbf{J} \right] \left. \vphantom{\frac{d(\psi/\theta)}{dt}} \right\} (8)$$

Equations of the same form as the above hold for the environment (in fact, one set holds for each phase if there are more than two phases). At interfaces, we have boundary conditions of two sorts: those prescribing the stress  $\mathcal{P}$  at the boundary, and those prescribing the diffusion flux. The latter are of the form

$$\mathbf{J}_i = \mathbf{J}_{iS}, \quad (i \text{ over class } 2)$$

$$\mathbf{J}_\alpha = 0 \quad (\alpha \text{ over class } 1)$$

The quantity  $J_{iS}$  is generally given by

$$\widehat{J}_{iS} = n(a_i C_{iS} - a'_i C'_{iS})$$

the subscript  $S$  denoting surface values, the primes denoting the "external" or adjoining phase, and  $n$  being the unit external normal to the surface of the phase.

The cell shape is related to the system as follows: if the equation of the cell surface is  $S(x, y, z, t) = 0$ , then

$$\frac{dS}{dt} = \frac{\partial S}{\partial t} + \mathbf{V}_1 \cdot \nabla S = 0 \quad (9)$$

This equation can be solved if  $\mathbf{V}_1$ , the solution of the second hydrodynamical equation, is obtained. Since  $\mathbf{V}_1$  depends on  $R_1$ , the cell shape is thus related to its metabolism.

Of interest in connection with the problem of growth are the equations for the total mass  $M$  and total volume  $V_0$  of any region ( $d\tau =$  element of volume).

$$\left. \begin{aligned} \frac{dM}{dt} &= \frac{d}{dt} \int m d\tau = - \int \nabla \cdot \mathbf{J} d\tau \\ \frac{dV_0}{dt} &= \frac{d}{dt} \int d\tau = \int \nabla \cdot \mathbf{V}_1 d\tau \end{aligned} \right\} (10)$$

For a region sufficiently small to be approximately homogeneous, those take the simpler form

$$\left. \begin{aligned} \frac{dM}{dt} &= - V_0 \nabla \cdot \mathbf{J} \\ \frac{dV_0}{dt} &= V_0 \nabla \cdot \mathbf{V}_1 \end{aligned} \right\} (11)$$

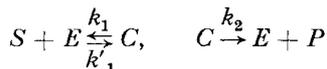
See Refs. 3, 11, and 12.

## 2. Kinetics of Enzyme Catalyzed Reactions

**2.1. Simple reactions** (Refs. 4 and 5). The basic assumption of the theory is that enzyme and substrate form a complex, which then reacts to yield the product or products together with the free enzyme, which can now enter another cycle. The simplest possible case has been described in equations first derived by Victor Henri (frequently incorrectly attributed to Michaelis and Menten).

Denote the substrate by  $S$ , product by  $P$ , free enzyme by  $E$ , enzyme-

substrate complex by  $C$ , total enzyme by  $E_0$  (all expressed as concentrations, e.g., in moles  $\text{cm}^{-3}$ ). The stoichiometric relations are



We have, moreover,

$$E_0 = E + C$$

The further assumptions that the first reaction is in equilibrium and that the overall reaction rate is determined by the transformation of  $C$  to  $E$  and  $P$  give

$$V = k_2 C = k_2 \frac{S}{K + S} E_0 \quad (1)$$

where  $K = k'_1/k_1$ .

Haldane's modification of the theory assumes (instead of equilibrium of the complex-forming reaction) a steady state for the complex. That is,

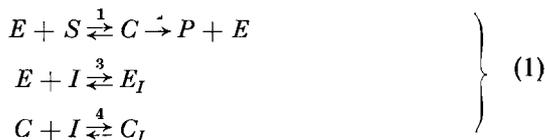
$$dC/dt = 0$$

This yields for the reaction rate

$$V = k_2 \frac{S}{K' + S} E_0 \quad (2)$$

where  $K' = K + k_2/k_1$ . The functional form is the same, but  $K'$  no longer has the significance of the dissociation constant of the complex, so that  $1/K'$  does not measure exclusively the affinity of enzyme for substrate.

**2.2. Inhibitors** (Refs. 1, 2, 7, 13). The effect of substances that inhibit enzymatic reactions is due to their action on the free enzyme molecules, on enzyme-substrate complex, or on both. Such reactions can be treated if stoichiometric combination or its formal equivalent is assumed. The equations are



where  $I$  is the free inhibitor,  $E_I$  is the enzyme-inhibitor complex,  $C_I$  is the enzyme-substrate-inhibitor complex, and the other symbols are as before.

We have the conservation equations

$$\left. \begin{aligned} E_0 &= E + C + E_I + C_I \\ I_0 &= I + E_I + C_I \end{aligned} \right\} \quad (2)$$

(assuming combination in 1 : 1 proportions as above and representing total inhibitor by  $I_0$ ).

We take  $C$  in the steady state as before, and assume that reactions involving inhibitor are in equilibrium (which is true for many but not necessarily for all inhibitions). Thus we have

$$ES = K_1C, \quad EI = K_3E_I, \quad CI = K_4C_I \quad (3)$$

where  $K_1 = k'_1/k_1 + k_2/k_1$ ,  $K_3 = k'_3/k_3$ ,  $K_4 = k'_4/k_4$ .

This solution of this system gives for the inhibited reaction rate,

$$V_i = k_2C = \frac{1}{2} \cdot \frac{k_2}{k} \left[ - \left( \frac{k}{m} - \Delta \right) + \sqrt{\left( \frac{k}{m} - \Delta \right)^2 + 4 \frac{k}{m} E_0} \right] \quad (4)$$

where  $k = K_1/S + 1$ ,  $m = K_1/SK_3 + 1/K_4$ ,  $\Delta = E_0 - I_0$ .

It is also convenient to plot results of inhibition experiments in terms of the fractional inhibition  $i$  or the fractional residual activity  $\rho$ , defined by

$$i = \frac{E_I + C_I}{E_0}$$

$$\rho = V_i/V$$

where  $V$  is the uninhibited rate as determined in the preceding section. These quantities are related by  $i + \rho = 1$ . The theoretical equations are

$$I_0 = iE_0 + \frac{k}{m} \cdot \frac{i}{1-i} \quad (5)$$

for the plot of  $I_0$  against  $i$ , and

$$E_0 = \frac{I_0}{1-\rho} - \frac{k}{m} \cdot \frac{1}{\rho} \quad (6)$$

for the plot of  $E_0$  against  $\rho$ , or

$$I_0 = (1-\rho)E_0 + \frac{k}{m} \frac{1-\rho}{\rho} \quad (7)$$

for  $I_0$  against  $\rho$ .

The theory demands in general an infinite value of  $I_0$  for complete inhibition, and an infinite value of  $E_0$  for the complete absence of inhibition.

Some special cases of interest have been worked out in the past, and are readily obtained from the above results. If the inhibitor reacts only with free enzyme, we have what is usually called competitive inhibition, since it is believed that substrate and inhibitor compete for the same grouping on the enzyme. In this case  $1/K_4 = 0$ ,  $k/m = K_3(1 + S/K_1)$ . If this is substituted in the  $i, I_0$  relation,

$$I_0 = iE_0 + K_3 \left( 1 + \frac{S}{K_1} \right) \frac{i}{1-i} \quad (8)$$

and the amount of inhibitor required to produce a given fractional inhibition increases with the concentration of substrate.

If inhibitor combines impartially with  $E$  and  $C$  and has the same affinity for both,  $K_3 = K_4$ . In this case,  $k/m = K_3$ , and the relation of  $I_0$  to  $i$  is independent of  $S$ . This sort of inhibition has been termed noncompetitive.

So-called "uncompetitive" inhibition results if inhibitor combines only with  $C$ . Then

$$1/K_3 = 0 \quad (9)$$

and

$$\frac{k}{m} = K_4 \left( \frac{K_1}{S} + 1 \right) \quad (10)$$

The  $i, I_0$  equation now reads

$$I_0 = iE_0 + K_4 \left( \frac{K_1}{S} + 1 \right) \frac{i}{1-i} \quad (11)$$

Increasing the substrate concentration now decreases the amount of inhibitor required to produce a given degree of inhibition, as should be expected.

If the combination of inhibitor with  $E$  and  $C$  is irreversible, we have  $K_3 = K_4 = 0$ , and therefore  $k/m = 0$ . In this case, substitution in the  $i, I_0$  equation gives  $i = I_0/E_0$ .

Moreover, the relation of reaction rate to  $E_0$  takes the special form of a broken line. For  $0 \leq E_0 \leq I_0$ ,  $V_i = 0$ , while for  $E_0 > I_0$ ,

$$V_i = \frac{k_2}{k} (E_0 - I_0) \quad (12)$$

This form of inhibition has been referred to as "titration" of the enzyme by the inhibitor. The same result is obtained with competitive and non-competitive inhibition if  $K_3 = 0$ , and for uncompetitive inhibition if  $K_4 = 0$ .

### 3. The Cell

**3.1. Metabolism and concentration distributions.** The simplest theoretical model of a living cell is based on the minimal set of characteristics which all such cells have in common. Nutrient metabolites diffuse into the cell from the environment, the chemical reactions that constitute metabolism go on inside the cell, and products of metabolism diffuse out of the cell into the environment.

The occurrence of these characteristics can be expressed by a modified form of the classical partial differential equation of diffusion. For a substance undergoing no chemical reactions, this equation has the form

$$\frac{\partial C}{\partial t} = -\nabla \cdot \mathbf{J} \quad (1)$$

where  $C [= C(x, y, z, t)]$  is the concentration of the substance in gm cm<sup>-3</sup> (or

moles  $\text{cm}^{-3}$ ) and  $\mathbf{J}$  is the vector of diffusion flux in  $\text{gm cm}^{-2} \text{sec}^{-1}$  (or moles  $\text{cm}^{-2} \text{sec}^{-1}$ ). When chemical reactions also occur, they are embodied in a term for "sources" and "sinks," and the equation is

$$\frac{\partial C}{\partial t} = -\nabla \cdot \mathbf{J} + Q \quad (2)$$

where  $Q$  is the net rate of reaction producing the substance in  $\text{gm cm}^{-3} \text{sec}^{-1}$  (or moles  $\text{cm}^{-3} \text{sec}^{-1}$ ). If the substance in the aggregate is removed by reaction rather than supplied,  $Q < 0$ . In general, one must consider groups of substances which are related to one another by chemical transformations. Thus, one would have simultaneous systems of equations like the foregoing for a set of concentrations  $C_1, C_2, \dots, C_n$ . Moreover,  $Q$  will in this general case be different in each equation, and each  $Q_i$  will be a function  $Q_i(C_1, C_2, \dots, C_n)$  of several or all of the functions  $C_j$ . However, much information may be obtained even from the oversimplified case in which each substance is treated independently, i.e., in which  $Q_i = Q_i(C_i)$  or  $Q_i = \text{constant} = q_i$ . (Such a situation may hold approximately for at least one of a group of related substances if all the others are present in sufficient excess.)

To solve the diffusion equation, it is necessary to find an expression for the flux vector  $\mathbf{J}$ . In many cases a satisfactory form is given by Fick's law,

$$\mathbf{J} = -D\nabla C$$

where  $D$  is a constant known as the diffusion coefficient, and is in general different for each substance (and for each kind of cell or tissue). With this relation, the diffusion equation becomes

$$\frac{\partial c}{\partial t} = D\nabla^2 C + Q \quad (3)$$

As was indicated in Section 1, a separate equation holds for each distinct phase (e.g., for the cell and for its environment). At the surface separating the phases, boundary conditions hold. For the diffusion problem, these express the condition that the flux into the surface from one side equals the flux across the surface equals the flux away from the surface on the other side. Thus for two phases, the interior of a cell and its environment, denoting the corresponding  $C$  functions by  $C_i$  and  $C_e$ , and by  $\partial/\partial\nu$  the normal derivative (with respect to the external normal to the surface), we have

$$-D_i \frac{\partial C_i}{\partial \nu} = -D_e \frac{\partial C_e}{\partial \nu} = J_S \quad (\text{at the surface}) \quad (4)$$

The surface flux is generally of the form

$$J_S = h_i C_i - h_e C_e$$

where  $h_i$  and  $h_e$  are constants (for each substance and each cell). A simple approximation to this, which is frequently used, occurs if  $h_i \cong h_e$ , so that

$$J_s = h(C_i - C_e)$$

and  $h$  is termed the permeability coefficient. In many cases, the solution of the diffusion equation,  $C(x, y, z, t)$ , with increasing time approaches a stationary value  $C(x, y, z)$  which represents a solution of the equation

$$D\nabla^2 C + Q = 0$$

obtained from the more general equation by setting  $\partial C/\partial t$  equal to zero. To estimate the time required to reach practically this stationary state, one can perform an approximate calculation which shows that the time-dependent transient term of  $C(x, y, z, t)$  is proportional to  $e^{-Dt/a^2}$ , where  $a$  is a measure of the linear dimensions of the cell. Since  $D$  for a number of important metabolites is known to be  $\sim 10^{-7}$  cm<sup>2</sup> sec<sup>-1</sup>, for a cell of linear dimensions  $\sim 10^{-3}$  cm, we have  $D/a^2 \sim 10^{-1}$  sec<sup>-1</sup>. In this case the transient term will drop to  $1/e$  of its initial value in 10 seconds, and become virtually negligible after 1 minute. Thus many problems may be treated satisfactorily in terms of the stationary diffusion equation.

A solution satisfying the boundary conditions is readily found if the cell has a spherical shape. For the case where  $Q$  is a constant  $q$ , the solution is given by

$$\left. \begin{aligned} C_e &= C_0 + \frac{qr_0^3}{3D_e} \cdot \frac{1}{r} \\ C_i &= C_0 + \frac{qr_0}{3h} + \frac{q}{6D_i} (r_0^2 - r^2) + \frac{qr_0^2}{3D_e} \end{aligned} \right\} \quad (5)$$

where the coordinate  $r$  is the radial distance from the center of the cell,  $r_0$  is the radius of the cell, and  $C_0$  is the limiting concentration of the substance at a great (strictly speaking, infinite) distance from the cell. For  $q > 0$ , the concentration distribution has a maximum at the center of the cell, and decreases as one moves outward, with a discontinuity of  $qr_0/3h$  at the surface. For  $q < 0$ , there is a minimum at the center of the cell and an increase as one moves outward.

For nonspherical cells, the solution of the boundary value problem rapidly becomes unmanageable, or at best so cumbersome as not to justify the effort expended. Rashevsky introduced a method of approximation that permits most problems to be handled with relative ease (Ref. 10). Consider a cell of roughly oblong shape, with "half-width"  $r_2$  and "half-length"  $r_1$ . Let the mean concentration of metabolite, halfway between periphery and center,

be  $\bar{c}$ . Let the average peripheral concentration inside the cell at the ends be  $c_1$ , at the "sides" be  $c_2$ , when the corresponding values just outside the cell are  $c'_1$  and  $c'_2$ . Finally let  $\delta$  be a length, of the order of magnitude of the cell dimensions, that distance from the cell in which the concentration changes from  $c'_1$  and  $c'_2$  to the limiting value  $c_0$ . The boundary conditions (two sets, one for the ends and one for the sides) take the form

$$\left. \begin{aligned} 2D_i(\bar{c} - c_1) &= r_1 h(c_1 - c'_1) \\ 2D_i(\bar{c} - c_2) &= r_2 h(c_2 - c'_2) \\ \frac{2D_i}{r_1}(\bar{c} - c_1) &= \frac{D_e}{\delta}(c'_1 - c_0) \\ \frac{2D_i}{r_2}(\bar{c} - c_2) &= \frac{D_e}{\delta}(c'_2 - c_0) \end{aligned} \right\} \quad (6)$$

The (nonstationary) diffusion equation becomes the equation of continuity.

$$\frac{d\bar{c}}{dt} = q - 3D_i \left( \frac{\bar{c} - c_1}{r_1^2} + 2 \frac{\bar{c} - c_2}{r_2^2} \right) \quad (7)$$

With the help of the boundary conditions this takes the form

$$\frac{d\bar{c}}{dt} = q - \frac{\bar{c} - c_0}{\Lambda} \quad (8)$$

where

$$\Lambda = \frac{r_1 r_2}{3hD_i D_e} \times \frac{(2D_i D_e + 2\delta D_i h + r_1 h D_e)(2D_i D_e + 2\delta D_i h + r_2 h D_e)}{2(2D_i D_e + 2\delta D_i h + r_1 h D_e)r_1 + (2D_i D_e + 2\delta D_i h + r_2 h D_e)r_2}$$

is termed the total diffusion resistance of the cell.

The solution of the continuity equation is

$$\bar{c} = c_0 + \Lambda q - C\Lambda e^{-t/\Lambda} \quad (9)$$

where  $C$  is a constant of integration. In the stationary state,

$$\bar{c} = c_0 + \Lambda q$$

**3.2. Diffusion forces and cell division** (Refs. 10 and 15). The relation of cell movements and cell division to metabolic activity is based on the production of concentration gradients and differences by metabolism. All concentrations become equal to  $c_0$  if  $q = 0$ , and the discontinuity  $c_i - c_e$  at  $r = r_0$  likewise vanishes with  $q$ . The presence of gradients and surface discontinuities for nonvanishing  $q$  leads to volume forces and surface pressures of "osmotic" character. The surface pressure is given by

$$p_0 = \frac{RT}{M}(c_i - c_e) \quad (1)$$

where  $c_i$  and  $c_e$  are evaluated at the cell surface;  $R$  is the gas constant,  $T$  the absolute temperature, and  $M$  the molecular weight of the solute. The volume force is derivable from a pressure which in the first instance is given by

$$p = \frac{RT}{M} c, \quad F_V = -\frac{RT}{M} \nabla c \quad (2)$$

A more refined calculation takes into account the modification of the distribution  $c$  by the molecule or particle subjected to this thermal bombardment (e.g., an enzyme or protein molecule). Thus the next approximation gives

$$F_V = -\frac{3}{2} \cdot \frac{RT}{M} \alpha V \nabla c \quad (3)$$

for the force on a particle of volume  $V$ , where  $\alpha$  is a constant  $\sim 1$ . The dependence of  $c$  on  $q$  then leads to the general result that the volume and surface forces are directed outward for  $q > 0$  and inward for  $q < 0$ .

The possibility that these forces will cause division of the cell can be analyzed by calculating the energy change  $\Delta E$  which results when a spherical cell of radius  $r_0$  divides into two equal spherical cells of radius  $r_1 = 0.8r_0$ . The calculation makes use of the well-known device of an imaginary expansion of the cell to infinity followed by condensation to two half-cells. The first component of the energy change is due to the surface tension, the second to the surface pressure, and the third to the volume force on the enzyme molecules, giving

$$\Delta E = \Delta E_S + \Delta E_m + \Delta E_V = 1.12\pi\gamma r_0^2 - \frac{\pi RT q r_0^4}{2Mh} - \frac{3}{20} \cdot \frac{\pi RT \alpha \mu q r_0^5}{DM} \quad (4)$$

where  $\gamma$  is the surface tension in ergs  $\text{cm}^{-2}$ ,  $D$  is an average of  $D_i$  and  $D_e$ , and  $\mu$  is the relative volume occupied by the enzyme particles. For small  $r_0$ ,  $\Delta E > 0$ ; for larger values  $\Delta E < 0$ . There is thus a critical value  $r_0^*$  of  $r_0$  for which  $\Delta E = 0$ , where the cell becomes unstable (if  $q > 0$ ). Then  $r_0^*$  is the solution of the cubic equation

$$1.12\gamma - \frac{RT q r_0^{*2}}{2Mh} - \frac{3}{20} \cdot \frac{RT \alpha \mu q r_0^{*3}}{DM} = 0 \quad (5)$$

The exact solution is cumbersome, but two simple limiting cases are easily studied. If  $h$  is very large,

$$r_0^* = \sqrt[3]{\frac{7.5\gamma DM}{RT \alpha \mu q}} \quad (6)$$

If  $D$  is very large,

$$r_0^* = \sqrt{\frac{2.24\gamma Mh}{RTq}} \quad (7)$$

With plausible values of the constants ( $\gamma \sim 1$ ;  $\alpha\mu = 1$ ;  $q = 10^{-6}$  gm cm $^{-3}$  sec $^{-1}$ ;  $M = 100$ ; and  $D = 10^{-7}$  cm $^2$  sec $^{-1}$ ,  $h = \infty$ , or  $h = 10^{-4}$  cm sec $^{-1}$ ,  $D = \infty$ ), we get  $r_0^* \sim 10^{-3}$  cm, which corresponds well to average cell sizes. Relatively large variations in the constants, however, result in relatively much smaller changes in  $r_0^*$ .

A more precise analysis of the stability of the cell uses as a criterion the virtual work of small arbitrary deformations of the cell, taking into account the redistribution of concentrations due to the deformation. The condition of instability leads to more complex expressions for  $r_0^*$ , but gives essentially the same numerical values. The condition is ( $n$  an integer)

$$\frac{RT}{M} \alpha\mu \frac{2hqr_0^2 + D_e(n+1)qr_0}{D_i D_e n(n+1) + h[D_e(n+1) + D_i n]r_0} (n-1) + \frac{2}{3} \times \frac{RT}{M} \times \frac{[D_i n(n-1) - D_e(n^2-1)]qr_0}{D_i D_e n(n+1) + h[D_e(n+1) + D_i n]r_0} > \frac{2(n-1)(n+2)}{r_0^2} \gamma$$

A novel result arises if  $q < 0$ , for now, if certain relations among the constants hold, the condition of instability may be satisfied in a region between the lower and the higher values of  $r_0$ . Within this range an infinitesimal elongation of the cell results in a decrease of energy. But we have seen that for  $q < 0$  the division of the cell gives an increase of energy. Thus the energy cannot continue to decrease as the deformation goes on, and an intermediate, nonspherical equilibrium shape must result. Neither of these calculations is adequate to predict the entire course of deformation of a cell and its eventual division or stabilization in a nonspherical shape. This can be done by applying the laws of plastic flow, in combination with the approximation method for diffusion in nonspherical cells. A theorem of Betti, first applied to the problem by G. Young (Ref. 15), gives for the average relative rate of change of any dimension of a body of any shape the following sort of expression.

$$\left. \begin{aligned} \frac{1}{l_z} \cdot \frac{dl_z}{dt} = \frac{1}{3\eta V} \left\{ \iiint_V [zZ - \frac{1}{2}(yY + xX)] dV + \right. \\ \left. \iint_S [zZ_v - \frac{1}{2}(yY_v + xX_v)] dS \right\} \quad (8) \end{aligned} \right\}$$

where  $l_z$  is the length of the body at time  $t$  in the direction of the  $z$  axis,  $X$ ,  $Y$ , and  $Z$  are the components of the volume force in the  $x$ ,  $y$ , and  $z$  directions, and  $X_v$ ,  $Y_v$ , and  $Z_v$  are the components of the surface pressure, and the integrals are extended over the volume  $V$  and surface  $S$ , respectively, of the body, whose viscosity is  $\eta$ .

For the volume force we use the previously cited expression,

$$\mathbf{F} = -\frac{3}{2} \cdot \frac{RT\alpha\mu}{M} \nabla c$$

while the surface pressures on the ends and sides of the cell respectively are

$$\left. \begin{aligned} p_1 &= \frac{RT}{M} (c_1 - c'_1) \\ p_2 &= \frac{RT}{M} (c_2 - c'_2) \end{aligned} \right\} \quad (9)$$

We put the  $z$  axis along the largest dimension of the cell, so that  $l_z = r_1$ . Solving for the concentrations by means of the approximate method as before, we obtain

$$\frac{1}{r_1} \cdot \frac{dr_1}{dt} = \frac{RT}{2M\eta} \cdot \frac{[3\alpha\mu\delta h + (3\alpha\mu - 2)D_e]hD_iD_e(r_1 - r_2)(\bar{c} - C_0)}{(2D_iD_e + 2\delta D_i h + r_1 h D_e)(2D_iD_e + 2\delta D_i h + r_2 h D_e)} \quad (10)$$

A more general relation is obtained if we take into account the effect of surface tension, which produces at the "ends" of the cell a surface force  $-2\gamma/r_2$  and along the "sides" a force  $-\gamma(1/r_1 + 1/r_2)$ , which results in a contribution to the relative rate of elongation of  $-(\gamma/2\eta)(r_1 - r_2)/r_1 r_2$ . Introducing the approximate stationary value  $\Lambda q$  for  $\bar{c} - c_0$ , we get, finally,

$$\begin{aligned} \frac{1}{r_1} \cdot \frac{dr_1}{dt} &= \frac{RT}{6M\eta} \cdot \frac{[3\alpha\mu\delta h + (3\alpha\mu - 2)D_e]r_1 r_2 (r_1 - r_2)q}{2(2D_iD_e + 2\delta D_i h + r_1 h D_e)r_1 + (2D_iD_e + 2\delta D_i h + r_2 h D_e)r_2} \\ &\quad - \frac{\gamma}{2\eta} \cdot \frac{r_1 - r_2}{r_1 r_2} \end{aligned} \quad (11)$$

Since  $r_1 - r_2 > 0$ , then for  $q > 0$  one necessary condition for elongation to occur (since usually  $3\alpha\mu - 2 < 0$ ) is

$$\delta > \frac{2 - 3\alpha\mu}{3\alpha\mu} \cdot \frac{D_e}{h}$$

Since  $\delta$  is of the order of the cell size (e.g.,  $\delta \cong r_2$ ), this means that elongation will occur for sufficiently large cell sizes. As  $r_1$  increases,  $r_2$  decreases. In fact, if the cell volume remains approximately constant during the elongation,  $r_2$  can be expressed in terms of  $r_1$  ( $r_2 \sim 1/\sqrt{r_1}$ ) by virtue of the approximate expression for the cell volume.

$$V = \frac{4\pi}{3} r_1 r_2^2 \quad (12)$$

Thus for very large values of  $r_1$  (where  $\delta \sim r_2$ ),  $dr_1/dt$  varies as  $A r_1^{1/2} - B r_1^{3/2}$  where  $A$  and  $B$  are constants. This expression will vanish for some suf-

ficiently large value of  $r_1$ , so that the elongation will proceed only to a finite extent. However, Betti's formula gives only the average rate of elongation. In point of fact, the middle of the cell, which is subject to the maximum force, will elongate and constrict more rapidly than the ends, and the process may continue at the middle even when the average elongation has reached its limit. The final stages of cell division may then be treated approximately in terms of a dumbbell-shaped figure, essentially two spheres of radius  $r_2''$ , whose centers are separated by a distance  $r_1''$  and connected by a cylindrical "neck" of radius  $r$ . The spheres are pulled apart by diffusion forces, due to metabolites produced in each sphere and acting on the other sphere, giving the effect of a repulsion between the spheres. An approximate expression for the total force is

$$F = \frac{RT\alpha\mu q(r_2'')^6}{6MD_e(h_1'')^2} \quad (13)$$

This force is applied to the total surface of the end of the neck,  $\pi r^2$ , giving a surface pressure  $F/\pi r^2$ . The surface forces due to surface tension in the neck are  $-2\gamma/r$  dynes  $\text{cm}^{-2}$  at the ends, and  $-\gamma/r$  on the lateral surface. Thus Betti's theorem gives

$$\frac{1}{l} \cdot \frac{dl}{dt} = \frac{1}{3\pi\eta} \frac{F - \pi r\gamma}{r^2} \quad (14)$$

Since for a viscous incompressible body the relative lateral constriction is half the relative elongation,

$$\frac{1}{r} \cdot \frac{dr}{dt} = -\frac{1}{2l} \cdot \frac{dl}{dt} \quad (15)$$

Thus we have

$$\frac{dr}{dt} = P - \frac{Q}{r}$$

where  $P = \frac{\gamma}{6\eta}$ ,  $Q = \frac{RT\alpha\mu q r_2''^6}{36\eta D_e M r_1''^2}$

For constriction to occur, we must have always

$$Q/r > P$$

The differential equation has the solution

$$P(r - r') + Q \ln \frac{Q - Pr}{Q - Pr'} = P^2 t \quad (16)$$

where  $r'$  is the initial value of  $r$ . From this it can be seen that  $r$  vanishes and division is complete at a time  $\tau$  given by

$$P^2 \tau = Q \ln \frac{Q}{Q - Pr'} - Pr' \quad (17)$$

It is easy to see that  $\tau$  is real and positive if  $Q - Pr' > 0$  and that  $\tau$  decreases as  $Q - Pr'$  increases. Thus the time required to complete division is smaller, among other things, as the metabolic rate  $q$  increases. It is also obvious that division will never occur if  $q < 0$ , for in this case  $dr/dt > 0$  always.

**3.3. Cell polarity and its maintenance** (Ref. 10). A model for the self-regulation of cell polarity depends on the effect of diffusion forces on a negative catalyst. Consider a spherical cell whose hemispheres have mean concentration  $\bar{c}_1$ , and  $\bar{c}_2$  of some metabolite. The reaction rate is  $q$ . The treatment of the problem is as usual, except that the internal flux  $\pi r_0 D(\bar{c}_1 - \bar{c}_2)$  must be taken into account. We get finally

$$\bar{c}_1 - \bar{c}_2 = \frac{r_0^2(2D + r_0 h)(q_1 - q_2)}{3D(2D + 3r_0 h)} \tag{1}$$

which vanishes if  $q_1 = q_2$ . The diffusion forces will act on colloidal particles of mean concentration  $n$ , volume  $V$ , and molecular weight  $M$ , to produce a concentration ratio in the two hemispheres

$$\frac{n_1}{n_2} = e^{-\bar{\alpha}(\bar{c}_1 - \bar{c}_2)} \tag{2}$$

where

$$\bar{\alpha} = \frac{3}{2} \cdot \frac{NV\alpha}{M}$$

Putting  $x = \bar{c}_1 - \bar{c}_2$ , and noting that  $n = (n_1 + n_2)/2$ , we have

$$n_2 - n_1 = 2n \tanh\left(\frac{1}{2}\bar{\alpha}x\right) \tag{3}$$

Suppose the particles act as negative catalysts on the reaction rate, so that for example,

$$q = q_0 - an$$

Then

$$q_1 - q_2 = a(n_2 - n_1) \tag{4}$$

A representation of an asymmetric distribution of the particles follows from the elimination of the  $q$ 's and  $n$ 's from the above relations.

$$x = 2Aan \tanh\left(\frac{1}{2}\bar{\alpha}x\right)$$

where

$$A = \frac{r_0^2(2D + r_0 h)}{3D(2D + 3r_0 h)}$$

Approximately, for small  $\bar{\alpha}x$ , this is

$$x = Aan\bar{\alpha}x\left(1 - \frac{1}{12}\bar{\alpha}^2x^2\right)$$

This has a root (besides  $x = 0$ ),

$$x^* = \frac{2}{\bar{\alpha}} \sqrt{\frac{3(Aan\bar{\alpha} - 1)}{Aan\bar{\alpha}}}$$

which is real and positive if  $Aan\bar{\alpha} > 1$ .

This root corresponds to a stable configuration, so that the asymmetry will be maintained against disturbances such as division of the cell. A similar result holds for a cell with impermeable membrane, in which the metabolite is produced at rate  $q$  and consumed at rate  $bc$ , except that the constant  $A$  is now given by

$$A = \frac{r_0^2}{r_0^2 b + 3D}$$

**3.4. Cell permeability** (Ref. 12). An analysis of interface and membrane permeability in terms of kinetic theory requires a calculation of the velocity distribution in the presence of a concentration gradient. An adaptation of a procedure used by Lorentz in the theory of conductivity was used. If the Maxwell distribution of velocities  $c$  is  $f_0(c)$ , the perturbed distribution is approximated by

$$f = f_0 + uF(c) \quad (1)$$

where  $u$  is the component of  $c$  in the direction of the gradient. The equation of Boltzmann is used to evaluate the correction term, giving

$$F(c) = - \left( \frac{L}{c} \right) \partial f_0 / \partial x \quad (2)$$

where  $L$  is the mean free path, and the  $x$  axis of a rectangular coordinate system has been placed in the direction of the gradient. We can now evaluate the diffusion current  $J$ .

$$J = \iiint_{-\infty}^{+\infty} u f d u d v d w = - \frac{L}{3} \left( \frac{8kT}{\pi m} \right)^{1/2} \partial n / \partial x \quad (3)$$

where  $m$  is molecular mass,  $T$  absolute temperature,  $n$  is concentration at  $x$ , and  $k$  is Boltzmann's constant. This is identical with Fick's law if the diffusion coefficient  $D$  is

$$D = \frac{L}{3} \left( \frac{8kT}{\pi m} \right)^{1/2}$$

At a phase boundary, the integral splits into two parts, since the parameters of the distribution for molecules approaching from one phase are in general different from those for molecules approaching from the other side. We

denote values at the boundary in the "left" and "right" phases by subscripts 1 and 2 respectively.

If a field with potential  $V(x)$  acts inside a phase, it adds  $-Mn\partial V/\partial x$  to the expression for  $J$ , where the mobility  $M = D/kT$ . At the boundary,  $V$  may undergo a finite change, and a potential barrier may also occur. Let the potential in phase 1 at the boundary be  $V_1$ , in phase 2  $V_2$ , and the barrier  $V$ . Then the potential jump going from 1 to 2 is  $U_1 = V - V_1$ , and from 2 to 1 is  $U_2 = V - V_2$ . The lower limits of the velocity integrals for  $J$  all given now by  $\frac{1}{2}mc^2 = U_1$  and  $\frac{1}{2}mc^2 = U_2$ . The diffusion current at the boundary is therefore

$$J_S = a_1 n_1 - a_2 n_2 \quad (4)$$

with

$$a_1 = a\phi_1/[1 - \frac{1}{2}(\phi_1 + \phi_2)]$$

$$a_2 = a\phi_2/[1 - \frac{1}{2}(\phi_1 + \phi_2)]$$

$$a = \frac{1}{2}(2\pi kT/m)^{1/2}$$

$$\phi_1 = e^{-U_1/kT}(1 + U_1/kT)$$

$$\phi_2 = e^{-U_2/kT}(1 + U_2/kT)$$

The constants  $a_1$  and  $a_2$  are called the coefficients of permeability. It is readily shown that values of the potentials can be chosen such that the flow will have a sign opposite to that of  $n_1 - n_2$  ("anomalous" diffusion, diffusion against a gradient).

In the case of a membrane of finite but small thickness  $d$ , we can apply the foregoing results. The potential barriers at the two boundaries are  $V$  and  $W$ , and the boundary potentials in the membrane are  $V_{m_1}$  and  $V_{m_2}$ . We write  $U_1 = V - V_1$ ,  $U_2 = W - V_2$ ,  $U_{m_1} = V - V_{m_1}$ ,  $U_{m_2} = W - V_{m_2}$ . The diffusion current in the membrane is, to a good approximation,

$$J_m = \frac{D_m(n_{m_1} - n_{m_2})}{d} \quad (5)$$

where  $D_m$  is the diffusion coefficient in the membrane. Noting that the left and right boundary fluxes are equal to each other, to  $J_m$ , and to  $J_S$  (continuity of flux across the membrane),

$$J_{S_1} = J_{S_2} = J_m = J_S$$

we get, finally,

$$J_S = \frac{(a_1/a_{m_1})n_1 - (a_2/a_{m_2})n_2}{1/a_{m_1} + 1/a_{m_2} + d/D_m}$$

$$\text{with } \left. \begin{aligned}
 a_1 &= \frac{a\phi_1}{1 - \frac{1}{2}(\phi_1 + \phi_{m_1})}, & a_2 &= \frac{a\phi_2}{1 - \frac{1}{2}(\phi_2 + \phi_{m_2})} \\
 a_{m_1} &= \frac{a\phi_{m_1}}{1 - \frac{1}{2}(\phi_1 + \phi_{m_1})}, & a_{m_2} &= \frac{a\phi_{m_2}}{1 - \frac{1}{2}(\phi_2 + \phi_{m_2})} \\
 \phi_1 &= e^{-U_1/kT}(1 + U_1/kT), & \phi_2 &= e^{-U_2/kT}(1 + U_2/kT) \\
 \phi_{m_1} &= e^{-U_{m_1}/kT}(1 + U_{m_1}/kT), & \phi_{m_2} &= e^{-U_{m_2}/kT}(1 + U_{m_2}/kT)
 \end{aligned} \right\} (6)$$

#### 4. The Neurone and Behavior

**4.1. Excitation and conduction in the neurone** (Ref. 10). The biophysical theory of nerve activity is a modification by Rashevsky of a theory introduced by Blair. The central concept of the theory is that of a pair of antagonistic "factors," referred to as "excitatory" and "inhibitory" and denoted by  $\epsilon$  and  $j$ , respectively. The nature of the factors is unspecified, though the analogy of antagonistic ions is very suggestive.

If an exciting current  $I$  is applied, it is assumed that both  $\epsilon$  and  $j$  increase at a rate proportional to  $I$ , and decrease at a rate proportional to the excess of  $\epsilon$  and  $j$  over their respective resting values  $\epsilon_0$  and  $j_0$ . Thus

$$\frac{d\epsilon}{dt} = KI - k(\epsilon - \epsilon_0), \quad \frac{dj}{dt} = MI - m(j - j_0) \quad (1)$$

where  $K$ ,  $M$ ,  $k$ , and  $m$  are constants. The condition for excitation of the nerve is  $\epsilon \geq j$ ; hence, of course,  $\epsilon_0 < j_0$ . If a constant current is applied at  $t = 0$ , the solution is

$$\left. \begin{aligned}
 \epsilon &= \epsilon_0 + \frac{KI}{k}(1 - e^{-kt}) \\
 j &= j_0 + \frac{MI}{m}(1 - e^{-mt})
 \end{aligned} \right\} (2)$$

Under the conditions

$$m \ll k, \quad M \ll K, \quad \frac{K}{k} \leq \frac{M}{m}, \quad \frac{K}{k} \sim \frac{M}{m}$$

excitation will occur at the cathode only when the current is established, and at the anode when it is broken, provided  $I$  is sufficiently great. The intensity-time curve for excitation at the cathode at make (from  $\epsilon = j$ ) is

$$I = \frac{j_0 - \epsilon_0}{(K/k)(1 - e^{-kt}) - (M/m)(1 - e^{-mt})} \quad (3)$$

and at the anode at break,

$$I = \frac{j_0 - \epsilon_0}{(M/m)e^{-mt} - (K/k)e^{-kt}} \tag{4}$$

The threshold or rheobase values of the current at cathode and anode, respectively (from  $\epsilon = j$  and  $d\epsilon/dt = dj/dt$ ), are

$$R_c = \frac{j_0 - \epsilon_0}{(K/k)[1 - (M/K)^{k/(k-m)}] - (M/m)[1 - (M/K)^{m/(k-m)}]} \tag{5a}$$

$$R_a = \frac{j_0 - \epsilon_0}{(M/m)(M/K)^{m/(k-m)} - (K/k)(M/K)^{k/(k-m)}} \tag{5b}$$

with the approximate value

$$R_c \sim [(j_0 - \epsilon_0)/K]k, \quad R_a \sim [j_0 - \epsilon_0]/M]m$$

The solution for a slowly rising current,  $I = \lambda t$ , is

$$\left. \begin{aligned} \epsilon &= \epsilon_0 + \frac{K\lambda}{k} \left\{ t - \frac{1}{k} (1 - e^{-kt}) \right\} \\ j &= j_0 + \frac{M\lambda}{m} \left\{ t - \frac{1}{m} (1 - e^{-mt}) \right\} \end{aligned} \right\} \tag{6}$$

For sufficiently small  $\lambda$ , no excitation occurs as long as  $K/k \leq M/m$ . For alternating current,  $I = I_0 \sin \omega t$ , a solution obtained under the condition  $K/k = M/m$  gives an empirically verifiable relationship between the threshold value of  $I_0$  and the frequency  $\omega$ .

$$\frac{I_0}{R_c} = \sqrt{\left(1 + \frac{\omega^2}{k^2}\right) \left(1 + \frac{m^2}{\omega^2}\right)} \tag{7}$$

where

$$R_c = \frac{j_0 - \epsilon_0}{K - M} k$$

This case has also been solved without the restriction  $K/k = M/m$ . Another interesting relation derivable from the theory is that between the duration  $\bar{t}$  of a constant current pulse and the threshold intensity  $I$  required to produce anodic excitation at break

$$I_c = \frac{(1 - e^{-k\bar{t}})^{1/[(k/m)-1]} \left(\frac{k}{m}\right)^{1/[(k/m)-1]}}{(1 - e^{-m\bar{t}})^{1/[1-(m/k)]}} \tag{8}$$

The theory of excitation is at present largely phenomenological, as is evident from the foregoing. The theory of conduction of the excitation along the nerve is a simple physical one, however, and is essentially the theory of a core conductor. The nerve is pictured as a cylinder with a core of radius  $r$  and specific resistance  $\rho$ , surrounded by a sheath of thickness  $\delta$  and specific

resistance  $\bar{\rho}$ . Also  $\delta \ll r$ . To a first approximation, neglecting the distributed capacity of the fiber, the distribution of current is given at  $t = 0$  by

$$i(x) = Ie^{-\alpha x} \quad (9)$$

where  $I$  is the current at the initially excited region,  $x$  is distance from the excited region to a point along the nerves, and

$$\alpha = \sqrt{\frac{\gamma + 1}{\gamma} \frac{2\rho}{\delta \bar{\rho} r}}$$

where  $\gamma$  is the ratio of resistance per unit length of the core to resistance per unit length of the sheath.

The distribution is propagated along the nerve, so that at any later time we have at any point a distribution,

$$i(S) = Ie^{-\alpha S} \quad (10)$$

where  $S$  is the distance between the point considered and the excited region at the moment  $t$ . If the velocity of propagation is  $v(t)$ , then at a point  $x_0$  we have

$$S = x_0 - \int_{t_1}^t v(t) dt = x_0 - u(t)$$

where  $t_1$  is the time from application of current  $I$  to occurrence of excitation at the electrode, and is given by

$$t_1 = \frac{1}{k} \log \frac{KI}{KI - k\epsilon_1}$$

where  $\epsilon_1 = \epsilon^* - \epsilon_0$ , and  $\epsilon^*$  is the value of  $\epsilon$  at the electrode when  $\epsilon = j$ . From  $t = 0$  to  $t_1$ , the current at  $x_0$  is  $Ie^{-\alpha x_0}$ . After  $t_1$ , it varies according to

$$i(x_0, t) = Ie^{-\alpha x_0 + \alpha u(t)} \quad (11)$$

Excitation at the point  $x_0$  by the local current  $i(x_0, t)$  obeys the differential equations:

$$\left. \begin{aligned} \frac{d\epsilon}{dt} &= Ki - k(\epsilon - \epsilon_0) \\ \frac{dj}{dt} &= Mi - m(j - j_0) \end{aligned} \right\} \quad (12)$$

Solving, and putting  $\epsilon(x_0, t) = j(x_0, t)$  for excitation, we finally obtain the differential equation

$$\alpha \frac{dv}{dt} = -\alpha^2 v^2 - \left( m + k - \frac{K - M}{j_0 - \epsilon_0} I \right) \alpha v - \left( mk + \frac{Mk - Km}{j_0 - \epsilon_0} I \right) \quad (13)$$

If (as is probably the case, from available values of the constants),

$$\Delta = a^2 - 4b > 0$$

the right side of the differential equation has two real roots,

$$\alpha v_1 = \frac{1}{2}(a - \sqrt{\Delta}), \quad \alpha v_2 = \frac{1}{2}(a + \sqrt{\Delta}) \tag{14}$$

where

$$-a = m + k - \frac{K - M}{j_0 - \epsilon_0} I, \quad b = mk + \frac{Mk - Km}{j_0 - \epsilon_0} I$$

The velocity  $v(t)$  is given by

$$v = \frac{v_1 - Av_2 e^{\sqrt{\Delta}t}}{1 - Ae^{\sqrt{\Delta}t}} \tag{15}$$

where

$$A = e^{-\sqrt{\Delta}t_1} \frac{(m + \alpha v_2) [j_1(m + \alpha v_1) - MI]}{(m + \alpha v_1) [j_1(m + \alpha v_2) - MI]}$$

At  $t = t_1$ ,

$$j_1 = j^* - j_0$$

$$v_1 < v < v_2$$

With increasing  $t_1$ ,  $v$  approaches  $v_2$ , which is a stable value.

**4.2. Behavior and the structure of the central nervous system** (Ref. 10). The biophysical theory of the behavior of organisms with a central nervous system is based on what might be called the network postulate : that the units of the central nervous system follow the same simple laws as isolated peripheral neurones, and that the complexities of behavior result from the interaction of such units arranged in networks of varying degrees of complexity.

It is known that a continuous physiological stimulus produces a volley of nerve impulses rather than a single impulse. The frequency  $\nu$  of the volley increases with the intensity  $S$  of the stimulus. The intensity  $I$  of the impulses is independent of  $S$  according to the "all-or-none law."

We define the intensity of excitation of a fiber,  $E$ , by

$$E = I\nu \tag{1}$$

and write as an approximate expression for the relation between  $\nu$  and  $S$ ,

$$\nu = \alpha(S - h)$$

where  $h$  is the threshold of the fiber and  $\alpha$  a constant of the fiber. Thus

$$E = \alpha I(S - h) = \beta(S - h) \tag{2}$$

The neuroelement produces factors  $\epsilon$  and  $j$  according to the differential equations

$$\frac{d\epsilon}{dt} = A\epsilon - a\epsilon, \quad \frac{dj}{dt} = BE - bj \quad (3)$$

The neuroelements may be divided into two classes, excitatory and inhibitory, according as the asymptotic values of  $\epsilon$  exceed those of  $j$  or vice versa, which depends on certain relations among the constants. A simplified version of this classification occurs if the neuroelements produce only one factor, either  $\epsilon$  or  $j$  alone; such neuroelements are termed purely excitatory or purely inhibitory.

One further postulate is required to establish the influence of the neuroelements in the network on one another. We consider the neuroelements as linear (possibly with collateral branches). They are polar: one end receives the stimulus, and this is propagated along the element to its other end. This end may make a connection with the stimulus-receiving end of a second neuron. Such connections may be multiple, i.e., more than one neuroelement may enter or leave such a connection. We now postulate that at any connection, if  $\epsilon > j$ , then  $\epsilon - j$  acts as the stimulus intensity  $S$  for any neuroelement leaving the connection. (It is understood that, if several neuroelements enter the connection, their contributions to  $\epsilon$  and  $j$  are additive.)

Space will permit only a few illustrations of the many applications of this scheme which have been made.

a. *Reaction time.* Consider a network in which two elements I and III converge in a connection to an element II. Let I be purely excitatory and III be simply excitatory. Suppose a warning stimulus  $S_3$  is applied to III at a time  $t_w$  units before  $S_1$  is applied to I. Then the reaction time  $t_r$  for response to  $S_1$  via I and II is related to  $t_w$  by

$$t_r = t_0 - \frac{1}{a_1} \log [M + J(e^{-b_3 t_w} - e^{-a_3 t_w})] \quad (4)$$

where 
$$M = 1 - \frac{a_1 h_2}{A_1 E_1}, \quad J = \frac{A_3 E_3 a_1}{A_1 E_1 a_3}$$

and  $t_0$  is the constant time due to conduction on the efferent side and delays at the end organs.

b. *Discrimination.* Discrimination problems of various sorts are analyzed in terms of networks with fundamentally similar characteristics: series of excitatory neuroelements run parallel to one another, and send collateral branches, both excitatory and inhibitory, to each other's connections. A

simple example consists of  $n$  elements I connecting with  $n$  elements II at connections  $c_i (i = 1, \dots, n)$ . A branch of each element  $i$  of I connects at  $c_i$  to a set of inhibitory elements III which join every connection  $c_i (h \neq i)$ . Thus every  $c_i$  receives an excitatory path from the periphery and  $n - 1$  inhibitors from other neuroelements. If all stimuli have the same intensity  $S$ , we have for  $\epsilon - j$  at  $c_i$  (asymptotically)

$$\epsilon - j = \left( \frac{A_e}{a_e} - \frac{B_e}{b_e} \right) E_1 + (n - 1) \left( \frac{A_j}{a_j} - \frac{B_j}{b_j} \right) E_3 \quad (5)$$

with

$$E_1 = \alpha_1 I_1 (S - h_1)$$

$$E_3 = \alpha_3 I_3 [P \alpha_1 I_1 (S - h_1) - h_3]$$

$$P = \frac{A_e}{a_e} - \frac{B_e}{b_e}$$

The subscripts  $e$  and  $j$  refer to excitatory and inhibitory parameters, the subscripts 1 and 3 to element I and III. If

$$h_1 < S < h_1 + \frac{h_3}{P \alpha_1 I}$$

then  $E_3 = 0$  and  $\epsilon - j > 0$ . If also

$$S > h_1 + \frac{h_2}{P \alpha_1 I_1}$$

which is possible only if  $h_2 < h_3$ , then  $\epsilon - j > h_2$ , and all II pathways are excited. But if

$$S > h_1 + \frac{h_3}{P \alpha_1 I_1}$$

then, for sufficiently large  $n$ ,  $\epsilon - j < 0$ ; i.e., if

$$n > 1 + \frac{P}{Q} \cdot \frac{\alpha_1 I_1}{\alpha_3 I_3} \cdot \frac{S - h_1}{P \alpha_1 I (S - h_1) - h_3}$$

where

$$Q = - \left( \frac{A_j}{a_j} - \frac{B_j}{b_j} \right)$$

In this case complete inhibition occurs at all  $c_i$ . But if  $m < n$  of the pathways are stimulated with  $S' > S$ , then at the  $c_i^m$  connections of these  $m$  paths

$$(\epsilon - j)_m = P E'_1 - (m - 1) Q E'_3 - (n - m) Q E_3 \quad (6)$$

while at the other  $n - m$  connections  $c_i^{n-m}$ ,

$$(\epsilon - j)_{n-m} = P E_1 - (n - m - 1) Q E_3 - m Q E'_3 \quad (7)$$

where

$$E'_1 = \alpha_1 I_1 (S' - h'), \quad E'_3 = \alpha_3 I_3 (PE'_1 - h_3)$$

and the other symbols are as before. Now

$$(\epsilon - j)_{n-m} < P\alpha_1 I_1 (S - h_1) - (n-1)Q\alpha_3 I_3 [P\alpha_1 I_1 (S - h_1) - h_3] \quad (8)$$

since  $S' > S$ . Thus  $(\epsilon - j)_{n-m} < 0$  for the same conditions as made  $\epsilon - j < 0$  before. But  $(\epsilon - j)_m > h_2$  whenever

$$S' > h_1 + \frac{h_2 + Q\alpha_3 I_3 [(n-m)P\alpha_1 I_1 (S - h_1) - (n-1)h_3]}{P\alpha_1 I_1 [1 - (m-1)Q\alpha_3 I_3]}$$

Thus, if  $S'$  is sufficiently greater than  $S$ , the  $m$  pathways will respond, while the  $n - m$  fail to respond to  $S$ .

c. *Self-exciting circuits.* Consider a closed circuit consisting of pure excitatory elements I and II. The differential equations are

$$\frac{d\epsilon_1}{dt} = AE_2 - a\epsilon_1, \quad \frac{d\epsilon_2}{dt} = AE_1 - a\epsilon_2 \quad (9)$$

The approximate relation  $E = \alpha I(S - h)$  leads to the physically absurd result that  $E_1$  and  $E_2$  become infinite if the circuit is excited at all. The next best approximation is

$$E = \frac{I}{\theta} [1 - e^{-\alpha\theta(S-h)}]$$

giving in this case

$$\left. \begin{aligned} \frac{d\epsilon_1}{dt} &= \frac{AI_2}{\theta_2} [1 - e^{-\alpha\theta_2(\epsilon_2 - h_2)}] - a\epsilon_1 \\ \frac{d\epsilon_2}{dt} &= \frac{AI_1}{\theta_1} [1 - e^{-\alpha\theta_1(\epsilon_1 - h_1)}] - a\epsilon_2 \end{aligned} \right\} \quad (10)$$

An analytic solution is not known. But a graphical analysis is readily carried out in terms of  $\epsilon_1$  and  $\epsilon_2$  as Cartesian coordinates in a plane. Then, setting  $d\epsilon_1/dt = 0$  and  $d\epsilon_2/dt = 0$ , we derive two curves in this plane, which in general intersect in two points. One of these points represents a stable equilibrium and the other an unstable one, while a third stable point is  $\epsilon_1 = \epsilon_2 = 0$ . There is a curve passing through the unstable point, which divides the positive quadrant of the plane into two regions, such that, starting at any point in one region, one passes to the origin, while from any point in the second region one arrives at the stable nonzero equilibrium. Thus, if the circuit is sufficiently excited by some external stimulus, it will arrive at a stable excitatory equilibrium, in which it will remain unless externally inhibited.

d. *Conditioned reflexes.* Consider two pathways, one consisting of elements  $I^u$  and  $II^u$ , the other of elements  $I^c$  and  $II^c$ , with I-II connections  $c_u$  and  $c_c$ , respectively. Let  $II^u$  and  $II^c$  converge at a connection  $c$ , which leads by further paths to a response  $R$ . A collateral of  $I^u$  leads to  $c_c$ . Also connected to  $c_c$  is a self-exciting circuit  $C$  of the type just described; the external excitation needed to start  $C$  is  $h^*$ , and the stable excitation value of  $C$  is  $\epsilon_0$ . Pathway  $I^c$  has threshold  $h_c$ , while  $II^c$  has threshold  $h'$ . We use for  $E_u$  and  $E_c$  the exponential expression of the preceding paragraph; the values of the constants are such that the limiting values of  $E_u$  and  $E_c$ ,  $I_u/\theta_u$  and  $I_c/\theta_c$ , satisfy

$$P \frac{I_c}{\theta_c} < h', \quad P = \frac{A_e}{a_c} - \frac{B_e}{b_c}, \quad P \frac{I_c}{\theta_c} < h^*, \quad P \frac{I_u}{\theta_u} < h^*$$

but 
$$P \left( \frac{I_u}{\theta_u} + \frac{I_c}{\theta_c} \right) > h^*, \quad P \frac{I_c}{\theta_c} + \epsilon_0 > h'$$

Now if  $S_u > h_u$  is applied to  $I^u$ ,  $R$  results. But  $S_c$  applied to  $I^c$ , no matter how strong, does not give  $R$ . But if  $S_u$  and  $S_c$  are applied simultaneously for a sufficient time,  $\epsilon - j$  at  $c_c$  will be  $P(F_u + E_c)$ ; and for sufficiently large  $S_u$  and  $S_c$  to bring  $E_u$  and  $E_c$  close to their limiting values  $I_u/\theta_u$  and  $I_c/\theta_c$ , this  $\epsilon - j$  will exceed  $h^*$ . Now  $C$  is in an excited state with  $\epsilon = \epsilon_0$ , even when external stimuli are removed. If  $S_c$  is now applied alone,  $\epsilon$  at  $c_c$  is  $PE_c + \epsilon_0$ ; and by the last inequality, for sufficiently large  $S_c$ , this will exceed  $h'$ , and elicit  $R_1$ . This is a simple scheme which contains the essential features of the conditioned reflex. Various modifications have been worked out which account for the finer details of the phenomenon.

e. *Learning.* The biophysical theory of learning utilizes the properties of the self-exciting circuit, contained in a larger cycle which has the property that has been rather loosely compared with feedback in electronic networks. If one of two alternatives is to be learned, as in many experimental setups in psychology, consider a pair of parallel pathways, containing several elements in series, one path originating in stimulus  $S_c$  and terminating in response  $R_c$  ("correct" response to choice) the other going from  $S_w$  to  $R_w$  ("wrong" response to choice). (The usual cross-inhibitory elements run from the I-II connections  $c_c$  and  $c_w$  to higher connections in the pathways.) Let  $R_c$  produce the event  $R_1$ , and  $R_w$  produce  $R_2$ . Here  $R_1$  ("reward") acts as stimulus to a pathway which includes a self-exciting circuit  $C$ , and terminates with an excitatory element at  $c_c$ ;  $R_2$  ("punishment") serves as stimulus to a path which includes a self-exciting circuit  $C'$  and terminates with an inhibitory element at  $c_w$ . ( $C$  and  $C'$  actually consist of two large groups of circuits arranged in parallel, and having a distribution of threshold values, so that they

will not all be activated at once, but will be activated in increasing numbers with repetition of the stimulus to them from  $R_1$  and  $R_2$ .) Now  $S_c$  and  $S_w$  are presented simultaneously on many successive occasions. Response is random at first, but  $C$  and  $C'$  are progressively activated, so that the strength of response  $R_c$  is reinforced and that of  $R_w$  is weakened. The relation between number of wrong responses  $w$  and number of trials  $n$  is

$$w = \frac{1}{k(b - \beta)} \log \frac{2be^{k(\epsilon_{0c} - \epsilon_{0w})}}{2be^{k(\epsilon_{0c} - \epsilon_{0w})} - (b - \beta)(1 - e^{-kbn})} \quad (11)$$

Here  $\epsilon_{0c}$  and  $\epsilon_{0w}$  are the initial values of  $\epsilon$  at  $C_c$  and  $C_w$ ,  $b$  is the increase in  $\epsilon$  at  $c_c$  per correct response,  $\beta$  is the decrease in  $\epsilon$  at  $c_w$  per wrong response, and  $k$  is a constant.

A generalization for  $N$  choices, with  $M$  associations to be learnt, with an allowance for prompting by the experimenter in a fraction  $(1 - f)$  of the trials, and taking into account the effect of  $M$  on the parameter  $b$ , gives

$$w = \frac{(N - 1)e^{\varphi M}}{\eta A} \log \frac{N}{e^{-\eta M e^{-\varphi M}} + N - A} \quad (12)$$

where

$$A = Nf - f - \beta/b$$

and  $\eta$  and  $\varphi$  are constants.

The logical calculus of neural nets : the foregoing work on the biophysics of behavior consists essentially in constructing networks and seeing what kind of behavior they will give. An alternative treatment by McCulloch and Pitts is capable of solving the inverse problem : for a given behavior pattern, to determine the corresponding network. This treatment employs the analogy between two-valued logic and the all-or-none character of nerve activity. Numbering the neurones, we represent by " $N_1(t)$ " the proposition " $\text{Neurone \#1 fires at time } t$ ." In the same way we write " $\sim N_2(t)$ " for " $\text{Neurone \#2 does not fire at time } t$ ," the symbol  $\sim$  being the classical negation sign of symbolic logic in the Russell-Whitehead notation. We shall also use " $V$ ", the classical disjunctive symbol (" $\dots$  or  $\dots$ , or both"). It is convenient to take the synaptic delay as the unit of time. It is also convenient to assume that inhibition is absolute; i.e., if any inhibitory neurone terminates on a second neurone, its firing will always inhibit the second neurone. However, it can be shown that nothing would be essentially altered in the results if one abandons this assumption, which merely simplifies the symbolic manipulations. The threshold of a neurone, taken to be an integer  $\theta$ , is for simplicity identified with the number of terminal bulbs, synapsing on it from other (excitatory) neurones, which must be excited simultaneously in order to stimulate it. This assumption facilitates dia-

grammatic representation of networks, but is otherwise not essential; there is, however, some evidence for its reality. Consider now that neurone 1 terminates on neurone 2 with a number of terminal bulbs equal to  $\theta$  for #2. The necessary and sufficient condition for #2 to fire at  $t$  is simply that #1 fired at  $t - 1$ .

$$N_2(t). \equiv .N_1(t - 1) \tag{13}$$

where  $\equiv$  is the logical sign of equivalence ("if and only if"), and the dots follow the dot punctuation conventions of Russell and Whitehead. If  $\theta = 2$ , and neurons 1 and 2 terminate on 3 with only one terminal bulb each, both must fire at once

$$N_3(t). \equiv .N_1(t - 1) \cdot N_2(t - 1) \tag{14}$$

If 1 and 2 synapse on 3 with two bulbs each, and  $\theta = 2$ , the firing of either will excite 3.

$$N_3(t). \equiv .N_1(t - 1)VN_2(t - 1) \tag{15}$$

If 1 synapses on 3 with 2 bulbs ( $\theta = 2$ ), and 2, an inhibitory neurone, synapses on 3, then 1 must fire while 2 is not firing to excite 3.

$$N_3(t). \equiv .N_1(t - 1) \cdot \sim N_2(t - 1) \tag{16}$$

These basic circuits are useful in constructing more complex ones, as will be seen. It is convenient to introduce the functor (operator) " $S$ ", defined by

$$SN_1(t). \equiv .N_1(t - 1)$$

so that a sentence like  $N_2(t). \equiv .N_1(t - 1)$  becomes

$$N_2(t). \equiv .SN_1(t) \tag{17}$$

Repetitions of the operation are represented by powers. Thus

$$S[SN_1(t)]. \equiv .S^2N_1(t) \tag{18}$$

Obviously, the operator  $S$  commutes with  $.$  and  $V$ .

Any network can be represented by a number of equivalences, as just illustrated, one for each neurone in the net except the initial ones (the peripheral afferents, defined by the fact that no neurone of the net terminates on them). (We neglect nets containing cycles in this presentation, since their theory is a far more elaborate one). Anormal form is readily obtained. If the equivalence for  $N_i(t)$  contains on the right side  $N_j$ , where  $j(\neq i)$  is not a peripheral afferent, then  $N_j$  can be eliminated by means of its own equivalence. This elimination can be carried out consistently and with a unique

result, until only the  $N$ 's of peripheral afferents appear on the right sides (since no cycles occur in the nets). The resulting form, called a temporal propositional expression, expresses each  $N_i(t)$  as a disjunction of conjunctions of propositions of the form  $S^n N_k(t)$  and their negations, where  $n \geq 1$  and  $k$  is a peripheral afferent. No term in the disjunction can consist wholly of negations.

To illustrate the application of the above, we treat the "illusion of heat and cold." If a cold object is touched briefly to the skin and removed, a sensation of heat is felt; only cold is felt if the contact is more prolonged. We number the cutaneous heat and cold receptor neurones 1 and 2, the corresponding central neurones whose activity gives the heat and cold sensations 3 and 4, respectively.

The phenomenon can then be expressed by

$$\left. \begin{aligned} N_3(t) &: \equiv :N_1(t-1) \cdot V \cdot N_2(t-3) \cdot \sim N_2(t-2) \\ N_4(t) &: \equiv \cdot N_2(t-2) \cdot N_2(t-1) \end{aligned} \right\} (19)$$

where we have for simplicity assumed the required contact for cold sensation to be two synaptic delays as against one for heat. These relations can be rewritten with the aid of the operator  $S$ .

$$\left. \begin{aligned} N_3(t) &: \equiv \cdot S\{N_1(t) V S[(S N_2(t) \cdot \sim N_2(t))]\} \\ N_4(t) &: \equiv \cdot S\{[S N_2(t)] \cdot N_2(t)\} \end{aligned} \right\} (20)$$

The problem is to connect neurones 1, 2, 3, 4, and introduce other neurones if necessary, such that the normal forms for the network will contain the above sentences. To do this, we construct nets for the partial expressions, beginning with those included in the largest number of brackets and proceeding outward.

Introduce a neurone  $a$ , upon which two terminal bulbs from neurone 2 synapse (assume for simplicity  $\theta = 2$  for all neurones of the net). Then

$$N_a(t) \equiv \cdot S N_2(t)$$

and we can substitute this expression above. Now let a single bulb from  $a$  and a single bulb from 2 terminate on 4. Then

$$N_4(t) \equiv \cdot S[N_a(t) \cdot N_2(t)] \equiv \cdot S[(S N_2(t)) \cdot N_2(t)]$$

Introduce neurone  $b$ , receiving an inhibitory terminal from 2 and two excitatory terminals from  $a$ . Then

$$N_b(t) \equiv \cdot S[N_a(t) \cdot \sim N_2(t)]$$

which is the square bracket in the expression for  $N_3(t)$ .

Now let neurones 1 and *b* each send two terminals to 3. Then

$$N_3(t) \equiv .S[N_1(t)VN_b(t)] \equiv .S\{N_1(t)VS[(SN_2(t) \cdot \sim N_2(t))]\} \quad (21)$$

This completes the solution of the problem, since our systematically constructed network leads to the desired expression for  $N_3(t)$  and  $N_4(t)$ .

The nature of the logical formalism for cyclic nets may be briefly indicated. If a self-exciting circuit is firing at time *t*, it is not true, as for simple neurones, that it was stimulated at *t* - 1. One can only say that it must have been stimulated at *t* - 1 or some earlier moment. We introduce the logical existential operator  $\exists$ , which is such that  $(\exists x)N(x)$  means, "There is an *x* for which *N(x)* holds." With the aid of this operator, some simple examples of cyclic nets may be given. Let neurone 1 terminate on neurone 2 with terminals less than  $\theta$  in number. Let 1 also terminate on a self-exciting circuit (with threshold number of terminals). Each neurone of the circuit sends a branch to 2; the total number of terminals from this source equals or exceeds  $\theta$ . This circuit is represented by

$$N_2(t) \equiv (\exists x)N_1(t - x - 1) \quad (22)$$

Again, let neurone 1 have a branch to a self-exciting circuit, each neurone of which sends a branch to 1. Then

$$N_1(t) \equiv (\exists x)N_1(t - x - 2) \quad (23)$$

Thus for cyclic nets we may have  $N_i$  expressed in terms of  $N_i$ , which is never true for noncyclic nets.

## 5. The Evolution and Interaction of Populations

**5.1. The general laws of populations** (Ref. 8). The elementary units of a population may be of quite diverse sorts: molecules, as in chemical kinetics; cells, as in embryology; or organisms, as in demography and ecology. The general character of the laws is the same for all these cases. The laws are differential or integrodifferential equations (or systems of equations), of first order in the time. The dependent variables are quantities which express the number of units, the total mass, or some such extensive property of each species or type of units in the population. Thus we have equations of the form

$$\frac{dX_i}{dt} = F_i(X_1, \dots, X_n; P) \quad (1)$$

where *P* represents a set of parameters (e.g., temperature, volume of space available to the population, etc.). In most cases, the time *t* does not appear

explicitly in the  $F_i$ . But the parameters  $P$  may vary with the time independently of the  $X_i$ , as in the case of long-range or seasonal climatic variations, or diurnal variations of temperature; and these variations may not always be neglected. For the moment, however, we ignore them.

These equations define certain steady states, which occur when all the  $dX_i/dt$  vanish, so that

$$F_1 = F_2 = \dots = F_n = 0$$

These  $n$  equations in general determine one or more sets of values

$$X_1 = C_1, \quad X_2 = C_2, \quad \dots, \quad X_n = C_n$$

for which the system is at rest. Some of these solutions are stable, however, and some unstable. It is convenient to introduce the new set of variables,

$$x_i = X_i - C_i$$

whence the system of equations becomes

$$\frac{dx_i}{dt} = f_i(x_1, \dots, x_n; P) \quad (2)$$

If the functions  $f_i$  can be expanded in Taylor series, the general solution of the system can be written

$$x_1 = G_{11}e^{\lambda_1 t} + G_{12}e^{\lambda_2 t} + \dots + G_{1n}e^{\lambda_n t} + G_{111}e^{2\lambda_1 t} + \dots \quad (3)$$

where the  $G$ 's are constants, of which  $n$  are arbitrary and are fixed by the initial conditions. The  $\lambda_i$  are roots of the characteristic equation

$$|a_{ij} - \delta_{ij}\lambda| = 0 \quad (4)$$

where the  $a_{ij}$  are the coefficients of the linear terms in the Taylor series, and  $\delta_{ij}$  is the Kronecker delta,

$$\delta_{ii} = 1, \quad \delta_{ij} = 0 \quad \text{for } i \neq j$$

If all  $\lambda_i$  are real and negative, the steady state is stable. If some  $\lambda_i$  are complex with negative real parts, damped oscillations occur, but the steady state is eventually approached. Pure imaginary  $\lambda_i$  result in permanent oscillations, however. The steady state is unstable if any  $\lambda_i$  is positive or has a positive real part.

**5.2. Equations of biological populations** (Ref. 6). In a large number of cases, biological populations are well represented by equations in which the  $F_i$  are quadratic in the  $X_i$ .

Thus

$$\frac{dX_i}{dt} = \alpha_i + \sum_j \epsilon_{ij} X_j - X_i \sum_j h_{ij} X_j, \quad (i = 1, \dots, n) \quad (1)$$

The  $\alpha_i$  may represent immigration and emigration at constant rates. The linear terms represent increase due to excess of births over deaths, and to movements from one species to another. The quadratic terms represent interactions between members of the same or different species; they may be due to parasitism, predatory activity, metabolic products, physical conflict, competition for food, or the like. If we neglect transition between groups, which might result from mutation, metamorphosis, etc., and confine ourselves to closed populations, a useful and not too special case results.

$$\frac{dX_i}{dt} = X_i(\epsilon_i - \sum_j h_{ij} X_j), \quad (i = 1, \dots, n) \quad (2)$$

The  $\epsilon_i$ , termed coefficients of multiplication, may be interpreted as excess of birth rate over death rate. There are  $2^n$  possible steady states. The simplest is

$$C_1 = 0, \quad C_2 = 0, \quad \dots, \quad C_n = 0 \quad (3)$$

This is stable only if all  $\epsilon_i < 0$ , and so is not very significant. There are  $n$  states of the type

$$C_k = \frac{\epsilon_k}{h_{kk}}, \quad C_i = 0 \quad \text{for } i \neq k \quad (4)$$

These are stable if

$$\epsilon_k > 0, \quad h_{kk} > 0, \quad \epsilon_s h_{kk} < h_{sk} \epsilon_k, \quad (s \neq k)$$

There are  $n(n-1)/2$  states like

$$C_1 = \frac{\epsilon_1 h_{22} - \epsilon_2 h_{21}}{h_{11} h_{22} - h_{12} h_{21}}, \quad C_2 = \frac{\epsilon_2 h_{11} - \epsilon_1 h_{12}}{h_{11} h_{22} - h_{12} h_{21}}, \quad C_3 = 0, \quad \dots, \quad C_n = 0 \quad (5)$$

One can continue in this fashion, finally arriving at a steady state in which none of the groups vanishes. This is given by the solutions  $C_i$  of the linear equations:

$$\sum_j h_{ij} C_j = \epsilon_i, \quad (i = 1, \dots, n) \quad (6)$$

This is stable if all the roots of the secular equation are negative or have negative real parts. The secular equation is of course

$$\left| \frac{\partial F_i}{\partial C_j} - \delta_{ij} \lambda \right| = 0 \quad (7)$$

where  $\partial F_i / \partial C_j$  stands for  $\partial F_i / \partial X_j$  evaluated at  $X_1 = C_1, \dots, X_n = C_n$ .

Thus in the present case

$$\left. \begin{aligned} \frac{\partial F_i}{\partial C_i} &= \epsilon_i - 2h_{ii}C_i - \sum_{j \neq i} h_{ij}C_j = -h_{ii}C_i \\ \frac{\partial F_i}{\partial C_j} &= -h_{ij}C_i, \quad (i \neq j) \end{aligned} \right\} \quad (8)$$

**5.3. Simple populations; effect of wastes, nutriment, and space** (Ref. 9). If  $p$  is the number of elements of a simple closed population,

$$\dot{p} = \epsilon p - hp^2 \quad (1)$$

The solution is

$$p = \frac{Cp_0}{p_0 + (C - p_0)e^{-\epsilon t}} \quad (2)$$

where  $p_0$  is the value of  $p$  at  $t = 0$ , and  $C = \epsilon/h$  is the stationary value of  $p$ . This is the so-called logistic law of growth. If  $h \ll \epsilon$ ,  $C$  is large, and

$$\dot{p} \cong p_0 e^{\epsilon t} \quad (3)$$

the Malthusian law of growth. If the accumulated metabolites are toxic, we get

$$\dot{p} = \epsilon p - hp^2 - cp \int_0^t K(t - \tau) p(\tau) d\tau \quad (4)$$

Putting for simplicity

$$K(t - \tau) = 1$$

we get

$$\dot{p} = \epsilon p - hp^2 - cpP \quad (5)$$

where

$$P(t) = \int_0^t p(\tau) d\tau$$

The solution is obtained in parametric form.

$$p = \left( p_0 - \frac{\epsilon}{h} - \frac{c}{h^2} \right) e^{-hP} + \frac{\epsilon}{h} + \frac{c}{h^2} - \frac{c}{h} P = F(P) \quad (6)$$

$$t = \int_0^P \frac{dS}{F(S)}$$

Now  $p = 0$  for a finite value of  $P$  attained as  $t \rightarrow \infty$ . But if  $p_0 < \epsilon/h$ ,  $p$  increases for small  $t$ . Hence  $p$  has a maximum  $p_m$ , which is given by

$$p_m = \frac{\epsilon}{h} - \frac{c}{h^2} \log \frac{c + \epsilon h - p_0 h^2}{c} < \frac{\epsilon}{h} \quad (7)$$

We can find approximate representations of  $p$ .

$$\left. \begin{aligned} p &\cong \frac{p_0 p_m}{p_0 + (p_m - p_0)e^{-\epsilon t}}, & (t < t_m) \\ p &\cong \frac{p_m}{ch^2 \frac{c(t - t_m)}{2}}, & (t > t_m) \end{aligned} \right\} \quad (8)$$

Space is one of the important limiting factors for a population. Suppose the space occupied per unit volume by living or dead members is  $s$ , the effective volume of a living member  $\alpha$ , that of a dead member  $\beta$ . The birthrate is  $n$ , death rate  $m$ . Births are proportional to  $p$  and available free space  $1 - s$ , deaths to  $p$  and to  $s$ . Then

$$\left. \begin{aligned} \dot{p} &= pn(1 - s) - nps - hp^2 \\ s &= p\alpha + m\beta \int_0^t p(u)s(u)du \end{aligned} \right\} \quad (9)$$

The solution in parametric form is

$$p = \frac{n}{h} - ZS_0 e^{-\varphi(Z)}, \quad t = \int_Z^{Z_0} \frac{du}{F(u)p(u)} \quad (10)$$

where

$$F(Z) = \alpha h Z^2 + Z(h - \alpha n - \alpha m + \beta m) - (m + n)$$

$$\varphi(Z) = \int_{Z_0}^Z \frac{\alpha hu - \alpha n - \alpha m + \beta m}{F(u)} du$$

and the parameter  $Z$  is defined by  $Z = (n - hp)/hs$ .

An interesting treatment in the case where nutriment is the only limiting factor is that of Monod. He writes in general

$$\frac{dp}{dt} = \epsilon(C)p \quad (11)$$

where  $C$  is the concentration of the limiting metabolite. He assumes further

$$\epsilon(c) = \epsilon_0 \frac{C}{K_1 + C}$$

where  $\epsilon_0$  and  $K_1$  are constant. This expression, proposed by Monod as an approximation to the solution of the differential equation

$$\frac{d\epsilon}{dC} = B(1 - \epsilon) \quad (12)$$

is interesting for its formal resemblance to the rate of an enzyme-catalyzed reaction limited by substrate.

The final relation needed is

$$-\frac{dC}{dt} = K \frac{dp}{dt} \quad (13)$$

which is an obvious assumption for the relation of food consumption to growth rate. In integrated form,

$$C - C_0 = K(p_0 - p)$$

it expresses the constancy of the "material efficiency of growth." The final solution, after  $C$  is eliminated, is

$$(1 + P) \ln \frac{p}{p_0} - P \ln \left( Q - \frac{p}{p_0} \right) = \epsilon_0 t + P \ln \frac{Kp_0}{C_0} \quad (14)$$

$$P = \frac{K_1}{C_0 + Kp_0}, \quad Q = \frac{C_0 + Kp_0}{Kp_0}$$

The asymptotic stationary value of  $p$  is

$$p_\alpha = p_0 Q$$

The curve has an inflection point, with a  $p$  value of

$$p_i = p_0 Q [1 + P - \sqrt{P(1 + P)}]$$

and in general is not symmetrical, as is the Verhulst logistic.

**5.4. Interaction of two species** (Refs. 8 and 14). The interaction of groups in a population has been analyzed principally by Lotka and Volterra. An interesting case is that in which all members of both groups compete for some common necessity like food. Let the effect of this competition on the food supply be  $F(p_1, p_2)$ . Then

$$\left. \begin{aligned} \frac{dp_1}{dt} &= p_1[\epsilon_1 - \gamma_1 F(p_1, p_2)] \\ \frac{dp_2}{dt} &= p_2[\epsilon_2 - \gamma_2 F(p_1, p_2)] \end{aligned} \right\} \quad (1)$$

where the constants  $\gamma_1$  and  $\gamma_2$  represent the effect of the food curtailment on the growth of the two groups. An integral of this pair of equations is

$$\frac{p_1^{\gamma_2}}{p_2^{\gamma_1}} = C e^{(\gamma_2 \epsilon_1 - \gamma_1 \epsilon_2) t} \quad (2)$$

where  $C$  is a constant of integration. If  $\gamma_2 \epsilon_1 > \gamma_1 \epsilon_2$ , the system approaches a steady state where

$$p_2 = 0, \quad F_1(p_1, 0) = \epsilon_1 / \gamma_1$$

If  $\gamma_2\epsilon_1 < \gamma_1\epsilon$ , the steady state reverses the fates of  $p_1$  and  $p_2$ . If species 1 is the sole food of the predatory species 2 (neglecting for simplicity the intragroup competition), we have

$$\left. \begin{aligned} \frac{dp_1}{dt} &= p_1(\epsilon_1 - h_{12}p_2) \\ \frac{dp_2}{dt} &= p_2(-\epsilon_2 + h_{21}p_1) \end{aligned} \right\} (3)$$

where the negative sign before  $\epsilon_2$  takes cognizance of the fact that species 2 would die out in the absence of its prey. Integration yields (with  $C$  a constant of integration)

$$p_1^{\epsilon_2} p_2^{\epsilon_1} e^{-h_{21}p_1 - h_{12}p_2} = C$$

This represents a family of nonintersecting closed curves. The system is therefore periodic. If terms for intragroup competition are included, however, the oscillations are damped, and the system spirals into a steady state. In the above case,  $p_1$  will never be completely wiped out by the predator if its initial value is positive. But suppose a third group is present, also a prey for group 2. Then

$$\left. \begin{aligned} \frac{dp_1}{dt} &= p_1(\epsilon_1 - h_{12}p_2) \\ \frac{dp_2}{dt} &= p_2(-\epsilon_2 + h_{21}p_1 + h_{23}p_3) \\ \frac{dp_3}{dt} &= p_3(\epsilon_3 - h_{32}p_2) \end{aligned} \right\} (4)$$

Consider, for instance, in the neighborhood of the  $p_3$  axis the approximate relation

$$\frac{dp_1}{dp_2} = \frac{p_1\epsilon_1}{p_2(-\epsilon_2 + h_{23}p_3)}$$

This is positive for sufficiently large  $p_3$ . The integral curve in that case has a positive slope, and may therefore intersect the  $p_2 - p_3$  plane; that is,  $p_1$  may become extinct. That the presence of an alternative prey may have such an effect has been experimentally verified, and the mechanism is obvious upon reflection.

**5.5. Embryonic growth** (Ref. 6). Consider a free embryo in the presence of a limited supply of nutriment (yolk). Suppose that the rate at which it consumes this is  $ap + bpn$ , where  $n$  is the nutriment at time  $t$ .

Let the toxic effect of wastes be  $-cpP$ , where

$$P = \int_0^t p dt$$

The differential equations of the system are

$$\left. \begin{aligned} \frac{dp}{dt} &= \tau(ap + bpn) - hp^2 - cpP \\ \frac{dn}{dt} &= -ap - bpn \end{aligned} \right\} \quad (1)$$

The solution in parametric form is

$$\left. \begin{aligned} n &= \left( n_0 + \frac{a}{b} \right) e^{-bP} - \frac{a}{b} \\ p &= \frac{\tau(n_0 b + a)}{h - b} (e^{-bP} - e^{-hP}) + \left( p_0 - \frac{c}{h^2} \right) e^{-hP} + \frac{c}{h^2} - \frac{cP}{h} = F(P) \\ t &= \int_0^P \frac{dS}{F(S)} \end{aligned} \right\} \quad (2)$$

The function  $n$  vanishes when

$$P = \frac{1}{b} \log \left( 1 + \frac{n_0 b}{a} \right)$$

If the reserve  $n_0$  is so inadequate that

$$\tau(n_0 b + a) < p_0 h$$

then  $dp/dt < 0$  at  $t = 0$  and the embryo dies. If the converse inequality holds,  $p$  increases to a maximum before decreasing. It is reasonable to assume that the egg is mature and hatches at or near the maximum. If this is also to correspond to the time of disappearance of  $n$ , we have a relation between  $p_0$  and  $n_0$ .

$$p_0 = \frac{1}{h} \left[ - \left( \frac{c}{h} + \frac{ab\tau}{h-b} \right) \left( 1 + \frac{n_0 b}{a} \right)^{h/b} + \frac{h\tau(n_0 b + a)}{h-b} + \frac{c}{h} \right] \quad (3)$$

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