

On the Theory of Natural Optical Activity

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Optical activity is a useful tool in structural chemistry because of its sensitivity to the arrangement of the atoms in a molecule. Whereas the refractivity depends on the *amount* of polarizable matter in a molecule, optical activity depends on its *distribution* within the molecule.¹ Thus, a helical arrangement of atoms, and therefore of polarizability, leads to optical activity. The topic has been considered in recent articles by Schellman,² Bosnich,³ Harada and Nakanishi,⁴ Geiger and Wagnière,⁵ Barrett,⁶ and Bayley;^{7a} Ruch^{7b} has considered algebraic aspects of chirality.

The Rosenfeld equation⁸ for optical rotation requires wave functions for the molecular ground and excited states and is rigorous for an isotropic distribution of isolated molecules with dimensions small compared with the wavelength of light. However, this equation gives little physical insight into the sensitive relationship between molecular structure and optical activity. Despite important efforts by Born,⁹ de Malleman,¹⁰ Kuhn,¹¹ and Boys,¹² a general approach to the structural theory of optical activity remained unrealized until the work of Kirkwood¹³ in 1937.

The present Account aims at expounding and extending the approach of Kirkwood¹³ to the theory of optical activity. This approach is based on the assumption that an optically active molecule can be separated into electronically independent optically inactive bonds or functional groups. The optical activity is attributed to electric multipole interactions among the subunits. Equations describing the optical activity emerge in terms of the properties (such as polarizability and electric dipole moment) of the subunits and their relative spatial distribution in the molecule.

One of the chief aims of theories of optical activity is to relate optical rotatory power, and particularly optical rotatory dispersion (ORD) and circular dichroism (CD) spectra, to molecular structure. For molecules of known conformation the absolute configuration is implicit in the signs of the Cotton effects.

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Unfortunately the chemical literature contains numerous examples of incorrect assignments of absolute structure (see ref 14 and 15). This is alarming, especially in view of the fact that a chemist without any chiroptical data has a 50% chance of guessing the correct configuration. The problem of predicting the conformation of a molecule of known configuration can also be hazardous unless the number of possible conformers is small and their gyrotory powers differ considerably.

Induced Multipole Moments

Changes in the direction of polarization of a light beam passing through a medium can be related by refractivity or scattering theory to the point electric and magnetic multipoles induced in each molecule by the electric and magnetic fields, \mathbf{E} and \mathbf{B} , of the light wave.¹⁶⁻¹⁹ Electric dipoles induced by the oscillating magnetic field of a plane-polarized light wave falling on optically active molecules in an isotropic medium have a component perpendicular to the plane of polarization of the electric vector. In transparent spectral regions these induced dipoles oscillate out of phase with the optical driving field at each molecule—they are proportional to $\partial\mathbf{B}/\partial t$. Radiation scattered in the forward direction by these electric dipoles, and by the magnetic dipoles induced by $\partial\mathbf{E}/\partial t$, combines with the unscattered beam to

(1) Other "higher" polarizabilities such as the dipole-quadrupole polarizability A in eq 1 are dependent on the distribution of polarizable matter within the molecule; A determines both the electric dipole induced by an electric field gradient and the quadrupole induced by an electric field.

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(19) A. D. Buckingham, *Advan. Chem. Phys.*, **12**, 107 (1967).

produce optical rotation. A particularly lucid account of this process has been given by Kauzmann.¹⁷

The electric dipole μ (with components μ_α) induced in a molecule by the electric field $\mathbf{E} = \mathbf{E}^0 \cos \omega(t - \mathbf{r} \cdot \mathbf{k}/c)$ and magnetic field $\mathbf{B} = \mathbf{B}^0 \cos \omega(t - \mathbf{r} \cdot \mathbf{k}/c)$ of a light wave of frequency $\omega/2\pi$ can be expressed¹⁹ in terms of the electrooptical polarizability tensor \mathbf{a} , the gyration polarizability β , and the electric dipole-quadrupole polarizability \mathbf{A} by eq 1,^{19,20}

$$\mu_\alpha = a_{\alpha\beta} E_\beta - \omega^{-1} \beta_{\alpha\beta} \dot{B}_\beta + \frac{1}{3} A_{\alpha\beta\gamma} E_{\beta\gamma} + \dots \quad (1)$$

where $E_{\beta\gamma}$ is the electric field gradient $\partial E_\gamma / \partial r_\beta$ and \dot{B}_β is the time derivative of the magnetic field. Equation 1 and subsequent equations make use of the cartesian tensor suffix notation and summation convention²¹⁻²³ for repeated Greek suffixes. This leads to concise and explicit formulas that are lengthy or ambiguous in most other representations. The first term on the right of eq 1 is by far the largest, but it is insensitive to the *distribution* of polarizable matter in the molecule. To discriminate between the responses of *R* and *S* isomers it is necessary to include additional small contributions from β and \mathbf{A} . The light beam also induces a magnetic dipole¹⁹

$$m_\alpha = \chi_{\alpha\beta} B_\beta + \omega^{-1} \beta_{\beta\alpha} \dot{E}_\beta + \frac{1}{3} \omega^{-1} D'_{\alpha\beta\gamma} \dot{E}_{\beta\gamma} + \dots \quad (2)$$

where χ is the molecular magnetizability tensor.

The polar tensors²⁴ of even rank, $a_{\alpha\beta}$ and $\chi_{\alpha\beta}$, have nonzero mean values $a = \frac{1}{3} a_{\alpha\alpha}$ and $\chi = \frac{1}{3} \chi_{\alpha\alpha}$, even for atoms. Polar tensors of odd rank like $A_{\alpha\beta\gamma}$ have nonzero components for molecules which lack a center of inversion, but axial tensors²⁴ of odd rank such as $D'_{\alpha\beta\gamma}$ may have nonzero components even if the molecule is centrosymmetric. The gyration polarizability $\beta_{\alpha\beta}$ is a second-rank axial tensor and, as its name implies, has a nonzero mean value $\beta = \frac{1}{3} \beta_{\alpha\alpha}$ for all optically active molecules. Molecules which are optically inactive have $\beta = 0$ but may possess individual nonzero components $\beta_{\alpha\beta}$.²³

If the molecules are in their electronic ground states, a quantum-mechanical analysis of the time-dependent optical perturbation

$$V = -\mu_\alpha E_\alpha - m_\alpha B_\alpha - \frac{1}{3} \theta_{\alpha\beta} E_{\alpha\beta} + \dots \quad (3)$$

in which the electric dipole, magnetic dipole, and electric quadrupole operators are defined by

$$\mu_\alpha = \sum_i e_i r_{i\alpha} \quad (4)$$

$$m_\alpha = \sum_i \frac{e_i}{2m_i} (\epsilon_{\alpha\beta\gamma} r_{i\beta} p_{i\gamma} + g_i s_{i\alpha}) \quad (5)$$

(20) The gyration polarizability β is equal to $-G'$ in ref 18 and 19.

(21) H. Jeffreys, "Cartesian Tensors," Cambridge University Press, 1931.

(22) G. Temple, "Cartesian Tensors," Methuen, London, 1960.

(23) R. R. Birss, "Symmetry and Magnetism," North-Holland Publishing Co., Amsterdam, 1964.

(24) A polar vector changes sign and an axial vector is unchanged on inversion of the coordinate frame. Thus the position and momentum vectors \mathbf{r} and \mathbf{p} are polar, but the angular momentum $\mathbf{r} \times \mathbf{p}$ is axial. Polar and axial tensors of the n th rank are multiplied by $(-1)^n$, and $(-1)^{n+1}$, respectively, on inversion. The α component of the vector product $\mathbf{A} \times \mathbf{B}$ is written in tensor notation as $(\mathbf{A} \times \mathbf{B})_\alpha = \epsilon_{\alpha\beta\gamma} A_\beta B_\gamma$ where $\epsilon_{\alpha\beta\gamma}$ is the unit skew-symmetric tensor and is +1 or -1 if $\alpha\beta\gamma$ is an even or odd permutation of xyz and is zero otherwise. Hence $\epsilon_{xyz} = \epsilon_{yxz} = -\epsilon_{yxz} = 1$, $\epsilon_{xxy} = 0$.

and

$$\theta_{\alpha\beta} = \frac{1}{2} \sum_i e_i (3r_{i\alpha} r_{i\beta} - r_i^2 \delta_{\alpha\beta}) \quad (6)$$

yields¹⁹

$$a_{\alpha\beta} = 2\hbar^{-1} \sum_{n \neq 0} \omega_{no} f(\omega, \omega_{no}, \Gamma_{no}) \operatorname{Re} \mu_\alpha^{\text{on}} \mu_\beta^{\text{no}} = a_{\beta\alpha} \quad (7)$$

$$\beta_{\alpha\beta} = 2\hbar^{-1} \omega \sum_{n \neq 0} f(\omega, \omega_{no}, \Gamma_{no}) \operatorname{Im} \mu_\alpha^{\text{on}} m_\beta^{\text{no}} \quad (8)$$

$$A_{\alpha\beta\gamma} = 2\hbar^{-1} \sum_{n \neq 0} \omega_{no} f(\omega, \omega_{no}, \Gamma_{no}) \operatorname{Re} \mu_\alpha^{\text{on}} \theta_{\beta\gamma}^{\text{no}} = A_{\alpha\gamma\beta} \quad (9)$$

$$\chi_{\alpha\beta} = 2\hbar^{-1} \sum_{n \neq 0} \omega_{no} f(\omega, \omega_{no}, \Gamma_{no}) \operatorname{Re} m_\alpha^{\text{on}} m_\beta^{\text{no}} + \langle 0 | \sum_i \frac{e_i^2}{4m_i} (r_{i\alpha} r_{i\beta} - r_i^2 \delta_{\alpha\beta}) | 0 \rangle = \chi_{\beta\alpha} \quad (10)$$

and

$$D'_{\alpha\beta\gamma} = -2\hbar^{-1} \omega \sum_{n \neq 0} f(\omega, \omega_{no}, \Gamma_{no}) \operatorname{Im} m_\alpha^{\text{on}} \theta_{\beta\gamma}^{\text{no}} = D'_{\alpha\gamma\beta} \quad (11)$$

In eq 4-11 e_i is the charge and m_i the mass of particle i with position vector \mathbf{r}_i , linear momentum \mathbf{p}_i , spin angular momentum \mathbf{s}_i , and g value g_i ; $f(\omega, \omega_{no}, \Gamma_{no})$ is a frequency factor with dimensions of ω^{-2} and for a Lorentzian line shape it takes the form

$$f(\omega, \omega_{no}, \Gamma_{no}) = \frac{\omega_{no}^2 - \omega^2}{(\omega_{no}^2 - \omega^2)^2 + \omega^2 \Gamma_{no}^2} \quad (12)$$

where Γ_{no} is approximately the width at half-height of the $n \leftarrow 0$ absorption spectral line of frequency $\omega_{no}/2\pi$. The unperturbed molecular ground state ψ_0 is labeled 0 and transition moments like $\int \psi_0^* \mu \psi_n d\tau$ between the states ψ_0 and ψ_n are written as μ^{on} . We shall take the wave functions to be real, but this is no restriction for molecules with an even number of electrons in the absence of a static magnetic field.

The Rosenfeld Equation

In an isotropic fluid of number density N the rotation ϕ per unit path length satisfies the Rosenfeld equation⁸

$$\phi = \mu_0 N \omega \beta \quad (13)$$

$$= \frac{2}{3} \mu_0 N \hbar^{-1} \omega^2 \sum_{n \neq 0} f(\omega, \omega_{no}, \Gamma_{no}) R_{no} \quad (14)$$

in which the rotatory strength of the $n \leftarrow 0$ transition is defined as $R_{no} = \operatorname{Im} \mu^{\text{on}} \cdot \mathbf{m}^{\text{no}}$ and μ_0 is the permeability of free space ($\mu_0/4\pi = 10^{-7}$ H m⁻¹ = 1 emu). The rotatory strength of a transition can be measured from the CD spectrum by integrating the circular dichroism $\Delta\epsilon = \epsilon_L - \epsilon_R$, where ϵ_L and ϵ_R are the molar extinction coefficients (in [mol l.⁻¹ cm]⁻¹) for left and right circularly polarized light, over the absorption band according to

$$\begin{aligned}
 R_{\text{no}} &= \frac{3000hc \ln 10}{32\pi^3 N_A} \int_{\text{band}} \omega^{-1} \Delta \epsilon d\omega \\
 &= 22.965 \times 10^{-40} \int_{\text{band}} \omega^{-1} \Delta \epsilon d\omega \text{ cgs units} \\
 &= 0.24763 \int_{\text{band}} \omega^{-1} \Delta \epsilon d\omega \text{ debye bohr magneton}
 \end{aligned}
 \tag{15}$$

Equations 13 and 15 require modification if the optical activity is measured in an anisotropic medium, as in an oriented sample or crystal, for then there is a contribution to the optical activity from **A** as well as from β .^{18,25-28}

Optical Activity due to the Interaction of Achiral Chromophores

(a) The Dynamic-Coupling (DC) Mechanism.

Consider a molecule composed of two achiral groups, 1 and 2. When an incident plane-polarized light wave strikes 2 it induces electric multipole moments. If 2 is dissymmetrically disposed relative to 1, that is, if the combined groups 1 and 2 are distinguishable from their mirror image, as in Figure 1, the oscillating local electric field at 1 due to these induced moments in 2 produces a magnetic dipole which is parallel to and out of phase with the electric field of the light wave. This is a necessary and sufficient condition for the molecule to exhibit optical rotation. Our analysis of these interactions, given in the Appendix, leads to²⁹

$$\begin{aligned}
 \beta(\text{DC}) &= \frac{1}{6} \omega \epsilon_{\alpha\beta\gamma} R_{\beta}^{(21)} a_{\gamma\delta}^{(2)} T_{\delta\epsilon}^{(21)} a_{\epsilon\alpha}^{(1)} - \\
 &\quad \frac{1}{18} \omega \epsilon_{\alpha\beta\gamma} R_{\beta}^{(21)} (a_{\gamma\delta}^{(2)} A_{\alpha\epsilon\delta}^{(1)} - \\
 &\quad a_{\alpha\delta}^{(1)} A_{\gamma\delta\epsilon}^{(2)}) T_{\delta\epsilon\phi}^{(21)} + \frac{1}{3} \sum_{\substack{i,j=1 \\ i \neq j}}^2 [\beta_{\alpha\beta}^{(i)} T_{\alpha\gamma}^{(ji)} a_{\gamma\beta}^{(j)} - \\
 &\quad \frac{1}{3} D'_{\alpha\beta\gamma}^{(i)} T_{\beta\gamma\delta}^{(ji)} a_{\delta\alpha}^{(j)}] + \dots \tag{16}
 \end{aligned}$$

Superscripts denote the group to which the property tensor refers and the vector $\mathbf{R}^{(21)}$ connects the origin on group 1 to that on 2. The choice of the positions of these origins is in general arbitrary. Their relative positions determine the tensors **T**

$$T_{\alpha}^{(ji)} = -(4\pi\epsilon_0)^{-1} R_{\alpha}^{(ji)} / (R^{(ji)})^3 = -T_{\alpha}^{(ij)} \tag{17}$$

$$\begin{aligned}
 T_{\alpha\beta}^{(ji)} &= (4\pi\epsilon_0)^{-1} [3R_{\alpha}^{(ji)} R_{\beta}^{(ji)} - \\
 &\quad (R^{(ji)})^2 \delta_{\alpha\beta}] / (R^{(ji)})^5 = T_{\alpha\beta}^{(ij)} = T_{\beta\alpha}^{(ji)} \tag{18}
 \end{aligned}$$

$$\begin{aligned}
 T_{\alpha\beta\gamma}^{(ji)} &= -3(4\pi\epsilon_0)^{-1} [5R_{\alpha}^{(ji)} R_{\beta}^{(ji)} R_{\gamma}^{(ji)} - \\
 &\quad (R^{(ji)})^2 (R_{\alpha}^{(ji)} \delta_{\beta\gamma} + R_{\beta}^{(ji)} \delta_{\gamma\alpha} + R_{\gamma}^{(ji)} \delta_{\alpha\beta})] / \\
 &\quad (R^{(ji)})^7 = -T_{\alpha\beta\gamma}^{(ij)} = T_{\gamma\alpha\beta}^{(ji)}, \text{ etc.} \tag{19}
 \end{aligned}$$

where ϵ_0 is the permittivity of free space ($4\pi\epsilon_0 = 1.11265 \times 10^{-10} \text{ F m}^{-1} = 1 \text{ esu}$).

Group additivity of a molecular property tensor

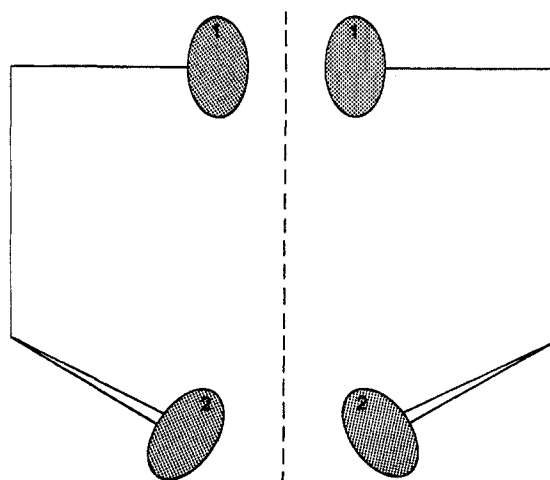


Figure 1. Dissymmetric arrangements of two achiral groups 1 and 2.

can be achieved in quantum mechanics by assigning an independent set of wave functions to each group and expressing the molecular wave function as the product of group wave functions. Thus, if group 2 differs from the chromophore 1, the dynamic-coupling (DC) component of the rotational strength of the molecular transition associated with the $n_1 \leftarrow o_1$ transition of angular frequency ω_{n_1} in 1 follows from (14) and (16) as

$$\begin{aligned}
 R_{\text{no}}(\text{DC}) &= \frac{1}{2} \omega_{n_1} \epsilon_{\alpha\beta\gamma} R_{\beta}^{(21)} a_{\gamma\delta}^{(2)} T_{\delta\epsilon}^{(21)} \mu_{\alpha}^{o_1 n_1} \mu_{\epsilon}^{n_1 o_1} - \\
 &\quad \frac{1}{6} \omega_{n_1} \epsilon_{\alpha\beta\gamma} R_{\beta}^{(21)} a_{\gamma\delta}^{(2)} T_{\delta\epsilon\phi}^{(21)} \mu_{\alpha}^{o_1 n_1} \theta_{\epsilon\phi}^{n_1 o_1} + \\
 &\quad \frac{1}{6} \omega_{n_1} \epsilon_{\alpha\beta\gamma} R_{\beta}^{(21)} A_{\gamma\delta\epsilon}^{(2)} T_{\delta\epsilon\phi}^{(21)} \mu_{\alpha}^{o_1 n_1} \mu_{\phi}^{n_1 o_1} + \\
 &\quad \text{Im } \mu_{\alpha}^{o_1 n_1} m_{\beta}^{n_1 o_1} T_{\alpha\gamma}^{(21)} a_{\gamma\delta}^{(2)} + \\
 &\quad \beta_{\alpha\beta}^{(2)} T_{\alpha\gamma}^{(21)} \mu_{\beta}^{o_1 n_1} \mu_{\gamma}^{n_1 o_1} (\omega_{n_1} / \omega) + \\
 &\quad \frac{1}{3} \text{Im } m_{\alpha}^{o_1 n_1} \theta_{\beta\gamma}^{n_1 o_1} T_{\beta\gamma\delta}^{(21)} a_{\delta\alpha}^{(2)} + \\
 &\quad \frac{1}{3} D'_{\alpha\beta\gamma}^{(2)} T_{\beta\gamma\delta}^{(21)} \mu_{\alpha}^{o_1 n_1} \mu_{\delta}^{n_1 o_1} (\omega_{n_1} / \omega) + \dots \tag{20}
 \end{aligned}$$

The first term in (16) and (20) was discovered by Kirkwood^{13,30} who derived it from the Rosenfeld equation. It describes the rotatory strength induced in an electric-dipole-allowed transition in group 1 by an anisotropically polarizable perturbing group 2. This contribution to the rotatory strength falls off as the inverse square of $R^{(21)}$. The third, fifth, and seventh terms of (20) describe additions to the Kirkwood term and vary as the third and fourth inverse powers of R . Terms two and four in R^{-3} contain contributions from the isotropic polarizability of the perturbing group. Term six^{31,32} in R^{-4} gives the leading dynamic-coupling contribution for electric-dipole-forbidden transitions. It also contains contributions from the mean polarizability of the perturber.

These formulas can readily be extended to molecules containing more than two groups. In such molecules we sum all pairwise and multiple interactions. Molecules containing three groups were considered by de Malleman,¹⁰ and Boys^{12,33} examined the

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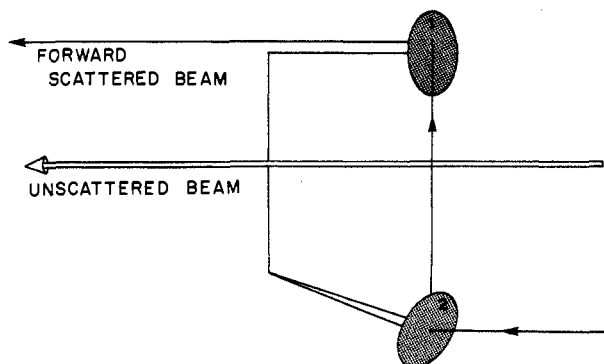


Figure 2. Dynamic coupling mechanism for optical rotation. The light wave interacts with both achiral groups before interfering with the unscattered wave.

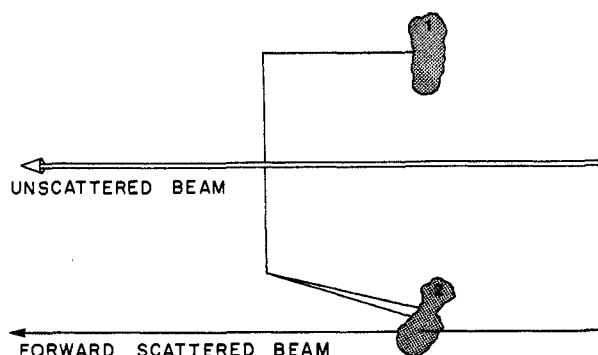


Figure 3. Static coupling mechanism for optical rotation. Distortion of each achiral group, 1 and 2, by the electrostatic field of the other causes it to become dissymmetric. Both groups then scatter as if they were chiral molecules.

case of four spherical groups, 1, 2, 3, and 4, at the apices of an irregular tetrahedron. In our notation Boys' formula is

$$\beta = \frac{1}{6} \omega a_1 a_2 a_3 a_4 \sum_{i=2}^4 \sum_{j \neq i} \sum_{k \neq i, j} \sum_{l \neq i, j, k} \epsilon_{\alpha\beta\gamma} R_{\beta}^{(i)} T_{\gamma}^{(ji)} T_{\delta}^{(kj)} T_{\epsilon}^{(lk)} \quad (21)$$

Two interacting spheres form an anisotropically polarizable pair, and it follows that the de Malleman model of two atoms in the presence of an anisotropic oscillator and the Boys model are closely related to the Kuhn-Kirkwood system with its two anisotropic oscillators. Applequist³³ has critically discussed polarizability formulas derived from point-electric-dipole models for the molecular subunits.

(b) **The Static-Coupling (SC) Mechanism.** In 1937 Condon, Altar, and Eyring³⁴ pointed out that local electrostatic fields due to the permanent charge distribution in a perturbing group could distort an achiral chromophore so that a light beam falling on the chromophore would induce a magnetic dipole parallel to the electric component of the optical field. In the presence of the electrostatic field $F_{\gamma}^{(i)}$ and field-gradient $F_{\gamma\delta}^{(i)}$ the perturbed gyration tensor of group i is

$$\beta_{\alpha\beta}^{(i)}(F_{\gamma}^{(i)}, F_{\gamma\delta}^{(i)}) = \beta_{\alpha\beta}^{(i)} + J_{\alpha\beta\gamma}^{(i)} F_{\gamma}^{(i)} + K_{\alpha\beta\gamma\delta}^{(i)} F_{\gamma\delta}^{(i)} + \dots \quad (22)$$

The tensor $J_{\alpha\beta\gamma}$ measures the oscillating magnetic dipole induced through the joint action of the static electric field F_{γ} and the optical field E_{β} and is equal to $-J_{\alpha,\beta,\gamma}$ as used elsewhere.³⁵ The expression for \mathbf{K} , the field-gradient analog of \mathbf{J} , can be obtained by replacing each matrix element μ_{γ}^{lm} in $J_{\alpha\beta\gamma}$ by $\frac{1}{3}\theta_{\gamma\delta}^{lm}$. The field at group i can be expressed in terms of the electric moments of group j (see eq A6 and A7 in the Appendix) and the static-coupling contribution to the gyration polarizability may be written as²⁹

$$\beta(\text{SC}) = \frac{1}{3} \sum_{\substack{i,j=1 \\ i \neq j}}^2 \{ J_{\alpha\beta\gamma}^{(i)} [T_{\beta}^{(ji)} q^{(j)} + T_{\beta\gamma}^{(ji)} \mu_{\gamma}^{(j)} + \frac{1}{3} T_{\beta\gamma\delta}^{(ji)} \theta_{\gamma\delta}^{(j)} + \dots] - K_{\alpha\beta\gamma}^{(i)} [T_{\beta\gamma}^{(ji)} q^{(j)} + T_{\beta\gamma\delta}^{(ji)} \mu_{\delta}^{(j)} + \dots] + \dots \} \quad (23)$$

In (23) $q^{(j)}$ is the charge on group j , and $\mu^{(j)}$ and $\theta^{(j)}$ are its permanent dipole and quadrupole moments. The static-coupling contribution to the rotatory strength of the $n_1 \leftarrow o_1$ transition in chromophore 1 follows from (14) and (23) as

$$R_{n_1}(\text{SC}) = J_{\alpha}^{(1)} [T_{\alpha}^{(21)} q^{(2)} + T_{\alpha\beta}^{(21)} \mu_{\beta}^{(2)} + \frac{1}{3} T_{\alpha\beta\gamma}^{(21)} \theta_{\beta\gamma}^{(2)} + \dots] - K_{\alpha\beta}^{(1)} [T_{\alpha\beta}^{(21)} q^{(2)} + T_{\alpha\beta\gamma}^{(21)} \mu_{\gamma}^{(2)} + \dots] + \dots \quad (24)$$

where

$$J_{\alpha}^{(1)} = \sum_{k \neq n} (\hbar\omega_{k_1 n_1})^{-1} \text{Im} (\mu^{o_1 k_1} \cdot \mathbf{m}^{n_1 o_1} + \mu^{o_1 n_1} \cdot \mathbf{m}^{k_1 o_1}) \mu_{\alpha}^{n_1 k_1} + \sum_{k \neq o} (\hbar\omega_{k_1 o_1})^{-1} \text{Im} (\mu^{k_1 n_1} \cdot \mathbf{m}^{n_1 o_1} + \mu^{o_1 n_1} \cdot \mathbf{m}^{n_1 k_1}) \mu_{\alpha}^{o_1 k_1} \quad (25)$$

and $K_{\alpha\beta}^{(1)}$ is obtained from (25) by replacing each μ_{α} in (25) by $\frac{1}{3}\theta_{\alpha\beta}$.

The total rotatory strength of a transition is the sum of the dynamic and static coupling contributions, which are depicted schematically in Figures 2 and 3. Equations 20 and 24 present the leading contributions to the rotatory strength; in higher orders there are terms involving mixed contributions from the dynamic and static coupling mechanisms.

Exciton Theory for Identical Chromophores

Consider a dissymmetric dimer $A_1 A_2$ composed of two identical and achiral chromophores, A_1 and A_2 , whose electronic states are nondegenerate. Corresponding to the excited dipole-allowed state n of the monomer there are two states in the dimer, the appropriate zero-order wave functions being $\psi_{n\pm} = 2^{-1/2} [\psi_o(A_1)\psi_n(A_2) \pm \psi_n(A_1)\psi_o(A_2)]$. The rotational strengths $\text{Im} \mu^{on\pm} \cdot \mathbf{m}^{n\pm o}$ of the two dimer transitions follow from $\mu = \mu(A_1) + \mu(A_2)$ and the quantum analog of (A3) as^{36,37}

$$R_{n_0}^{\pm} = \pm \frac{1}{2} \{ \frac{1}{2} \omega_{n_0} \mathbf{R}^{(A_2 A_1)} \cdot \mu^{on}(A_2) \times \mu^{on}(A_1) + \text{Im} [\mu^{on}(A_1) \cdot \mathbf{m}^{no}(A_2) + \mu^{on}(A_2) \cdot \mathbf{m}^{no}(A_1)] \} \quad (26)$$

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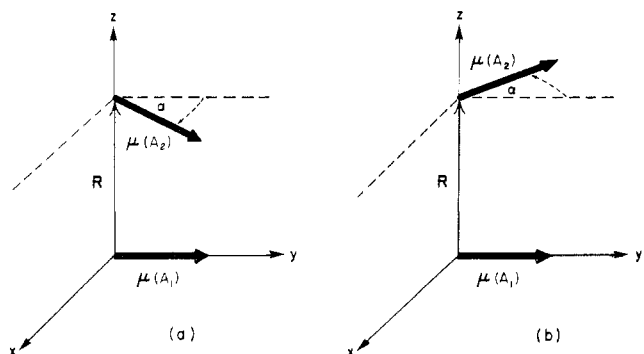


Figure 4. Dissymmetric configurations of electric transition dipoles in an optically active molecule with two identical chromophores. The enantiomeric configurations are labeled a and b.

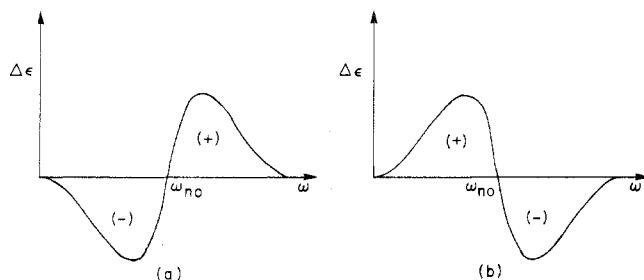


Figure 5. Exciton splittings in the CD spectra corresponding to configurations 4a and 4b respectively.

The appearance of the CD spectrum depends strongly on the magnitude of the exciton splitting

$$\Delta E =$$

$$2 \left| \int \int \psi_n^*(A_1) \psi_o^*(A_2) V^{A_1 A_2} \psi_o(A_1) \psi_n(A_2) d\tau(A_1) d\tau(A_2) \right| \quad (27)$$

where $V^{A_1 A_2}$ is the potential energy of interaction between A_1 and A_2 . The displacements of the symmetric and antisymmetric components from the center of the couplet are given by eq 28 in the point-dipole

$$E^\pm = \mp \mu_\alpha^{on}(A_1) \mu_\beta^{on}(A_2) T_{\alpha\beta}^{(A_2 A_1)} \quad (28)$$

approximation.

Figures 4 and 5 illustrate an application of this theory to the determination of absolute configuration for a pair of chromophores of which the electric transition dipoles, depicted for the symmetric case, are parallel to the XY plane. If the " μ - m " contribution to the rotatory strength is secondary to that from the scalar triple product in (26), the CD spectra of configurations 4a and 4b appear as in 5a and 5b, respectively. In both cases the symmetric coupling mode occurs at the higher frequency. In this simple example the sign of either the lower or higher frequency CD absorption is determined by the relative configuration of the transition dipoles in the molecular moieties and hence by the absolute configuration of the dimer.

Interesting applications of theories of this type are provided by the work of Weigang and Nugent³⁸ on monosubstituted [2.2]paracyclophanes and by Mason and Vane^{39,40} on aromatic alkaloids. Bosnich³ and

Harada and Nakanishi⁴ have described the application of exciton theory to the determination of the structures of inorganic complexes⁴¹ and organic natural products. A recent study by Hezemans and Groenewege⁴² of (+)-(1,5)-diaminotriptycene has confirmed a theoretical expectation³⁷ that the error incurred by ignoring the μ - m terms in (26) is not always negligible; for this molecule an incorrect absolute configuration had previously been assigned.¹⁵

Symmetry Rules for Circular Dichroism

Inspection of a two-component model of an optically active molecule, one group of which has C_{2v} symmetry and the other spherical symmetry, reveals that a quadrant rule governs the sign of the optical rotation. If the sphere is reflected through either of the two symmetry planes of the C_{2v} group one enantiomer transforms into the other. Similarly, an octant rule is the stereochemical symmetry rule for a group of D_{2h} symmetry perturbed by another of spherical symmetry.

Although stereochemical symmetry rules for spherical perturbing groups can be determined by inspection, eq 20 and 24 show that we should consider orbital symmetry of the chromophoric transition as well as the spatial symmetry of the perturbing group in order to find the sector rule which applies in a given spectral region. We illustrate this by developing sector rules for the electric-dipole-forbidden 300-nm $\pi^* \leftarrow n$ transition and for the allowed 190-nm $\sigma^* \leftarrow n$ transition in a carbonyl chromophore perturbed by an axially symmetric group with a permanent dipole moment μ and polarizability anisotropy $a_{\parallel} - a_{\perp}$. Components of \mathbf{a} , β , \mathbf{A} , \mathbf{D}' , and μ for perturbing groups with axial ($C_{\infty v}$) and spherical symmetry are listed in Table I. Selection rules for the leading electromagnetic transition multipoles in a chromophore of C_{2v} symmetry are given in Table II.

(a) The $\pi^* \leftarrow n$ Carbonyl Transition ${}^1A_2 \leftarrow {}^1A_1$ (C_{2v}). Using Tables I and II we see that only the sixth term of (20) and the second term of (24) contribute to the dynamic and static coupling mechanisms. Thus

$$R_{no} = -\frac{\text{Im } m_z^{on} \theta_{xy}^{no}}{4\pi\epsilon_0 R^7} \{10[a_{\perp} + (a_{\parallel} - a_{\perp})l_z^2]XYZ + 2(a_{\parallel} - a_{\perp})[X(5Y^2 - R^2)l_y l_z + Y(5X^2 - R^2)l_x l_z]\} + \frac{6\mu K_{xy}}{4\pi\epsilon_0 R^7} [5XYZl_z + X(5Y^2 - R^2)l_y + Y(5X^2 - R^2)l_x] \quad (29)$$

where l_x , l_y , and l_z are the direction cosines of the symmetry axis of the perturbing group with the right-handed x, y, z axes fixed in the carbonyl chromophore ($z \parallel \text{CO}$, y in the plane of the local nuclei). Both terms in (29) were first derived by Höhn and Weigang.³²

Because $\text{Im } m_z^{on} \theta_{xy}^{no}$ is positive for this transition and the polarizability anisotropy is normally positive for axially symmetric substituents, the first

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Table I
Non-Zero Components of Tensors describing the Perturbing Group

	Point-group symmetry of perturber $C_{\infty v}$	Spherical
$\alpha\alpha\beta$	$a_{zz} = a_{ }$ $a_{xx} = a_{yy} = a_{\perp}$	$a_{zz} = a_{yy} =$ $a_{xx} = a$
$\beta\alpha\beta$	$\beta_{xy} = -\beta_{yx}$	None
$A_{\alpha\beta\gamma}$	$A_{zzz} = A_{ }$ $A_{zzx} = A_{zyy} = -1/2 A_{ }$ $A_{xxx} = A_{zzx} = A_{yyz} = A_{yzy} = A_{\perp}$	None
$D'_{\alpha\beta\gamma}$	$D'_{xyz} = D'_{zxy} = -D'_{yzz} = -D'_{yzz}$	None
$\mu\alpha$	μ_z	None

Table II
Selection Rules for C_{2v} Chromophores^a

Transition symmetry	Non-zero transition multipoles
$A_1 \leftarrow A_1$	$\mu_z, \theta_{zz}, \theta_{xx}, \theta_{yy} = -\theta_{xx} - \theta_{zz}$
$A_2 \leftarrow A_1$	$m_z, \theta_{xy} = \theta_{yx}$
$B_1 \leftarrow A_1$	$\mu_x, m_y, \theta_{zz} = \theta_{xx}$
$B_2 \leftarrow A_1$	$\mu_y, m_x, \theta_{yz} = \theta_{zy}$

^a The z axis is the twofold rotation axis.

line of (29) is responsible for the observed octant rule.^{31,32,43,44} The other terms can lead to deviations from octant behavior. The sign of K_{xy} can only be determined by detailed calculations, but if the substituent is nonpolar this static-coupling term can be neglected. For a weakly polar perturbing group like a methyl substituent in cyclohexanone the dynamic coupling dominates, but the octant rule from the first term in (29) is modified by the other term in the polarizability anisotropy of the substituent. This term (i) enhances the octant effect associated with α -axial and β -equatorial substitution, (ii) diminishes the octant effect of β -axial substitution, and (iii) makes a negligible contribution for α -equatorial substitution.

(b) **The 190-nm Carbonyl Transition.** The recent observations of Kirk, *et al.*,^{44,45} can be interpreted if it is assumed that the 190-nm transition involves a $\sigma^* \leftarrow n$ excitation of local symmetry ${}^1B_2 \leftarrow {}^1A_1$ (C_{2v}). The second term in (24) and all terms except the sixth in (20) contribute to the rotatory strength, but only the second and fourth members of (20) can produce a quadrant rule if the perturbing group is uncharged. For an axially symmetric perturbing group the rotatory strength due to this pair of dynamic-coupling terms is²⁹

$$R_{no} = \frac{a_{\perp}XY}{4\pi\epsilon_0R^5} [3 \operatorname{Im} \mu_y^{\text{on}} m_x^{\text{no}} + \omega_{no} \mu_y^{\text{on}} \theta_{yz}^{\text{no}}] + \frac{(a_{||} - a_{\perp})}{4\pi\epsilon_0R^7} \{ 3 \operatorname{Im} \mu_y^{\text{on}} m_x^{\text{no}} [XYl_x^2 + (Y^2 - 1/3R^2)l_xl_y + YZl_xl_z] R^2 + \omega_{no} \mu_y^{\text{on}} \theta_{yz}^{\text{no}} [XYR^2l_z^2 + 5XYZ^2(l_x^2 - l_z^2) + YZ(5Z^2 - 5X^2 - R^2)l_xl_z + Z(5Y^2 - R^2)(Zl_xl_y - Xl_yl_z)] \} \quad (30)$$

(43) W. Moffitt, R. B. Woodward, A. Moscovitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, **83**, 4013 (1961); D. A. Lightner and T. C. Chang, *J. Amer. Chem. Soc.*, **96**, 3015 (1974).

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If $\operatorname{Im} \mu_y^{\text{on}} m_x^{\text{no}}$ and $\mu_y^{\text{on}} \theta_{yz}^{\text{no}}$ are positive, the first line implies a quadrant rule whose signs agree with those found experimentally.^{44,45} Terms in $(a_{||} - a_{\perp})XY/R^5$ also contribute to this quadrant rule if the polarizability anisotropy is positive. Equation 30 indicates that in cyclohexanones with nonpolar and axially symmetric substituents these terms (i) enhance the quadrant effect associated with α -axial and β -axial substitution, (ii) diminish the quadrant effect associated with β -equatorial substitution, and (iii) make negligible contributions in the case of α -equatorial substitution. Experimental data^{44,45} appear to support these conclusions. Terms such as Kirkwood's may tend to oppose i and ii, but (30) probably gives the most important dynamic-coupling contributions.

Simple symmetry rules have met with only limited success. This is hardly surprising, for in the formalism of this article they can be justified only if the perturbing group is isotropically polarizable³² or carries a net charge.⁴⁶ Although "through-space" mechanisms depending on polarizability anisotropy and bond polarity may account for many deviations from simple sector-rule behavior, interaction through bonds⁴⁷ and other delocalization mechanisms⁴⁸ which lie outside the scope of this formalism cannot be neglected.⁴⁹⁻⁵²

Induced Optical Activity

Investigations by Blout and Stryer,⁵³ Bosnich,⁵⁴ and Hayward, *et al.*,^{55,56} have shown that electronic transitions in a chromophore of an achiral molecule interacting stereospecifically with an optically active substrate⁵³ or solvent⁵⁴⁻⁵⁶ often acquire significant rotatory strength. This type of optical activity arises from the same dynamic and static coupling mechanisms invoked to account for the circular dichroism of molecules composed of two symmetric groups. In particular, the fifth dynamic-coupling term in (20) always contains a nonzero component $\mu_{\alpha}^{\text{o}1n_1} \cdot \mu_{\beta}^{\text{n}1\text{o}1} T_{\alpha\beta}^{(2)} \beta^{(2)} \omega_{no} / \omega$ when the perturbing molecule, 2, is optically active. The contribution of this term to the induced optical activity is

$$R_{no} = (4\pi\epsilon_0)^{-1} D^{(1)} \beta^{(2)} \langle (3 \cos^2 \theta - 1) / R^3 \rangle \omega_{no} / \omega \quad (31)$$

where $D^{(1)} = \mu_{\alpha}^{\text{o}1n_1} \cdot \mu_{\beta}^{\text{n}1\text{o}1}$ is the electric dipole strength of the $n \leftarrow o$ transition in molecule 1 and θ is the angle between the transition dipole and the position vector \mathbf{R} of 2 relative to 1. The angular brackets denote statistical averaging over all configurations of 1 and 2.

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Vibrational Effects

A number of papers dealing with the effects of nuclear motion on CD bands are available;⁵⁷⁻⁶¹ often there is pronounced vibrational structure in electronic CD bands. Optical activity arising from isotopic substitution is of current interest⁶²⁻⁶⁵ and has been partially examined from the Kirkwood point of view by Fickett.^{66,66a} Raman circular intensity differentials⁶⁷ which give information about the vibrational dependence of the gyration polarizability have recently been measured.^{68,69} Efforts are being made to extend CD measurements into the infrared.^{70,71}

Solvent Effects

Solvent effects in ORD spectroscopy have been incorporated by inserting a Lorentz factor of $(n^2 + 2)/3$ on the right-hand side of (13). However this procedure makes no allowance for stereospecific interactions with the solute. The Kirkwood formalism is ideally suited to deal with the effects of weak molecular interactions on CD and ORD spectra.

Conclusion

The Kirkwood formalism, as expounded and extended in this article, is a helpful but not a foolproof guide to the relationship between molecular structure and natural optical activity. Great care must be exercised in choosing a model that adequately reflects the molecule being investigated. Some day our improving knowledge of molecular wave functions may make the Rosenfeld equation the method of choice, but the Kirkwood formalism remains important for the light it throws on the interactions responsible for a molecule's rotatory strength.

We thank Professor D. P. Craig for helpful criticisms of the manuscript.

Appendix: Classical Derivation of the Gyration Polarizability due to Two Interacting Groups

The magnetic dipole induced in the molecule by the light wave is assumed to be the sum of the dipoles induced in the component groups 1 and 2 (referred to local origins) together with the magnetic dipole of group 2 referred to the local origin on 1. Thus

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$$\overline{m_\alpha} = \overline{m_\alpha^{(1)}} + \overline{m_\alpha^{(2)}} + \overline{m_\alpha^{(21)}} \quad (\text{A1})$$

where the bar denotes a vibronic expectation value in the presence of the optical field. We note that

$$\overline{m_\alpha^{(21)}} = \frac{1}{2} \left[\mathbf{R}^{(21)} \times \sum_j e_j \dot{\mathbf{r}}_j^{(2)} \right]_\alpha = \frac{1}{2} \epsilon_{\alpha\beta\gamma} R_\beta^{(21)} \sum_j e_j \dot{r}_{j\gamma}^{(2)} \quad (\text{A2})$$

and that $\sum_j e_j \dot{r}_{j\gamma}^{(2)}$ is equal to the time derivative of the electric dipole induced in 2 by the light wave; Σ_j is a sum over all charges in group 2. It follows that

$$\overline{m_\alpha} = \frac{1}{2} \epsilon_{\alpha\beta\gamma} R_\beta^{(21)} \overline{\dot{\mu}_\gamma^{(2)}} + \overline{m_\alpha^{(1)}} + \overline{m_\alpha^{(2)}} \quad (\text{A3})$$

Thus, the magnetic moment is dependent on the origin if there is a time-dependent electric dipole. The first term in (A3) leads directly to Kirkwood's polarizability formula which can be deduced using the result

$$\dot{\mu}_\gamma^{(2)} = a_{\gamma\delta}^{(2)} [\dot{E}_\delta + \dot{F}_\delta^{(2)}] + \frac{1}{3} A_{\gamma\delta\epsilon}^{(2)} [\dot{E}_{\delta\epsilon} + \dot{F}_{\delta\epsilon}^{(2)}] + \dots \quad (\text{A4})$$

where $F_\delta^{(2)}$ and $F_{\delta\epsilon}^{(2)}$ are the dynamic field and field-gradient at 2 due to the oscillating electric multipoles induced in 1.

The local magnetic dipoles $\overline{m_\alpha^{(1)}}$ and $\overline{m_\alpha^{(2)}}$ are expanded as in eq 2 and 22

$$m_\alpha^{(i)} = \chi_{\alpha\beta}^{(i)} B_\beta + \omega^{-1} [\beta_{\beta\alpha}^{(i)} + J_{\beta\alpha\gamma}^{(i)} F_\gamma^{(i)} + K_{\beta\alpha\gamma\delta}^{(i)} F_{\gamma\delta}^{(i)}] [\dot{E}_\beta + \dot{F}_\beta^{(i)}] + \frac{1}{3} \omega^{-1} D'_{\alpha\beta\gamma}^{(i)} [\dot{E}_{\beta\gamma} + \dot{F}_{\beta\gamma}^{(i)}] + \dots \quad (\text{A5})$$

in which $F_\gamma^{(i)}$ and $F_{\gamma\delta}^{(i)}$ are the local electrostatic field and field-gradient at group i due to the charge distribution on group j . Using the standard results¹⁹

$$F_\gamma^{(i)} = T_\gamma^{(ji)} Q^{(j)} + T_{\gamma\delta}^{(ji)} \mu_\delta^{(j)} + \dots \quad (\text{A6})$$

$$F_{\gamma\delta}^{(i)} = -T_{\gamma\delta}^{(ji)} Q^{(j)} - T_{\gamma\delta\epsilon}^{(ji)} \mu_\epsilon^{(j)} + \dots \quad (\text{A7})$$

$$F_\beta^{(i)} = T_{\beta\gamma}^{(ji)} \dot{\mu}_\gamma^{(j)} + \frac{1}{3} T_{\beta\gamma\delta}^{(ji)} \dot{\theta}_{\gamma\delta}^{(j)} + \dots = T_{\beta\gamma}^{(ji)} a_{\gamma\delta}^{(j)} \dot{E}_\delta + \frac{1}{3} T_{\beta\gamma\delta}^{(ji)} A_{\epsilon\gamma\delta}^{(j)} \dot{E}_\epsilon + \dots \quad (\text{A8})$$

and

$$\dot{F}_{\beta\gamma}^{(i)} = -T_{\beta\gamma\delta}^{(ji)} \dot{\mu}_\delta^{(j)} + \dots = -T_{\beta\gamma\delta}^{(ji)} a_{\delta\epsilon}^{(j)} \dot{E}_\epsilon + \dots \quad (\text{A9})$$

we find that (A4) and (A5) when substituted into (A3) and

$$\beta = \frac{1}{3} \omega \partial m_\alpha / \partial \dot{E}_\alpha \quad (\text{A10})$$

give (16) and (23).