so kann β und näherungsweise für kleine β auch $|v_3|$ als das Verhältnis der Materiegeschwindigkeit in der x_3-Richtung zur Lichtgeschwindigkeit gedeutet werden. Aus den Feldgln. (9), (14) läßt sich v_3 als Funktion von λ, ν gewinnen:

$$\begin{aligned} 4(\lambda_{|1|1} + \lambda_{|2|2} + \nu_{|1}^2 + \nu_{|2}^2 - \Delta\nu)\, \Delta\boldsymbol{\nu} \cdot v_3^2 \\ = (\lambda_{|1|1} + \lambda_{|2|2} + \nu_{|1}^2 + \nu_{|2}^2)^2 \qquad (81) \\ - \left(\frac{\lambda_{|1}}{x_1} - \nu_{|1}^2 + \nu_{|2}^2\right)^2 - \left(\frac{\lambda_{|2}}{x_1} - 2\,\nu_{|1}\,\nu_{|2}\right)^2. \end{aligned}$$

Setzt man hierin $v_3 = 0$ ein, so wird man auf die Gl. (44) zurückgeführt, die für unsere statischen Lösungen von entscheidender Bedeutung war. Die 17 Feldgln. der BECHERTschen Theorie (9) bis (12) lassen sich auf drei nichtlineare, noch einigermaßen übersichtliche Diff.-Gln. zurückführen, deren Lösungsmöglichkeiten von BECHERT und LINDNER untersucht werden. Beim Aufsuchen von Lösungen kann man einmal von erweiterten Lösungen der statischen Modelle ausgehen, zum anderen läßt sich der ungefähre Verlauf der elektromagnetischen Feldstärken in größerer Entfernung von einer rotierenden Ladungsverteilung aus klassischen Überlegungen gewinnen.

Mein herzlicher Dank gilt Herrn Professor BECHERT, der mich nicht nur bei vielen unbefriedigend verlaufenen Lösungsversuchen seiner Feldgleichungen unermüdlich beraten hat, sondern auch an dem Auffinden der geschilderten Lösungen mitbeteiligt war. Der Studienstiftung des Deutschen Volkes und dem Lande Rheinland-Pfalz danke ich für die großzügige Bereitstellung von Geldmitteln zur Durchführung dieser Untersuchungen.

Theory of Optical Activity of Molecules, Polymer Chains and Crystals

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The polarisability theory of optical activity has been fully worked out in tensor notation, giving formulae for birefringence and optical activity of a crystal kept in an arbitrary orientation in a beam of light. It is shown that the theory so developed can also be applied to a simple molecule or a polymer chain of fixed orientation, with some minor modifications. Compact formulae have been obtained useful for these cases, which also bring out the idea of "coupled oscillators" for the occurrence of optical activity. The formulae can also be averaged over all orientations and this leads to an expression for the specific rotation of a solution of a polymer containing helical chains. The theory, as applied to the α-helix and other helices occurring in proteins and polypeptides is being reported separately.

Theories of optical activity are generally of two types, either involving coupled oscillators [1], or purely in terms of optical principles, usually referred to as the polarisability theory [2]. KIRKWOOD [3] has shown that the quantum mechanical formulation of the coupled oscillators leads to the polarisability theory when certain reasonable approximations are made. RAMACHANDRAN [4] has applied the polarisability theory for calculating the rotatory power of β-quartz and some other crystals of simple structure, and has found reasonably satisfactory agreement with experiment. But similar calculations, from first principles, cannot be attempted on crystals having a more complicated structure, because of the forbidding nature of the numerical computations. In this paper a general mathematical formulation of the polarisability theory is presented. Formulae are given in a very compact form by making use of tensor notation, and they may be conveniently used in calculating the rotatory power of crystals or solutions, i. e., randomly orientied molecules or chains of molecules. The method also leads to similar compact formulae for calculating the refractive indices of crystals for different directions. The theoretical formulae derived here have been applied to calculate the optical activity of helical structures such as polypeptides. This will be reported separately.

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[1] eg. M. BORN, Phys. Z. **16**, 251 [1915].

[2] eg. G. N. RAMACHANDRAN, Proc. Ind. Acad. Sci. A **33**, 217 [1951], which contains also detailed references to earlier literature.

[3] J. G. KIRKWOOD, J. Chem. Phys. **5**, 479 [1937].

[4] G. N. RAMACHANDRAN, Proc. Ind. Acad. Sci. A **33**, 309 [1951]; **34**, 127 [1951].

1. The electromagnetic theory

We shall first work out the theory for a crystal kept in an arbitrary orientation in a beam of light. The theory so developed can also be applied to a simple molecule or a polymer chain of fixed orientation, with some minor modifications. The result of the latter can then be averaged over all orientations so as to obtain the specific rotation of a solution.

Considering the case of the crystal, if the coordinate axes are taken along the principal axes of the crystal, the components of the displacement vector $\mathfrak{D}$ and the electric vector $\mathfrak{E}$ of a linearly polarised wave will be connected by the relations [5]

$$D_x = K_1 E_x + i(\mathfrak{G}\times\mathfrak{E})_x \quad \text{etc.,} \tag{1}$$

$$G_x = g_{11} S_x + g_{12} S_y + g_{13} S_z \quad \text{etc.} \tag{2}$$

where K_1, K_2, K_3 are the principal dielectric constants and $\mathfrak{G}$ is the gyration vector whose components are given by (2) as linear functions of the components of the unit vector $\mathfrak{S}$ specifying the direction of the wave normal. The parameters g_{ij} form a tensor of rank two, which in general need not be symmetric. However, the rotatory power along any direction in the crystal depends only on the symmetric part, neamly $\frac{1}{2}(g_{ij}+g_{ji})$. It can be shown [5] that the behaviour of an optically active crystal depends essentially on the parameter

$$G = \mathfrak{S}\cdot\mathfrak{G}\,. \tag{3}$$

Thus, if n_0', n_0'' are the two refractive indices, the crystal would have in the absence of optical activity for propagation along $\mathfrak{S}$, then the refractive indices of the two elliptically polarised waves that can be transmitted in the actual crystal are the positive roots n', n'' of the equation

$$(n^2 - n_0'^2)\,(n^2 - n_0''^2) = G^2. \tag{4}$$

For propagation along an optic axis, or along any direction if the crystal is isotropic, $n_0' = n_0'' = \bar{n}$, say. Equation (4) then gives $n^2 - \bar{n}^2 = \pm G$ and since G is small, the refractive indices of the two circularly polarised waves may be written

$$n_{\mathrm{l}} = \bar{n} + \frac{G}{2\bar{n}}\,, \qquad n_{\mathrm{r}} = \bar{n} - \frac{G}{2\bar{n}} \tag{5}$$

and the rotatory power of the crystal is

$$\varrho = \frac{\pi}{\lambda_0}\,\frac{G}{\bar{n}}\ \text{rad./cm.} \tag{6}$$

This equation is in agreement with the sign convention for optical activity adopted by writers on optics (e. g. Ref. 5), i. e. laevorotation corresponds to positive ϱ. However, in chemical literature, the opposite convention is used, particularly for solutions, so that when we calculate the specific rotation $[\alpha]$ of a solution, it will be related to ϱ by a negative sign as in (41).

It is obvious from the above that an actual rotation of the plane of polarisation of magnitude given by (6) occurs only in isotropic bodies and along the optic axes of an anisotropic crystal. For any other direction, the medium can be considered to have an optical rotatory power (6), where G is given by (3), which is the value it would have if there were no birefringence. So also, we may consider the medium to possess a birefringence $\Delta n = n_0' - n_0''$ in addition to its rotatory power. If δ is the phase difference introduced per unit length due to the birefringence, then the phase difference Δ between the two elliptically polarised waves propagated along a general direction is given by [5]

$$\Delta^2 = \delta^2 + (2\,\varrho)^2, \tag{7}$$

where ϱ is given by (6), with the value (3) of G. In (6) one uses the mean refractive index $\bar{n}$ given by [5]

$$\bar{n}^3 = \frac{n_0'^2\, n_0''^2}{\frac{1}{2}(n_0' + n_0'')}\,. \tag{8}$$

It is known that this "method of superposition" gives results closely agreeing with observed facts for anisotropic optically active crystals. The problem of calculating the optical activity of a crystal therefore reduces to the determination of the parameter G for various directions, i. e. the components of the tensor g_{ij}. Since this tensor is directly connected to the expression (1) for $\mathfrak{D}$ in terms of $\mathfrak{E}$, occurring as it does only in the imaginary part of $\mathfrak{D}$, it should be sufficient to obtain an expression for the displacement vector $\mathfrak{D}$ in terms of the crystal structure and the polarisability tensor of its constituent parts. It is then possible to obtain an expression for g_{ij} in terms of the structural parameters.

This is the basic idea of the theory. For a molecule oriented at random, it comes out that in equation (6), G is just equal to $(g_{11} + g_{22} + g_{33})/3$ so that this becomes a special case of the general treatment.

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[5] G. N. Ramachandran and S. Ramaseshan, Crystal Optics, Handbuch der Physik, Bd. **24**. Springer-Verlag, Berlin (in press).

2. Basic formulae for curvilinear coordinates

In view of the fact that the theory is to be applied particularly to helical structures, the formulae have been developed using a general curvilinear coordinate system, and using the tensor notation for such a system. Obviously, such formulae will also be valid for any special coordinate system appropriate to a particular problem, e. g. an orthogonal cartesian system, or an oblique system as will be used for crystals of low symmetry.

The standard notations of tensor analysis have been followed throughout. Indices occur both as superfixes and suffixes, the former denoting contravariance and the latter covariance. The indices take on the values 1, 2, 3. Coupled indices, such as l in equation (10), denote summation for the three values of the index, and no separate symbol for this summation is used. Indices are also used for denoting particular quantities, e. g. (jk) in $R_l^{(jk)}$. Such indices are enclosed in brackets and they do not possess tensorial character.

Associated tensors are formed by the usual process of raising or lowering the indices. For example, S_t and S^l occurring in (11) are connected by the relation $S_t = a_{tl} S^l$ where a_{tl} is the metric tensor in the covariant form. Its relationship to the metric tensor in the contravariant form is given by $a_{tl}\, a^{sl} = \delta_t^s$ where δ_t^s is the KRONECKER delta. Associated tensors represent the same physical quantity, though their components may be different.

In a general coordinate system equations (1) and (2) of the electromagnetic theory take the tensorial form

$$D_s = K_{sq} E^q + i\, \varepsilon_{stq}\, G^t E^q\,, \tag{9}$$

$$G^t = g_l^{\,t} S^l \tag{10}$$

where G^t is the gyration vector, $g_l^{\,t}$ is the gyration tensor and S^l is the unit vector specifying the direction of the wave normal. Also

$$\varepsilon_{stq} = \sqrt{a}\; e_{stq}$$

and

$$a = \det(a_{jk})$$

where e_{stq} is the skew symmetric tensor whose components are ± 1 according as $s\,t\,q$ is an even or odd permutation of 123, and zero in all other cases. The parameter G of equation (6) may now be written

$$G = S_t\, G^t = g_l^{\,t}\, S_t\, S^l\,. \tag{11}$$

Equations (9) and (10) determine the optical properties of the crystal. The refractive index is given by the tensor K_{sq} and the optical rotation along any direction is given by the tensor $g_l^{\,t}$. Both these can be obtained if we can get the relation between the displacement vector D_s and the electric vector E^q from the structure. We now proceed to obtain this relation.

3. Calculation from crystal structure

Let the incident plane polarised wave be represented by

$$E^q \exp \frac{i\, 2\, \pi\, n}{\lambda_0}\, (v\, t - R_l\, S^l)$$

where n is the refractive index and λ_0 the wavelength in vacuo. Leaving out the time factor $\exp \frac{i\, 2\, \pi\, n}{\lambda_0}\, v\, t$ let the macroscopic field at atom j be E^q. The position of an atom k with respect to j may be specified by a vector $R_l^{(jk)}$ defined at j. Then, the field at atom k, including the LORENTZ field may be written

$$f^q_{(k)} = \left(E^q + \frac{4\, \pi\, P^q}{3}\right) \exp \frac{-i\, 2\, \pi\, n}{\lambda_0}\, R_l^{(jk)}\, S^l \tag{12}$$

where P^q is the electric moment per unit volume. The induced moment in atom k, neglecting interaction of neighbours is $\alpha^{(k)}_{pq}\, f^q_{(k)}$ where $\alpha^{(k)}_{pq}$ is the polarisability tensor of atom k. The contribution to the field at atom j by the dipole moment induced in atom k is thus given by

$$F^m_{(j)} = T^{mp}_{(jk)}\, \alpha^{(k)}_{pq}\, f^q_{(k)} \tag{13}$$

where $T^{mp}_{(jk)}$ is the dipole-dipole interaction tensor which may be written in the form

$$T^{mp}_{(jk)} = \frac{1}{r^5}\, (3\, R^m_{(jk)}\, R^p_{(jk)} - r^2\, a^{mp}) \tag{14}$$

where $r^2 = a_{st}\, R^s_{(jk)}\, R^t_{(jk)}$

i. e., r is the distance between atoms j and k. In writing equation (13) it is presumed that the induced field at atom j is in phase with the moment of atom k, and hence out of phase with the macroscopic field E^q at atom j. This is true because $r \ll \lambda$, the ratio being of the order of 1/1000 for the atoms in the immediate neighbourhood. The LORENTZ field, on the other hand, is a contribution by the more distant regions of the medium, and may be taken to be in phase with E^q. This implies that in optically active crystals the LORENTZ field is real even though P^q is complex, and must be taken as $\frac{4\, \pi}{3} P^q(\text{real})$.

The effective field at atom j is then

$$E^m + \frac{4\, \pi}{3}\, P^m(\text{real}) + \sum_{j \neq k = 1}^{N} F^m_{(j)} \tag{15}$$

where N is the number of atoms within the LORENTZ's sphere. The induced moment in atom j is

$$M_s^{(j)} = \alpha_{sm}^{(j)} \left[E^m + \frac{4\pi}{3} P^m(\text{real}) + \sum_{j \neq k = 1}^{N} F_{(j)}^m \right]$$

$$= \left(E^q + \frac{4\pi}{3} P^q(\text{real}) \right) \qquad (16)$$

$$\cdot \left[\alpha_{sq}^{(j)} + \alpha_{sm}^{(j)} \sum_{j \neq k = 1}^{N} T_{(jk)}^{mp} \alpha_{pq}^{(k)} \left(1 - \frac{i\, 2\pi n}{\lambda_0} R_l^{(jk)} S^l \right) \right]$$

where we have replaced the exponential function in $F_{(j)}^m$ by the first two terms of its power series on account of the smallness of the argument. Also since

$$P_s = \frac{1}{V} \sum_{j=1}^{N'} M_s^{(j)}$$

where V is the volume of the unit cell and N' the number of atoms in it, we have

$$P_s = \left(E^q + \frac{4\pi}{3} P^q(\text{real}) \right) (\Phi_{sq} + i\, \Phi'_{sq}) \qquad (17)$$

$$\text{where } \Phi_{sq} = \frac{1}{V} \sum_{j=1}^{N'} \left(\alpha_{sq}^{(j)} + \alpha_{sm}^{(j)} \sum_{j \neq k = 1}^{N} T_{(jk)}^{mp} \alpha_{pq}^{(k)} \right) \qquad (18)$$

and

$$i\, \Phi'_{sq} = -\frac{i\, 2\pi n}{\lambda_0} \frac{1}{V} \sum_{j=1}^{N'} \sum_{j \neq k = 1}^{N} \alpha_{sm}^{(j)} T_{(jk)}^{mp} \alpha_{pq}^{(k)} R_l^{(jk)} S^l . \qquad (19)$$

The real and imaginary parts of equation (17) may be solved separately, the real part leading to birefringence and the imaginary part to optical activity.

4. Formula for birefringence

By equating the real parts of (17) we get

$$\psi_{sq} P^q(\text{real}) = E^q \Phi_{sq}$$

$$\text{where} \qquad \psi_{sq} = a_{sq} - \frac{4\pi}{3} \Phi_{sq}$$

which on solving yields

$$P^q(\text{real}) = \overline{\psi}^{sq} \Phi_{st} E^t$$

where $\overline{\psi}^{sq}$ is the cofactor of ψ_{sq} in the determinant $\det(\psi_{sq})$ divided by $\det(\psi_{sq})$. Thus the susceptibility tensor

$$\chi_t^q = \overline{\psi}^{sq} \Phi_{st} \qquad (20)$$

is completely known in terms of the crystal structure. From $\chi_t{}^q$ the dielectric constant tensor may be evaluated, since

$$K_t^q = \delta_t^q + 4\pi \chi_t^q . \qquad (21)$$

The two refractive indices of the crystal for the given wave normal may than be calculated by the usual methods of the electromagnetic theory, or with the help of the indicatrix.

5. Formula for optical activity

(a) *General formula*

The optical activity of a crystal is completely determined by the gyration tensor which ultimately depends only on the structure of the crystal. However, in the polarisability theory, we assume that the incident wave is propagated through the crystal with the appropriate refractive index for the particular direction. As already mentioned, we may consider birefringence and optical activity separately, and consider them to be superposed in the crystal, to a good degree of approximation *. In fact in the previous section 4 dealing with refractive index, we had neglected optical activity. In the same way, we shall neglect the birefringence in this section and consider the wave to be propagated with a uniform mean refractive index n along any given direction. The best value for this mean index is given by (8) and this value is to be used on the right hand side of (19).

Thus, equating the imaginary parts of (17) we get

$$P_s(\text{imag.}) = \frac{n^2+2}{3} E^q \left(-\frac{i\, 2\pi n}{\lambda_0} \right)$$

$$\cdot \frac{1}{V} \sum_{j=1}^{N'} \sum_{j \neq k = 1}^{N} \alpha_{sm}^{(j)} T_{(jk)}^{mp} \alpha_{pq}^{(k)} R_l^{(jk)} S^l .$$

Since $\qquad D_s = E_s + 4\pi P_s \qquad$ we have

$$D_s(\text{imag.}) = 4\pi P_s(\text{imag.}) = -i\, c\, E^q \gamma_{lsq} S^l \qquad (22)$$

$$\text{where} \qquad c = n \frac{n^2+2}{3} \frac{8\pi^2}{\lambda_0} \frac{1}{V} \qquad (23)$$

$$\text{and} \qquad \gamma_{lsq} = \sum_{j=1}^{N'} \sum_{j \neq k = 1}^{N} \alpha_{sm}^{(j)} T_{(jk)}^{mp} \alpha_{pq}^{(k)} R_l^{(jk)} . \qquad (24)$$

Since E^q is arbitrary, by comparing (22) with (9) we get

$$\varepsilon_{stq} G^t = -c\, \gamma_{lsq} S^l$$

which on solving yields

$$G^t = \tfrac{1}{2} c\, \varepsilon^{tsq} \gamma_{lsq} S^l . \qquad (25)$$

Again, since S^l is arbitrary, comparison with (10) gives

$$g_l{}^t = \tfrac{1}{2} c\, \varepsilon^{tsq} \gamma_{lsq} . \qquad (26)$$

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* For a discussion of the degree of validity of the superposition principle, see Ref. 5.

(b) *Formulation in terms of pairs of atoms*

The summation involved in (24) may now be modified so as to obtain a formula which represents γ_{lsq} as arising out of interactions in pairs. This way of writing the result is particularly useful in the case of molecules, and even for crystals or helices, it helps to make the numerical calculations more systematic. Also, it brings out the relationship to the idea of "coupled oscillators". We may thus write

$$\gamma_{lsq} = \tfrac{1}{2} \sum_{j=1}^{N'} \sum_{j \neq k=1}^{N} (\alpha_{sm}^{(j)} T_{(jk)}^{mp} \alpha_{pq}^{(k)} R_l^{(jk)} + \alpha_{sm}^{(k)} T_{(kj)}^{mp} \alpha_{pq}^{(j)} R_l^{(kj)})$$

in which the contribution of each pair of atoms such as j and k is counted twice. Instead we may delete the factor $\frac{1}{2}$ and count each pair once only. Thus

$$\gamma_{lsq} = \sum_{k=j+1}^{N''} \sum_{j=1}^{N'} (\alpha_{sm}^{(j)} T_{(jk)}^{mp} \alpha_{pq}^{(k)} R_l^{(jk)} + \alpha_{sm}^{(k)} T_{(kj)}^{mp} \alpha_{pq}^{(j)} R_l^{(kj)})$$

where the atoms 1 to N' lie within the unit cell and those from $N'+1$ to N'' lie in one half of the Lorentz's sphere. Also since

$$R_l^{(kj)} = -R_l^{(jk)} \text{ and } T_{(kj)}^{mp} = T_{(jk)}^{mp} \text{ we have}$$

$$\varepsilon^{tsq} \gamma_{lsq} = \sum_{k=j+1}^{N''} \sum_{j=1}^{N'} (\varepsilon^{tsq} \alpha_{sm}^{(j)} T_{(jk)}^{mp} \alpha_{pq}^{(k)} R_l^{(jk)} - \varepsilon^{tsq} \alpha_{sm}^{(k)} T_{(jk)}^{mp} \alpha_{pq}^{(j)} R_l^{(jk)}) .$$

Now interchanging the coupled indices s, q and also m, p in the second term and remembering that the polarisability tensors and the interaction tensors are all symmetric, we get

$$\varepsilon^{tsq} \gamma_{lsq} = 2 \sum_{k=j+1}^{N''} \sum_{j=1}^{N'} \varepsilon^{tsq} \alpha_{sm}^{(j)} T_{(jk)}^{mp} \alpha_{pq}^{(k)} R_l^{(jk)} . \qquad (27)$$

Therefore the gyration tensor (26) may now be written

$$g_l{}^t = c \sum_{k=j+1}^{N''} \sum_{j=1}^{N'} \varepsilon^{tsq} \alpha_{sm}^{(j)} T_{(jk)}^{mp} \alpha_{pq}^{(k)} R_l^{(jk)} \qquad (28)$$

where c is given by (23). Since there are less number of terms in the summation (27) than in (24), the expression (28) for the gyration tensor is preferable to (26). From the method of derivation it is clear that in evaluating c from equation (23) we should use the mean refractive index of the crystal for the particular direction of propagation. Having obtained $g_l{}^t$, the parameter G corresponding to any direction S^l may be evaluated according to (11), and the rotatory power may then be calculated by means of (6) which also involves the mean refractive index. If the propagation is parallel to the optic axis, the mean index is just equal to the corresponding refractive index.

(c) *Special case of symmetrical polarisability tensor*

If the polarisability tensors of the atoms or groups have axes of symmetry, then using relation (46) of Appendix II we may write the gyration tensor (28) in the more explicit form

$$g_l{}^t = c \sum_{k=j+1}^{N''} \sum_{j=1}^{N'} \alpha^{(j)} \beta^{(j)} \alpha^{(k)} \beta^{(k)} \varepsilon^{tsq} R_l^{(jk)} \qquad (29)$$
$$\cdot \left[\frac{3\,\sigma(j)}{r^5} R_s^{(jk)} b_q^{(k)} R_{(jk)}^p b_p^{(k)} + \frac{3\,\sigma(k)}{r^5} b_s^{(j)} R_q^{(jk)} R_{(jk)}^m b_m^{(j)} + T_{(jk)}^{mp} b_m^{(j)} b_p^{(k)} b_s^{(j)} b_q^{(k)} \right]$$

where $b_s^{(j)}$ is the unit vector specifying the direction of the optical symmetry axis of group j, $\alpha^{(j)}$ is its mean polarisability, $\beta^{(j)}$ is the anisotropy ratio and $\sigma^{(j)} = \frac{1}{\beta(j)} - \frac{1}{3}$. $\alpha^{(j)}$ and $\beta^{(j)}$ may be defined in terms of the principal components of the polarisability tensor, namely $\alpha_{11}'^{(j)}$, $\alpha_{22}'^{(j)}$ and $\alpha_{33}'^{(j)}$, by means of the relations

$$\alpha^{(j)} = \tfrac{1}{3}(\alpha_{11}'^{(j)} + 2\,\alpha_{22}'^{(j)}) \quad \text{and} \quad \beta^{(j)} = \frac{1}{\alpha(j)}(\alpha_{11}'^{(j)} - \alpha_{22}'^{(j)}). \qquad (30)$$

6. Optical activity of a randomly orientied system

(i) It is obvious that the above theory is equally valid for a molecule kept in a specific orientation in a beam of light. In this case, both N' and N'' will be equal to the number of atoms in the molecule. Since in any experiment, either with gases or solutions, the molecules will be orientied at random, it would be worthwhile to calculate the mean value of the optical rotation for all orientations. In such a case, the mean value of the scalar parameter G may be obtained by replacing the tensor $S_t S^l$ occurring in (11) by its mean value over all directions of the wave normal. According to (44) Appendix I, the mean value is $\frac{1}{3}\,\delta_t{}^l$, and hence the scalar parameter reduces to

$$\overline{G} = \tfrac{1}{3}\, g_l{}^l . \qquad (31)$$

In a dilute solution the molecules of the optically active substance are far apart. Therefore in computing the effective field at the place occupied by an atom belonging to a molecule, we need only take into account the contribution of the rest of the atoms in the molecule. That is, we may consider each molecule as a separate unit consisting of N atoms and occupying a volume $\bar{V} = V'/N_0$ where V' is the volume of the solution containing one gram-molecule of the solute and N_0 is AVOGADRO's number. Then, analogous to (28), the gyration tensor for the molecule may be written as

$$g_l^{\,t} = \bar{c} \sum_{k=j+1}^{N} \sum_{j=1}^{N-1} \varepsilon^{tsq} \alpha_{sm}^{(j)} T_{(jk)}^{mp} \alpha_{pq}^{(k)} R_l^{(jk)} \tag{32}$$

where

$$\bar{c} = n \frac{n^2+2}{3} \frac{8\pi^2}{\lambda_0} \frac{1}{\bar{V}} \tag{33}$$

and using (31) the mean value of the scalar parameter may be written in the form

$$\bar{G} = \tfrac{1}{3} \bar{c} L \tag{34}$$

where

$$L = \sum_{k=j+1}^{N} \sum_{j=1}^{N-1} L_{(jk)} \tag{35}$$

and

$$L_{(jk)} = \varepsilon^{lsq} \alpha_{sm}^{(j)} T_{(jk)}^{mp} \alpha_{pq}^{(k)} R_l^{(jk)}. \tag{36}$$

In equation (33) we should use for n the refractive index of the solution; and the same value of the index is to be used in formula (6) also, in calculating the rotatory power ϱ. To evaluate $L_{(jk)}$ we may use (36) as such, choosing any convenient coordinate system, or adapt it for computation by vector analysis, as follows:

Let $\bar{a}_{uv}^{(j)}$ be the polarisability tensor of group j in the coordinate system of its principal axes, and let $y_{(j)}^{i}$ represent the coordinates in this system, the corresponding curvilinear coordinates being x^i. Then

$$\alpha_{sm}^{(j)} = \frac{\partial y_{(j)}^u}{\partial x^s} \frac{\partial y_{(j)}^v}{\partial x^m} \bar{\alpha}_{uv}^{(j)} = \sum_{u=1}^{3} \frac{\partial y_{(j)}^u}{\partial x^s} \frac{\partial y_{(j)}^u}{\partial x^m} \bar{\alpha}_{uu}^{(j)}. \tag{37}$$

We may now interpret $\partial y_{(j)}^u / \partial x^s$ $(s = 1, 2, 3)$ as the covariant components of the unit vector $b_{(u)s}^{(j)}$ parallel to $y_{(j)}^u$ axis, and write

$$\alpha_{sm}^{(j)} = \sum_{u=1}^{3} b_{(u)s}^{(j)} b_{(u)m}^{(j)} \bar{\alpha}_{uu}^{(j)}. \tag{38}$$

Expressing $\alpha_{pq}^{(k)}$ similarly and substituting these in (36) we get

$$\begin{aligned} L_{(jk)} &= \sum_{u,v=1}^{3} \bar{\alpha}_{uu}^{(j)} \bar{\alpha}_{vv}^{(k)} T_{(jk)}^{mp} b_{(u)m}^{(j)} b_{(v)p}^{(k)} \varepsilon^{lsq} R_l^{(jk)} b_{(u)s}^{(j)} b_{(v)q}^{(k)} \\ &= \sum_{u,v=1}^{3} \bar{\alpha}_{uu}^{(j)} \bar{\alpha}_{vv}^{(k)} \boldsymbol{b}_{(u)}^{(j)} \cdot T_{(jk)} \cdot \boldsymbol{b}_{(v)}^{(k)} \boldsymbol{R}^{(jk)} \cdot \boldsymbol{b}_{(u)}^{(j)} \times \boldsymbol{b}_{(v)}^{(k)} \end{aligned} \tag{39}$$

where

$$\boldsymbol{b}_{(u)}^{(j)} \cdot T_{(jk)} \cdot \boldsymbol{b}_{(v)}^{(k)} = \frac{1}{r^5} [3 (\boldsymbol{R}^{(jk)} \cdot \boldsymbol{b}_{(u)}^{(j)}) (\boldsymbol{R}^{(jk)} \cdot \boldsymbol{b}_{(v)}^{(k)}) - r^2 (\boldsymbol{b}_{(u)}^{(j)} \cdot \boldsymbol{b}_{(v)}^{(k)})] \tag{40}$$

and $\boldsymbol{R}^{(jk)} \cdot \boldsymbol{b}_{(u)}^{(j)} \times \boldsymbol{b}_{(v)}^{(k)}$ is the scalar triple product. Here $\boldsymbol{b}_{(u)}^{(j)}$, $\boldsymbol{b}_{(v)}^{(k)}$ $(u, v = 1, 2, 3)$ are unit vectors defining the principal optical axes of groups j and k respectively and $\boldsymbol{R}^{(jk)}$ is the vector joining them from j to k, r being its length. This results is closely analogous to that given by KIRKWOOD [3].

The specific rotation of a solution is connected with the rotatory power ϱ by means of the relation

$$[\alpha]_{\lambda_0} = -\frac{1800}{\pi} \varrho \frac{V'}{M} \text{ deg./dm./(gm./cc.)} \tag{41}$$

Now combining (6), (33), (34), and (41) we arrive at the general formula

$$[\alpha]_{\lambda_0} = -\frac{4800\,\pi^2}{\lambda_0^{\,2}} \frac{N_0}{M} \frac{n^2+2}{3} L \tag{42}$$

where L is given by (35) and (36).

If the polarisability tensors have axes of symmetry, combining (35), (36) and (47) of Appendix II, L may be expressed in the form

$$L = \sum_{k=j+1}^{N} \sum_{j=1}^{N-1} \alpha^{(j)} \beta^{(j)} \alpha^{(k)} \beta^{(k)} T_{(jk)}^{mp} b_m^{(j)} b_p^{(k)} \cdot \varepsilon^{lsq} R_l^{(jk)} b_s^{(j)} b_q^{(k)} \tag{43}$$

where $b_m^{(j)}$ and $b_p^{(k)}$ are unit vectors defining the optical symmetry axes of the groups j and k respectively. Equation (42) with L as given by (43) represents KIRKWOOD's [6] formula in tensorial form. The apparent reversal of sign is due to the fact that the interaction tensor used by KIRKWOOD is the negative of the one used here.

(ii) The problem arises whether the above results are also valid for a suspension of a crystalline powder, in which the crystallites are oriented at random. Here, a simple answer cannot be given for it is closely connected with the propagation of light in a birefringent, optically active medium. If the crystallite size is large enough so that the electromagnetic equations for the solid in bulk are valid (i. e. large compared to the wavelength of light), then the mean optical rotation will be practically zero, for the effective rotation is very small for all directions except those very close to the optic axis (or axes). On the other hand, if the crystallite size is very small, as it occurs for instance in solutions of pro-

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[6] W. W. WOOD, W. FICKETT and J. G. KIRKWOOD, J. Chem. Phys. **20**, 561 [1952].

teins or polypeptides, where an ordered helical chain exists and yet the dimensions are only of the order of a few hundred Angstroms, then the above formulae may be valid. However, since it is known from optical theory [5] that birefringence always decreases the optical rotation in such cases, the experimental value should be expected to be smaller than the theoretical specific rotation. A more detailed account of this problem is beyond the scope of the present paper.

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Appendix I

The tensor $S_t\, S^l$ and its mean value

We shall find the mean value of the tensor in a special coordinate system (c. s.) and then transform the result to the general curvilinear c. s. Taking an orthogonal cartesian c. s. the contravariant and covariant components of any vector are equal, and the components of a unit vector are simply its direction cosines $\cos\alpha$, $\cos\beta$, $\cos\gamma$. Hence

$$S^1 = S_1 = \cos\alpha\,; \quad S^2 = S_2 = \cos\beta\,; \quad S^3 = S_3 = \cos\gamma\,.$$

Consequently, in component form

$$S_t\, S^l = \begin{pmatrix} \cos^2\alpha & \cos\alpha\cos\beta & \cos\alpha\cos\gamma \\ \cos\beta\cos\alpha & \cos^2\beta & \cos\beta\cos\gamma \\ \cos\gamma\cos\alpha & \cos\gamma\cos\beta & \cos^2\gamma \end{pmatrix}.$$

Since $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$ for any direction of the wave normal S_t, the sum of the diagonal components of the mean tensor must also be unity. Denoting the mean value by a bar over the quantity, we therefore have

$$\overline{\cos^2\alpha} = \overline{\cos^2\beta} = \overline{\cos^2\gamma} = 1/3\,.$$

The mean value of all other components must vanish. Taking for example the component $\cos\alpha\cos\beta$, for a given value of $\cos\beta$ there are two directions for which $\cos\alpha$ will be equal and opposite, and therefore

$$\overline{\cos\alpha\cos\beta} = 0\,.$$

Hence

$$\overline{S_t\, S^l} = \tfrac{1}{3}\,\delta_t{}^l \tag{44}$$

in an orthogonal cartesian c. s., and since Kronecker deltas transform into themselves on a change of c. s., the above result is valid in any curvilinear c. s.

Appendix II

The polarisability tensor with an axis of symmetry

If α_{pq} has an axis of symmetry, it may be written in the form

$$\alpha_{pq} = \alpha\,\beta\,(\sigma\, a_{pq} + b_p\, b_q) \tag{45}$$

where b_p is the unit vector in the direction of the symmetry axis and α, β, σ are constants which may be defined in terms of the components of the tensor in the coordinate system of the principal axes. Denoting these by primes we can readily show

$$\alpha = (\alpha'_{11} + 2\,\alpha'_{22})/3\,, \qquad \beta = (\alpha'_{11} - \alpha'_{22})/\alpha$$

and $\sigma = \dfrac{1}{\beta} - \dfrac{1}{3}$. It is now seen that α is the mean polarisability and β is the anisotropy ratio.

Using polarisability tensors of the above form in the product

$$\varepsilon^{tsq}\,\alpha^{(j)}_{sm}\,T^{mp}_{(jk)}\,\alpha^{(k)}_{pq}$$

which occurs in the expression (28) for the gyration tensor, we have

$$\begin{aligned}\varepsilon^{tsq}\,\alpha^{(j)}_{sm}\,T^{mp}_{(jk)}\,\alpha^{(k)}_{pq} &= \alpha^{(j)}\,\beta^{(j)}\,\alpha^{(k)}\,\beta^{(k)}\,\varepsilon^{tsq}\,T^{mp}_{(jk)} \\ &\quad\cdot(\sigma^{(j)}\,a_{sm} + b^{(j)}_s\,b^{(j)}_m)\,(\sigma^{(k)}\,a_{pq} + b^{(k)}_p\,b^{(k)}_q)\,.\end{aligned}$$

The partial products may be simplified separately as follows:

$$\varepsilon^{tsq}\,T^{mp}_{(jk)}\,\sigma^{(j)}\,a_{sm}\,\sigma^{(k)}\,a_{pq} = \varepsilon^{tsq}\,T^{(jk)}_{sq}\,\sigma^{(j)}\,\sigma^{(k)} = 0\,,$$

$$\begin{aligned}\varepsilon^{tsq}\,T^{mp}_{(jk)}\,\sigma^{(j)}\,a_{sm}\,b^{(k)}_p\,b^{(k)}_q &= \frac{\sigma^{(j)}}{r^5}\,\varepsilon^{tsq}\,(3\,R^{(jk)}_s\,R^p_{(jk)} \\ &\qquad - r^2\,\delta^p_s)\,b^{(k)}_p\,b^{(k)}_q \\ &= \frac{3\,\sigma^{(j)}}{r^5}\,\varepsilon^{tsq}\,R^{(jk)}_s\,R^p_{(jk)}\,b^{(k)}_p\,b^{(k)}_q\end{aligned}$$

and similarly

$$\varepsilon^{tsq}\,T^{mp}_{(jk)}\,\sigma^{(k)}\,a_{pq}\,b^{(j)}_s\,b^{(j)}_m = \frac{3\,\sigma^{(k)}}{r^5}\,\varepsilon^{tsq}\,R^m_{(jk)}\,R^{(jk)}_q\,b^{(j)}_s\,b^{(j)}_m\,.$$

Thus

$$\begin{aligned}\varepsilon^{tsq}\,\alpha^{(j)}_{sm}\,T^{mp}_{(jk)}\,\alpha^{(k)}_{pq} &= \alpha^{(j)}\,\beta^{(j)}\,\alpha^{(k)}\,\beta^{(k)}\,\varepsilon^{tsq} \\ &\quad\cdot\Big[\frac{3\,\sigma^{(j)}}{r^5}\,R^{(jk)}_s\,b^{(k)}_q\,R^p_{(jk)}\,b^{(k)}_p + \frac{3\,\sigma^{(k)}}{r^5}\,b^{(j)}_s\,R^{(jk)}_q\,R^m_{(jk)}\,b^{(j)}_m \\ &\qquad + T^{mp}_{(jk)}\,b^{(j)}_m\,b^{(k)}_p\,b^{(j)}_s\,b^{(k)}_q\Big]\end{aligned} \tag{46}$$

and hence

$$\begin{aligned}&\varepsilon^{lsq}\,\alpha^{(j)}_{sm}\,T^{mp}_{(jk)}\,\alpha^{(k)}_{pq}\,R^{(jk)}_l \\ &\quad = \alpha^{(j)}\,\beta^{(j)}\,\alpha^{(k)}\,\beta^{(k)}\,T^{mp}_{(jk)}\,b^{(j)}_m\,b^{(k)}_p\,\varepsilon^{lsq}\,R^{(jk)}_l\,b^{(j)}_s\,b^{(k)}_q\,.\end{aligned} \tag{47}$$

This is the value of $L_{(jk)}$, occurring in (36), when the polarisability tensors have axes of symmetry.