

## On the Theory of Optical Rotatory Power

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**Measured energy in Japan**  
David von Seggern  
(vonneg@seismo.unr.edu) University of Nevada  
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The article by Thorne Lay and Hiroo Kanamori is an editorial comment on the article by David von Seggern.

By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck ball. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon, later becomes released in a new event. Perhaps calculations of one added that in, while another's calculations did not. E.M.C.

Written by Edgar McCarroll, 14 July 2012 19:59

Rossini,<sup>18</sup> while the values for the olefins are obtained by combining the heat of hydrogenation<sup>14</sup> with the heat of formation of the resulting paraffin. In the case of ethylene, precise heat of combustion data<sup>19</sup> are available and the value used is a compromise one. The remaining calculations were made using the data and methods described in this and the preceding paper.<sup>6</sup> All values of the constants of formation are based on H<sub>2</sub> gas and  $\beta$ -graphite. The contribution due to nuclear spin is omitted from all entropies. In obtaining the values listed in Tables V and VI the following constants were used either in the present work or that of Rossini.

For  $\text{H}_{2(g)} + 1/2\text{O}_{2(g)} = \text{H}_2\text{O}_{(l)}$ ,  
 $\Delta H^\circ_{298.1} = -63.313 \pm 0.01$  kcal./mole,

$\text{C}_{(\beta\text{-graphite})} + \text{O}_{2(g)} = \text{CO}_{2(g)}$ ,  
 $\Delta H^\circ_{298.1} = -94.24 \pm 0.10$  kcal./mole,

$\text{C}_{(\text{diamond})} = \text{C}_{(\beta\text{-graphite})}$ ,  
 $\Delta H^\circ_{298.1} = -0.22 \pm 0.07$  kcal./mole,

<sup>18</sup> Rossini, Nat. Bur. Stand. J. Research **13**, 21 (1934); **15**, 357 (1935); J. Chem. Phys., **3** 438 (1935).

<sup>19</sup> Rossini, Nat. Bur. Stand. J. Research **17**, 629 (1936).

1 kcal. = 1000 cal. = 4183.3 int. joules;

for  $\text{H}_2$ ,  $S^\circ_{298.1} = 31.23$  cal./deg. mole

and  $(H^\circ_{298.1} - H^\circ_0) = 2.028$  kcal./mole;

for  $\text{C}_{(\beta\text{-graphite})}$ ,  $S^\circ_{298.1} = 1.36$  cal./deg. mole

and  $(H^\circ_{298.1} - H^\circ_0) = 0.25$  kcal./mole.

In Table VI some of the values have been obtained by graphical interpolation. The values for 450, 1000 and 1500°K were directly calculated while those calculated for 298.1 and 763°K (in Tables III and V) were also used in making the interpolations. The slope of the curve at 298.1°K was made to correspond to the known  $\Delta H^\circ$  at that temperature. It should be noted that the values in Table VI are not sufficiently precise to allow accurate differences to be taken. Thus heat contents and heat capacities must be calculated separately if other than very rough estimates are desired.

The data in Table VI should be useful in obtaining equilibrium constants for a large number of hydrocarbon reactions.

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## On the Theory of Optical Rotatory Power

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The Born theory of optical activity in quantum-mechanical form is simplified with the aid of certain approximations. It leads to a simple expression for the rotatory parameter of an active molecule in terms of the geometrical configuration and the polarizability tensors of its constituent groups. Optical anisotropy of the component groups and inhibited internal rotation are found to play an

important role in determining rotatory power. The proposed theory has points of similarity both with the polarizability theories of Gray, de Mallemann, and Boys and also with Kuhn's specialization of Born's classical theory of optical activity. To illustrate its use, the absolute configuration and the specific rotation of *d*-secondary butyl alcohol are calculated.

### I

**A** PHYSICAL theory of optical activity was first formulated by Fresnel,<sup>1</sup> who attributed the phenomenon to circular double refraction. In seeking a structural explanation in crystals he postulated a helicoidal arrangement of the atoms, anticipating the screw axis revealed by modern x-ray investigations of crystal structure.

This type of structural explanation was inadequate to account for the optical activity of liquids and solutions, discovered by Biot.<sup>2</sup> It was necessary to attribute the optical rotatory power of a liquid to a characteristic structure of its component molecules, themselves, rather than to their arrangement. The principles of stereochemistry, enunciated by Le Bel and van't

<sup>1</sup> Fresnel, Bull. Soc. Philomat., p. 147 (1824).

<sup>2</sup> Biot, Bull. Soc. Philomat., p. 190 (1815).

Hoff,<sup>3</sup> led to the important empirical rule that the absence of a plane or center of symmetry was a necessary condition for molecular rotatory power. Drude<sup>4</sup> made an attempt to develop a theory of optical rotatory power both in crystals and liquids, based upon the classical theory of dispersion. However, he was forced to postulate the existence of electric charges constrained to vibrate in helicoidal paths, a point of view not substantiated by modern views of molecular structure.

A satisfactory molecular theory of optical rotatory power was first formulated by Born<sup>5</sup> in the frame of the classical oscillator theory of dispersion. In Born's theory, optical rotatory power is to be found in a second-order term of the dispersion formula, arising from the retardation of the radiation field over the space occupied by an active molecule. A theory similar to that of Born was almost simultaneously proposed by Oseen<sup>6</sup> and certain refinements were introduced by Gans.<sup>7</sup> The classical theory has been extensively applied by Kuhn,<sup>8</sup> using a special model consisting of a pair of anisotropic dispersion oscillators. Recently Born<sup>9</sup> has applied the theory to a model consisting of four isotropic oscillators. With the advent of quantum mechanics, Born's theory was reformulated on the basis of the quantum-mechanical theory of dispersion.<sup>10</sup> It is here that an adequate theory of rotatory power, free from the defects of the artificial oscillator theory, is to be sought. We shall endeavor to put the quantum-mechanical theory into manageable form with the aid of certain approximations.

Paralleling the Born theory, a theory of rotatory power, similar in principle, but starting

directly from the forced vibrations produced in a molecule by the radiation field, has been developed by Gray,<sup>11</sup> de Mallemann,<sup>12</sup> and Boys.<sup>13</sup> We shall refer to this theory as the polarizability theory of optical activity, since it allows the expression of the rotatory power of a molecule in terms of the configuration and polarizabilities of its constituent groups. We shall show how the quantum-mechanical formulation of the Born theory leads directly to the polarizability theory when certain reasonable approximations are introduced. The initial term in the polarizability theory, which we believe to be chiefly responsible for rotatory power, has not, however, been considered by other writers on the polarizability theory, since they have either treated the groups constituting an active molecule as optically isotropic or as possessing optical axes of symmetry along the bonds linking them to an asymmetric carbon atom. The formula, which we shall obtain involves the interaction of pairs of optically anisotropic groups. Its analog in the oscillator theory is to be found in Kuhn's specialization of Born's classical formula. However, anisotropic polarizable groups replace the hypothetical dispersion oscillators, and the coupling parameter is explicitly calculated from the electrostatic interaction of the groups.

## II

Optical rotatory power in a dispersive medium can be formally attributed to a difference in its refractive indices,  $n_r$  and  $n_l$ , for right and left circularly polarized light. A beam of plane polarized light may be regarded as a superposition of two right and left circularly polarized components of equal intensity. A phase difference between the two circular components is set up in an optically active medium, which is equivalent to a rotation of the plane of polarization of their resultant plane polarized wave. The angle,  $\vartheta$ , through which the plane of polarization is rotated per centimeter of path is given by

$$\vartheta = (\pi/\lambda_0)(n_r - n_l), \quad (1)$$

where  $\lambda_0$  is the wave-length of the light in vacuum.

<sup>3</sup> Le Bel, *Bull. Soc. Chim.* **22**, 337 (1874); van't Hoff, *La Chimie dans L'Espace* (1875).

<sup>4</sup> Drude, *Theory of Optics*, English translation (Longmans, 1902), p. 400.

<sup>5</sup> Born, *Physik. Zeits.* **16**, 251 (1915); *Optik* (Springer, Berlin, 1930).

<sup>6</sup> Oseen, *Ann. d. Physik* **48**, 1 (1915).

<sup>7</sup> Gans, *Zeits. f. Physik* **17**, 353 (1923); **27**, 164 (1924); *Ann. d. Physik* **79**, 548 (1926).

<sup>8</sup> W. Kuhn, *Zeits. f. physik. Chemie* **B4**, 14 (1929); *Ber.* **63**, 190 (1930); *Trans. Faraday Soc.* **26**, 293 (1930). Kuhn and Freudenberg, *Drehung der Polarisationsebene des Lichtes* (Leipzig, 1932).

<sup>9</sup> Born, *Proc. Roy. Soc. London* **A150**, 84 (1935); Oke, *ibid.* **153**, 339 (1935).

<sup>10</sup> Rosenfeld, *Zeits. f. Physik* **52**, 161 (1928); Born and Jordan, *Elementare Quantenmechanik* (Springer, Berlin, 1930), p. 250.

<sup>11</sup> Gray, *Phys. Rev.* **7**, 472 (1916).

<sup>12</sup> de Mallemann, *Rev. Gen. Sci.* **38**, 453 (1927).

<sup>13</sup> Boys, *Proc. Roy. Soc. London* **A144**, 655, 675 (1934).

From the standpoint of the electromagnetic theory,<sup>5, 10</sup> the optical properties of a substance may be characterized by the manner in which its electric polarization  $\mathbf{P}$  and magnetic polarization  $\mathbf{M}$  are related to the field vectors of an electromagnetic wave. In an isotropic optically active medium these relations have the following form

$$\begin{aligned}\mathbf{P} &= \chi_e \mathbf{E} + \sigma \mathbf{H} - (\rho/c) \partial \mathbf{B} / \partial t, \\ \mathbf{M} &= \chi_m \mathbf{H} + \sigma \mathbf{E} + (\rho/c) \partial \mathbf{E} / \partial t,\end{aligned}\quad (2)$$

where  $\mathbf{E}$  is the electric vector,  $\mathbf{H}$  the magnetic vector and  $\mathbf{B}$  the magnetic induction.  $\chi_e$  and  $\chi_m$  are the ordinary electric and magnetic susceptibilities, and  $\rho$  is a constant which determines the rotatory power of the medium. The constant  $\sigma$  does not influence the rotatory power and is of no importance for our purposes. The rotation in radians per centimeter of a plane polarized wave is given by

$$\vartheta = 16\pi^3 \rho / \lambda_0^2. \quad (3)$$

It is associated with a corresponding difference in the refractive indices for right and left circularly polarized light, but the decomposition of the plane polarized wave into circular components is unessential. The specific rotation,  $[\alpha]$ , in degrees per decimeter per gram of active substance per cubic centimeter is equal to  $1800\vartheta/\pi M$ , where  $M$  is the molecular weight and  $v$  is the volume occupied by a mole of the substance.

$$[\alpha] = 2.880 \times 10^4 (\pi^2 \rho v / M \lambda_0^2). \quad (4)$$

The constant  $\rho$  can be related to a molecular rotatory parameter  $g$ . We shall presently show that the average electric moment,  $\mathbf{u}_{00}'$ , induced in an active molecule by a plane electromagnetic wave can be expressed in the following form

$$\mathbf{u}_{00}' = \alpha \mathbf{F} + \gamma (\mathbf{a}_1 \times \mathbf{F}) + g \nabla \times \mathbf{F}, \quad (5)$$

where  $\mathbf{a}_1$  is a unit vector normal to the wave front and  $\mathbf{F}$  is the internal electric vector of the light. The Lorentz field, equal to  $(n^2+2)\mathbf{E}/3$  where  $n$  is the refractive index, is a fairly good approximation to  $\mathbf{F}$ , even in polar liquids for frequencies equal to or greater than those of the visible spectrum. From Maxwell's equation,  $\nabla \times \mathbf{E} = -(1/c) \partial \mathbf{B} / \partial t$ , and the definition of  $\mathbf{P}$  as the density of electric moment, we see that the rotatory part of the electric polarization is equal

to  $-[(n^2+2)/3v](Ng/c) \partial \mathbf{B} / \partial t$ . By comparison with Eq. (1), we obtain

$$\rho = \frac{n^2+2}{3} \frac{Ng}{v}, \quad (6)$$

where  $N$  is Avogadro's number. The specific rotation may then be written in the form

$$[\alpha] = 2.880 \times 10^4 \frac{\pi^2 N}{M \lambda_0^2} \frac{n^2+2}{3} g. \quad (7)$$

If we insert numerical values for the constants,  $[\alpha]_D$ , the specific rotation for the  $D$  line of sodium,  $\lambda_0 = 5893\text{\AA}$ , may be calculated from the formula

$$[\alpha]_D = 4.960 \times 10^{37} \frac{n^2+2}{3M} g. \quad (8)$$

If the angstrom instead of the centimeter is employed as the unit of length in the calculation of the rotatory parameter,  $g$ , which has dimensions of length to the fourth power, we may write

$$[\alpha]_D = 4.960 \times 10^5 \frac{n^2+2}{3M} g, \quad (9)$$

$g$ , of course, depends upon the frequency of the light, but varies slowly outside regions of anomalous rotatory dispersion.

### III

We shall now undertake the calculation of the molecular rotatory parameter  $g$ , following the general outlines of the theory of Born.<sup>10</sup> We consider a polyatomic molecule situated in a Lorentz cavity in a dispersive medium of refractive index  $n$ , through which a plane electromagnetic wave of frequency,  $\nu$ , is passing. We suppose that the ground electronic state of the molecule is non-degenerate, although the ground state as a whole may have vibrational degeneracy, which is unimportant for the dispersion. The orientation of the molecule, that is to say the orientation of the average configuration of its atomic nuclei, is assumed to be fixed relative to a set of mutually orthogonal unit vectors,  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , and  $\mathbf{a}_3$ , specifying the directions of the wave normal, electric vector, and magnetic vector of the wave. Later we average over all molecular orientations. By the principle of spectroscopic stability, this is equiva-

lent to averaging over spatial quantum numbers. The Lorentz field  $\mathbf{F}$  at a point,  $\mathbf{R}$ , referred to some convenient origin, may be written

$$\mathbf{F} = \mathbf{a}_2 F \cos 2\pi[\nu t - \mathbf{R} \cdot \mathbf{a}_1/\lambda], \quad (10)$$

where the amplitude  $F$  is equal to the product of  $(n^2+2)/3$  and the amplitude  $\mathbf{E}$  of the electric vector. The field  $\mathbf{F}$  may be derived from the following vector potential

$$\begin{aligned} \mathbf{F} &= -(1/c)\partial\mathbf{A}/\partial t \\ \mathbf{A} &= -\mathbf{a}_2(cF/2\pi\nu) \sin 2\pi[\nu t - \mathbf{R} \cdot \mathbf{a}_1/\lambda]. \end{aligned} \quad (11)$$

From the quantum-mechanical theory of dispersion,<sup>14</sup> we obtain the following expression for the electric moment induced in the ground state of the molecule by the electromagnetic field.

$$\begin{aligned} \mu_{00}' &= -\frac{eF}{4\pi i m h \nu} \sum_n' \left\{ \frac{\mathbf{u}_{0n} \mathbf{p}_{n0}^+ \cdot \mathbf{a}_2 - \mathbf{u}_{n0} \mathbf{p}_{0n}^+ \cdot \mathbf{a}_2}{\nu_{n0} + \nu} \right. \\ &\quad \times \exp(2\pi i[\nu t - \mathbf{R}_0 \cdot \mathbf{a}_1/\lambda]) \\ &\quad - \frac{\mathbf{u}_{0n} \mathbf{p}_{n0}^- \cdot \mathbf{a}_2 - \mathbf{u}_{n0} \mathbf{p}_{0n}^- \cdot \mathbf{a}_2}{\nu_{n0} - \nu} \\ &\quad \left. \times \exp(-2\pi i[\nu t - \mathbf{R}_0 \cdot \mathbf{a}_1/\lambda]) \right\}, \end{aligned} \quad (12)$$

where  $\mathbf{R}_0$  specifies the position of the molecular center of gravity and the sum extends over all excited states of the molecule, associated with the spectroscopic frequencies  $\nu_{n0}$ . An integral over continuous parts of the spectrum is implied in the summation. The constants  $h$ ,  $e$ , and  $m$  are Planck's constant, the electronic charge, and the electronic mass. The quantities,  $\mathbf{u}_{n0}$ , are the matrix elements of the electric moment of the molecule, and  $\mathbf{p}_{n0}^+$  and  $\mathbf{p}_{n0}^-$  are matrix elements of operators defined below.

$$\begin{aligned} \mathbf{u} &= \sum_s e \mathbf{r}_s = \sum_s \mathbf{u}_s, \\ \mathbf{p}^+ &= \sum_s \exp(-2\pi i \mathbf{r}_s \cdot \mathbf{a}_1/\lambda) \mathbf{p}_s \\ &= \mathbf{p} - \frac{2\pi i}{\lambda} \sum_s \mathbf{a}_1 \cdot \mathbf{r}_s \mathbf{p}_s, \quad (13) \\ \mathbf{p}^- &= \sum_s \exp(+2\pi i \mathbf{r}_s \cdot \mathbf{a}_1/\lambda) \mathbf{p}_s \\ &= \mathbf{p} + \frac{2\pi i}{\lambda} \sum_s \mathbf{a}_1 \cdot \mathbf{r}_s \mathbf{p}_s, \end{aligned}$$

<sup>14</sup> Sommerfeld, *Atombau und Spektrallinien, Wellenmechanischer; Ergänzungsband*, p. 193, Vieweg, Braunschweig (1929); Dirac, *Quantum Mechanics*, Chap. XII, (Oxford, 1930).

where the sum extends over all electrons of the molecule,  $\mathbf{r}_s$  is the position of electron  $s$  relative to the molecular center of gravity,  $\mathbf{p}_s$  is its momentum operator, and  $\mathbf{p}$  the total electronic momentum. It is sufficient to retain only the first two terms in the expansions of  $\mathbf{p}^+$  and  $\mathbf{p}^-$ . The second terms are responsible for optical activity. Substitution of the expressions (13) in Eq. (12) yields after some algebraic simplification

$$\begin{aligned} \mu_{00}' &= [\alpha \cdot \mathbf{a}_2 + \gamma \cdot \mathbf{a}_2] F \cos 2\pi[\nu t - \mathbf{R}_0 \cdot \mathbf{a}_1/\lambda] \\ &\quad + (2\pi/\lambda) \mathbf{g} \cdot \mathbf{a}_2 F \sin 2\pi[\nu t - \mathbf{R}_0 \cdot \mathbf{a}_1/\lambda], \end{aligned} \quad (14)$$

where the tensors  $\alpha$ ,  $\gamma$ , and  $\mathbf{g}$  are written in dyadic form below. The expression for  $\alpha$ , the familiar polarizability tensor, is simplified by use of the relation,  $e\mathbf{p}_{n0} = 2\pi i m \nu_{n0} \mathbf{u}_{n0}$ ,

$$\begin{aligned} \alpha &= -\frac{2}{h} \sum_n' \frac{\nu_{n0} \mathbf{u}_{0n} \mathbf{u}_{n0}}{\nu_{n0}^2 - \nu^2}, \\ \gamma &= \frac{e}{\lambda m h \nu} \sum_{r,s} \sum_n' \frac{\nu_{n0}}{\nu_{n0}^2 - \nu^2} [(\mathbf{u}_r)_{0n} \mathbf{a}_1 \cdot (\mathbf{r}_s \mathbf{p}_s)_{n0} \\ &\quad - (\mathbf{u}_r)_{n0} \mathbf{a}_1 \cdot (\mathbf{r}_s \mathbf{p}_s)_{0n}], \end{aligned} \quad (15)$$

$$\begin{aligned} \mathbf{g} &= \frac{e}{2\pi i m h} \sum_{r,s} \sum_n' \\ &\quad \times \frac{(\mathbf{u}_r)_{0n} (\mathbf{a}_1 \cdot \mathbf{r}_s \mathbf{p}_s)_{n0} - (\mathbf{u}_r)_{n0} (\mathbf{a}_1 \cdot \mathbf{r}_s \mathbf{p}_s)_{0n}}{\nu_{n0}^2 - \nu^2}. \end{aligned}$$

We need not concern ourselves further with  $\gamma$ , since it does not contribute to the rotation but simply gives rise to the term  $\sigma \mathbf{H}$  in Eq. (2). The tensor  $\mathbf{g}$  gives rise to the rotatory power. We now average  $\mu_{00}'$  over all orientations of the molecule with respect to the fixed set of axes ( $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$ ). We make use of the formulas

$$\begin{aligned} ((\mathbf{v}_1 \cdot \mathbf{a}_1)(\mathbf{v}_2 \cdot \mathbf{a}_1)(\mathbf{v}_3 \cdot \mathbf{a}_2))_{Av} &= 0, \\ ((\mathbf{v}_1 \cdot \mathbf{a}_2)(\mathbf{v}_2 \cdot \mathbf{a}_1)(\mathbf{v}_3 \cdot \mathbf{a}_2))_{Av} &= 0, \\ (\mathbf{v}_1 \cdot \mathbf{a}_3)(\mathbf{v}_2 \cdot \mathbf{a}_1)(\mathbf{v}_3 \cdot \mathbf{a}_2) &= -\frac{1}{6} \mathbf{v}_1 \cdot (\mathbf{v}_2 \times \mathbf{v}_3), \end{aligned} \quad (16)$$

where  $\mathbf{v}_1$ ,  $\mathbf{v}_2$ , and  $\mathbf{v}_3$  are any set of vectors fixed in the molecule. Thus the vector  $(\mathbf{g} \cdot \mathbf{a}_2)_{Av}$  is equal to  $(\mathbf{a}_3 \cdot \mathbf{g} \cdot \mathbf{a}_2)_{Av} \mathbf{a}_3$  and  $(\gamma \cdot \mathbf{a}_2)_{Av}$  is equal to  $(\mathbf{a}_3 \cdot \gamma \cdot \mathbf{a}_2)_{Av} \mathbf{a}_3$ . From Eq. (11), we may calculate

$$\begin{aligned} \nabla \times \mathbf{F}_0 &= (2\pi/\lambda) F \mathbf{a}_3 \sin 2\pi[\nu t - \mathbf{R}_0 \cdot \mathbf{a}_1/\lambda], \\ \mathbf{a}_1 \times \mathbf{F}_0 &= F \mathbf{a}_3 \cos 2\pi[\nu t - \mathbf{R}_0 \cdot \mathbf{a}_1/\lambda]. \end{aligned} \quad (17)$$

Denoting  $(\mathbf{a}_3 \cdot \mathbf{g} \cdot \mathbf{a}_2)_{\text{av}}$  by  $g$  and  $(\mathbf{a}_3 \cdot \boldsymbol{\gamma} \cdot \mathbf{a}_2)_{\text{av}}$  by  $\gamma$ , we obtain from Eqs. (14) and (16)

$$(\mathbf{u}_{00'})_{\text{av}} = \alpha \mathbf{F}_0 + \gamma (\mathbf{a}_1 \times \mathbf{F}_0) + g \nabla \times \mathbf{F}_0, \quad (18)$$

which is identical with Eq. (5). The constant  $\alpha$  is the mean polarizability of the molecule, equal to one-third of the sum of the diagonal elements of  $\alpha$ . In carrying out the averaging of  $\mathbf{a}_3 \cdot \mathbf{g} \cdot \mathbf{a}_2$ , we may first express the tensors  $(\mathbf{r}_s \mathbf{p}_s)_{n0}$  in terms of an orthogonal set of unit vectors fixed in the molecule and then sum the result.

$$g = -\frac{e^2}{12\pi i m h} \sum_{r,s} \sum_n' \frac{(\mathbf{r}_r)_{0n} \cdot (\mathbf{r}_s \times \mathbf{p}_s)_{n0} - (\mathbf{r}_r)_{n0} \cdot (\mathbf{r}_s \times \mathbf{p}_s)_{0n}}{\nu_{n0}^2 - \nu^2}. \quad (19)$$

If we remember that the magnetic moment  $\mathbf{m}$  of the molecule is given by

$$\mathbf{m} = (e/2mc) \sum_s \mathbf{r}_s \times \mathbf{p}_s \quad (20)$$

we may write  $g$  in a slightly different form

$$g = \frac{c}{6\pi i h} \sum_n' \frac{\mathbf{m}_{0n} \cdot \mathbf{u}_{n0} - \mathbf{m}_{n0} \cdot \mathbf{u}_{0n}}{\nu_{n0}^2 - \nu^2}. \quad (21)$$

An analysis similar to the preceding one except for the fact that the retardation of the wave over the molecule may be neglected entirely yields for  $\mathbf{m}_{00'}$ , the average magnetic moment induced in the ground state of the molecule.

$$(\mathbf{m}_{00'})_{\text{av}} = (g/c) \partial \mathbf{F}_0 / \partial t + \gamma \mathbf{F}_0. \quad (22)$$

Eqs. (19) and (21) are Born's equations<sup>10</sup> for the optical rotatory parameter, put in a slightly more explicit form.

We shall attempt to simplify the general formula for  $g$  with the aid of certain approximations, which will allow its calculation from the properties of the groups or radicals constituting the molecule. We suppose that the molecule consists of  $N$  groups coupled to an inactive central group by valence bonds. The central group may be the asymmetric carbon atom in simple optically active organic compounds or it may be a hydrocarbon radical of rigid configuration as in the spirane compounds. The subsidiary groups may themselves be optically active as in the sugars or other compounds containing two or more asymmetric carbon atoms. When this is true, the group in question may be further decomposed into secondary groups.

The sum over all electrons in Eq. (19) may be replaced by a sum over the  $N+1$  groups by means of the following relations

$$\begin{aligned} \sum_r (\mathbf{u}_r)_{0n} &= \sum_{i=1}^{N+1} \mathbf{u}_{0n}^{(i)}, \\ \sum_s (\mathbf{r}_s \times \mathbf{p}_s)_{n0} &= \sum_{k=1}^{N+1} \left[ \mathbf{R}_k \times \mathbf{p}_{n0}^{(k)} + \frac{2mc}{e} \mathbf{m}_{n0}^{(k)} \right], \\ \mathbf{m}_{n0}^{(k)} &= \frac{e}{2mc} \sum_s^{(k)} (\mathbf{r}_s^{(k)} \times \mathbf{p}_s)_{n0}, \end{aligned} \quad (23)$$

where  $\mathbf{u}^{(i)}$  is the electric moment of group  $i$ ,  $\mathbf{p}^{(k)}$  is the total electronic momentum of group  $k$ , and  $\mathbf{m}^{(k)}$  is its total magnetic moment referred to the center of gravity of group  $k$ , situated at a point  $\mathbf{R}_k$  from center of gravity of the molecule as a whole. Since nondiagonal matrix elements of any constant vanish, the shift in origin from the center gravity of the molecule to the center of gravity of the group does not affect the matrix elements  $\mathbf{u}_{0n}^{(i)}$ . The replacement of the sums over electrons by sums over groups is strictly valid only when electron exchange between groups can be neglected, since otherwise the assignment of a definite number of electrons to a given group is ambiguous. However, when structural resonance involving two or more of the groups is absent, it is an adequate approximation to neglect exchange between groups except for the bonding electrons between each subsidiary group and the central group. The ambiguity in the assignment of electrons to the various groups may then be removed by including the bonding electrons between a subsidiary group and the central group in the sums (23) for both groups with a factor,  $\frac{1}{2}$ , in each case. In the absence of structural resonance, electron exchange between subsidiary groups can be neglected. From Eqs. (19), (21) and (23) and the relation,  $e\mathbf{p}_{n0}^{(k)} = 2\pi i m \nu_{n0} \mathbf{u}_{n0}^{(k)}$ , we obtain

$$\begin{aligned} g &= g^{(0)} + g^{(1)} + \sum_{k=1}^{N+1} g_k, \\ g^{(0)} &= \frac{1}{6h} \sum_{i \neq k=1}^{N+1} \sum_n' \frac{\nu_{n0}}{\nu_{n0}^2 - \nu^2} [\mathbf{R}_k \cdot (\mathbf{u}_{0n}^{(i)} \times \mathbf{u}_{n0}^{(k)}) \\ &\quad + \mathbf{R}_k \cdot (\mathbf{u}_{n0}^{(i)} \times \mathbf{u}_{0n}^{(k)})], \\ g^{(1)} &= \frac{c}{6\pi i h} \sum_{i \neq k=1}^{N+1} \sum_n' \frac{\mathbf{m}_{0n}^{(k)} \cdot \mathbf{u}_{n0}^{(i)} - \mathbf{m}_{n0}^{(k)} \cdot \mathbf{u}_{0n}^{(i)}}{\nu_{n0}^2 - \nu^2}, \end{aligned} \quad (24)$$

where  $g_k$  is the internal rotatory parameter of group  $k$ , itself. In simple optically active compounds the  $g_k$  vanish. If the retardation of the electromagnetic wave over all parts of each group is approximated by its value at the center of gravity of the group,  $g^{(1)}$  vanishes, and the rotatory parameter reduces to  $g^{(0)}$ . We shall make this approximation in the present article, remarking that it is common to all previous theories of optical activity based upon localized oscillators.

For the calculation of  $g^{(0)}$ , we start with approximate molecular wave functions  $\psi_n^0$ , which are the eigenfunctions of a Hamiltonian including the interactions of the subsidiary groups with the central group, but not the interactions of the subsidiary groups among themselves. Because of the interaction between the subsidiary groups the wave functions will undergo a perturbation. We suppose that the subsidiary groups are sufficiently distant from each other that it is sufficient to retain only the dipole term in the potential,  $V$ , of their interaction

$$V = \sum_{i>j=1}^N \mathbf{u}^{(i)} \cdot \mathbf{T}_{il} \cdot \mathbf{u}^{(j)}, \quad (25)$$

$$\mathbf{T}_{il} = \frac{1}{R_{il}^3} \left[ 1 - 3 \frac{\mathbf{R}_{il} \mathbf{R}_{il}}{R_{il}^2} \right].$$

The use of this potential, of course, requires the neglect of electron exchange between the subsidiary groups. If any of the states  $n$  are degenerate, we select for the corresponding  $\psi_n^0$ , a set of linear combinations of the eigenfunctions of the degenerate state, which diagonalize  $V$ . This can in general be done with real linear combinations and it will be convenient to have all the  $\psi_n^0$  real in subsequent calculations.

The spectrum associated with the approximate wave functions  $\psi_n^0$  is, of course, not the actual spectrum of the molecule, since the mutual perturbation of the secondary groups has been neglected. However, in the absence of structural resonance the two spectra will not be expected to differ much. Thus the spectrum of an organic radical retains to a large extent its identity in different compounds of which it is a substituent and is influenced considerably only by groups which are its nearest neighbors, in this case the

central group. The approximate additivity of atomic refractions and atomic volumes of organic compounds are related to this fact. Moreover, for the same reasons, the zero-order spectrum can be characterized by sets of quantum numbers  $n_1, n_2, \dots, n_{N+1}$  associated with the individual groups of the molecule, corresponding to a set of normalized orthogonal wave functions,  $\psi_n^0 = \psi_{n_1, n_2, \dots, n_{N+1}}^0$  with the following property

$$[f(q_i)]_{n'} = [f(q_i)]_{n_i'} \prod_{l \neq i=1}^{N+1} \delta_{n_l' n_l}, \quad (26)$$

where  $f(q_i)$  is any function of the coordinates,  $q_i$ , of the electrons of group  $i$  alone. This amounts to assuming that the wave functions,  $\psi_n^0$ , can be expressed in the form,  $\prod_{i=1}^{N+1} \varphi_{n_i}(q_i)$ , where  $\varphi_{n_i}(q_i)$  depends only on the coordinates of the electrons of group  $i$ . The function  $\varphi_{n_i}(q_i)$  may be regarded as a generalized "self-consistent field" function of group  $i$  as a whole in the presence of the central group. Thus exchange between the subsidiary groups and the central group is really neglected. Accordingly the above wave functions would be poor in the neighborhood of the valence bonds and quite unsuitable for the calculation of bond energies. However, since the number of bonding electrons between the central group and the subsidiary groups is small in comparison with the total number of electrons in the molecule, these wave functions should be adequate for the calculation of the optical properties of the molecule, unless the bonding electrons make abnormally large contributions. It is to be remarked that electron exchange within the groups themselves is not neglected. The perturbation of the wave functions of the molecule resulting from the mutual interaction of the subsidiary groups may be calculated by the usual methods. The perturbed wave functions  $\psi_{n_1, n_2, \dots, n_{N+1}}$  may be written to the first order in the following form when use is made of Eqs. (25) and (26).

$$\psi_{n_1, \dots, n_{N+1}} = \psi_{n_1, \dots, n_{N+1}}^0 - \frac{1}{h} \sum_{l>j=1}^N \sum_{n' l n' j} \frac{(V_{jl})_{n_j' n_l'; n_j n_l} \psi_{n_1^0 \dots n_j' \dots n_l' \dots n_{N+1}}}{\nu_{n_j' n_j} + \nu_{n_j' n_l}}. \quad (27)$$

Calculation of  $\mathbf{u}_{n0}^{(i)} \times \mathbf{u}_{n0}^{(k)}$  with these wave functions leads to the result,

$$\begin{aligned} \mathbf{u}_{0n}^{(i)} \times \mathbf{u}_{n0}^{(k)} = & -\frac{1}{h} \sum_{n_k'} \left\{ \frac{(V_{ik})_{n_i 0; 0 n_k'} (\mathbf{u}^{(i)}_{0 n_i} \times \mathbf{u}^{(k)}_{n_k' 0})}{\nu_{n_k' 0} - \nu_{n_i 0}} \right. \\ & + \left. \frac{(V_{ik})_{n_i n_k'; 0 0} (\mathbf{u}^{(i)}_{0 n_i} \times \mathbf{u}^{(k)}_{0 n_k'})}{\nu_{n_k' 0} + \nu_{n_i 0}} \right\} \prod_{l=1 \neq i}^{N+1} \delta_{n_l 0} \quad (28) \\ & -\frac{1}{h} \sum_{n_i'} \left\{ \frac{(V_{ik})_{n_i' 0; 0 n_k} (\mathbf{u}^{(i)}_{0 n_i'} \times \mathbf{u}^{(k)}_{n_k 0})}{\nu_{n_i' 0} - \nu_{n_k 0}} \right. \\ & + \left. \frac{(V_{ik})_{0 0; n_i' n_k} (\mathbf{u}^{(i)}_{n_i' 0} \times \mathbf{u}^{(k)}_{n_k 0})}{\nu_{n_i' 0} + \nu_{n_k 0}} \right\} \prod_{l=1 \neq k}^{N+1} \delta_{n_l 0}. \end{aligned}$$

With the wave functions (27), the sum in Eq. (24), defining  $g^{(0)}$ , of course, becomes a multiple sum over  $n_1, n_2, \dots, n_{N+1}$  and  $\nu_{n0}$  becomes  $\nu_{n_1 0} + \nu_{n_2 0} + \dots + \nu_{n_{N+1} 0}$ , where  $\nu_{n_i 0}$  is a frequency of group  $i$ . Substituting Eq. (28) in Eq. (24), and making use of the fact that all  $\mathbf{u}_{n0}^{(i)}$  are real and thus equal to  $\mathbf{u}_{0n}^{(i)}$ , since the  $\psi_n^0$  have been chosen real, we obtain after some algebraic simplification

$$\begin{aligned} g^{(0)} = & -\frac{2}{3h^2} \sum_{i \neq k=1}^N \sum_{n_i} \sum_{n_k}' \\ & \times \frac{\nu_{n_i 0} \nu_{n_k 0} (\mathbf{u}^{(i)}_{n_i 0} \cdot \mathbf{T}_{ik} \cdot \mathbf{u}^{(k)}_{n_k 0}) \mathbf{R}_k \cdot (\mathbf{u}^{(i)}_{n_i 0} \times \mathbf{u}^{(k)}_{n_k 0})}{(\nu_{n_i 0}^2 - \nu^2)(\nu_{n_k 0}^2 - \nu^2)}. \quad (29) \end{aligned}$$

Actually the initial substitution of (28) in (24) yields two sums, one over  $n_i$  and  $n_k'$  and one over  $n_i'$  and  $n_k$ . Since the labeling is entirely arbitrary, both are relabeled as sums over  $n_i$  and  $n_k$ , and combined. We remark that the polarizability tensor of group  $i$  has the form

$$\alpha^{(i)} = -\frac{2}{h} \sum_{n_i}' \frac{\nu_{n_i 0} \mathbf{u}^{(i)}_{n_i 0} \mathbf{u}^{(i)}_{n_i 0}}{\nu_{n_i 0}^2 - \nu^2}, \quad (30)$$

so that we may write

$$\begin{aligned} \alpha^{(i)} \mathbf{T}_{ik} \cdot \alpha^{(k)} = & -\frac{4}{h^2} \sum_{n_i} \sum_{n_k}' \\ & \times \frac{\nu_{n_i 0} \nu_{n_k 0} (\mathbf{u}^{(i)}_{n_i 0} \cdot \mathbf{T}_{ik} \cdot \mathbf{u}^{(k)}_{n_k 0}) \mathbf{u}^{(i)}_{n_i 0} \mathbf{u}^{(k)}_{n_k 0}}{(\nu_{n_i 0}^2 - \nu^2)(\nu_{n_k 0}^2 - \nu^2)}. \quad (31) \end{aligned}$$

From Eqs. (16), (29) and (31), we see that  $g^{(0)}$

may be expressed in the following form

$$g^{(0)} = - \sum_{i \neq k=1}^N ((\mathbf{a}_3 \cdot \alpha^{(i)} \cdot \mathbf{T}_{ik} \cdot \alpha^{(k)} \cdot \mathbf{a}_2) (\mathbf{R}_k \cdot \mathbf{a}_1))_{Av}, \quad (32)$$

a formula which allows the calculation of  $g^{(0)}$  from the polarizability tensors of the subsidiary groups and the geometry of the molecule. Eq. (32) would have been the first term in Boys' polarizability theory, had he not assumed the groups to be optically isotropic. By a very tedious extension of the perturbation calculation, the next approximation of the polarizability theory, considered by de Malleman, involving sets of three groups has been verified, although small additional terms connected with frequency shifts caused by the perturbation appear. The Boys term would appear only if third-order terms were included in the perturbed wave function (27). If the groups are optically isotropic, the Boys term is the first one which does not vanish. Although the anisotropy of the groups might introduce only a moderate correction to the Boys term itself, it cannot be neglected for it enters into a much earlier approximation. It is our opinion that the Boys term and the one preceding it are seldom very important in comparison with the initial term in the polarizability theory given by Eq. (32). This will be substantiated by calculations based upon reasonable assumptions as to the geometry of the active molecule. Nevertheless, we see that the polarizability theory is correct in principle, since it can be obtained from Born's quantum-mechanical theory with not unreasonable methods of approximation. Unless the bonding electrons between the central group and the subsidiary groups make disproportionately large contributions to the optical rotatory power, which does not seem likely, the polarizability theory should be adequate as a good first approximation.

Let us suppose that  $\mathbf{b}_1^{(i)}, \mathbf{b}_2^{(i)}, \mathbf{b}_3^{(i)}$  are unit vectors defining the principal optical axes of group  $i$  and  $\mathbf{b}_1^{(k)}, \mathbf{b}_2^{(k)}, \mathbf{b}_3^{(k)}$  a set of vectors specifying those of group  $k$ . Then from Eqs. (16) and either (29) or (32),  $g^{(0)}$  may be expressed as follows.

$$\begin{aligned} g^{(0)} = & -\frac{1}{6} \sum_{i \neq k=1}^N \sum_{r,s=1}^3 \alpha_{rr}^{(i)} \alpha_{ss}^{(k)} \\ & \times (\mathbf{b}_r^{(i)} \cdot \mathbf{T}_{ik} \cdot \mathbf{b}_s^{(k)}) \mathbf{R}_k \cdot (\mathbf{b}_r^{(i)} \times \mathbf{b}_s^{(k)}), \quad (33) \end{aligned}$$



where  $\alpha_{rr}^{(i)}$  and  $\alpha_{ss}^{(k)}$  are the elements of the diagonalized polarizability tensors of the two groups. If each group possesses an optical axis of symmetry, the formula may be simplified. We may designate the symmetry axes of the two groups  $i$  and  $k$  by unit vectors,  $\mathbf{b}_i$  and  $\mathbf{b}_k$ . The polarizability tensor of group  $i$  may be written in the form

$$\alpha^{(i)} = \alpha_i \left[ (1 - \beta_i/3) + \beta_i \mathbf{b}_i \mathbf{b}_i \right],$$

$$\beta_i = \frac{\alpha_{11}^{(i)} - \alpha_{22}^{(i)}}{\alpha_i} = 3 \frac{\alpha_{11}^{(i)} - \alpha_{22}^{(i)}}{\alpha_{11}^{(i)} + 2\alpha_{22}^{(i)}} \quad (34)$$

where  $\alpha_i$  is the mean polarizability of group  $i$  and  $\alpha_{11}^{(i)}$  and  $\alpha_{22}^{(i)}$  are the components of  $\alpha^{(i)}$  parallel and perpendicular to  $\mathbf{b}_i$ . After some algebraic simplification the averaging process indicated in Eq. (32) yields with the use of polarizability tensors of the above form

$$g^{(0)} = -\frac{1}{6} \sum_{i>k=1}^N \alpha_i \alpha_k \beta_i \beta_k G_{ik} \mathbf{R}_{ik} \cdot (\mathbf{b}_i \times \mathbf{b}_k), \quad (35)$$

$$G_{ik} = \mathbf{b}_i \cdot \mathbf{T}_{ik} \cdot \mathbf{b}_k = \frac{1}{R_{ik}^3} \left[ \mathbf{b}_i \mathbf{b}_k - 3 \frac{(\mathbf{b}_i \cdot \mathbf{R}_{ik})(\mathbf{b}_k \cdot \mathbf{R}_{ik})}{R_{ik}^2} \right],$$

$$\mathbf{R}_{ik} = \mathbf{R}_k - \mathbf{R}_i,$$

where the sum includes each pair of groups only once, as indicated by the notation  $i > k$ . Each term in  $g^{(0)}$  vanishes not only if either group is isotropic but also if  $\mathbf{b}_i$  and  $\mathbf{b}_k$  are coplanar, since in the latter case the three vectors  $\mathbf{R}_{ik}$ ,  $\mathbf{b}_i$  and  $\mathbf{b}_k$  are coplanar and the triple vector product vanishes. Thus any pair of groups,  $i$  and  $k$ , with optical axes of symmetry parallel to the respective bonds linking them to an asymmetric carbon atom, make no contribution to  $g^{(0)}$ . Such symmetry would result if there were free rotation of polyatomic groups about the bonds linking them to an asymmetric carbon atom, and it would be necessary to seek the rotatory power of the group in the next approximation of the polarizability theory, which is usually very small. However, by means of an hypothesis about restricted rotation, we shall see that  $g^{(0)}$  cannot be expected to vanish. We suppose that the ground electronic state of the molecule comprises a number of torsional vibrational states,  $v$ , associated with rotation around the valence bonds between the subsidiary groups and the

central group. Some of these states may be degenerate and some closely spaced relative to  $kT$ , the product of Boltzmann's constant and the absolute temperature. The parameter  $g^{(0)}$  for the molecule will then be the average value of the  $g_v^{(0)}$  of these states

$$g^{(0)} = \frac{\sum_v g_v^{(0)} e^{-E_v/kT}}{\sum_v e^{-E_v/kT}}, \quad (36)$$

where  $E_v$  is the energy of state,  $v$ , referred to the lowest of the states as zero. In particular if there are  $n$  equivalent sharp minima in the potential function associated with the relative orientations of the groups, permitted by rotation about the bonds linking them to the central group, while all other minima are higher by an energy difference large relative to  $kT$ ,  $g^{(0)}$  may be approximately calculated by the formula

$$g^{(0)} = \frac{1}{n} \sum_{n=1}^n g_r^{(0)}, \quad (37)$$

where  $g_r^{(0)}$  is to be calculated from Eq. (35) for the orientation  $r$  and the sum extends over all orientations of equal potential energy. This formula implies that the amplitude of vibration in lowest vibrational state of each minimum is so small that fluctuations in the orientations can be neglected. We shall presently employ this formula in the calculation of  $g^{(0)}$  for simple optically active molecules. As an illustration let us consider secondary butylalcohol. We tentatively assume that due to van der Waals forces and polarization forces, there are two orientations of equal energy for the C—C bond of the ethyl group, which makes a tetrahedral angle with the bond to the asymmetric carbon atom, C\*. In one of these, the axis of the ethyl group is coplanar with the C\*—OH bond and in the other with the C\*—CH<sub>3</sub> bond. The third possible orientation in which the axis is coplanar with the C\*—H bond is supposed to correspond to a minimum higher than the other two by an energy fairly large relative to  $kT$ . If this orientation had a probability equal to that of the other,  $g^{(0)}$  would vanish. These assumptions are entirely reasonable in the light of recent evidence<sup>15</sup> relative to restricted rotation in ethane itself. Due probably

<sup>15</sup> Kemp and Pitzer, J. Am. Chem. 59, 276 (1937).

to van der Waals forces between the hydrogen atoms, there appear to be three equivalent relative orientations of the methyl groups, separated by energy barriers greater than 3000 cal. When some of the hydrogens of each methyl group are replaced by larger radicals with greater capacity for van der Waals attraction than hydrogen, not only would the sharpness of the minima be enhanced, but also differences in depth large relative to  $kT$  at ordinary temperatures could be expected.

Some general remarks about the equations of the present theory are perhaps appropriate at this point. The rotatory parameter may be written in the form

$$g = \frac{e^2}{m} \sum_n' \frac{g_{n0}}{\nu_{n0}^2 - \nu^2}, \quad (38)$$

where the  $g_{n0}$  satisfy the following sum rule according to the general theory of Born.<sup>5, 10</sup>

$$\sum_n' g_{n0} = 0. \quad (39)$$

It may be readily verified by use of familiar commutation rules that the approximate  $g_{n0}^{(0)}$  entering into the expression for  $g^{(0)}$  of Eq. (24) satisfy the sum rule (39). Thus the polarizability theory is in accord with the general theory in this respect. The use of Eq. (29) with appropriate modification to allow for radiation damping, is not to be recommended in the immediate neighborhood of an absorption band of the molecule, because of the likelihood of poor convergence of the perturbation calculation under these conditions. However, the Cotton effect, involving a change in sign of the parameter  $g$  in the neighborhood of an absorption band, can be qualitatively understood from Eqs. (29), (33) and (35). The absorption frequencies associated with different components of the polarizability tensor of a group will in general have different selection rules. It is easy to see that these selection rules could operate to produce a change in sign in one or more of the constants  $\beta_i$  of Eqs. (34) and (35), with a resultant change of sign in  $g^{(0)}$  when certain absorption bands are traversed. Objection<sup>8, 9</sup> has been raised to the polarizability theories of de Malleman, Gray and Boys on the ground that measurements of circular dichroism show that the major contributions to the rotatory

parameter  $g$  generally come from relatively weak absorption bands of the molecule, whereas the major contributions to the polarizability of the molecule as a whole, come from the strongest bands. This objection seems untenable as far as the general polarizability theory is concerned, for several reasons. In the first place, a large part of the existent data on circular dichroism refers to complicated molecules and is difficult to interpret from the standpoint of structure. It may very well happen that the strongest absorption bands are associated with groups which do not contribute to the sum of Eq. (35) because of unfavorable orientation of their optical axes relative to those of other groups in the molecule. In the second place, there is nothing in the polarizability theory which requires the  $g_{n0}$  of Eq. (24) to be proportional to the  $f_{n0}$ , the corresponding dispersion  $f$  values of the molecule. The  $f_{n0}$  of the molecule as a whole involve sums of the  $f$  values of its constituent groups, while the  $g_{n0}$  values, according to the polarizability theory, involve products of the  $f$  values of the groups. From Eq. (29), it is evident that overlapping regions in the absorption bands of the zero-order spectra of two groups might well make the most important contributions to the rotatory parameter.<sup>16</sup> Although no general statement can be made, there is no reason to suppose that such overlapping ordinarily occurs in the absorption bands of maximum intensity for two groups of different structure.

### III

In order to apply the present theory, it is necessary to have information about the polarizability tensors,  $\alpha^{(i)}$ , of the groups constituting an active molecule. The mean polarizability,  $\alpha_i$ , equal to one-third the diagonal sum of  $\alpha^{(i)}$ , may be estimated from the atomic refractions,  $A_s$ , of the atoms constituting the group by means of the formula,

$$\alpha_i = \frac{3}{4\pi N} \sum_s^{(i)} A_s, \quad (40)$$

where the sum extends over all atoms of the

<sup>16</sup> Degeneracy arising from such overlapping has been taken care of in the perturbation calculation by choosing for the  $\Psi_n^{(0)}$  linear combinations which diagonalize  $V$ .

group.<sup>17</sup> The determination of the anisotropy ratios,  $\beta_i$ , defined by Eq. (34), and the relative orientation of the optical axes of the subsidiary groups in an active molecule is considerably more difficult. The polarizability tensors entering into Eq. (35) for  $g^{(0)}$  are calculated with a wave function which includes the interaction of each subsidiary group with the central group, but not the mutual interaction of the subsidiary groups themselves. When the central group is an asymmetric carbon atom, it is reasonable to estimate the anisotropy induced in a subsidiary group  $R$  by the central group from a study of the optical properties of the compound  $RCH_3$ . In the case of a polyatomic group with intrinsic anisotropy, the properties of the compound  $RH$  may also be used. For this purpose, we shall turn to measurements of the degree of depolarization of light scattered by the vapors of the compounds  $RCH_3$  and  $RH$  at an angle of  $90^\circ$  to the incident beam. The Kerr effect also furnishes information about molecular anisotropy, but there are few data on the vapors of nonpolar substances, and its interpretation in the case of polar substances is complicated by the role of the permanent dipole moment.

The principal polarizabilities of a molecule,  $\alpha_{11}$ ,  $\alpha_{22}$ , and  $\alpha_{33}$  are related to the degree of depolarization,<sup>18</sup>  $\Delta$ , of light scattered by the vapor, in the following manner.

$$\begin{aligned} [(\alpha_{11} - \alpha_{22})^2 + (\alpha_{11} - \alpha_{33})^2 + (\alpha_{22} - \alpha_{33})^2] / \alpha^2 \\ = 90\Delta / (6 - 7\Delta), \quad (41) \\ \alpha = \frac{1}{3}[\alpha_{11} + \alpha_{22} + \alpha_{33}]. \end{aligned}$$

We may define a general anisotropy ratio  $\beta$  by the relation.

$$\begin{aligned} \beta^2 = [(\alpha_{11} - \alpha_{22})^2 + (\alpha_{11} - \alpha_{33})^2 + (\alpha_{22} - \alpha_{33})^2] / 2\alpha^2, \\ \beta = \pm (45\Delta / (6 - 7\Delta))^{\frac{1}{2}}. \quad (42) \end{aligned}$$

When the molecule possesses an optical axis of symmetry,  $\alpha_{22} = \alpha_{33}$ , the above definition of  $\beta$  becomes identical with that of Eq. (34), employed for the groups of an active molecule. The positive or negative sign is to be taken

TABLE I.

	$\alpha \cdot 10^{24}(\text{cc})$	$\beta$
$\text{CH}_3$	2.25	0.35
$\text{C}_2\text{H}_5$	4.07	.35
OH	1.03	.35
Cl	2.35	.35
$\text{NH}_2$	1.78	.25*
COOH	2.86	.55
$\text{C}_6\text{H}_5$	9.89	-.58

according to whether the polarization ellipsoid is prolate or oblate.

Although we shall not attempt to develop a molecular theory of anisotropy at the present time, we shall suppose, for purposes of approximation, that in a molecule consisting of two groups, not only the mean polarizability but also each component of its polarizability tensor may be expressed as the sum of the corresponding components of polarizability tensors of the two groups, referred to a common set of axes. If the groups have a common axis of symmetry, directed along the bond between them, the anisotropy ratio,  $\beta$ , of the molecule may be expressed in the form  $(\alpha_1\beta_1 + \alpha_2\beta_2) / (\alpha_1 + \alpha_2)$ , where  $\alpha_1$ ,  $\alpha_2$ ,  $\beta_1$  and  $\beta_2$  are the mean polarizabilities and anisotropy ratios of the respective groups. Although the anisotropy ratio of each group may be expected to depend somewhat upon the nature of the other, we shall arbitrarily assume that  $\text{CH}_3$  has the same anisotropy ratio in different compounds  $\text{CH}_3\text{R}$  in which  $\text{R}$  is a monatomic group or a simple polyatomic group. From the degree of depolarization,  $\Delta$ , of ethane, 0.016, we calculate a value of  $\beta$  equal to 0.35. According to the above considerations this is also the anisotropy ratio of one methyl group in the presence of another. The compounds  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{Cl}$  have values of  $\Delta$  equal to 0.016 and 0.015, respectively. Assuming the anisotropy ratio of  $\text{CH}_3$  to be the same in these compounds as in  $\text{C}_2\text{H}_6$ , we assign a value of  $\beta$  equal to 0.35 to both OH and Cl, bonded to carbon. It is of course questionable to treat the group OH in methylalcohol as having an axis of symmetry along the C—O bond, although this will be true on the average, since the O—H can doubtless assume three equivalent positions with respect to the three C—H bonds in the methyl group. In the case of polyatomic groups, the anisotropy of which may be expected to be largely internally

<sup>17</sup> Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, Hw. II, 985; Eisenlohr, *Zeits. f. physik. Chemie* **75**, 585 (1910); **79**, 129 (1912).

<sup>18</sup> Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, Eg IIa 88; Eg III, 1204.

determined, we make use of the compounds RH. From formic acid,  $\Delta=0.038$ , we obtain a value of  $\beta$  equal to 0.55 for the carboxyl group. As a rough approximation the carboxyl group may be treated as having an axis of symmetry parallel to a vector joining the oxygen atoms, since the polarizability along this axis doubtless differs from either of the two polarizabilities in a plane perpendicular to it by an amount considerably greater than their own difference. From benzene,  $\Delta=0.042$ , a value of  $\beta$  for the phenyl group of  $-0.58$  is obtained. This value is in substantial agreement with that obtained from measurements of the Kerr effect in benzene vapor.<sup>19</sup> The mean polarizabilities and the anisotropy ratios, estimated in the manner described, for several common organic groups are listed in Table I. The value of  $\beta$  for  $\text{NH}_2$  obtained from the degree of depolarization of methylamine is 0.11. Since the compound has been measured by only one investigator and 0.11 seems rather too low, the value 0.25 is suggested as more probable. Although structural resonance is present in the group  $\text{COOH}$  and  $\text{C}_6\text{H}_5$ , the present theory of rotatory power may be applied to compounds containing these groups, providing their structure is such that resonance cannot extend outside these groups. The estimates of the anisotropy ratios given in Table I are admittedly rough and subject to revision, for not only is the method of calculation rather crude, but also the measurements of depolarization are very sensitive to error. Nevertheless, we believe that they are of the correct magnitude.

For the calculation of the functions  $G_{ik}$  in Eq. (35), it is necessary to know the configuration of the active molecule and its dimensions. For this purpose we use the atomic radii tabulated by Pauling and Huggins.<sup>20</sup> The most important interatomic distances are C—C, 1.54Å; C=C, 1.38Å; C—N, 1.47Å, and C—O, 1.43Å. These distances together with the trigonometric functions of the tetrahedral angle suffice to characterize the geometry of a number of simple organic molecules.

We shall not undertake a systematic calculation of optical rotation in the present article, but we shall illustrate the application of Eqs.

(35) and (37) in the case of secondary butyl-alcohol. The central group is here an asymmetric carbon atom  $\text{C}^*$  and the subsidiary groups are H, OH,  $\text{CH}_3$ , and  $\text{C}_2\text{H}_5$ . We suppose that the groups H, OH, and  $\text{CH}_3$  have optical axes of symmetry directed along their bonds to  $\text{C}^*$ . Because of its small size and polarizability and since the C—H bond is somewhat polar, it would probably be better to treat H as a part of the central group. In the present case we shall see that it does not contribute directly to the rotatory parameter. We could assign to the ethyl group an optical axis directed along the C—C bond as in ethane. However, the central group,  $\text{C}^*$ , might be expected to tilt the optical axis (not the geometrical axis) of the ethyl group toward itself. There is evidence in the degree of depolarization of propane for an effect of this sort. A reasonable assignment of the optical axis would be to place it in the plane of  $\text{C}^*$  and the C—C bond of the ethyl inclined at one-half the tetrahedral angle to the C—C bond. As outlined in an earlier section we assume two orientations of the ethyl group of equal probability, in which the C—C bond of the ethyl group is coplanar with the  $\text{C}^*\text{—OH}$  and with the  $\text{C}^*\text{—CH}_3$  bonds, respectively. We shall designate these orientations as *a* and *b*. The third possible orientation beneath the C—H bond is assumed to be of negligible probability because of a small Boltzmann factor. This does not mean that there is not free rotation of the ethyl group through this position in the sense of the organic chemist's use of the term since the potential barriers hindering the rotation of the ethyl group doubtless correspond to low activation energies.

From Eq. (35) we see that the mutual interaction of the three groups H, OH, and  $\text{CH}_3$  cannot contribute to the rotatory parameter since the optical axes of each pair terminate in  $\text{C}^*$  and are therefore coplanar with the corresponding  $\mathbf{R}_{ik}$ . Moreover, no contribution can arise from the interaction of the groups  $\text{C}_2\text{H}_5$  and H, if the ethyl group has two equivalent orientations beneath the C— $\text{CH}_3$  and C—OH bonds, since  $\mathbf{R}_{ik} \cdot (\mathbf{b}_i \times \mathbf{b}_k)$  merely changes sign in passing from position *a* to position *b* and all other factors remain the same, with a resultant cancellation of the contributions from the two

<sup>19</sup> H. A. Stuart, *Molekülstruktur* (Berlin, 1934), p. 173.

<sup>20</sup> Pauling and Huggins, *Zeits. f. Krist.* **87**, 205 (1934).

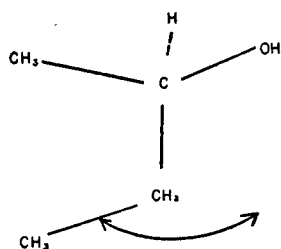


FIG. 1. Configuration of *d*-secondary butyl alcohol. The hydrogen atom bonded to the asymmetric carbon is behind the plane of the paper.

positions. In position *a*, the only other non-vanishing term in  $g^{(0)}$  arises from the groups  $C_2H_5$  and  $CH_3$ , while in position *b*, the only other contribution arises from the groups  $C_2H_5$  and  $OH$ . If we designate the values of  $g^{(0)}$  in the two positions by  $g_a^{(0)}$  and  $g_b^{(0)}$  (omitting for simplicity the canceling terms for H), the mean rotatory parameter of the molecule may be expressed in the form,

$$(g^{(0)})_A = \frac{1}{2}(g_a^{(0)} + g_b^{(0)}),$$

$$g_a^{(0)} = -\frac{1}{6}\alpha_1\alpha_2\beta_1\beta_2G_{12}\mathbf{R}_{12} \cdot (\mathbf{b}_1 \times \mathbf{b}_2), \quad (43)$$

$$g_b^{(0)} = -\frac{1}{6}\alpha_1\alpha_3\beta_1\beta_3G_{13}\mathbf{R}_{13} \cdot (\mathbf{b}_1 \times \mathbf{b}_3),$$

where the subscripts 1, 2, and 3 in the expressions for  $g_a^{(0)}$  and  $g_b^{(0)}$  refer to the groups ethyl, methyl, and hydroxyl, respectively. The distances  $C^*-CH_3$ , and  $C^*-OH$  are taken as 1.54Å and 1.43Å, respectively, and the center of the ethyl group is located at the midpoint of its C—C bond, a distance of 0.77Å from either carbon. The distance of the asymmetric carbon atom from the ethyl carbon to which it is bonded is 1.54Å. The bond angles are all taken as the tetrahedral angle,  $109^\circ 28'$ . These data suffice to fix the configuration of the groups in the two orientations, *a* and *b*, and allow the calculation of  $G_{12}$ ,  $G_{13}$ ,  $\mathbf{R}_{12} \cdot (\mathbf{b}_1 \times \mathbf{b}_2)$ , and  $\mathbf{R}_{13} \cdot (\mathbf{b}_1 \times \mathbf{b}_3)$  once we have fixed the optical axis  $\mathbf{b}_1$  of the ethyl group. We shall first assume it to be directed along the C—C bond. For the dextro configuration, Fig. 1, in which the groups  $CH_3$ ,  $OH$ , and H appear in clockwise order when the molecule is viewed with the ethyl group toward the observer, the following values of  $g_a^{(0)}$ ,  $g_b^{(0)}$ , and  $(g^{(0)})_A$  are obtained

$$g_a^{(0)} = 9.88 \times 10^{-3} A^4,$$

$$g_b^{(0)} = -4.86 \times 10^{-3}, \quad (44)$$

$$(g^{(0)})_A = +2.51 \times 10^{-3}.$$

When the optical axis  $\mathbf{b}_1$  of the ethyl group is

tilted to an angle of  $54^\circ 44'$  with the C—C bond, remaining in the plane of this bond and the  $C^*-C_2H_5$  bond, the dextro configuration remains unchanged, but somewhat different values of  $g^{(0)}$  are obtained

$$g_a^{(0)} = 4.26 \times 10^{-3} A^4,$$

$$g_b^{(0)} = -2.12 \times 10^{-3}, \quad (45)$$

$$(g^{(0)})_A = 1.07 \times 10^{-3}.$$

The refractive index of pure secondary butylalcohol corresponds to a value of  $(n^2+2)/3$  of 1.32 at  $20^\circ\text{C}$ . Substitution of the values of  $(g^{(0)})_A$  calculated above, into Eq. (8) leads to the following values for the specific rotation of *d*-secondary butylalcohol.

$$[\alpha]_{D^{20}} = 21.9^\circ \quad (g = 2.51 \times 10^{-3})$$

$$= 9.5^\circ \quad (g = 1.07 \times 10^{-3})$$

$$= 13.9^\circ \quad (\text{observed}).$$

The observed rotation<sup>21</sup> lies between the values corresponding to the two extreme orientations of the optical axis of the ethyl group. The calculated values are definitely of the correct magnitude, although their numerical values might be shifted somewhat by small changes in the relative distribution of the ethyl group between positions *a* and *b* and by small reorientations of the optical axes of the groups. Probably the most serious defect in the calculation lies in the treatment of the hydroxyl group as axially

<sup>21</sup> To meet the possible objection that the rotatory power of pure secondary butylalcohol might be materially influenced by intermolecular interaction through the alcoholic hydroxyl groups, we call attention to the fact  $3[\alpha]_{D^{20}}/(n^2+2)$  has approximately the same value in the pure alcohol as in its solutions in benzene and carbon disulfide. (Pickard and Kenyon, J. Chem. Soc. 105, 883 (1914).)

<i>d</i> -secondary butylalcohol	
Solvent	$[3/(n^2+2)][\alpha]_{D^{20}}$
pure alcohol	10.4°
benzene	10.3
carbon disulfide	11.1

The assumption that in secondary butylalcohol the two orientations of the ethyl group, below the hydroxyl group and below the methyl group, are of about equal probability is entirely reasonable. The van der Waals energy of the ethyl group and the methyl group is doubtless a little greater than that of the ethyl group and hydroxyl. However, this difference will tend to be compensated by the energy of polarization of the ethyl group by the hydroxyl dipole and by the fact that the minimum distance between the ethyl and hydroxyl groups is a little smaller than that between the ethyl and methyl groups. It is interesting to remark that an abnormally strong interaction between the ethyl and hydroxyl group, fixing the ethyl group beneath the hydroxyl would leave the proposed absolute configuration of *d*-secondary butylalcohol unchanged, but would lead to far too high a value of  $[\alpha]_{D^{20}}$  unless the optical axes of the groups were reoriented.

symmetric relative to the C—O bond, since the hydroxyl hydrogen may produce some anisotropy in the plane perpendicular to this bond. Whether this is an important effect must await subsequent calculations. The absolute configuration of *d*-secondary butylalcohol shown in Fig. 1 must be regarded as tentative for these reasons, but it is probably correct.

The next approximation in the polarizability theory has not been calculated, but the third approximation has been estimated from Boys' formula,<sup>3</sup> with the center of the ethyl group fixed on the C\*—C<sub>2</sub>H<sub>5</sub> bond at a distance of 2.17Å from the asymmetric carbon atom, a position which is actually its projection on this bond in any orientation. The carbon hydrogen distance is taken as 1.05Å. The centers of the groups C<sub>2</sub>H<sub>5</sub>, CH<sub>3</sub>, OH, and H are then situated at the vertices of a tetrahedron, the edges of which are approximately the pairwise sums of the distances 1.79; 1.25; 1.18; and 0.92Å. With these dimensions the Boys term makes a contribution of less than 0.1° to  $[\alpha]_D^{20}$ . Boys' term is very sensitive to the dimensions of the molecule. He himself obtained a much larger value for secondary butylalcohol, but with very improbable values for the inter-group distances. It is interesting to note, that both the present theory and that of Boys lead to the same absolute configuration for *d*-secondary butylalcohol. This will not always be the case, however, and it does not seem possible to predict absolute configurations by Boys' simple rule based upon the sizes of the substituent groups.

The example which has just been discussed serves to illustrate the possibilities of the present theory. At a later time a systematic application of the theory will be presented. The presence of inhibited rotation will generally be of considerable importance in determining the rotatory power of a molecule. It seems likely that it may be the key to an understanding of the dependence of rotatory power on temperature and upon the solvent in which the active molecule is dissolved.<sup>22</sup> From Eq. (36), the rotatory parameter would be expected to be sensitive to temperature if two or more orientations are associated with energies differing by an amount comparable with  $kT$ . Again a change of solvent could very

well alter the probability distribution of a group among several possible orientations and so produce a marked change in the rotatory power of a molecule.

The present theory is, of course, crude in many respects and can never be expected to give more than a first approximation. A major improvement could be made if it were possible to avoid treating the electric moments induced in the groups of an active molecule as though they were localized at the centers of gravity. Moreover, we remark again that the theory may be expected to break down badly whenever there is structural resonance between groups.

*Note added in Proof:* It should be emphasized that the present theory is not limited by the special stereochemical model we have employed for secondary butylalcohol. Although the model is a plausible one, it is not entirely above reproach, because of the possibility of steric hindrance arising from repulsive forces between the groups. For this reason, we shall discuss two other models.

(1) Repulsive forces between the methyl groups make the *cis*-position, orientation (b), one of small probability. Under these conditions, it is reasonable to suppose that the potential energy has a minimum of appreciable depth only for orientation (a), in which the ethyl group lies beneath the hydroxyl group. The corresponding values of  $[\alpha]_D^{20}$  for the two orientations of the optical axis of the ethyl group are 86° and 38°. Neither value is in good agreement with the experimental rotation. The dextro configuration remains as shown in Fig. 1.

(2) Steric hindrance from both the methyl group and the hydroxyl group constrains the ethyl group to lie beneath the hydrogen, bonded to the asymmetric carbon. The corresponding values of  $[\alpha]_D^{20}$  are -44° and -19°. The latter value agrees fairly well with the rotation of the laevo alcohol. The absolute configuration is inverted and Fig. 1 represents the laevo form.

Our first model appears to give the best agreement with experiment and indeed seems to be the most probable one. On the other hand certain writers have suggested that steric hindrance may occur in compounds of the type of secondary butylalcohol. Thus Stuart, *Phys. Rev.* **38**, 1372 (1931), advances the view that in *n*-butane, the *cis*-position of the terminal methyl groups is one of small probability because of steric hindrance. However, his conclusion is based upon thermochemical evidence, the interpretation of which is not entirely unambiguous. From x-ray scattering experiments, Debye, *Physik. Zeits.* **31**, 142 (1930), concludes that 1,2-dichlorethane exists almost exclusively in the *trans* form. However, repulsive forces between the dipoles of the C—Cl bonds are sufficient to account for this fact.

It would be highly desirable to investigate the stereochemistry of secondary butylalcohol by the electron diffraction method. Once the most probable locations of the ethyl group are determined, the present theory of rotatory power can be applied without ambiguity.

<sup>22</sup> Beckmann and Cohen, *J. Chem. Phys.* **4**, 784 (1936).