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Theories of Optical Rotatory Power

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1. INTRODUCTION

BY optical rotatory power is meant the property of a medium to rotate the plane of polarization of linearly polarized light that is transmitted through it. The first effect of this kind was discovered by Arago in 1811. He found that quartz had this property in the direction of the optical axis, the direction along with ordinary double refraction vanishes.

The sense of rotation bears a fixed relation to the direction of propagation of the light, so if the light traverses the same medium once in each of two opposite directions—as when it is returned through the active medium by reflection at a mirror—the net rotation just vanishes. A substance is said to show positive rotation if the plane of polarization is turned in a clockwise sense as viewed by an observer into whose eye the light is entering. The rotation is proportional to the thickness of the active medium traversed and the rotatory power is defined as the angle through which the plane of polarization is turned per unit path in the medium.

The discovery of optically active liquids is due to Biot.[1] Here, since there is no preferred orientation of the molecules the effect must be due to a structural peculiarity of the individual molecules. The modern theories which relate this property of a fluid to the structure of the individual molecules is the subject of this report.[2]

Conventionally the rotatory power of a medium is given in degrees/decimeter. This quantity will be denoted by φ. In the c.g.s. system it is measured in radian/cm, and evidently one has to multiply the value in degree/cm by $\pi/1800$ to convert to radian/cm.

Another measure of rotatory power called the specific rotatory power is also in common use. It is the rotatory power divided by the density of the active material in gram/cm^3. It will be denoted by $[\varphi]$. It is more common in the experimental literature to denote these quantities by α and $[\alpha]$, respectively, but this departure from the common notation is introduced here because it is desired to reserve the letter α for molecular polarizability corresponding to another well-established usage.

Still another measure of rotatory power is in common use which is called the molecular rotatory power. It is defined as being the specific rotatory power $[\varphi]$ in degree/decimeter per gram/cm^3, multiplied by one one-hundredth of the molecular weight and is denoted by $[M]$. That is,

$$[M]=[\varphi]/100; \qquad [\varphi]=\varphi/\rho, \tag{1}$$

in which ρ is the density and M the molecular weight.

In the theoretical formulas the combination $\varphi M/\rho$ often occurs where φ is the rotatory power in radian/cm. It is convenient to remember the relation,

$$\varphi M/\rho=(\pi/18)[M]. \tag{2}$$

The basic feature of propagation in an optically active medium that is responsible for rotating the plane of polarization is circular double refraction. This was recognized by Fresnel.[3] A substance is said to be double refracting if in a given direction the phase velocity of propagation of light waves is different for two different states of polarization. In the case of optical activity the velocity is different for right and left circularly polarized waves respectively.

Although Fresnel's work greatly antedates the electromagnetic theory of light it is convenient to discuss the situation at once in terms of the modern theory. In the electromagnetic theory there are two vectors associated with the wave that are transverse to the direction of propaga-

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[1] Biot, Bull soc. philomath. 190 (1815).

[2] The book by T. M. Lowry, *Optical Rotatory Power* (Longmans, Green, 1935), contains a very thorough account of the experimental and empirical side of the subject. In this report the general principles are briefly reviewed and the main emphasis is devoted to a review of the applications of dispersion theory to our understanding of the phenomenon.

[3] Fresnel, Ann. Chim. Phys. **28**, 147 (1925); *Oeuvres complètes* **1**, 731, Paris (1866).

tion. These are the electric induction, **D**, and the magnetic induction, **B**. Suppose the wave is traveling in the direction of the unit vector **k** with a velocity c/n where n is the index of refraction. If we introduce unit vectors, **i** and **j**, mutually orthogonal and orthogonal to **k** in such a way that (**i**, **j** **k**) form the basis of a right-handed coordinate system, then **D** and **B** may be written in the forms,

$$\mathbf{D}=R\{\mathbf{D}_0e^{i\psi}\},\quad \mathbf{B}=R\{\mathbf{B}_0e^{i\psi}\},\qquad \psi=2\pi\nu(t-n\mathbf{k}\cdot\mathbf{r}/c), \tag{3}$$

where $\mathbf{D}_0$ and $\mathbf{B}_0$ are constant vectors, expressible in terms of **i** and **j**, and ψ is the phase of the wave at time t and place **r**, it being supposed that ν is the frequency of the wave. The symbol $R\{\ \}$ means that the real part of the complex expression is to be taken.

For a right circularly polarized wave the constant amplitude will be of the form of a constant multiplying into $(\mathbf{i}+i\mathbf{j})$, say $D(\mathbf{i}+i\mathbf{j})$ for, on taking the real part of this expression, we have

$$D(\mathbf{i}\cos\psi-\mathbf{j}\sin\psi).$$

When $\psi=0$ the vector **D** is parallel to **i** and as times goes on ψ increases and the vector **D** rotates in the clockwise sense as viewed by an observer faced in the $-\mathbf{k}$ direction, that is, faced so the light enters his eyes. Similarly a left circularly polarized wave is represented by a constant multiplying into $(\mathbf{i}-i\mathbf{j})$.

These results contain expression of the fact that circularly polarized light can be regarded as the superposition of two plane polarized waves having the proper phase relation. The factor i in $(\mathbf{i}+i\mathbf{j})$ may be written $e^{i\pi/2}$ from which it is clear that the phase of the linearly polarized constituent along **j** is a quarter-cycle ahead of the linearly polarized constituent along **i**. Similarly in the left circularly polarized wave the component along **j** lags a quarter-cycle behind the component along **i**.

Linearly polarized light may likewise be regarded as arising from the superposition of two circularly polarized waves. Consider the wave made up of a superposition of a right circularly polarized wave with a phase $e^{i\delta}$ and a left circularly polarized wave with a phase $e^{-i\delta}$. The expression for **D** assumes the form,

$$\mathbf{D}\approx R\{(\mathbf{i}+i\mathbf{j})e^{i\delta}+(\mathbf{i}-i\mathbf{j})e^{-i\delta}\}$$
$$=2(\mathbf{i}\cos\delta-\mathbf{j}\sin\delta). \tag{4}$$

For $\delta=0$ this represents a linearly polarized wave whose plane of polarization is given by the vector **i** and for $\delta>0$ the plane of polarization is turned clockwise through an angle δ with respect to the **i** axis.

Now let us suppose that the medium has different refractive indices for right and left circularly polarized waves which may be denoted by n_r and n_l, respectively. Suppose the light enters at the plane $\mathbf{k}\cdot\mathbf{r}=0$ and leaves at the plane $\mathbf{k}\cdot\mathbf{r}=d$, so d is the length of path traversed. Further suppose that the light enters linearly polarized along **i**. At the exit plane the phases of the two components will be

$$\psi_r=2\pi\nu(t-n_rd/c),$$
$$\psi_l=2\pi\nu(t-n_ld/c),$$

so we can write. $(\psi_r,\ \psi_l)=\psi\pm\delta$,

where $\psi=2\pi\nu(t-\tfrac{1}{2}(n_r+n_l)d/c)$

is the phase corresponding to the mean index of refraction and

$$\delta=\pi(n_l-n_r)d/\lambda\qquad(\lambda=c/\nu) \tag{5}$$

arises from the difference of the two indices of refraction.

But as we have seen, an advance in phase δ for the right and a retardation in phase δ of the left circularly polarized components results in their superposing to produce linearly polarized light whose plane of polarization is turned through an angle δ. Hence the rotation per unit path length is δ/d or the rotatory power φ is expressed directly in terms of the difference of the two indices of refraction:

$$\varphi=(\pi/\lambda)(n_l-n_r). \tag{6}$$

In this equation if φ is expressed in degree/decimeter, then the vacuum wave-length λ must be expressed in decimeters and $\pi=180$.

Owing to the fact that λ is very small compared to macroscopic values of d, the quantity d/λ in (5) is large compared to unity and so appreciable rotations are produced in spite of (n_l-n_r) being small compared to unity. It is convenient to remember that the sense of the rotation is that of the circularly polarized component that travels most rapidly.

Just as optical activity is produced as an indirect effect of the difference in velocity of propagation of right and left circularly polarized waves, so also there is an indirect effect, known as circular dichroism, arising from differential absorption of the two kinds of waves. It was discovered by Cotton[4] in 1896. It is well known that in the case of ordinary refraction the refractivity is closely associated with the absorption bands, strong absorption bands producing more refractivity. In the case of optically active liquids the difference (n_l-n_r) is of the order of a few parts in a million. The general connection between refraction and absorption suggests that a difference of this order in the absorption coefficients is all that can be expected. In view of the difficulties surrounding intensity measurements it cannot be expected that such a small difference in absorption can be detected by measuring separately absorption coefficients for the two kinds of circularly polarized light.

Instead we have to look for a differential effect whose very existence is due to the difference in the two absorption coefficients. This is provided by studying the propagation of a linearly polarized wave through the absorbing medium. Let ϵ_l and ϵ_r be the absorption coefficients for left and right circularly polarized waves and write

$$(\epsilon_l,\ \epsilon_r)=\epsilon\pm\epsilon', \tag{7}$$

where ϵ is the mean absorption coefficient and ϵ' is half the difference. Then since the intensity of light varies as $\mathbf{D}^2$, the amplitude of $\mathbf{D}$ is subject to exponential decrease by the factors $e^{-\epsilon_r d/2}$ and $e^{-\epsilon_l d/2}$ for right and left circularly polarized waves respectively after traversing a thickness d of the medium. Hence the two components which initially unite to give a linearly polarized wave are of unequal amplitude after traversing the medium. As a result they recombine to give elliptically polarized light the ellipticity of which is connected with the difference of the two absorption coefficients.

Each amplitude will be reduced by the common factor $e^{-\epsilon d/2}$ corresponding to the mean absorption coefficient, but after going through a thickness d the amplitude will in addition to this factor be given by

$$e^{\epsilon' d/2}(\mathbf{i}+i\mathbf{j})e^{i\delta}+e^{-\epsilon' d/2}(\mathbf{i}-i\mathbf{j})e^{-i\delta}.$$

Denoting by $\mathbf{i}(\delta)$ and $\mathbf{j}(\delta)$ the unit vectors obtained by making a clockwise rotation through δ of the unit vectors $\mathbf{i}$ and $\mathbf{j}$, this can be written

$$\mathbf{i}(\delta)\cosh\epsilon' d/2+i\mathbf{j}(\delta)\sinh\epsilon' d/2. \tag{8}$$

This represents, for $\epsilon>0$, a right elliptically polarized wave whose major amplitude is rotated by δ from the original direction of the linear polarization. The ellipticity is conventionally measured by an angle Ψ whose tangent is equal to the ratio of the minor to the major amplitudes, that is,

$$\tan\Psi=\tanh\epsilon' d/2, \tag{9}$$

if we adopt the convention that the ellipticity is positive for a right elliptically polarized wave and negative for left elliptic polarization.

The observable phenomenon known as circular dichroism consists in this appearance of elliptic polarization when linearly polarized light is partially absorbed in passing through an active medium. In view of the fact that ϵ' will be small compared to ϵ and that we must choose d such that ϵd is not very great in order to have an appreciable amount of light transmitted, we shall always have $\epsilon' d\ll 1$ and therefore

$$\Psi=\tfrac{1}{2}\epsilon' d=\tfrac{1}{4}(\epsilon_l-\epsilon_r)d, \tag{10}$$

so the ellipticity will be proportional to the thickness d. Bruhat[5] has shown that the relative error in measurement of δ and Ψ is a minimum when such a thickness of material is chosen that the amplitude is reduced by the factor e^{-1}, that is the energy reduced by e^{-2}, or to 13.5 percent of its initial value.

2. Electromagnetic Theory

After the general introduction of the preceding section we now turn to the problem of generalizing the ordinary elementary treatments of the electromagnetic theory of light in such a way as to give circular double refraction. The

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[4] Cotton, Ann. Chim Phys. **8**, 347 (1896).

[5] Bruhat, Ann. de physique **3**, 232 (1915).

starting point is, of course, Maxwell's equations:

$$\begin{aligned} &\operatorname{div}\mathbf{D}=0, &&\operatorname{div}\mathbf{B}=0,\\ &\operatorname{curl}\mathbf{E}=-(1/c)\dot{B}, &&\operatorname{curl}\mathbf{H}=(1/c)\dot{D},\\ &\mathbf{D}=E+4\pi\mathbf{P}, &&\mathbf{B}=\mathbf{H}+4\pi\mathbf{I}. \end{aligned} \tag{11}$$

The properties of the medium find their expression entirely in that they give rise to **P**, the electric moment per unit volume and to **I**, the magnetic moment per unit volume. The theory of wave propagation, underlying all kinds of dispersion effects, needs, in addition to Eqs. (11), a connection which relates **P** and **I** to **E** and **H**. This connection will be provided by a detailed application of electrodynamics to a particular model of the material of the medium.

In the simple theory of isotropic media we have

$$\mathbf{P}=\kappa\mathbf{E}, \qquad \mathbf{I}=\kappa'\mathbf{H},$$

where κ and κ' are scalars. Then

$$\begin{aligned} \mathbf{D}&=(1+4\pi\kappa)\mathbf{E}=\epsilon\mathbf{E},\\ \mathbf{B}&=(1+4\pi\kappa')\mathbf{H}=\mu\mathbf{H}, \end{aligned} \tag{12}$$

where ϵ and μ are the usual dielectric constant and magnetic permeability. This simple connection leads, as is well known, to the propagation of waves with an index of refraction given by $n^2=\epsilon\mu$. As a general rule $\kappa'\approx 10^{-4}\kappa$ except for strongly magnetic substances which absorb light anyway, so it is generally permissible to write, $n^2=\epsilon$.

The theory of crystal optics, so far as ordinary double refraction is concerned, is given as a generalization in which κ and κ' are replaced by tensors, although usually κ' is neglected in comparison with κ and the whole refraction regarded as due to the electric polarization.

To get a theory of optical activity we need a different kind of generalization of the material connections. It turns out that the essential point is that there be a part of **P** that is proportional to $\dot{B}$ and a part of **I** that is proportional to $\dot{D}$. We shall assume for the moment that we have a molecular theory which leads to connections of the form

$$\begin{aligned} \mathbf{D}&=\epsilon\mathbf{E}-g\dot{H},\\ \mathbf{B}&=\mathbf{H}+g\dot{E} \end{aligned} \quad \text{or} \quad \begin{aligned} \mathbf{E}&=\epsilon^{-1}\mathbf{D}+\epsilon^{-1}g\dot{B},\\ \mathbf{H}&=\mathbf{B}-\epsilon^{-1}g\dot{D} \end{aligned} \tag{13}$$

and proceed to find solutions of the Maxwell equations using these connections. Every vector may be assumed to be a constant amplitude multiplied into $e^{i\psi}$ where ψ is the phase as in (3). The equations $\operatorname{div}\mathbf{D}=0$ and $\operatorname{div}\mathbf{B}=0$ lead to $\mathbf{k}\cdot\mathbf{D}=0$ and $\mathbf{k}\cdot\mathbf{B}=0$ so **D** and **B** are transverse to the direction of propagation.

Next consider the curl equations. These give

$$\begin{aligned} n\mathbf{k}\times\mathbf{E}&=\mathbf{B},\\ n\mathbf{k}\times\mathbf{H}&=-\mathbf{D} \end{aligned}$$

and the material connections (13) give

$$\begin{aligned} \mathbf{E}&=\epsilon^{-1}\mathbf{D}+i\gamma\mathbf{B},\\ \mathbf{H}&=\mathbf{B}-i\gamma\mathbf{D}, \end{aligned}$$

where $\gamma=2\pi\nu g\epsilon^{-1}$.

With these we may eliminate **E** and **H** from the curl equations and obtain

$$\begin{aligned} n(\epsilon^{-1}\mathbf{k}\times\mathbf{D}+i\gamma\mathbf{k}\times\mathbf{B})&=\mathbf{B},\\ n(-i\gamma\mathbf{k}\times\mathbf{D}+\mathbf{k}\times\mathbf{B})&=-\mathbf{D}. \end{aligned}$$

Written out in terms of two components for **B** and **D** these are four homogeneous equations for the four unknown components. To make them consistent the determinant of their coefficients must vanish. This condition gives an equation for n whose roots give the possible values of the index of refraction. Writing

$$\begin{aligned} \mathbf{D}&=D_1\mathbf{i}+D_2\mathbf{j},\\ \mathbf{B}&=B_1\mathbf{i}+B_2\mathbf{j}, \end{aligned}$$

the equations are

$$\begin{array}{r|l} -n(\epsilon^{-1}D_2+i\gamma B_2)=B_1 & n(i\gamma D_2-B_2)=-D_1\\ n(\epsilon^{-1}D_1+i\gamma B_1)=B_2 & n(-i\gamma D_1+B_1)=-D_2. \end{array}$$

The permissible values of the index of refraction are readily found to be

$$n^{-2}=(\epsilon^{-\frac{1}{2}}\pm\gamma)^2. \tag{14}$$

The two negative roots correspond to propagation in the direction $-\mathbf{k}$ and are not of interest. The two positive roots give the indices for propagation in the direction $+\mathbf{k}$. The root with the positive sign for γ is easily seen to correspond to a solution for **D** and **B** of the form of a right circularly polarized wave, the other to left circular polarization. Since γ is a small quantity compared with unity, it follows therefore that

$$\begin{aligned} n_r&=\epsilon^{\frac{1}{2}}-2\pi\nu g,\\ n_l&=\epsilon^{\frac{1}{2}}+2\pi\nu g. \end{aligned} \tag{15}$$

This result combined with (6) gives a connection between the rotatory power of the medium and the parameter g introduced in (13) as follows:

$$\varphi=(2\pi/\lambda)^2 cg. \tag{16}$$

The next problem is to see what kind of response of the individual molecules to the fields of the light wave is needed to give terms in the macroscopic field equations of the type introduced in (13). The effective electric field acting on a molecule is not only the **E** vector of the macroscopic field theory but an average field due to the neighboring molecules. Lorentz[6] showed that for a medium in which the molecules are distributed at random we have to take for the effective field, **E**′,

$$\mathbf{E}'=\mathbf{E}+(4\pi/3)\mathbf{P}. \tag{17}$$

Similar considerations hold in principle for the magnetic field but as the intensity of magnetization of the medium is practically negligible in comparison with **H** this need not be considered.

Now let us suppose that the theory of the response of individual molecules to the external fields leads to formulas,

$$\begin{aligned}\mathbf{p}&=\alpha\mathbf{E}'-(\beta/c)\dot{H},\\ \mathbf{m}&=+(\beta/c)\dot{E}',\end{aligned} \tag{18}$$

in which **p** is the induced electric moment and **m** is the induced magnetic moment of an individual molecule. The essential point is the introduction of the term involving the parameter β. Here α is the usual polarizability term giving an induced electric moment proportional to the applied electric field.

The total electric and magnetic moments in unit volume are

$$\mathbf{P}=N_1\mathbf{p}, \qquad \mathbf{I}=N_1\mathbf{m}, \tag{19}$$

where N_1 is the number of molecules in unit volume. In case the medium consists of a simple mixture of different kinds of molecules there will be different coefficients α_i and β_i for each species and then **P** and **I** will be given by a sum of terms one for each species each $\mathbf{p}_i$ and $\mathbf{m}_i$ being multiplied by the corresponding N_i, the number of molecules of the ith species present in unit volume.

Combining (19), (18) and (17) one can easily find that the implied connections of **D** and **B** with **E** and **H** are those given by (13) as already assumed. The new result is the connection between the individual molecular parameters α and β and the molar parameters ϵ and g, which turn out to be

$$4\pi N_1\alpha/3=(\epsilon-1)/(\epsilon+2), \tag{20}$$

which is familiar from the ordinary theory of dispersion, and the analogous expression for the rotatory parameter, g,

$$4\pi N_1(\beta/c)/3=g/(\epsilon+2). \tag{21}$$

Using the familiar expression $n^2=\epsilon$ where n is the mean index of refraction and combining (21) with (16) one may arrive at a formula giving a direct connection between the rotatory power and the molecular parameter β:

$$\varphi=\frac{16\pi^3 N_1\beta}{\lambda^2}\cdot\frac{n^2+2}{3}. \tag{22}$$

This is the main result of the electromagnetic theory in that it refers the activity of the medium back to the parameter β. This parameter has to be explained in terms of detailed molecular theories as will be seen in later sections.

From its definition in (18) we see that molecules with a nonvanishing β have the property that an increasing electric field produces a magnetic moment in them, and an increasing magnetic field produces an electric moment. Let us try to visualize how this can come about.

The main effect when the molecule is put in an electric field is that measured by the polarizability α; positive charges are displaced in the direction of **E** and negative charges the other way, the amount being proportional to the field strength, resulting in the production of an induced dipole moment in the molecule. If the electric field is increasing the charges are moving to provide the increasing displacement necessary to go with the increasing dipole moment. Suppose now the molecular structure is such that these flowing charges are not allowed to move directly from their initial to their final positions but are constrained to move in somewhat helical paths so that there is a circulatory component of motion around $\dot{E}$, accompanying the general forward motion in the direction of **E**.

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[6] Lorentz, *Theory of Electrons*, p. 305.

The currents associated with the circulatory component of the motion give rise to a magnetic moment that is proportional to the amount of $\dot{E}$ and in the same direction as E. This is a simple pictorial view of the mechanism underlying the term involving β in the equation for the induced magnetic moment.

Conversely, suppose the molecule is in a changing magnetic field. The changing flux through the molecule sets up induced currents in the molecule, that is, induces a flow of charges around the direction of $\dot{H}$ in the sense given by Lenz' law. The same constraints which previously required a circulatory motion to accompany a general displacement, now will require a displacement of positives one way and negatives the other to accompany the induced circulatory currents. Thus there will be produced a separation of positive and negative charges as a result of the action of the induced currents. This is the simple pictorial view of the production of electric moment by a changing magnetic field, the minus sign relative to the other effect being a simple consequence of Lenz' law for induced currents.

At this point it is well to emphasize that the pictorial description may with equal validity be stated in other terms. Thus in Maxwell's equations a changing electric field is invariably associated with an inhomogeneity of the magnetic field. It is therefore meaningless to say whether the magnetic moment we have formally and pictorially associated with changing electric field is really "due to" the changing electric field rather than "due to" the inhomogeneities of the magnetic field. A similar remark holds, of course, for the electric moment associated here with a changing magnetic field.

In writing this section it has seemed best to put all references to the original literature at the end. It is not really worth while to trace back the history completely for it leads into phenomenological extensions of the old elastic solid theory of light which today are only of antiquarian interest. Apparently the first theory of the kind given in this section is due to Gibbs.[7] Others who contributed to the application of the electromagnetic theory to the problem of optical activity are Drude,[8] Lorentz[9] and Livens.[10]

3. The Parameter β and Rotatory Dispersion

In the next section we shall develop the quantum-mechanical theory of dispersion in a form which includes the theory of the parameter β. Before doing this it will be of interest to consider the empirical data in relation to the theory. It will be shown that β is given by

$$\beta_a = \frac{c}{3\pi h} \sum_b \frac{R_{ba}}{\nu_{ba}^2 - \nu^2}. \tag{23}$$

Here β_a is the value of β appropriate to molecules in the quantum state a, ν_{ba} is the frequency of the light absorbed in the jump $a \rightarrow b$ and R_{ba} is a constant characteristic of that particular absorption line which we shall call the ***rotational strength*** of the line ν_{ba}.

If the molecules are distributed over various states in the thermal equilibrium appropriate to the temperature of the medium, the number per unit volume in the state a is $N_1(a)$ where this will be given by a Boltzmann distribution formula. Then the effective value of β to be used in (22) is

$$N_1\beta = \sum_a N_1(a)\beta_a. \tag{24}$$

Equation (23) for β_a is analogous to the better-known equation for the polarizability α_a of molecules in the quantum state a. This formula, due to Kramers and Heisenberg,[11] is

$$\alpha_a = \frac{2}{3h} \sum_b \frac{\nu_{ba} S_{ba}}{\nu_{ba}^2 - \nu^2}, \tag{25}$$

in which S_{ba} is another characteristic of the line ν_{ba} which is called the *strength* of the line.[12] The strength of the line should not be confused with the *oscillator strength* which is another measure of the intensity of a line, important in

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[7] Gibbs, *Collected Works*, Vol. 2, p. 195. Originally published in Am. J. Science **25**, 460 (1882).

[8] Drude, *Göttinger Nachrichten* (1892), p. 366.

[9] Lorentz, *Versuch einer Theorie* . . . (Leipzig, 1906).

[10] Livens, Phil. Mag. **25**, 817 (1913); **26**, 362, 535 (1913); **27**, 468, 994 (1914); **28**, 756 (1914); Physik. Zeits. **15**, 385 (1914).

[11] Kramers and Heisenberg, Zeits. f. Physik **31**, 681 (1925); Ladenburg, Zeits. f. Physik **4**, 451 (1921).

[12] Condon and Shortley, *The Theory of Atomic Spectra* (Cambridge, 1935), p. 98.

dispersion theory. The oscillator strength is usually denoted by f_{ba}. It is dimensionless and is defined by the equation,

$$f_{ba}=(8\pi^2\mu/3e^2h)\nu_{ba}S_{ba}, \tag{26}$$

in which e and μ are the charge and mass of the electron. In terms of the oscillator strengths the formula (25) for the polarizability becomes

$$\alpha_a=\frac{e^2}{4\pi^2\mu}\sum_b\frac{f_{ba}}{\nu_{ba}{}^2-\nu^2}. \tag{27}$$

The oscillator strengths satisfy an important sum rule,

$$\sum_b f_{ba}=n. \tag{28}$$

which was discovered independently by Thomas and Kuhn.[13] In (28) the letter n stands for the total number of electrons in the molecule. Eq. (28) is true for each state a of the molecule, the sum extending over all other states.

Instead of the rotational strengths of the lines, Kuhn[14] has introduced another measure of the importance of a line in contributing to the rotatory power. This he calls the anisotropy factor for the line. In the notation that is being used here, Kuhn's anisotropy factor, g_{ba}, is

$$g_{ba}=R_{ba}/S_{ba}. \tag{29}$$

The anisotropy factor is easily seen to be a pure number.

Let us now turn to the empirical data in its relation to these equations. When one first approaches the study of optical activity he is apt to be overwhelmed at the large amount of data that exists. But as soon as one tries to use it in connection with the theory, however, he finds that very little of the data is complete enough to be of any real use. In the first place many of the measurements have been made for a single wave-length, usually the sodium D lines, so it is insufficient to determine the constants R_{ba} and ν_{ba} of a dispersion formula for β. This deficiency has been emphasized by Lowry[2] to whose efforts is largely due the recent tendency of experimentalists to secure more complete dispersion data. In the second place, the index of refraction is usually not measured so that one is forced to make an estimate of the $(n^2+2)/3$ factor which appears in (22).

Ordinarily we may assume that all of the molecules are in the lowest electronic state so an averaging over initial states as in (24) is not needed, in which case β_a refers to the normal electronic state of the molecule. Combining (23) and (22) we have

$$\frac{\varphi M/\rho}{\frac{1}{3}(n^2+2)}=\frac{16\pi^2N}{3hc}\sum_b\frac{R_{ba}\nu^2}{\nu_{ba}{}^2-\nu^2}, \tag{30}$$

in which M is the molecular weight, ρ the density and N is Avogadro's number. In this equation φ is the rotation in radian/cm. Referring to (2) one may write this as an equation for the molecular rotatory power $[M]$ in the conventional units of §1. The result is

$$\frac{[M]}{\frac{1}{3}(n^2+2)}=\frac{96\pi N}{hc}\sum_b\frac{R_{ba}\nu^2}{\nu_{ba}{}^2-\nu^2}. \tag{31}$$

An ordinary transparent liquid will have its absorption frequencies ν_{ba} in the ultraviolet and ordinarily the data on $[M]$ will be confined to the visible part of the spectrum. As a consequence if there are a great number of different absorption bands in the same general region of the ultraviolet, this will not be recognizable in the data which refer simply to the visible spectrum. Instead all of these frequencies will lump together to produce a single effective term having for its effective ν_{ba} some kind of average of the individual ν_{ba} of the actual lines, and having an effective rotational strength, R_{ba} that is essentially the sum of the separate rotational strengths. This is a situation that is quite familiar in the discussion of the dispersion formula for ordinary refractivity.

A good example of the use of (31) and the related formulae just developed is provided by discussing the data of Hunter[15] on d-sec octyl alcohol which has the rare virtue of including refractive index measurements. His data are given in Table I, which he represents by these

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[13] Thomas, Naturwiss. **13**, 627 (1925); Kuhn, Zeits. f. Physik **33**, 408 (1925).

[14] Kuhn, Trans. Faraday Soc. "Discussion on Optical Rotatory Power," p. 299 (1930).

[15] Hunter, J. Chem. Soc. **123**, 1671 (1923).

TABLE I. *Index of refraction and specific rotation of d-sec octyl alcohol. (Hunter.)*

λ	n	$[\varphi]$
6438	1.4238	8.12
5896	1.4256	9.86
5461	1.4273	11.65
5086	1.4292	13.58
4800	1.4311	15.46
4678	1.4320	16.42
4358	1.4349	19.49
4251		20.6
3969		24.2
3790		27.3
3650		29.9

empirical formulas,

$$n^2=1.6913+0.313\lambda^2/(\lambda^2-0.0283),$$
$$[\varphi]=3.14/(\lambda^2-0.0283),$$

in which λ is in microns.

According to (31) it is not $[\varphi]$ or $[M]$ which satisfy a formula of the type used empirically but these quantities divided by $(n^2+2)/3$. But in this example the total variation in this factor from one end of the table to the other is from 1.34 to 1.36 so we may treat the factor as constant and equal to 1.35 without appreciable error. The molecular weight is $M=130$ and therefore by the use of Hunter's empirical formula one obtains

$$[M]/\tfrac{1}{3}(n^2+2)=107\sigma^2/(35.6-\sigma^2),$$

where σ is the wave number in reciprocal microns (10^4 cm^{-1}). Since σ is proportional to ν and the formula (31) is homogeneous in the frequency it follows that

$$96\pi NR_{ba}/hc=107,$$

where R_{ba} is the effective rotational strength of the group of ultraviolet bands whose effective wave number is 58,800 cm^{-1} that is, whose effective wave-length is 1700A. The combination of universal constants occurring here is

$$96\pi N/hc=0.943\times10^{42}$$

and therefore the effective rotational strength from the data is

$$R_{ba}=1.13\times10^{-40}.$$

There are not many cases for which the data on rotatory dispersion are complete enough to permit a calculation of this sort. Even so this merely represents the effect of lumping all the active absorption bands at one effective average frequency in the ultraviolet.

The quantum-mechanical theory of the next section gives a formula for the rotational strength, R_{ba}, of an individual line in terms of matrix components of the unperturbed molecule. There it is shown that

$$R_{ba}=\mathrm{Im}\{(a|\mathbf{p}|b)\cdot(b|\mathbf{m}|a)\}, \qquad (32)$$

in which $(a|\mathbf{p}|b)$ and $(b|\mathbf{m}|a)$ are, respectively, the matrix components connecting states b and a of the electric and magnetic dipole moments of the molecule. The symbol Im{ } means "imaginary part of" in the sense

$$\mathrm{Im}\{u+iv\}=v,$$

if u and v are real. The electric moment of a molecule is

$$\mathbf{p}=\sum e\mathbf{r}_i,$$

where $\mathbf{r}_i$ is the position vector of the ith electron. Nonvanishing matrix components of $\mathbf{p}$ may then be expected to be of the order of the electron charge times the radius of the first Bohr orbit, a_H, that is, of the order,

$$ea_H=2.53\times10^{-18} \text{ c.g.s.}$$

Similarly nonvanishing matrix components of the magnetic dipole moment may be expected to be of the order of the Bohr magneton, or roughly,

$$eh/2\mu c=0.92\times10^{-20} \text{ c.g.s.}$$

Hence on this crude estimation the expected order of magnitude of a rotational strength, R_{ba}, is

$$ea_H\cdot eh/2\mu c=2.32\times10^{-38} \text{ c.g.s.}$$

The value just found for octyl alcohol is about one two-hundredth of this crude estimate which is very reasonable, considering that the estimate was too large for a number of reasons: (a) generally the scalar product of the two matrix components will be smaller than the product of their magnitudes as they will usually not be parallel, (b) generally the product of the two matrix components will not be purely imaginary so part of the quantity is lost on taking the imaginary part and (c) the empirical value is the sum of the values referring to different absorption bands in the molecule some of which have negative and others positive values, so there is a tendency for the sum of many such terms to be smaller than the average individual term.

It is of interest to continue the discussion of the illustrative example and to handle the refractive index data in a manner comparable to what has been done for rotatory dispersion. The combination of (25) and (20) yields the formula,

$$\frac{(n^2-1)M/\rho}{\frac{1}{3}(n^2+2)}=\frac{8\pi N}{3hc}\sum_b \frac{\sigma_{ba}S_{ba}}{\sigma_{ba}{}^2-\sigma^2}, \tag{33}$$

in which σ_{ba} and σ are the wave number equivalents of the corresponding frequencies ν_{ba} and ν, and ρ is the density. The refractivity data on octyl alcohol already given then lead to

$$S_{ba}=83.7\cdot 10^{-36}\text{ c.g.s.},$$

as the effective strength of the ultraviolet absorption bands.

By the standard dispersion theory, the formula for S_{ba} which is the analog of (32) is

$$S_{ba}=|(a|\mathbf{p}|b)|^2, \tag{34}$$

so the expected order of magnitude of an S_{ba} term is

$$(ea_H)^2=6.40\cdot 10^{-36}\text{ c.g.s.}$$

The experimental value just found is 13.1 times this natural atomic unit, which is reasonable, for none of the reasons given for smallness of R_{ba} are applicable here.

We conclude the discussion of the example by calculating the effective f_{ba} (oscillator strength) and g_{ba} (anisotropy factor) for the ultraviolet bands lumped at 1700A. From (26) we have, in general,

$$f_{ba}=(4.79\times 10^{29})\sigma_{ba}S_{ba}$$

and hence using the values of σ_{ba} and S_{ba} we have

$$f_{ba}=2.36.$$

This shows that transitions of more than one electron are involved in the totality of bands which contribute to the dispersion in the empirical formula given by Hunter. Kuhn's anisotropy factor for these bands is readily calculated from (29) and found to be

$$g_{ba}=1.35\times 10^{-6}.$$

This value is typical of the values obtained for g_{ba} in the case of strong absorption bands for which f_{ba} is of the order of unity.

In discussing the example we have referred rather casually to the calculated R_{ba} as being an effective value representing the total contribution of a group of bands. To be more precise, suppose a group of bands to be represented by a single rotatory dispersion term. Then, say

$$\frac{R_1}{\nu_1{}^2-\nu^2}=\sum_b \frac{R_{ba}}{\nu_{ba}{}^2-\nu^2}, \tag{35}$$

where the equality holds for small values of ν. To get agreement of both sides in the first two terms of a power series development in ν one must have

$$\begin{aligned} \nu_1{}^{-2}&=(\textstyle\sum R_{ba}/\nu_{ba}{}^4)\div(\sum R_{ba}/\nu_{ba}{}^2),\\ R_1&=(\textstyle\sum R_{ba}/\nu_{ba}{}^2)^2\div(\sum R_{ba}/\nu_{ba}{}^4). \end{aligned} \tag{36}$$

Similarly, if one is representing a whole group of ultraviolet bands on the ordinary dispersion formula by a single lumped term, then the analogs of (35) and (36) are easily seen to be

$$\frac{\nu_1 S_1}{\nu_1{}^2-\nu^2}\approx\sum\frac{\nu_{ba}S_{ba}}{\nu_{ba}{}^2-\nu^2}, \tag{37}$$

where, to get agreement in the first two terms in a power series in the frequency, we must have

$$\begin{aligned} \nu_1{}^{-2}&=(\textstyle\sum S_{ba}/\nu_{ba}{}^3)\div(\sum S_{ba}/\nu_{ba}),\\ S_1{}^2&=(\textstyle\sum S_{ba}/\nu_{ba})^3\div(\sum S_{ba}/\nu_{ba}{}^3). \end{aligned} \tag{38}$$

As the formulas (36) and (38) are quite different there is no reason to expect that the effective frequency ν_1 in the ordinary dispersion formula will be the same as that in the rotatory dispersion formula, even though, of course, the individual frequencies, ν_{ba}, are the same. An interesting illustration of this point is provided by data obtained by Volkmann.[16] He found for limonene the critical wave-length in a single term formula for the refractivity to be 998A while that for a corresponding single term formula for rotatory power was 1878A, almost

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[16] Zeits. f. physik. Chemie **B10**, 161 (1930).

twice as great. This comes about because the R_{ba} are not all of the same sign so the contribution of various bands deep in the ultraviolet tends to cancel out. However, the S_{ba} are all positive so in the refractivity the deep ultraviolet bands are fully effective.

The case of ethyl tartrate is interesting in that it requires two terms in its rotatory dispersion formula. The empirical data are from measurements by Lowry and Cutter[17] and may be represented by the empirical formula

$$[\varphi]=\frac{25.005}{\lambda^2-0.03}-\frac{20.678}{\lambda^2-0.056}$$

corresponding to absorption bands of opposite rotatory power at 1730A and at 2360A. As a result of the joint action of these two different groups of absorption bands, the rotatory power of ethyl tartrate actually passes through zero with reversal of sign in the neighborhood of 4250A, although there is no characteristic frequency of the molecule at this place in the spectrum. The refractive index data are not given so we merely estimate $(n^2+2)/3$ to be 1.30 for want of anything better. Making the calculations exactly as for the previous calculation we arrive at the results:

Ethyl tartrate

$$\lambda_1=1730\text{A},\qquad \lambda_2=2360\text{A},$$
$$R_1=12.1\cdot 10^{-40},\quad R_2=5.42\cdot 10^{-40}.$$

The critical frequencies appearing in the empirically determined formulas for rotatory dispersion all lie in the ultraviolet or in the visible part of the spectrum if the substance absorbs in the visible. Such frequencies are associated with electronic transitions in the molecule. All of these compounds possess infrared absorption spectra corresponding to changes in the state of nuclear vibration so the question arises: is there any contribution to the rotatory power associated with the infrared absorption frequencies? Several investigations[18] bear on this question, the rotatory power of several substances having been measured out to a wave-length of 2.14 microns. No detectable irregularity in the rotation could be found that could be associated with the infrared absorption.

This is not surprising for we know from ordinary dispersion theory that the contribution to ordinary refractivity of the infrared bands is of the order of 2000 times smaller than electronic bands (of the order of the mass ratio), even for the fundamental vibrations in which the quantum number changes by but one unit. These investigations only went into the harmonic infrared region where the vibrational quantum number changes by two units which would make contributions from such bands extremely weak.

4. QUANTUM MECHANICS OF ROTATORY DISPERSION

Modern work on the problem of deriving the parameter β from a molecular model dates from the independent discovery by Born, Oseen and Gray[19] in 1915 that a calculation of β depends essentially on taking into account the finite ratio of the molecular diameter to the wave-length of light. In other words the fact that the phase of the light wave is different for different parts of a molecule is essential.

The molecular model used was that of a spatial distribution of coupled oscillators and corresponds to a natural extension of the form of electron theory of dispersion then in vogue. More or less independently of this work the same general view was also developed by Thomson, de Malleman and Boys.[20] Kuhn[21] has also contributed greatly to the problem by a detailed consideration of the most simple special case of the coupled oscillator model to show activity. His work on this has been very stimulating to the recent development of the subject.

The quantum-mechanical calculation of β was first formulated by Rosenfeld.[22] His calculations

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[17] Lowry and Cutter, J. Chem. Soc. London **121**, 532 (1922).

[18] Meyer, Ann. d. Physik **30**, 607 (1909); Ingersoll, Phil. Mag. **11**, 41 (1906); Phys. Rev. **23**, 489 (1906); Phys. Rev. **9**, 257 (1917); Lowry and Coude-Adams, Phil. Trans. **A226**, 391 (1927); Lowry and Snow, Proc. Roy. Soc. **A127**, 271 (1930).

[19] Born, Physik. Zeits. **16**, 251 (1915); Ann. d. Physik **55**, 177 (1918); Oseen, Ann. d. Physik **48**, 1 (1915); Gray, Phys. Rev. **7**, 472 (1916); Landé, Ann. d. Physik **56**, 225 (1918); Gans, Zeits. f. Physik **17**, 353 (1923); **27**, 164 (1924); Ann. d. Physik **79**, 548 (1926).

[20] J. J. Thomson, Phil. Mag. **40**, 713 (1920); de Malleman, Rev. gen des sci. **38**, 453 (1927); Boys, Proc. Roy. Soc. **144**, 655 (1934); Kirkwood, J. Chem. Phys. **5**, 479 (1937).

[21] Kuhn, Zeits. f. physik. Chemie **B4**, 14 (1929).

[22] Rosenfeld, Zeits. f. Physik **52**, 161 (1928). An account will also be found in Born and Jordan, *Elementare Quantenmechanik* (1930), p. 250.

lead to the formulas (23) and (32) which have already been discussed in the preceding section. This work unquestionably provides an approach that is much superior to that of the older coupled oscillator models so that one may hope that future work will be built on the quantum-mechanical theory rather than on further study of the coupled oscillator models.

In the rest of this section we give an account of the quantum-mechanical theory for β following essentially Rosenfeld's work but differing somewhat in the details of the calculations. Readers who are not interested in the details of quantum-mechanical calculations will find great pleasure in skipping the rest of this section, for all that will be accomplished will be the derivation of Eqs. (23) and (32).

The fields of a light wave traveling in the direction of the unit vector **k** are all derivable from the vector potential **A**:

$$A = R\{\mathbf{A}\exp(i(t-\mathbf{k}\cdot\mathbf{r}/c)E/\hbar)\}. \tag{39}$$

Here $E=h\nu$ represents the quantum energy associated with the wave. The electric and magnetic vectors of the wave are given by

$$\begin{aligned}\mathbf{E} &= -A/c = -(E/\hbar c)R\{i\mathbf{A}e^{+}\},\\ \mathbf{H} &= \text{curl }\mathbf{A} = -(E/\hbar c)R\{i\mathbf{k}\times\mathbf{A}e^{+}\},\end{aligned} \tag{40}$$

where the exponents of e are the same as in (39).

We may neglect the direct interaction of the atomic nuclei in a molecule with the light wave owing to their comparatively great mass. Hence the interaction gives rise to a perturbation term

$$\mathbf{H} = -(e/mc)\sum_{i}[\mathbf{p}_i\cdot\mathbf{A}_i+\mathbf{S}_i\cdot(\text{curl }A)_i]. \tag{41}$$

Here e/mc refers to the charge and mass of the electron and the subscript i on **A** and curl **A** means that they are to be evaluated at the position of the ith electron.

We have to find how the wave function for the molecule in a particular state labeled by quantum numbers a is affected by the perturbing action of the light wave. For the perturbed wave function we may write

$$\Psi = \psi(a)e^{-iW_a t/\hbar}+\psi_1(a), \tag{42}$$

where $\psi_1(a)$ has to be determined from the dynamical equation of quantum mechanics

$$i\hbar\partial\Psi/\partial t = (H_0+H)\Psi, \tag{43}$$

in which H_0 is the Hamiltonian for the unperturbed molecule. This leads to the following equation for $\psi_1(a)$

$$(H_0-i\hbar\partial/\partial t)\psi_1(a) = -H\psi(a)e^{-iW_a t/\hbar}. \tag{44}$$

This will now be solved in the usual way. The right-hand side is expanded in terms of the unperturbed wave functions so

$$\begin{aligned}-H\psi(a)e^{-iW_a t/\hbar} = \tfrac{1}{2}\sum_b\psi(b)[&(b|H_+|a)e^{i(E-W_a)t/\hbar}\\ &+(b|H_-|a)e^{-i(E+W_a)t/\hbar}],\end{aligned} \tag{45}$$

where the coefficients are

$$\begin{aligned}(b|H\pm|a) = \frac{e}{mc}\Big\{&\bar{\psi}(b)\\ &\times(\sum_i\mathbf{p}_i\exp(\mp i\mathbf{k}\cdot\mathbf{r}_i E/\hbar c))\psi(a)\cdot\mathbf{A}\\ &\mp\frac{iE}{\hbar c}\bar{\psi}(b)(\sum_i\mathbf{S}_i)\psi(a)\cdot(\mathbf{k}\times\mathbf{A})\Big\}.\end{aligned} \tag{46}$$

Here it is to be understood that $\bar{A}$ stands in place of **A** when the lower sign is used and the approximation has been made of neglecting the retardation factor in the small spin term on the second line. Integration of the wave functions over the configuration space of the molecule is also implied in (46).

If we now expand the retardation factor and save only the first two terms then by some easy reductions

$$\begin{aligned}(b|H\pm|a) = &\frac{i}{\hbar c}W_{ba}(b|\mathbf{p}|a)\cdot\mathbf{A}\\ &\pm\frac{EW_{ba}}{2\hbar^2c^2}\mathbf{k}\cdot(b|\mathfrak{R}|a)\cdot\mathbf{A}\mp\frac{iE}{\hbar c}(b|\mathbf{m}|a)\cdot(\mathbf{k}\times\mathbf{A}),\end{aligned} \tag{47}$$

where again $\bar{A}$ is to be written for **A** when the lower sign is used. In (47) the following abbreviations have been introduced:

$$W_{ba} = W_b - W_a,\quad \mathbf{p} = e\sum_i\mathbf{r}_i,\quad \mathfrak{R} = e\sum_i\mathbf{r}_i\mathbf{r}_i,$$

$$\mathbf{m} = \frac{e}{2mc}\sum_i(\mathbf{r}_i\times\mathbf{p}_i+2\mathbf{S}_i), \tag{48}$$

so **p**, $\mathfrak{N}$ and **m** are respectively the electronic contributions to the electric dipole moment, the electric quadrupole moment and the magnetic moment of the molecule.

The terms in the electric quadrupole moment do not introduce any new type of propagation of light through the medium. They give a small correction, of the order of a few parts in a million, to the ordinary connection between mean refractive index and the electric dipole moment and so will be neglected in what follows. Therefore when (47) is used in later calculations the terms in $\mathfrak{N}$ will simply be dropped.

Following the usual procedure one next assumes an expansion for $\psi_1(a)$ in terms of unperturbed wave functions and determines coefficients in the expansion by equating coefficients of both sides of (44). The resulting formula for $\psi_1(a)$ is

$$\psi_1(a)=\tfrac{1}{2}\sum_b\psi(b)\left[\frac{(b|H_+|a)e^{i(E-W_a)t/\hbar}}{W_{ba}+E}+\frac{(b|H_-|a)e^{-i(E+W_a)t/\hbar}}{W_{ba}-E}\right]. \quad (49)$$

The first-order correction to the diagonal matrix element of any observable F referring to atoms in the state a is then

$$2R\{\bar{\psi}(a)F\psi_1(a)e^{iW_at/\hbar}\}=R\sum_b\left\{\frac{(a|F|b)(b|H_+|a)}{W_{ba}+E}e^{iEt/\hbar}+\frac{(a|F|b)(b|H_-|a)}{W_{ba}-E}e^{-iEt/\hbar}\right\}. \quad (50)$$

What is needed are the special cases of (50) in which the values (47) are used for $(b|H_\pm|a)$ and F is identified with **p** and with **m**. If we denote the induced values of **p** and **m** by $\mathbf{p}_1$ and $\mathbf{m}_1$ we have

$$\mathbf{p}_1=\sum_b R\left\{\frac{(a|\mathbf{p}|b)(b|H_+|a)}{W_{ba}+E}e^{iEt/\hbar}+\frac{(a|\mathbf{p}|b)(b|H_-|a)}{W_{ba}-E}e^{-iEt/\hbar}\right\} \quad (51)$$

and a corresponding expression for $\mathbf{m}_1$. Substituting the expressions (47), with neglect of the quadrupole terms as already mentioned this can be written

$$\mathbf{p}_1=2\sum_b R\left\{\frac{W_{ba}}{W_{ba}{}^2-E^2}(a|\mathbf{p}|b)(b|\mathbf{p}|a)\cdot\mathbf{E}+i\frac{\hbar W_{ba}{}^2/E^2}{W_{ba}{}^2-E^2}(a|\mathbf{p}|b)(b|\mathbf{p}|a)\cdot\dot{E}+\frac{W_{ba}}{W_{ba}{}^2-E^2}(a|\mathbf{p}|b)(b|\mathbf{m}|a)\cdot\mathbf{H}+i\frac{\hbar}{W_{ba}{}^2-E^2}(a|\mathbf{p}|b)(b|\mathbf{m}|a)\cdot\dot{H}\right\} \quad (52)$$

and the corresponding expression for $\mathbf{m}_1$ becomes

$$\mathbf{m}_1=2\sum_b R\left\{\frac{W_{ba}}{W_{ba}{}^2-E^2}(a|\mathbf{m}|b)(b|\mathbf{p}|a)\cdot\mathbf{E}+\frac{iW_{ba}{}^2/E^2}{W_{ba}{}^2-E^2}(a|\mathbf{m}|b)(b|\mathbf{p}|a)\cdot\dot{E}\right\}. \quad (53)$$

Each of these expressions contains a term involving

$$\frac{W_{ba}{}^2/E^2}{W_{ba}{}^2-E^2}=E^{-2}+\frac{1}{W_{ba}{}^2-E^2}.$$

The contribution to $\mathbf{p}_1$ resulting from the E^{-2} part of this can be written

$$R\left\{\frac{2i\hbar}{E^2}\sum_b(a|\mathbf{p}|b)(b|\mathbf{p}|a)\cdot\dot{E}\right\}=\frac{2\hbar}{E^2}R\{i(a|\mathbf{pp}|a)\cdot\dot{E}\}$$

by the law of matrix multiplication. Now $(a|\mathbf{pp}|a)$ is a diagonal matrix element of a real observable so it is real; hence the expression whose real part is to be taken is purely imaginary, so the real part vanishes. A similar reduction can also be made in the case of the corresponding term in (53). Since the real part of iX is $-\text{Im}\{X\}$ where $\text{Im}\{X\}$ denotes the imaginary part of X the induced moment expressions can finally be written

$$\begin{aligned}\mathbf{p}_1=2\sum_b \frac{W_{ba}}{W_{ba}{}^2-E^2}&R\{(a|\mathbf{p}|b)(b|\mathbf{p}|a)\}\cdot\mathbf{E}\\ &-\frac{\hbar}{W_{ba}{}^2-E^2}\,\mathrm{Im}\,\{(a|\mathbf{p}|b)(b|\mathbf{p}|a)\}\cdot\dot{E}\\ &+\frac{W_{ba}}{W_{ba}{}^2-E^2}R\{(a|\mathbf{p}|b)(b|\mathbf{m}|a)\}\cdot\dot{\mathbf{H}}\\ &-\frac{\hbar}{W_{ba}{}^2-E^2}\,\mathrm{Im}\,\{(a|\mathbf{p}|b)(b|\mathbf{m}|a)\}\cdot\dot{H},\\ \mathbf{m}_1=2\sum_b \frac{W_{ba}}{W_{ba}{}^2-E^2}&R\{(a|\mathbf{m}|b)(b|\mathbf{p}|a)\}\cdot E\\ &-\frac{\hbar}{W_{ba}{}^2-E^2}\,\mathrm{Im}\,\{(a|\mathbf{m}|\mathbf{r})(b|\mathbf{p}|a)\}\cdot\dot{E}.\end{aligned}\tag{54}$$

These expressions give the coherent induced electric and magnetic moments which are needed for the calculation of the relations of **D** and **B** to **E** and **H** in the medium. They can now be further simplified by averaging over all orientations of the molecules in space. In the ordinary case this means that all orientations are equally likely. If they are not equally likely and the partial lining up of molecules is produced say by an external electric field then special effects may arise, such as that which has apparently been discovered by Kunz and Babcock[23]—the effect of an external electric field on the rotatory power of an active liquid.

The averaging over all orientations is carried out by the following argument. One has to average expressions of the type $\mathbf{pm}\cdot\mathbf{H}$ for all orientations of $\mathbf{p}$ and $\mathbf{m}$ keeping fixed the magnitudes of $\mathbf{p}$ and $\mathbf{m}$ and the angle between them. Now $\mathbf{pm}\cdot\mathbf{H}$ is a vector in the direction of $\mathbf{p}$. As $\mathbf{p}$ takes on all possible directions consistent with a fixed direction of $\mathbf{m}$ the average value of $\mathbf{pm}\cdot\mathbf{H}$ will be the component of this along $\mathbf{m}$, that is $\mathbf{p}\cdot\mathbf{m}_0\mathbf{m}\cdot\mathbf{H}\mathbf{m}_0$ where $\mathbf{m}_0$ is a unit vector in the direction of $\mathbf{m}$. Next we average over all directions of $\mathbf{m}$ by considering first those directions making a fixed angle θ with $\mathbf{H}$. The result will be a vector along $\mathbf{H}$ of magnitude $\mathbf{p}\cdot\mathbf{m}\cos^2\theta\mathbf{H}$. Finally averaging over all directions of θ weighting them per unit solid angle the end result is $\mathbf{p}\cdot\mathbf{m}\,(\cos^2\theta)_{\mathrm{Av}}\mathbf{H}=(1/3)\mathbf{p}\cdot\mathbf{m}\,\mathbf{H}$.

Hence after averaging over all orientations of the molecules the expressions for $\mathbf{p}_1$ and $\mathbf{m}_1$ simplify to

$$\begin{aligned}\mathbf{p}_1&=\alpha_a\mathbf{E}+\gamma_a\mathbf{H}-(1/c)\beta_a\dot{H},\\ \mathbf{m}_1&=\qquad\gamma_a\mathbf{E}+(1/c)\beta_a\dot{E},\end{aligned}\tag{55}$$

which are almost exactly like Eqs. (18) assumed in the phenomenological discussion of §2. Here, however, we have the additional results connecting α, β and γ with the quantum-mechanical description of the molecular model that is given in the following equations,

$$\alpha_a=\frac{2}{3h}\sum_b\frac{\nu_{ba}|(a|\mathbf{p}|b)|^2}{\nu_{ba}{}^2-\nu^2},\tag{56α}$$

$$2\pi\nu\beta_a/c=\frac{2}{3h}\sum_b\frac{\nu\,\mathrm{Im}\,\{(a|\mathbf{p}|b)\cdot(b|\mathbf{m}|a)\}}{\nu_{ba}{}^2-\nu^2},\tag{56β}$$

$$\gamma_a=\frac{2}{3h}\sum_b\frac{\nu_{ba}R\{(a|\mathbf{p}|b)\cdot(b|\mathbf{m}|a)\}}{\nu_{ba}{}^2-\nu^2}.\tag{56γ}$$

Here ν is written for the frequency of the light wave and $\nu_{ba}=W_{ba}/h$. The subscript a has been written on the coefficients α, β and γ to indicate that these are attributes of molecules in the state a.

The end result of the calculation is contained in (55) and (56). These equations with neglect of the terms in β and γ correspond to the ordinary theory of the refractive index in an isotropic medium. It is easy to see by work analogous to that of §2 that the term in γ has only a second order effect on the mean refractive index for right and left circularly polarized light.[24] There-

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[23] Kunz and Babcock, Phil. Mag. **22**, 616 (1937). See, however, Nature **140**, 194 (1937), in which further work is reported showing that the earlier results were due to suspended materials.

[24] The details are as follows: corresponding to introduction of g by (13) and (21), the quantity γ leads to introduction of an $f=4\pi N\gamma(1-4\pi N\alpha/3)^{-1}$ where N is the number of molecules per cm³ so in place of (11) one has

$$\begin{aligned}\mathbf{D}&=\mathbf{E}\mathbf{E}+f\mathbf{H}-g\dot{H},\\ \mathbf{B}&=\mathbf{H}+f\mathbf{E}+g\dot{E}.\end{aligned}$$

Using Maxwell's equations as in Section 4 and assuming

$$\begin{aligned}\mathbf{D}&=d_1(1-i\mathbf{m})+d_2(1+i\mathbf{m}),\\ \mathbf{B}&=\mathbf{b}_1(1-i\mathbf{m})+\mathbf{b}_2(1+i\mathbf{m}),\end{aligned}$$

one finds that the curl equations give

$$\begin{aligned}&(in^{-1}d_1-b_1+\bar{F}d_1)(1-i\mathbf{m})+(-in^{-1}d_2-b_2+\bar{F}d_2)(1+i\mathbf{m})=0,\\ &(in^{-1}b_1+\epsilon^{-1}d_1-Fb_1)(1-i\mathbf{m})\\ &\qquad\qquad+(-in^{-1}b_2+\epsilon^{-1}d_2-Fb_2)(1+i\mathbf{m})=0.\end{aligned}$$

One can equate to zero separately the coefficients of $(1-i\mathbf{m})$ and $(1+i\mathbf{m})$ in these equations to find the index fore its effect may be neglected and (55) reduces precisely to (18). We see that a calculation of the rotatory power of a given substance involves evaluation of the numerators,

$$R_{ba} = \mathrm{Im}\{(a|\mathbf{p}|b)\cdot(b|\mathbf{m}|a)\}, \tag{32}$$

which occur in the formula (56) for β. This part of the problem is discussed in later sections.

We observe that ν_{ba} appears in the formula for α at the place where ν appears in that for β, in the numerators. The appearance of ν_{ba} is what gives rise to the phenomenon of negative dispersion shown by substances having an appreciable number of atoms in electronically excited states.[25] This raises the question: is there an analogous negative rotatory dispersion? The question is rather of pure theoretic interest as it is unlikely that a sufficient concentration of excited optically active molecules could be obtained to study the question experimentally. The answer is in the affirmative, and consists simply in the theorem:

$$R_{ba} = -R_{ab}.$$

Since R_{ba} is the strength associated with resonance to the virtual jump from state a to state b by molecules actually in state a, it follows that R_{ab} is the strength associated with resonance to the virtual jump from state b to state a by molecules actually in state a. The equation just stated is obvious from (32), for interchanging a and b replaces the matrix components by their complex conjugates, which reverses the sign of the imaginary part.

5. GENERAL PROPERTIES OF ROTATORY STRENGTHS

By means of (31) the rotatory power of a medium is expressed entirely in terms of the rotatory strengths of the absorption lines, where the rotatory strengths are defined in terms of electric and magnetic dipole matrix components by (32). We wish now to consider certain properties of the R_{ba} which can be derived without specialization of the molecular model.

First of all there is a sum rule, analogous to (28),

$$\sum_b R_{ba} = 0, \tag{57}$$

which is true for all states, a, where the sum is extended over all other states, b. This rule was discovered by Kuhn in connection with the coupled oscillator model. It is easy to give a general quantum-mechanical proof in one line:

$$\sum_b R_{ba} = \mathrm{Im}\ \{\sum_b (a|\mathbf{p}|b)\cdot(b|\mathbf{m}|a)\}$$
$$= \mathrm{Im}\ \{(a|\mathbf{p}\cdot\mathbf{m}|a)\} = 0,$$

the equality to zero following from the fact that any diagonal matrix element of a real observable is real and therefore its imaginary part vanishes.

Because of the sum rule the optical activity of all substances must vanish in the limit in which $\nu \gg$ all ν_{ba} as is readily seen from (23) or (31). From (31) it is also evident that the rotatory power vanishes as $\nu \rightarrow 0$ because of the ν^2 factor in the numerator. Hence rotatory power is a property which tends to zero at both ends of the spectrum.

Next we may consider the symmetry properties of optical activity. This can be done independently of any special theory of the phenomenon and, in fact such considerations which are due to Pasteur, van't Hoff and Le Bel, lie at the foundation of modern stereochemistry. The basic result is: the quantity β is a pseudoscalar which means that it reverses sign on passing from a right-handed coordinate system to a left-handed system. This means that two molecules which are mirror images of each other will have equal and opposite rotatory strengths. This is in accord with (32) for electric dipole moment is a polar vector whereas magnetic dipole moment is an axial vector so their scalar product is a pseudoscalar rather than a true invariant.[26]

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of refraction for left and right circularly polarized light, respectively. Here

$$F = \epsilon^{-1}(f - 2\pi i\nu g)$$

and $\bar{F}$ is the complex conjugate. The resulting equations give

$$\epsilon^{\frac{1}{2}} n_e^{-1} = (1 - f^2/\epsilon)^{\frac{1}{2}} - 2\pi\nu g\epsilon^{-1},$$
$$\epsilon^{\frac{1}{2}} n_r^{-1} = (1 - f^2/\epsilon)^{\frac{1}{2}} + 2\pi\nu g\epsilon^{-1},$$

which shows that f enters only as a term in f^2 and does not affect the difference $(n_l - n_r)$. One has therefore

$$n_l = \epsilon^{\frac{1}{2}} + 2\pi\nu g \quad \text{and} \quad n_r = \epsilon^{\frac{1}{2}} - 2\pi\nu g$$

as in (15).

[25] Ladenburg, Rev. Mod. Phys. **5**, 243 (1933).

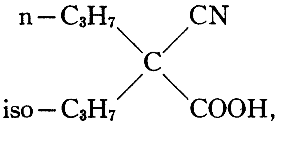
[26] Perhaps these remarks should be made more explicit since so little attention is paid to these points in the usual presentations of electromagnetic theory. Let $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ be the basic vectors of a right-handed system and $\mathbf{i}'$, $\mathbf{j}'$, $\mathbf{k}'$

The generality of the symmetry argument is also its weakness. It tells us that two molecules related as mirror images will have equal and opposite rotatory powers, but it does not give us the slightest clue as to what structural feature of the molecule is responsible for the activity—any pseudoscalar associated with the structure might be responsible for the activity and the symmetry argument would be unable to distinguish between them. The attempts to relate optical activity to structure without a detailed theory have been guided to this extent but no more.

Thus Crum Brown[27] proposed a formula for the case of a molecule in which a single asymmetric carbon atom was linked to four different atoms or radicals, A, B, C, D. If k is any scalar attribute of each of the four radicals then the quantity,

$$K=(k_A-k_B)(k_A-k_C)(k_A-k_D)\\ \times(k_B-k_C)(k_B-k_D)(k_C-k_D),$$

is evidently a pseudoscalar, for we may pass to the mirror image by interchanging any two of the groups and this reverses the sign of K. Of course, it vanishes if any two of the k's are equal. Crum Brown identified the attribute k with the mass of the attached group and achieved some success in correlating empirical data with it but it is now discredited. For example Walden showed that propyl-isopropyl-cyano-acetic acid,



is optically active in spite of the equal masses of the propyl and isopropyl groups. Later workers[28] have tried using other attributes of the groups in this type of formula but without much success.

6. The Coupled Oscillator Model

We now come to the problem of calculating the rotatory strengths for particular molecular models. These are of two classes: the coupled oscillator model of Born, Oseen[19] and Kuhn,[21] and the single oscillator model recently proposed by Condon, Altar and Eyring.[29] This section will be devoted to a discussion of the main results for the coupled oscillator model and the single oscillator model will be discussed in the next section.

It is convenient to consider first the extremely simple version of the coupled oscillator model which was devised by Kuhn as this shows all the essential features of this type of model.[30] Suppose we have two particles, the coordinates of which are $(x_1, 0, -d/2)$ and $(0, y_2, +d/2)$ where d is a constant. The arrangement in space is indicated in Fig. 1. Let the charges and masses be e_1, e_2 and m_1, m_2, respectively, and suppose each particle to be bound elastically to its own equilibrium position. Also let there be a quadratic interaction term so the potential energy of the system is given by

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be those of the left-handed system that is related to it by inversion,

$$\mathbf{i}'=-\mathbf{i},\quad \mathbf{j}'=-\mathbf{j},\quad \mathbf{k}'=-\mathbf{k}.$$

The point P whose coordinates are (x, y, z) in the r system has coordinates $(-x, -y, -z)$ in the l system. The coordinates of a point reverse sign on changing systems: any vector whose components do this is called a polar vector.

With regard to the vector products we have, in the r system,

$$\mathbf{i}\times\mathbf{j}=\mathbf{k},\quad \ldots,\quad \ldots,$$

so in the l system, $\mathbf{i}'\times\mathbf{j}'=-\mathbf{k}'$ on using the transformation equations. From this it is evident that the vector product of two polar vectors has components which do not reverse sign on transforming from the r system to the l system. Such a vector is called an axial vector.

It is easy to see that the differential operator

$$\nabla=\mathbf{i}\frac{\partial}{\partial x}+\mathbf{j}\frac{\partial}{\partial y}+\mathbf{k}\frac{\partial}{\partial z}=\mathbf{i}'\frac{\partial}{\partial x^1}+\ldots+\ldots$$

is a polar vector and that the curl of a polar vector field is an axial vector field while the curl of an axial vector field is a polar vector field. Hence if the curl equations of the electromagnetic field are to be invariant on passage from an r system to an l system, it must be that $\mathbf{B}$ and $\mathbf{E}$ are of opposite character and that $\mathbf{D}$ and $\mathbf{H}$ are of opposite character.

It is conventional to assume that $\mathbf{D}$ and $\mathbf{E}$ are polar vectors and $\mathbf{B}$ and $\mathbf{H}$ are axial vectors but all that the theory requires is that the two pairs be of opposite character. The choice is fixed by the assumption that charge density is a true scalar and that current density is a polar vector. If we have a simple connection whereby a vector of one type is equated to a scalar times a vector of the other type, it is evident that that scalar cannot be a true scalar but must reverse sign on passing from an r system to an l system. Such a scalar is called a pseudoscalar. Since $\mathbf{D}$ and $\mathbf{H}$ are of opposite type it follows that g in (13) must be a pseudoscalar and hence that β in (18) is also a pseudoscalar.

[27] Crum Brown, Proc. Roy. Soc. Edinburgh **17**, 181 (1890).

[28] Bose, Zeits. f. physik. Chemie **65**, 695 (1909); Physik. Zeits. **9**, 680 (1908); Bose and Wellers, Zeits. f. physik. Chemie **65**, 702 (1909); Walker, J. Phys. Chem. **13**, 574 (1909).

[29] Condon, Altar and Eyring, J. Chem. Phys. **5**, 753 (1937).

[30] The presentation here follows closely that given by Kuhn and Freudenberg, *Hand und Jahrbuch der chemischen Physik*, Vol. 8, part 3 (1932), p. 47.

$$U=\tfrac{1}{2}k_1x_1^2+k_{12}x_1y_2+\tfrac{1}{2}k_2y_2^2, \tag{58}$$

while the kinetic energy is given by

$$T=\tfrac{1}{2}m_1\dot{x}_1^2+\tfrac{1}{2}m_2\dot{y}_2^2. \tag{59}$$

The motion is expressed in terms of normal coordinates, ξ_1 and ξ_2, defined as follows:

$$\begin{aligned} x_1(m_1)^{\frac{1}{2}}&=\xi_1\cos\alpha+\xi_2\sin\alpha,\\ y_2(m_2)^{\frac{1}{2}}&=-\xi_1\sin\alpha+\xi_2\cos\alpha, \end{aligned} \tag{60}$$

where the parameter α has to be so chosen that the potential energy (58) transforms into a sum of squares in ξ_1 and ξ_2. The value of α is then easily seen to be given by

$$(k_1/m_1-k_2/m_2)\sin 2\alpha +k_{12}/(m_1m_2)^{\frac{1}{2}}\cos 2\alpha=0, \tag{61}$$

in which case the expressions for kinetic and potential energy become

$$T=\tfrac{1}{2}(\dot{\xi}_1^2+\dot{\xi}_2^2),\quad U=2\pi^2(\nu_1^2\xi_1^2+\nu_2^2\xi_2^2),$$

in which

$$\begin{aligned} (2\pi\nu_1)^2&=(k_1/m_1)\cos^2\alpha\\ &\quad-2(k_{12}/(m_1m_2)^{\frac{1}{2}})\sin\alpha\cos\alpha+(k_2/m_2)\sin^2\alpha,\\ (2\pi\nu_2)^2&=(k_1/m_1)\sin^2\alpha\\ &\quad+2(k_{12}/(m_1m_2)^{\frac{1}{2}})\sin\alpha\cos\alpha+(k_2/m_2)\cos^2\alpha. \end{aligned} \tag{62}$$

Hence the general motion is a superposition of a simple harmonic motion of ξ_1 with frequency ν_1 and a simple harmonic motion of ξ_2 with frequency ν_2. It is interesting to consider some qualitative features of the motion. Suppose that

$$k_{12}/(m_1m_2)^{\frac{1}{2}}\ll(k_1/m_1-k_2/m_2),$$

then (61) shows that α will be a small angle. Hence by (60) the motion in the ξ_1 mode is largely a motion of x_1 with a much smaller amplitude for y_2 (assuming the masses to be of the same order of magnitude). Similarly in the ξ_2 mode the y_2 motion is large compared to the x_1 motion. Qualitatively the two modes have vibration patterns as shown in Fig. 2. On the diagrams are indicated the opposite screw senses characteristic of the two modes. Here the screw sense is the direction of turn around the z axis associated with a displacement toward $+z$ needed to make the direction of the first particle's displacement coincide with that of the second particle.

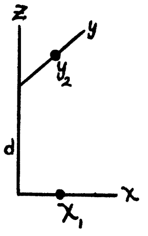

FIG. 1.

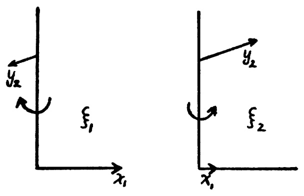

FIG. 2.

The next step in the classical discussion of the model consists in determining the forced oscillations set up by the fields of right and left circularly polarized waves, respectively. These forced oscillations give rise to coherent scattering which determines the index of refraction. This is given in full detail by Kuhn and Freudenberg[30] and so need not be repeated here. Instead we shall derive the formula for the rotatory power of this model by applying to it the quantum-mechanical theory of §4. This will provide an interesting variant of their treatment and at the same time give a proof that there is no difference between the classical and quantum-mechanical treatment of this model.

We need an expression for the variable part of the electric dipole moment. This is readily seen to be

$$\begin{aligned} \mathbf{p}&=e_1x_1\mathbf{i}+e_2y_2\mathbf{j}\\ &=(e_1/(m_1)^{\frac{1}{2}}\cos\alpha\mathbf{i}-e_2/(m_2)^{\frac{1}{2}}\sin\alpha\mathbf{j})\xi_1\\ &\quad+(e_1/(m_1)^{\frac{1}{2}}\sin\alpha\mathbf{i}+e_2/(m_2)^{\frac{1}{2}}\cos\alpha\mathbf{j})\xi_2. \end{aligned} \tag{63}$$

Similarly the magnetic moment of the orbital motion of the two charges is given by

$$\mathbf{m}=(1/2c)[e_1\mathbf{r}_1\times\mathbf{v}_1+e_2\mathbf{r}_2\times\mathbf{v}_2],$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors and $\mathbf{v}_1$ and $\mathbf{v}_2$ the velocities of the particles. When one uses

$$\begin{aligned} \mathbf{r}_1&=(-d/2)\mathbf{k}+x_1\mathbf{i}, & \mathbf{r}_2&=(+d/2)\mathbf{k}+y_2\mathbf{j},\\ \mathbf{v}_1&=\dot{x}_1\mathbf{i}, & \mathbf{v}_2&=\dot{y}_2\mathbf{j}, \end{aligned}$$

this can be written

$$\mathbf{m} = -(d/2c)(e_1\dot{x}_1\mathbf{j}+e_2\dot{y}_2\mathbf{i})$$
$$= -(d/2c)(e_1/(m_1)^{\frac{1}{2}}\cos\alpha\mathbf{j}-e_2/(m_2)^{\frac{1}{2}}\sin\alpha\mathbf{i})\dot{\xi}_1$$
$$-(d/2c)(e_1/(m_1)^{\frac{1}{2}}\sin\alpha\mathbf{j}+e_2/(m_2)^{\frac{1}{2}}\cos\alpha\mathbf{i})\dot{\xi}_2. \quad (64)$$

Next we have to calculate the matrix components of **p** and **m** in order to get the rotatory strengths given by (32). The energy levels will be labeled by two harmonic oscillator quantum numbers, n_1 and n_2, corresponding to the normal coordinates, ξ_1 and ξ_2. The energies are given by

$$W(n_1, n_2) = (n_1+\tfrac{1}{2})h\nu_1+(n_2+\tfrac{1}{2})h\nu_2 \quad (65)$$

and the corresponding wave functions are

$$\psi(n_1, n_2) = \varphi_{n_1}(\xi_1/a_1)\varphi_{n_2}(\xi_2/a_2), \quad (66)$$

where

$$\varphi_n(z) = \frac{1}{[2^n n!(\pi)^{\frac{1}{2}}]^{\frac{1}{2}}}H_n(z)e^{-z^2/2}, \quad (67)$$

in which $H_n(z)$ stands for the nth Hermitian polynomial and

$$a_i = (1/2\pi)(h/\nu_i)^{\frac{1}{2}} \quad (i=1, 2). \quad (68)$$

The necessary matrix components are those for ξ_1 and ξ_2, $\dot{\xi}_1$ and $\dot{\xi}_2$ appearing in (63) and (64). These are well known from the quantum mechanics of the harmonic oscillator:

$$(n_1n_2|\xi_1|n_1'n_2') = a_1(\bar{n}_1/2)^{\frac{1}{2}}\delta(n_2, n_2'). \quad (69)$$

Here $n_1' = n_1 \pm 1$ and $(\bar{n}_1)$ stands for the larger of n_1 and n_1'. Here the effective mass of the oscillator is unity so $\dot{\xi}_1$ is the same as the momentum, p_{ξ_1}, so the matrix components of $\dot{\xi}_1$ are

$$(n_1'n_2'|\dot{\xi}_1|n_1n_2) = \pm i(\hbar/a_1)(\bar{n}_1/2)^{\frac{1}{2}}\delta(n_2, n_2'), \quad (70)$$

in which $(\bar{n}_1)$ has the same meaning as before and the $\pm$ sign has the same value as occurs in $n_1' = n_1 \pm 1$. The formulas for matrix components for ξ_2 and $\dot{\xi}_2$ are obtained from (69) and (70) by obvious changes.

If we are calculating the parameter β for molecules in the state (n_1, n_2) there will be four other states for which there are nonvanishing values of the rotatory strength, namely,

$$(n_1+1,\ n_2) \quad \text{and} \quad (n_1-1,\ n_2).$$

Also $\quad (n_1,\ n_2+1) \quad$ and $\quad (n_1,\ n_2-1)$.

The pair in the first line will have the same resonance denominator in the formula (23) and the same is true of the pair on the second line, so although there are four quantum jumps which can contribute there will only be two critical frequencies in the dispersion formula.

If we write R_1 and R_2 for the two rotatory strengths, it is easy to calculate by a combination of (63), (64), (69) and (70) that

$$R_1 = -R_2 = \hbar(d/4c)\frac{e_1e_2}{(m_1m_2)^{\frac{1}{2}}}\sin\alpha\cos\alpha. \quad (71)$$

This result is in accord with the sum rule of §5 in giving $R_1+R_2=0$. In calculating this result it will be noticed that the upward virtual jump contributes an amount to R_1 that is proportional to (n_1+1), while the downward virtual jump contributes an amount proportional to $(-n_1)$ so the resultant effect of both contributions is an amount which is independent of the quantum number, n_1. This, it will be recalled, is exactly analogous to the quantum-mechanical theory of the ordinary dispersion by a harmonic oscillator. There the positive dispersion due to the upward virtual jump increases with the quantum number, but so also does the negative dispersion due to the downward virtual jump, and in fact in exactly the same way as here so that the difference is independent of the quantum number.

If we substitute these values in (23) and use the resulting value of β in (22), the final result for the rotatory power of a medium containing N_1 of these models in unit volume, oriented at random, is

$$\varphi = \frac{2\pi N_1}{3}\cdot\lambda^{-2}\cdot\tfrac{1}{3}(n^2+2)\cdot d\sin\alpha\cos\alpha$$
$$\cdot\frac{e_1e_2}{(m_1m_2)^{\frac{1}{2}}}\left[\frac{1}{\nu_1^2-\nu^2}-\frac{1}{\nu_2^2-\nu^2}\right]. \quad (72)$$

This corresponds exactly with the result given by Kuhn and Freudenberg[31] except for the factor (1/3) in (72) which arises because (72) is the final formula applying for random orientations of the molecules whereas the equations (46) and (46a)

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[31] Kuhn and Freudenberg, reference 30, p. 59, Eqs. (46) and (46a).

of Kuhn and Freudenberg have still to be averaged. (Compare reference 30, pp. 72–76.)

It is of interest to note how (72) exhibits the two essential features of the model: (1) the oscillators must be coupled, for if k_{12} is zero then by (61), $\sin 2\alpha = 0$ so the rotation vanishes; and (2) the oscillators must be offset by the distance d as is evident from the proportionality of φ to d that occurs explicitly in (72).

As the foregoing calculations illustrate all the essential features of the coupled oscillator model, it will not be necessary to present the detailed calculations of the general case here. This will be found in the original papers of Born and Oseen[19] and also in the Kuhn and Freudenberg article[30] already referred to, pp. 69–72.

The results of such calculations may be stated as follows: Let the model consist of s particles, the charge and mass of the κth particle being e_κ and m_κ and let x_κ, y_κ, z_κ be the equilibrium coordinates of the κth particle with respect to a coordinate system fixed in the molecule. The potential energy will be assumed to be a general quadratic form in the displacements of the particles from equilibrium, u_κ, v_κ, w_κ being the displacements of the κth particle. This means that in general there will be $3s$ different proper frequencies and $3s$ normal modes of vibration, described by $3s$ normal coordinates $(a = 1, 2 \cdots 3s)$. Analogous to (60) we may express the connection between the displacements and the normal coordinates by

$$\xi_a = \sum_{k=1}^{s} (m_\kappa)^{\frac{1}{2}} (\alpha_{\kappa a} u_\kappa + \beta_{\kappa a} v_\kappa + \gamma_{\kappa a} w_\kappa) \qquad (73)$$

for $a = 1, 2, \cdots 3s$. Here the coefficients $\alpha_{\kappa a}$, $\beta_{\kappa a}$, $\gamma_{\kappa a}$ define an orthogonal transformation which is determined as usual by the requirement that the potential energy be expressed as a sum of squares in terms of the ξ_a coordinates. The coefficients therefore depend on the coupling terms in the potential energy.

The end result of the calculations is to show that the rotatory power is given by

$$\varphi = \frac{2\pi N_1}{3} \cdot \lambda^{-2} \cdot \tfrac{1}{3}(n^2+2) \sum_{a=1}^{3s} \frac{\mathbf{L}_a \cdot \mathbf{M}_a}{\nu_a{}^2 - \nu^2}. \qquad (74)$$

Here ν_a is the frequency associated with the normal coordinate ξ_a, and the vectors $\mathbf{L}_a$ and $\mathbf{M}_a$ are defined by

$$\mathbf{L}_a = \sum_{\kappa=1}^{s} \frac{e_\kappa}{(m_\kappa)^{\frac{1}{2}}} (\alpha_{\kappa a}\mathbf{i} + \beta_{\kappa a}\mathbf{j} + \gamma_{\kappa a}\mathbf{k}),$$

$$\mathbf{M}_a = \sum_{\kappa=1}^{s} \frac{e_\kappa}{(m_\kappa)^{\frac{1}{2}}} (\alpha_{\kappa a}\mathbf{i} + \beta_{\kappa a}\mathbf{j} + \gamma_{\kappa a}\mathbf{k}) \times (x_\kappa\mathbf{i} + y_\kappa\mathbf{j} + z_\kappa\mathbf{k}). \qquad (75)$$

It is easy to see that the vector $\mathbf{L}_a$ is related to the electric dipole moment belonging to the ξ_a mode of vibration and that $\mathbf{M}_a$ is related to the corresponding magnetic dipole moment. Hence this classical formula is related to the quantum-mechanical formula in a manner analogous to that revealed by our detailed calculations of the Kuhn model.

7. The Single Oscillator Model

Drude[32] proposed a model for optical activity in which a single electron was constrained to move on a helix while being elastically bound to an equilibrium position on the curve. This model stood in the literature for many years until Kuhn[33] in 1933 pointed out an error in the calculations. Kuhn showed that when correctly treated this model has no rotatory power. This result was extremely interesting in that it provided a case in which the rotatory power vanished in spite of the proper kind of dissymmetry being present. From this result he was inclined to conclude that coupled oscillators of the type discussed in the preceding section were essential to optical activity. The statement that rotatory power *requires* the existence of coupled oscillators for its explanation has been made repeatedly in the literature in recent years.

This view can no longer be held since the work of Condon, Altar and Eyring[29] has shown that it is possible to build a model of a single charged particle moving in a dissymmetric field which has rotatory power. This section will be devoted to a brief summary of that work: for further details the original paper should be consulted.

Most of our thinking about molecular electronic

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[32] Drude, *Göttinger Nachrichten* (1892), p. 400.

[33] Kuhn, Zeits. f. physik. Chemie **B20**, 325 (1933).

structure nowadays is done in terms of the Hartree approximation. In this each electron is regarded in the first approximation as moving in a static potential field due to the average charge distribution of the nuclei and of the other electrons in the molecule. This has been shown to be an accurate way of accounting for the larger part of the interaction between electrons. The dynamic coupling of the electrons only comes in in higher approximations. Now the coupled oscillator model of Born, Oseen, Kuhn and others takes account of this dynamic coupling of the electrons, but the question arises: If we are proceeding in the sense of a Hartree development, does optical activity make its appearance at the outset, where each electron is moving in the *static* average dissymmetric field of the rest of the molecule, or does it vanish in this approximation and first make its appearance when the *dynamical* coupling of electrons is considered? Kuhn's elimination of the Drude helix model had tended to make it appear that dynamic coupling of more than one electron was a necessary condition, until the single oscillator model was developed.

The single oscillator model assumes that an electron moves in a dissymmetric potential field in which the potential energy as a function of Cartesian coordinates, x_1, x_2, and x_3, is given by

$$V=\tfrac{1}{2}k_1x_1^2+\tfrac{1}{2}k_2x_2^2+\tfrac{1}{2}k_3x_3^2+Ax_1x_2x_3. \quad (76)$$

The term in A is what produces the necessary dissymmetry.

It is easy to see that an equipotential surface of (76) is qualitatively like what one would get if he took an ellipsoid of three unequal axes and subjected it to a torsional stress. An equipotential surface has elliptical cross sections when cut by any of the planes parallel to the basic planes of the coordinate system. For definiteness think of the section of the surface $V=$ constant by a plane $x_3=$ constant. The section by the plane $x_3=0$ is an ellipse whose principal axes are the x_1 and x_2 axes. For positive x_3 the section is an ellipse whose principal axes have turned around in the sense of a right-handed screw if $k_1>k_2$ and $A>0$. The same screw sense holds for $x_3<0$. Hence there is a right-handed screw sense associated with the x_3 axis under the conditions stated.

The screw sense associated with the other coordinate axes is easily determined in the same way. It turns out that in every case there is a screw sense associated with each axis and that two of these are alike while the third one is different. Thus in the special case

$$k_1>k_2>k_3 \quad \text{and} \quad A>0,$$

it turns out that one has a right-hand screw sense associated with the first and third axes and a left-hand screw sense associated with the second axis.

In the actual calculations the $Ax_1x_2x_3$ term is handled by perturbation theory based on a starting solution of the anisotropic oscillator problem represented by the quadratic terms in the potential. Thus the stationary states are labeled by harmonic oscillator quantum numbers $(n_1n_2n_3)$, corresponding to the energy levels,

$$W(n_1n_2n_3)=(n_1+\tfrac{1}{2})h\nu_1 + (n_2+\tfrac{1}{2})h\nu_2+(n_3+\tfrac{1}{2})h\nu_3, \quad (77)$$

which are not affected by the perturbation energy in at least the first two approximations. Here ν_1, ν_2, ν_3 are the frequencies determined by the force constants, k_1, k_2, k_3, in the usual way, $\nu_i=(2\pi)^{-1}(k_i/\mu)^{\frac{1}{2}}$. By the standard form of perturbation theory the first-order wave functions are found and from these the matrix components of electric and magnetic dipole moment correct to the first order are computed.

If we consider that the "molecules" represented by the model are in their lowest quantum state (0 0 0) then in the zeroth approximation only three upper states may be reached by ordinary electric dipole absorption of light, namely (1 0 0), (0 1 0) and (0 0 1). Likewise in the zeroth approximation the magnetic dipole moment has nonvanishing matrix components connecting (0 0 0) only with (0 1 1), (1 0 1), and (1 1 0). As these selection rules are mutually exclusive it follows that there is no jump from the normal state which has simultaneously nonvanishing matrix components of both $\mathbf{p}$ and $\mathbf{m}$, hence the rotatory power vanishes.

In the first approximation, however, one may get nonvanishing rotatory power associated with transitions from the normal state to all six of the excited states just enumerated. It will be convenient to consider explicitly the pair (0 0 0)→(1 0 0) and (0 0 0)→(0 1 1), as the other two pairs behave in exactly the same way and the results for them can be obtained by cyclic permutation of the indices. With regard to $(0\,0\,0)\rightarrow(1\,0\,0)$, here one has a zero-order **p** matrix component and is provided with a first-order **m** matrix component by the dissymmetric perturbation. In consequence this line is strong in ordinary absorption and also contributes to the rotatory power. On the other hand, $(0\,0\,0)\rightarrow(0\,1\,1)$ has a vanishing zero-order **p** component so its ordinary absorption power will be weak as the **p** component arises entirely from the dissymmetric perturbation. Its rotatory strength however will be comparable with that of the other absorption line, and in fact comes out actually equal and opposite to it.

This important qualitative distinction between the two lines corresponds exactly to an empirical generalization made by Kuhn.[34] He points out that empirically the strong bands ($f\approx 1$) have very small anisotropy factors ($g\approx 10^{-5}$) whereas the weak absorption bands ($f\approx 10^{-3}$) have much greater anisotropy factors ($g\approx 10^{-2}$) so that in order of magnitude the rotatory strengths ($fg\approx 10^{-5}$) are all about the same.

This result receives a very simple interpretation on the single oscillator model independently of the special form assumed in (76) for the effective force field. The dissymmetry in the effective field in which a particular electron moves is due to the action of the other atoms than the one or two to which the electron essentially belongs and therefore is weak, because the other atoms are farther away and because the dissymmetry is a residual high order effect due to the joint action of several neighbors. Hence there is a tendency for the electron to be governed by the selection rules which would hold rigorously if the dissymmetry were absent. In these the selection rules are mutually exclusive, **p**'s matrix component vanishing when **m**'s does not, and *vice versa*. When the selection rule is broken down by the dissymmetric field this will produce two classes of active bands, those which have a rotatory strength arising from a large **p** factor and a small **m** which will also have a large f value, and those which arise from a large **m** combined with a small **p** which will have a small f value.

Continuing the discussion of the particular single oscillator model which uses the field (76) we find that the value of β for a particle of charge e and mass μ when it is in the normal state is

$$\beta_{0\,0\,0}=\frac{A\hbar e^2}{12(2\pi)^5\mu^3}\left\{\left(\frac{1}{\nu_2}-\frac{1}{\nu_3}\right)\frac{1}{(\nu_2+\nu_3)^2-\nu_1^2}\left[-\frac{1}{\nu_1^2-\nu^2}+\frac{1}{(\nu_2+\nu_3)^2-\nu^2}\right]+\left(\frac{1}{\nu_3}-\frac{1}{\nu_1}\right)\frac{1}{(\nu_3+\nu_1)^2-\nu_2^2}\right.$$
$$\left.\times\left[-\frac{1}{\nu_2^2-\nu^2}+\frac{1}{(\nu_3+\nu_1)^2-\nu^2}\right]+\left(\frac{1}{\nu_1}-\frac{1}{\nu_2}\right)\frac{1}{(\nu_1+\nu_2)^2-\nu_3^2}\left[-\frac{1}{\nu_3^2-\nu^2}+\frac{1}{(\nu_1+\nu_2)^2-\nu^2}\right]\right\}. \quad (78)$$

A similar formula may be obtained for molecules in an arbitrary state (n_1, n_2, n_3). The general formula is given by Condon, Altar and Eyring.[29] It is interesting here only in this connection: it can be written in such a way that Planck's constant cancels out of the expression for the rotatory power from which it follows, with the aid of the correspondence principle, that this same model would show optical activity even if it were treated by classical mechanics. In other words, the nonvanishing rotatory power of the model is not a specific effect of quantum mechanics but is an essential property of the model from either the classical or the quantum-theoretic point of view.

Turning now to the question of how this model is to be applied to actual molecules, we see that it is first necessary to make a definite postulate concerning the part of the molecule which is responsible for a particular absorption band. This part is generally called the *chromophoric group* and there exists a fairly good body of empirical material about absorption spectra of polyatomic molecules which enables a decision to be made. The strongest part of the field in which the chromophoric electron moves is that due to the atom to which it belongs or the two atoms which it is bonding. This part of the field has to be estimated by the methods which are being

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[34] Kuhn, Trans. Faraday Soc. "Discussion on Optical Rotatory Power," 300 (1930). Also Kuhn and Freudenberg, *Hand und Jahrbuch der chemischen Physik*, Vol. 8, part 3, p. 84.

developed in other connections for dealing with molecular orbitals.

Superimposed on this local field is the field due to the other atoms and it is this which produces the dissymmetry. One can calculate an approximation to this field by assuming it to be due to point charges located at the center of each atom, the magnitudes of these charges being chosen in such a way as to represent the observed values of the static dipole moments arising from each bond. Fairly definite information about this can be obtained from the literature on dipole moments.[35] However, at present one is balked to some extent by lack of information about the extent to which partially hindered free rotations are hindered and such questions. The relation of optical rotatory power to these questions however probably means that in future developments study of rotatory power can be made to throw light on these and related problems of molecular structure.

Having made the best assumption possible about the system of effective charges arising in this way one may next calculate the effect of this field on a particular electron by developing the field in powers of the displacement of that electron about its mean position. In this way quadratic and cubic terms of the type introduced in (76) arise which result in a nonvanishing rotatory strength for that electron's transitions. This method of handling the field due to neighboring atoms is, of course, very much the same as that used so successfully by Van Vleck and others[36] in dealing with the effects of crystalline fields on magnetic susceptibility.

Some detailed calculations of this type may be found in the paper of Condon, Altar and Eyring.[29]

7*a*. ROTATORY STRENGTH AND POLARIZABILITY OF GROUPS

Just as this review was being finished there appeared an important paper by Kirkwood[a] who shows how to relate the quantum-mechanical theory of rotatory power to the polarizability of the groups and their mutual coupling. This section provides a brief review and commentary of the paper, written as an insert after completion of the rest of the report so the equations here will be numbered in a separate sequence denoted by (1a), (2a), etc. The notation of Kirkwood's paper has been changed where necessary to conform to that used elsewhere in this report.

We suppose that the electrons in the molecule may be unambiguously assigned to N different groups attached to a central group. Then for the total electric dipole moment we may write

$$\mathbf{p}=\sum_{i=1}^{N+1}\mathbf{p}^{(i)} \tag{1a}$$

where $\mathbf{p}^{(i)}$ is the electric dipole moment of the ith group defined as

$$\mathbf{p}^{(i)}=\sum_s e\mathbf{r}_s$$

in which $\mathbf{r}_s$ is the position vector of an electron in the ith group referred to an origin at the center of mass of that group and not at the center of mass of the molecule as formerly. Let R_k be the position vector of the center of mass of the kth group relative to that of the entire molecule then for the magnetic moment we have

$$\mathbf{m}=\frac{e}{2mc}\sum_k\mathbf{R}_k\times\mathbf{P}_k+\sum_k\mathbf{m}^{(k)} \tag{2a}$$

in which $\mathbf{P}_k$ stands for the total electronic momentum of the electrons in the kth group and $m^{(k)}$ stands for the magnetic dipole moment of the kth group computed with the position vectors of the electrons measured from the center of mass of that group. Now if we consider the electric and magnetic dipole moments written as sums of terms from different groups as in (1a) and (2a) then the rotatory strength R_{ba} associated with any one transition $a\rightarrow b$ can be written, from (32)

$$\begin{aligned}R_{ba}=&\operatorname{Im}\{(a|\sum_i\mathbf{p}^{(i)}|b)\\&(b|(e/2mc)\sum_k\mathbf{R}_k\times\mathbf{P}_k+\sum_k\mathbf{m}^{(k)}|a)\}\\=&\operatorname{Im}\{\sum_i(a|\mathbf{p}^{(i)}|b)\cdot(b|\mathbf{m}^{(i)}|a)\\&+\sum_{i\neq k}(a|\mathbf{p}^{(i)}|b)\cdot\mathbf{R}_k\times(b|\mathbf{P}_k|a)(e/2mc)\\&+\sum_{i\neq k}(a|\mathbf{p}^{(i)}|b)\cdot(b|\mathbf{m}^{(k)}|a)\}.\end{aligned} \tag{3a}$$

This equation corresponds to (24) of Kirkwood's

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[35] See for example, C. P. Smyth, *Dipole Moments and Molecular Structure.*

[36] Bethe, Ann. d. Physik **3**, 133 (1929); Kramers, Proc. Amsterdam Acad. **32**, 1176; **33**, 959 (1929–30); Penney and Schlapp, Phys. Rev. **41**, 194 (1932); Van Vleck, *Electric and Magnetic Susceptibilities*, Chap. XI.

[a] Kirkwood, J. Chem. Phys. **5**, 479 (1937).

paper. On the first line we have the sum of the contributions from the separate groups. These have a nonvanishing value because of the action of the neighboring groups in producing a dissymmetric field as discussed in the preceding section. The second line corresponds to the part which is of most importance in the coupled oscillator theories and is here in a form which lends itself to a discussion which is the main point of Kirkwood's paper. The third line is dismissed by Kirkwood as unimportant but without a thorough investigation of its magnitude. This point deserves to be studied more carefully.

The terms of the second line will now be discussed more fully. From the commutation rules we have for any one electron $H\mathbf{r}_i - \mathbf{r}_i H = \hbar \mathbf{p}_i / im$ and hence summing over the electrons in any, say the kth group

$$H\mathbf{p}^{(k)} - \mathbf{p}^{(k)}H = (e\hbar/im)\mathbf{P}^{(k)} \tag{4a}$$

which enables us to express the electronic momentum matrix components in terms of those of the group dipole moments:

$$\frac{e}{2mc}(b|\mathbf{P}^{(k)}|a) = (\pi i \nu_{ba}/c)(b|\mathbf{p}^{(k)}|a)$$

and therefore the particular contribution to R_{ba} on the second line of (3a) which we denote denote with $R_{ba}{}^{\circ}$ is, since $\mathrm{Im}\{iz\} = R\{z\}$

$$R_{ba}{}^{\circ} = (\pi \nu_{ba}/c)R\{\sum_{i \neq k}(a|\mathbf{p}^{(i)}|b)\cdot R_k \times (b|\mathbf{p}^{(k)}|a)\}.$$

Using standard properties of the mixed triple product and the fact that $R\{\bar{z}\} = R\{z\}$ this can be written

$$R_{ba}{}^{\circ} = (\pi \nu_{ba}/2c)R\{\sum_{i \neq k}(\mathbf{R}_k - \mathbf{R}_i) \cdot (a|\mathbf{p}^{(k)}|b) \times (b|\mathbf{p}^{(i)}|a)\} \tag{5a}$$

In the sum each pair (i, k) appears twice, once as (i, k) and again as (k, i). This result exhibits clearly the features that were emphasized in §6 in the more classical discussion of the coupled oscillators: $R_{ba}{}^{\circ}$ has the same dimensions as the ordinary strength S_{ba} namely square of dipole moment, but is smaller for two reasons. Firstly $R_{ba}{}^{\circ}$ is small because of the fact that $(\mathbf{R}_k - \mathbf{R}_i)$, the vector distance from group i to group k, is divided by c/ν_{ba} the wave-length of the quantum jump frequency of the active band in question which is large compared to the size of the molecule. Secondly, $R_{ba}{}^{\circ}$ is small because it owes its existence entirely to the weak dynamic coupling between different groups.

To see this, consider the case in which the dynamic coupling between groups could be ignored. This means that the Hamiltonian can be represented adequately as a sum of separate Hamiltonians, one for each group and that the ensemble of quantum numbers symbolized by a and b would break up into sets referring separately to each group. This is, a would be $a_1 a_2 \cdots a_{n+1}$ where a_k refers only to the kth group. If this were the case then the only nonvanishing matrix components $(a|\mathbf{p}^{(i)}|b)$ would be those in which b is the same as a with regard to all other quantum numbers than those of the ith group and similarly for $(a|\mathbf{p}^{(k)}|b)$. Therefore, in the absence of dynamic coupling the selection rules for $\mathbf{p}^{(i)}$ and $\mathbf{p}^{(k)}$ are mutually exclusive and $R_{ba}{}^{\circ}$ vanishes. Therefore, to get a nonvanishing rotatory power it is really essential to consider the coupling of the electronic groups in the molecule.

Various assumptions about the nature of this coupling might be made but if one assumes ordinary Coulomb interaction between the electrons in the groups then the first term in a development in inverse powers of the distance is the dipole-dipole interaction energy. This can be written

$$V = \sum_{l>j=1}^{N} \mathbf{p}^{(l)} \cdot \mathbf{T}_{lj} \cdot \mathbf{p}^{(j)} \tag{6a}$$

where $\mathbf{T}_{lj} = R_{jl}{}^{-3}[1 - 3\mathbf{R}_{jl}\mathbf{R}_{jl}/R_{jl}{}^2]$.

The effect of this on the wave functions and hence on the matrix components can be taken into account by ordinary perturbation theory. The details of this will be found in Kirkwood's paper, the end result being a formula for the rotatory strengths which depends on the polarizabilities of the interacting groups.

8. Solvent Effect and the Effective Field Correction

According to the arguments of §2 which led up to (22), the parameter β is a property of individual active molecules. If the rotatory power, φ, is measured and the molecular density N_1 and the refractive index n are known, then by means of (22) one may calculate an empirical value of β. This will be the effective value of β for the active molecules in the average conditions in which they exist in the particular medium for which the measurements were made.

The question arises: Is the parameter β a constant property of the individual molecule quite independent of the molecular environment? In this section we wish to review the evidence which shows that the answer to this question is in the negative. It turns out that β is generally quite sensitive to the molecular environment. This is called the solvent effect. In this respect β is quite different from the ordinary polarizability α which generally shows a constant value leading to the well-known additivity laws for ordinary molecular refractivity.

First let us consider what happens on change of state from liquid to vapor. In the vapor state the molecules are far apart while in the liquid they are densely packed together. The simplest thing to assume would be that in spite of the change in average environment the value of β is the same in both states. If this is the case it s easily seen from (22) that

$$[\varphi]/\tfrac{1}{3}(n^2+2)$$

should be continuous at the change of state since N_1 is proportional to the density, ρ. For all vapors the index of refraction is so close to unity that one may set $\frac{1}{3}(n^2+2)=1$. For liquids, however, the factor is usually between 1.30 and 1.50. Hence if β does not change, the specific rotatory power $[\varphi]$ should show the same discontinuity at the change of state as the factor $\frac{1}{3}(n^2+2)$ namely a 30 to 50 percent decrease in going from liquid to vapor.

This is in conflict with the usual statement[37] that $[\varphi]$ itself is continuous with change of state. But the available data are quite meager. The most detailed investigation is that of Guye and Amaral.[38] Their results, however, are not accurate enough for a definite conclusion. Their final table of results (reference 38, p. 527) is given in Table II. From the table we see that there is no great discontinuity in $[\varphi]$ at the change of state, that in most cases $[\varphi]$ for liquid is greater than for the vapor as would be required by constant β but this is not true in every case and in no case are the data good enough for a definite check. It appears therefore that one can only say that β does not change much on change of state, if at all.

TABLE II. *Rotatory power in vapor and liquid states. (Guye and Amaral.)*

SUBSTANCE	$[\varphi]$ VAPOR	$[\varphi]$ LIQUID
Valeric aldehyde	7.1 to 6.4	14.6
Amyl acetate	2.6 3.2	2.8
Methyl valerate	14.3 14.5	16.4
Amyl chloracetate	1.9 1.6	3.1
Diamyl	10.7 10.9	11.1
Amyl amine	2.1 2.2	1.8
Amyl bromide	1.9	2.8
Amyl iodide	3.9 to 4.1	5.6
Amyl alcohol	5.8 6.5	5.1
Valeric acid	10.7 10.9	13.5

A modern investigation of the rotatory dispersion of camphor in the vapor phase has been made by Lowry and Gore.[39] They measured both the vapor at 180°C and a solution of camphor in cyclohexane at 20°C. These data are not comparable because of the difference in temperature involved.

Similarly in case of inactive solvents where there is very small disturbance of the solute molecules by those of the solvent we should expect to find the same value of β on applying (22) to the observed rotations independently of the choice of the solvent. This question was first studied from this point of view by Wolf and Volkmann[40] and has recently been the subject of a long series of experimental investigations by Rule[41] and his associates. In general the results indicate that for a nonpolar active substance in a nonpolar solvent the quantity $[\varphi]/\frac{1}{3}(n^2+2)$ is more nearly constant than $[\varphi]$. But in case of polar solvents and polar active substances there are great differences which indicate large changes in the effective value of β produced by solvation. Thus Pickard and

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[37] For example Lowry, *Optical Rotatory Power*, p. 102 or Bruhat, *Traité de Polarimetrie*, p. 194.

[38] Guye and Amaral, Arch. Sci. Phys. Nat. Geneva **33**, 409, 513 (1895).

[39] Lowry and Gore, Proc. Roy. Soc. **A135**, 13 (1932).

[40] Wolf and Volkmann, Zeits. f. physik. Chemie **B3**, 139 (1929); Volkmann, Zeits. f. physik. Chemie **B10**, 161 (1930).

[41] Rule, various papers in the J. Chem. Soc. London from 1931 to 1937, under the general heading, "Studies in Solvent Action."

Kenyon[42] found that the sign of the rotatory power is different for β-hexyl stearate in two different solvents:

$$[\varphi]=+20.21 \quad \text{in alcohol,}$$
$$[\varphi]=-\ 8.93 \quad \text{in carbon disulphide.}$$

A great deal of information of this kind is to be found in Lowry's book.

What is very important and what has been very much neglected hitherto is the study of rotatory dispersion in relation to solvent effect. Clearly one may expect the rotatory contributions of different chromophoric groups to be differently affected by association or loose compound formation with the solvent. The data ought to be complete enough to show how the individual rotatory strengths, R_{ba}, of the various bands, ν_{ba}, change on solution.

On the theoretical side a somewhat phenomenological treatment of solvent action has been given recently by Beckmann and Cohen.[43] In this they attempt to connect the solvent action principally with a deformation of the molecular frame.

9. Circular Dichroism

As mentioned in the introduction, circular dichroism consists in a difference in the absorption of right and left circularly polarized light by the medium. It is observed by determining the ellipticity of the elliptically polarized light transmitted by the active medium from a beam that is initially linearly polarized. It is the property that is related to optical rotatory power in the same way that ordinary dispersion is related to ordinary absorption.

Experimental technique for observing circular dichroism is described in the books by Lowry and by Bruhat already cited, also in the Cornell lectures of Jaeger.[44]

In the older electronic theories of dispersion the connection between refraction and dispersion is always obtained by formal introduction of a *damping* term in the equation of motion of the electron. The damping term is in the form of a force proportional to the velocity and opposite to it in direction so that no matter how the electron moves energy must always be given up to do work against this force. As is well known this acts to cut down the sharpness of resonance and leads to a considerable absorption of energy at frequencies near the resonant frequency where the forced oscillation is relatively great. Various proposals have been made to give a physical account of the origin of the damping term, the two most important being the *radiation damping* of Planck[45] and the *collision damping* of Lorentz.[46] On the radiation damping picture the loss of energy from the original beam is due to the scattering of radiation in all directions by the radiation due to the forced oscillations of the electron. The collision damping is the expression for the average energy loss associated with the interruption of the forced oscillations by collisions of other molecules with the resonator.[47]

In dealing with the absorption of light by matter a number of different measures of absorptive power are in common use. For theoretical purposes the most convenient mode of description is by means of the complex index of refraction, usually written $\mathbf{n}=n(1-i\kappa)$. With this form of the index of refraction in (3) the equation for the propagation of the electric induction for example is

$$\mathbf{D}=R\{D_0e^{i\psi}\}=\exp\left(-2\pi\nu n\kappa\mathbf{k}\cdot\mathbf{r}/c\right) \times R\{\mathbf{D}_0\exp\left(2\pi i\nu(t-n\mathbf{k}\cdot\mathbf{r}/c)\right)\}, \tag{79}$$

so the amplitude of $\mathbf{D}$ diminishes with an exponential factor which depends on the imaginary part of the index. Since the intensity of the light wave is proportional to the mean value of $\mathbf{D}^2$, the intensity falls off exponentially according to the formula,

$$I=I_0e^{-4\pi\nu n\kappa z/c}, \tag{80}$$

where z is the distance traveled in the medium. The coefficient of z in the exponential here is called the *extinction coefficient* of the medium and is usually (as in §1) denoted by ϵ so

$$\epsilon=\frac{4\pi\nu n\kappa}{c}=\frac{4\pi n\kappa}{\lambda}, \tag{81}$$

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[42] Pickard and Kenyon, J. Chem. Soc. **105**, 830 (1914).

[43] Beckmann and Cohen, J. Chem. Phys. **4**, 784 (1936).

[44] Jaeger, *Optical Activity and High Temperature Measurements* (McGraw-Hill, 1930), Appendix, page 215.

[45] Planck, Ann. d. Physik **60**, 577 (1897).

[46] Lorentz, Proc. Amsterdam Acad. **14**, 518, 577 (1906).

[47] For modern accounts of these theories see Margenau and Watson, Rev. Mod. Phys. **8**, 22 (1936); also Born, *Optik* (Berlin, 1933), Chapter 8.

where, as always in this report, λ means the *vacuum* wave-length. (In some accounts λ means the wave-length in the medium, i.e., our λ/n so the n does not appear explicitly in the numerator.)

The reader will have no difficulty in showing that (6) and (10) can be neatly unified with the aid of the complex index of refraction. Let us write φ' for Ψ/d, which is the ellipticity per unit length and consider φ and φ' to be united into the single complex quantity $(\varphi - i\varphi')$ which we shall call the *complex rotatory power.*

Then (6) and (10) can be combined into the single equation

$$(\varphi - i\varphi') = (\pi/\lambda)(\mathbf{n}_l - \mathbf{n}_r), \tag{82}$$

in which $\mathbf{n}_l$ and $\mathbf{n}_r$ are the *complex* indices of refraction for left and right circularly polarized light respectively. In other words, *the complex rotatory power is related to the complex indices in the same way that ordinary rotatory power is related to the real indices.* This compact result is extremely useful in discussing the connections of rotatory power and circular dichroism.

Before considering the theory of circular tichroism further it will be convenient to define another measure of absorptive power that is often found in the experimental literature. This is called the molecular or molar absorption and is also usually denoted by κ but will here be denoted by κ' to distinguish it from the imaginary part of the complex index of refraction. It is defined by the equation

$$I = I_0 10^{-\kappa' C z}, \tag{83}$$

in which z is in cm and C is the concentration of the absorbing material in mole/liter. The connection between κ' and ϵ is evidently

$$\epsilon = 2.303\kappa' C. \tag{84}$$

One can also introduce an easily visualized quantity which is closely related to the molecular absorption coefficient, namely the effective cross section of the molecule for absorption of a light quantum of the type under consideration. Let A be this effective cross section, then if there are N_1 absorbing molecules per cm^3 the probability of a light quantum getting through a thickness z without being absorbed is, by familiar arguments, $e^{-N_1 A z}$. On the other hand if the concentration is C mole/liter then $N_1 = NC/1000$ where N is Avogadro's number and therefore

$$A = (2.303/N)\kappa' = \kappa' \cdot 3.81 \cdot 10^{-21}\ \text{cm}^2. \tag{85}$$

As κ' in ordinary absorption bands is of the order 10 to 10^3 we see that the effective cross-sectional area of the molecules is in general small compared to the actual cross-sectional area of the molecule (10^{-16} cm^2).

In the classical electron theory the absorption is treated by introducing the damping term into the equation of motion of the electronic oscillator. If the electron is elastically bound to the origin so its natural frequency is ν_0 then its equation of motion is assumed to be

$$m\ddot{r} + 2\pi m \Gamma_0 \dot{r} + (2\pi\nu_0)^2 m r = e\mathbf{F}, \tag{86}$$

where Γ_0 measures the strength of the damping term and in what follows we assume that $\Gamma_0 \ll \nu_0$. Here $\mathbf{F}$ stands for the effective field acting on the electron and is the same as the $\mathbf{E}'$ of (17). If $\mathbf{F} = \mathbf{F}_0 e^{2\pi i \nu t}$ so the frequency of the light responsible for the forced vibrations is ν then the steady state solution of (86) becomes, in the familiar way,

$$e\mathbf{r} = e\mathbf{r}_0 e^{2\pi i \nu t} = \frac{e^2/m}{4\pi^2[(\nu_0^2 - \nu^2) + i\nu\Gamma_0]}\mathbf{F}. \tag{87}$$

This gives us the dipole moment due to the coherent forced oscillation and thus is the classical analog of the quantum-theoretic dispersion formula (56α). In establishing the correspondence the coefficient of $\mathbf{F}$ in (87) is multiplied by the oscillator strength f_{ba} as defined in (26) and equated to the coefficient of $\mathbf{F}$ in (87). If this be done we obtain for the polarizability a modified form of (27) in which the effect of damping is included in the denominator,

$$\alpha_a = \frac{2}{3h}\sum_b \frac{\nu_{ba} S_{ba}}{(\nu_{ba}^2 - \nu^2) + i\nu\Gamma_{ba}}. \tag{88}$$

This result, obtained by formal alteration of the denominators is correct for quantum theory, but the full proof of it is rather elaborate and leads into the Wigner-Weisskopf theory of natural line widths.[48] The corresponding generalization of the theory of rotatory power to include damping has not been worked out but from general considerations it is fairly clear that the

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[48] See Breit, Rev. Mod. Phys. 5, 91 (1933).

end result would be a similar alteration of (56β) or (23) with the same change in the resonance denominators. Thus it is probable that (23) would become

$$\beta_a=\frac{c}{3\pi h}\sum_b\frac{R_{ba}}{\nu_{ba}{}^2-\nu^2+2\pi i\nu\Gamma_{ba}},\tag{89}$$

in which the damping constants Γ_{ba} are the same as in (88). With this complex value for β_a we obtain for the complex rotatory power an obvious generalization of (22)

$$(\varphi-i\varphi')=\frac{16\pi^3N_1}{\lambda^2}\cdot\frac{n^2+2}{3}\cdot\beta.\tag{90}$$

Separating the real and imaginary parts we obtain formulas for the rotation per unit length and the ellipticity per unit length respectively,

$$\begin{aligned}\varphi&=\frac{16\pi^2N_1}{3hc}\sum_b\frac{\nu^2(\nu_{ba}{}^2-\nu^2)R_{ba}}{[(\nu_{ba}{}^2-\nu^2)^2+\nu^2\Gamma_{ba}{}^2]},\\ \varphi'&=\frac{16\pi^2N_1}{3hc}\sum_b\frac{\nu^3\Gamma_{ba}R_{ba}}{[(\nu_{ba}{}^2-\nu^2)^2+\nu^2\Gamma_{ba}{}^2]}.\end{aligned}\tag{91}$$

These formulas are of the same form as those obtained originally by Drude[49] except that they have been brought into correspondence with the quantum mechanically defined rotatory strengths, R_{ba}.

In applying these formulas to the experimental data the fact of the extreme smallness of the radiation damping coefficient must be borne in mind. Hence when experiment gives a broad band several hundred angstrom units in width it will not do to choose a Γ_{ba} large enough to make the absorption band extend over this great a region according to (91). (It is easy to see that Γ_{ba} has the meaning of being the full width from half-maximum absorption on the low frequency to half-maximum absorption on the high frequency side of the band.) To do this would call for impossibly large values of Γ_{ba} and would give the wrong shape to the absorption band in that weak absorption would persist to too great a frequency range around the maximum.

Instead the actual absorption bands due to molecules in the gas phase or especially when in solution have to be regarded as due to an enormous number of quite sharp lines corresponding to a vast number of possible rotation and vibration transitions. It is even convenient to think of the broadening of individual lines by collision in this same way. A broadened line may be regarded as the resultant effect of a large number of sharp lines all close together produced by different individual molecules which have been perturbed by the surrounding molecules to various degrees.

Equations of the form (91) were derived also by Natanson[50] in an important classical treatment of circular dichroism. In this paper was enunciated a generalization known as Natanson's rule: *The wave that is most strongly absorbed also travels more slowly, for frequencies less than the absorption frequency.* The equations were studied from an experimental point of view by Bruhat[51] who found that they represented his observations quite accurately, these being largely confined to studies on tartrates which involve metal ions with visible absorption like chromium and copper.

The modern work on circular dichroism is largely due to Kuhn and his associates.[52] Bielicki and Henri[53] showed that in many absorption bands the absorption coefficient for complicated molecular bands follows the law,

$$\epsilon(\nu)\sim e^{-(\nu-\nu_0)^2/\theta^2}.$$

This simply means that if the logarithm of the absorption coefficient is plotted against the frequency the resulting curve is a parabola with vertex upward. Kuhn and his associates have adopted a similar representation for the spectral distribution of rotatory power in an absorption band for the empirical representation of their data. This has proved to be much more satisfactory than the way which accounts for the width of the band by simply choosing a very large value of Γ for the band in question.

In the paper by Condon, Altar and Eyring[29] explicit calculations are carried out quantum-mechanically to show that the aborption transition probability for right and left circularly polarized light are different when the calculations are carried to the same degree of approximation as is necessary to get rotatory power as in §4.

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[49] Drude, Ann. d. Physik **48**, 536 (1896).

[50] Natanson, J. de phys. **8**, 321 (1909).

[51] Bruhat, Ann. d. Physik **3**, 232, 417 (1915).

[52] See especially Kuhn and Braun, Zeits. f. physik. Chemie **B8**, 281 (1930) and numerous other papers in the same journal subsequently.

[53] Bielicki and Henri, Physik. Zeits. **14**, 516 (1913).