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On the quantum mechanical theory of natural optical activity*

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Optical activity due to the coupling of molecular subunits is discussed in its dependence on various electromagnetic tensor properties of the subunits and on geometrical parameters. Certain approximation aspects of the theory are analyzed. Symmetry rules for dynamic-coupling terms are derived. Origin-dependent tensors are eliminated by referring their components to local frequency-dependent polarizability centers. Kirkwood's reduced first order result is revisited.

Key words: Natural optical activity—Symmetry rules—Polarizability centers—Kirkwood approach.

1. Introduction

A quantum mechanical theory of natural optical activity which relates optical rotatory power to molecular structure was formulated by Kirkwood [1]. It is based on a molecular model in terms of chemically distinguishable subunits without electron exchange between them, their relative spatial distribution, and their electric multipole interactions considered as a perturbation. The model is used for a perturbation treatment of the Rosenfeld expression [2] which is a standard approximation for the molecular rotatory power and the first term in a series of pseudoscalar products of molecular electric and magnetic transition multipole moments of equal rank [3]. The perturbation treatment, partly performed in [1], leads to an expression for the optical rotatory power in terms of electromagnetic properties of the subunits such as dipole moment and various

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polarizabilities as well as of geometrical parameters describing their steric arrangement (e.g. [4–8]). Thus, comparison of the optical rotation of molecules differing in the nature of their subunits at given molecular sites is made possible, and chemical relation can be taken into account.

This theory combines the conceptions of the dynamic- and static-coupling theories according to which optical activity is generated by the dynamic coupling of electronic motions on various subunits and, respectively, by the coupling of a chromophoric group to the electric field of the asymmetric static charge distribution of the remainder of the molecule (cf. [8]). For applications of the theory, a proper definition of the molecular subunits has to be used, and the zeroth-order Hamiltonian in the Born–Oppenheimer approximation has to be correspondingly specialized [1, 7, 9]. Additional approximations in this theory for deriving simple expressions for the rotatory parameter are: (1) restriction of the perturbation treatment of Rosenfeld's expression to first order, (2) truncation of the electric multipole expansion after the dipole–dipole term, (3a) disregard of the static-coupling terms or (3b) of the dynamic-coupling terms or (3c) of parts of the dynamic-coupling terms, (4) reduction of the geometrical parameters to distances between "centers of gravity" of the subunits. Such simplifications were already criticized by Hückel [10]. Since their use for obtaining quantitative results may lead to serious errors, the limits of their applicability have to be taken into account.

Approximation (1) leads to a linear combination of contributions to the optical rotatory power depending on properties of pairs of molecular subunits. If each pair is achiral, interactions of at least three subunits have to be considered and the rotatory power cannot be described by a first order expression. A typical example is the optical activity of so-called T_d-derivatives [7], i.e. molecules with a T_d-symmetrical skeleton and four different substituents whose symmetry elements are also symmetry elements of the C_{3v}-axes of the skeleton. Thus, the contribution to the optical rotatory power which appears in all chiral methane derivatives and which is the main contribution, if the deviations from the idealized situation in T_d-derivatives are small, is described in second-order perturbation theory. A first order perturbation calculation describes contributions to the optical rotation of methane derivatives which are based exclusively on deviations from the T_d-situation. In this respect, the order of the perturbation calculation is a doubtful criterion for the order of magnitude of the result. For such discussions an algebraic analysis of the optical activity of chiral molecules with a common achiral skeleton by Ruch and Schönhofer [11, 12] is used to best advantage. Approximation (2) requires the distance between two subunits to be much larger than the separation of charges within them and will, therefore, introduce errors in calculating the optical rotatory power of compact molecules. The optical rotation of ketones is explained by considering the electric dipole–quadrupole coupling of subunits [4, 6]. The static-coupling terms and, thus, approximation (3a) were analyzed by Schellman [13] in terms of the symmetry of subunits.

In spite of the considerable interest the coupling theory of natural optical activity has attracted (cf. [14]), the dynamic-coupling terms have not been systematically discussed in their dependence on the symmetry of subunits. In this note such an analysis and, thus, an analysis of approximation (3b) and of the special Kirkwood approximation (3c) is performed provided that approximations (1) and (2) are valid. The correlation between the approximations (3c) and (4) is examined in terms of local frequency-dependent polarizability centers.

2. Optical rotatory power in first-order coupling theory

The molecular optical rotatory power $[M]$ of randomly distributed chiral molecules of one sort in gas or liquid phase at transparent frequencies is given by the Rosenfeld expression [2, 15]

$$[M]=\frac{48\pi N_A}{c}\frac{n^2+2}{3}\nu^2\,\mathrm{tr}\,\boldsymbol{\gamma}, \qquad \boldsymbol{\gamma}=\frac{2}{h}\,\mathrm{Im}\sum_s\frac{\langle 0|\boldsymbol{m}|s\rangle\langle s|\boldsymbol{\mu}|0\rangle}{\nu_{s0}^2-\nu^2}. \tag{1}$$

$\langle 0|\boldsymbol{m}|s\rangle$ and $\langle 0|\boldsymbol{\mu}|s\rangle$ denote matrix elements of the molecular electric and magnetic dipole moment between the nondegenerate molecular ground state $|0\rangle$ and an excited state $|s\rangle$, ν_{s0} is the corresponding eigenfrequency, ν the frequency of the linearly polarized light wave whose plane of polarization is rotated, N_A is Avogadro's number, c the velocity of light, $(n^2+2)/3$ the Lorentz factor, Im denotes the imaginary part of the sum, tr the trace of the tensor $\boldsymbol{\gamma}$.

For the perturbation calculation of the rotatory parameter $\mathrm{tr}\,\boldsymbol{\gamma}$ according to Kirkwood's molecular model, the unperturbed subunits may be, for instance, completely isolated groups or ligands in the presence of an achiral molecular skeleton as in methane or allene derivatives. In the second case, the interaction between the skeleton and each ligand is considered in zeroth order so that perturbation results for $\mathrm{tr}\,\boldsymbol{\gamma}$ do not explicitly depend on electromagnetic properties of the skeleton. The zeroth-order molecular state vector $|s^0\rangle$ is a product of energy eigenstates $|s_i\rangle$ of the unperturbed subunits l_i, $i=1,2,\ldots,N$ (and the skeleton l_{N+1}). Spin effects are disregarded [16] and, correspondingly, the eigenfunctions are chosen to be real. The molecular moments are decomposed into moments of the N (or $N+1$) groups which are assumed to be electrically neutral. Thus, $\boldsymbol{m}=\sum_i \boldsymbol{m}^{(i)}$, $\boldsymbol{\mu}=\sum_i \boldsymbol{\mu}^{(i)}$ where the electric moments $\boldsymbol{m}$ and $\boldsymbol{m}^{(i)}$ are origin-independent, whereas the magnetic moments $\boldsymbol{\mu}$ and $\boldsymbol{\mu}^{(i)}$ are origin-dependent. If $\boldsymbol{\mu}$ is referred to $\boldsymbol{r}'$ instead of $\boldsymbol{r}$, it is

$$\langle s|\boldsymbol{\mu}(\boldsymbol{r}')|t\rangle=\langle s|\boldsymbol{\mu}(\boldsymbol{r})|t\rangle+\frac{i\pi}{c}\nu_{st}\langle s|\boldsymbol{m}|t\rangle\times(\boldsymbol{r}'-\boldsymbol{r}) \tag{2}$$

where

$$\boldsymbol{\mu}(\boldsymbol{r})=\sum_k\frac{q_k}{2M_kc}(\boldsymbol{r}_k-\boldsymbol{r})\times\boldsymbol{p}_k, \qquad \boldsymbol{m}=\sum_k q_k\boldsymbol{r}_k$$

and q_k, M_k, $\boldsymbol{p}_k$ denote charge, mass, and momentum of particle k at position $\boldsymbol{r}_k$. With the aid of (2), the origin-independence of $\mathrm{tr}\,\boldsymbol{\gamma}$ is verified; it holds true in each perturbation order.

In zeroth order, tr $\boldsymbol{\gamma}$ is the sum of the rotatory parameters tr $\boldsymbol{\gamma}^{(i)}$ of the molecular subgroups.

$$[\mathrm{tr}\,\boldsymbol{\gamma}]^{(0)} = \sum_{i=1}^{N(N+1)} \mathrm{tr}\,\boldsymbol{\gamma}^{(i)}, \qquad \boldsymbol{\gamma}^{(i)} = \frac{2}{h}\,\mathrm{Im}\sum_{s_i} \frac{\langle 0_i|\boldsymbol{m}^{(i)}|s_i\rangle\langle s_i|\boldsymbol{\mu}^{(i)}|0_i\rangle}{\nu_{s_i0_i}^2 - \nu^2}. \tag{3}$$

The unperturbed subunits (and the skeleton) are assumed to be achiral, and thus each tr $\boldsymbol{\gamma}^{(i)}$ vanishes.

The first-order dipole–dipole approximation of tr $\boldsymbol{\gamma}$ is written in the form [6, 7]

$$[\mathrm{tr}\,\boldsymbol{\gamma}]^{(1)} = \sum_{i<j=1}^{N} (H_1^{(ij)} + H_2^{(ij)}),$$

$$H_1^{(ij)} = -S_{ij} \sum_{\rho,\sigma} \Gamma_{\rho\rho\sigma}^{(i)}(\boldsymbol{r}_0)(\boldsymbol{e}_\sigma^{(i)} \cdot \boldsymbol{T}^{(ij)} \cdot \langle \boldsymbol{m}^{(j)}\rangle), \tag{4}$$

$$H_2^{(ij)} = -S_{ij} \sum_{\rho,\sigma,\rho',\sigma'} \alpha_{\rho\sigma}^{(i)} \gamma_{\rho'\sigma'}^{(j)}(\boldsymbol{r}_0)(\boldsymbol{e}_\rho^{(i)} \cdot \boldsymbol{e}_{\sigma'}^{(j)})(\boldsymbol{e}_\sigma^{(i)} \cdot \boldsymbol{T}^{(ij)} \cdot \boldsymbol{e}_{\rho'}^{(j)}),$$

where $H_n^{(ij)}$ depends on properties of the unperturbed subunits l_i and l_j only. S_{ij} is a symmetrizing operator with the property $S_{ij}f^{(ij)} = f^{(ij)} + f^{(ji)}$. $\boldsymbol{T}^{(ij)}$ is the dipole–diple tensor

$$\boldsymbol{T}^{(ij)} = \frac{1}{|\boldsymbol{R}^{(ij)}|^3}\left(\mathbf{1} - 3\frac{\boldsymbol{R}^{(ij)}\boldsymbol{R}^{(ij)}}{|\boldsymbol{R}^{(ij)}|^2}\right), \qquad \boldsymbol{R}^{(ij)} = \boldsymbol{R}^{(j)} - \boldsymbol{R}^{(i)}.$$

$\boldsymbol{R}^{(i)}$ and $\boldsymbol{R}^{(j)}$ are vectors directed to the centers of the electric multipole interaction between subunit l_i and l_j. The second-rank tensor $\boldsymbol{\alpha}^{(i)}$ is the familiar frequency-dependent polarizability; the third-rank tensor $\boldsymbol{\Gamma}^{(i)}$ describes the variation of $\boldsymbol{\gamma}^{(i)}$ by a static electric field which here is generated by the permanent electric dipole moment $\langle \boldsymbol{m}^{(j)}\rangle = \langle 0_j|\boldsymbol{m}^{(j)}|0_j\rangle$ of subunit l_j[1]. $\boldsymbol{\gamma}^{(i)}$ and $\boldsymbol{\Gamma}^{(i)}$ are origin-dependent tensors which, in equation (4), are referred to a common molecular origin $\boldsymbol{r}_0$. The tensors $\langle \boldsymbol{m}^{(i)}\rangle$, $\boldsymbol{\alpha}^{(i)}$, $\boldsymbol{\gamma}^{(i)}$, $\boldsymbol{\Gamma}^{(i)}$ are written according to $\boldsymbol{t}^{(i)} = \sum_{\rho,\sigma,\dots} t_{\rho\sigma\dots}^{(i)} \boldsymbol{e}_\rho^{(i)} \boldsymbol{e}_\sigma^{(i)} \dots$ where the $\boldsymbol{e}_\rho^{(i)}$, $\rho = 1, 2, 3$ are orthonormalized basis vectors of a coordinate system specific to subunit l_i.

The sum $\sum_{i<j} H_1^{(ij)}$ describes the contributions to the optical rotatory power in first-order dipole–dipole approximation generated by the static coupling of the subunits; $\sum_{i<j} H_2^{(ij)}$ is due to dynamic coupling and expressible in terms of the polarizabilities $\boldsymbol{\alpha}^{(k)}$, $\boldsymbol{\gamma}^{(k)}$. Differences between Eq. (4) and the corresponding Eq. (13) of Ref. [7] are based on different conceptions of the intramolecular interactions; they do not influence the following discussion.

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[1] The real tensors $\boldsymbol{\alpha}$, $\boldsymbol{\gamma}$, $\boldsymbol{A}$, $\boldsymbol{\Gamma}$ used in this note are identical with ${}^{(R)}\boldsymbol{\alpha}$, ${}^{(I)}\boldsymbol{\gamma}$, ${}^{(R)}\boldsymbol{A}$, ${}^{(I)}\boldsymbol{\Gamma}$ of Ref. [7] and correspond to $\boldsymbol{G}$, $\boldsymbol{\beta}$, $\boldsymbol{J}$ of Ref. [19] as follows: $\boldsymbol{\gamma} = -\nu^{-1}\boldsymbol{G}$, $\boldsymbol{A} = \boldsymbol{\beta}$, $\boldsymbol{\Gamma} = -\nu^{-1}\boldsymbol{J}$. The meaning of the operators $\boldsymbol{m}$ and $\boldsymbol{\mu}$ chosen here is identical with that of [7] and opposite to that of [19].

The terms $H_1^{(ij)}$ and $H_2^{(ij)}$ are each invariant with respect to a change of the molecular origin $\boldsymbol{r}_0$, as can be verified using the transformation equations

$$\sum_\sigma \gamma_{\rho\sigma}(\boldsymbol{r}')\boldsymbol{e}_\sigma = \sum_\sigma \gamma_{\rho\sigma}(\boldsymbol{r})\boldsymbol{e}_\sigma + \frac{\pi}{c}\sum_\sigma \alpha_{\rho\sigma}\boldsymbol{e}_\sigma \times (\boldsymbol{r}'-\boldsymbol{r}), \qquad \alpha_{\rho\sigma} = \alpha_{\sigma\rho} \tag{5a}$$

$$\sum_\sigma \Gamma_{\rho\sigma\tau}(\boldsymbol{r}')\boldsymbol{e}_\sigma = \sum_\sigma \Gamma_{\rho\sigma\tau}(\boldsymbol{r})\boldsymbol{e}_\sigma + \frac{\pi}{c}\sum_\sigma A_{\rho\sigma\tau}\boldsymbol{e}_\sigma \times (\boldsymbol{r}'-\boldsymbol{r}), \qquad A_{\rho\sigma\tau} = A_{\sigma\rho\tau} \tag{5b}$$

where the hyperpolarizability $\boldsymbol{A}$ describes the variation of $\boldsymbol{\alpha}$ by a static electric field. (5a) and (5b) are derived from the definition of the tensors $\boldsymbol{\alpha}$, $\boldsymbol{\gamma}$, $\boldsymbol{A}$, $\boldsymbol{\Gamma}$ and from Eq. (2). From (5a) and (5b), the corresponding transformation equations for single components $\gamma_{\rho\sigma}$ and $\Gamma_{\rho\sigma\tau}$ are obtained; from (5b) it follows that $\sum_\rho \Gamma_{\rho\rho\sigma}$ is origin-independent.

A consequence of not completely taking into account the Coulomb interaction energy is that the Rosenfeld expression in each perturbation order depends on the individual centers $\boldsymbol{R}^{(i)}$, $i = 1, 2, 3, \ldots, N$ of the subunits which are chosen as origins of the multipole expansion. Origins leading to optimal convergence of the expansion are supposed to nearly coincide with the charge centers of the polarizable electrons in each subunit [17, 18]. For the following discussion, the expansion points are chosen according to subunit symmetry as follows: $\boldsymbol{R}$ is a point of the mirror plane in a C_s-system, a point of the axis in a C_{nv}-system, and the center of mass in any other achiral system. Otherwise, the achiral subunit together with the expansion point would be treated as a system with lower symmetry or as a chiral system. In pure C_s- and C_{nv}-subunits, the identification of the expansion point with the center of mass is normally not optimal, since two isotopically distinct molecules have the same intramolecular Coulomb energy and do not differ to a high degree of accuracy in any electromagnetic property (cf. also [19]). Such differences in the choice of expansion points, however, are negligible for systems with a sufficiently large distance between each other as considered in dipole–dipole approximation.

3. Symmetry and optical rotation

For discussing the static- and dynamic-coupling contributions $H_1^{(ij)}$ and $H_2^{(ij)}$ in their dependence on the symmetry of the unperturbed achiral subunits, the special form of the electromagnetic tensors $\langle \boldsymbol{m} \rangle$, $\sum_{\rho,\sigma} \Gamma_{\rho\rho\sigma}\boldsymbol{e}_\sigma$, $\boldsymbol{\alpha}$, $\boldsymbol{\gamma}$ has to be determined for the corresponding symmetry groups G. The non-zero components of these tensors are found according to Neumann's principle [20]: components of a tensor describing a physical property are invariant under symmetry transformations of the coordinates. For this purpose, the coordinate system specific to a subunit is chosen as follows: the origin coincides with the multipole expansion point $\boldsymbol{R}$; the orthonormalized basis vectors $\boldsymbol{e}_\rho$, $\rho = 1, 2, 3$ are oriented arbitrarily in the case of pure C_i; in the case of pure C_s, $\boldsymbol{e}_3$ is perpendicular to the mirror plane; in the other achiral cases, $\boldsymbol{e}_3$ is parallel to an axis of highest order; in the case

Table 1. Non-zero components of $\langle \boldsymbol{m} \rangle$, $\sum_{\rho,\sigma} \Gamma_{\rho\rho\sigma} \boldsymbol{e}_\sigma$, $\boldsymbol{\alpha}$, $\boldsymbol{\gamma}(\boldsymbol{R})$

Achiral symmetry G[a]	m_ρ	$\Gamma_\sigma \equiv \sum_\rho \Gamma_{\rho\rho\sigma}$	$\alpha_{\rho\sigma} = \alpha_{\sigma\rho}$[b]	$\gamma_{\rho\sigma}(\boldsymbol{R})$[c]
C_i		$\Gamma_1, \Gamma_2, \Gamma_3$	$\alpha_{11}, \alpha_{22}, \alpha_{33}$ $\alpha_{12}, \alpha_{13}, \alpha_{23}$	
C_s	m_1, m_2	Γ_3	$\alpha_{11}, \alpha_{22}, \alpha_{33}$ α_{12}	γ_{13}, γ_{23} γ_{31}, γ_{32}
C_{2h}		Γ_3	$\alpha_{11}, \alpha_{22}, \alpha_{33}$ α_{12}	
$C_{nh}, S_{2n}(n \geq 3)$		Γ_3	$\alpha_{11} = \alpha_{22}, \alpha_{33}$	
C_{2v}	m_3		$\alpha_{11}, \alpha_{22}, \alpha_{33}$	γ_{12}, γ_{21}
$C_{nv}(n \geq 3)$	m_3		$\alpha_{11} = \alpha_{22}, \alpha_{33}$	$\gamma_{12} = -\gamma_{21}$
S_4		Γ_3	$\alpha_{11} = \alpha_{22}, \alpha_{33}$	$\gamma_{11} = -\gamma_{22}$ $\gamma_{12} = \gamma_{21}$
D_{2d}			$\alpha_{11} = \alpha_{22}, \alpha_{33}$	$\gamma_{12} = \gamma_{21}$
D_{2h}			$\alpha_{11}, \alpha_{22}, \alpha_{33}$	
$D_{nd}, D_{nh}(n \geq 3)$			$\alpha_{11} = \alpha_{22}, \alpha_{33}$	
$T_d, T_h, O_h, O(3)$			$\alpha_{11} = \alpha_{22} = \alpha_{33}$	

[a] A symmetry is called achiral if the symmetry group G contains an improper rotation.
[b] Non-diagonal components of $\boldsymbol{\alpha}$ vanish if principal axes are chosen.
[c] For S_4, the x- and y-axis can be chosen so that γ_{11} or γ_{12} vanishes.

of C_{2v} and D_{2d}, $\boldsymbol{e}_1$ lies in one of the mirror planes; for D_{2h}, the basis vectors are parallel to the rotation axes.

For these coordinate systems, the specification of the tensors needed is given in Table 1. There is no permanent electric dipole moment $\langle \boldsymbol{m} \rangle$ except for systems with pure symmetry C_s or C_{nv}. The vector $\sum_{\rho,\sigma} \Gamma_{\rho\rho\sigma} \boldsymbol{e}_\sigma$ vanishes if the system has symmetry C_{nv} or a higher symmetry. The symmetrical tensor $\boldsymbol{\alpha}$ has non-zero components for each system; its non-diagonal components vanish if principal axes are chosen; for C_s and C_{2h}, the 3-axis is a principal axis. The $\boldsymbol{\gamma}$-components referred to the axes introduced vanish except for the cases of C_s, C_{nv}, S_4, and D_{2d}; in the case of S_4, a proper choice of $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ leads to the vanishing of one of the two $\boldsymbol{\gamma}$-components; for the following discussion, only $\gamma_{12} = \gamma_{21}$ will be used for S_4 in correspondence with D_{2d}.

As can be seen from Table 1, the static-coupling term $H_1^{(ij)}$ vanishes for various combinations of subunit symmetries $G^{(i)}$ and $G^{(j)}$. For example:

$$\begin{aligned} H_1^{(ij)} = 0 \quad & \text{if } G^{(k)} \neq C_s, C_{nv}, k = i, j \\ & \text{or } G^{(k)} \supset C_{nv}, k = i, j \\ & \text{or } G^{(i)} = D_{nd}, D_{nh}, \text{cubic.} \end{aligned} \tag{6}$$

Apart from exceptions, $H_1^{(ij)}$ does not vanish if the subunits l_i, l_j form a chiral pair and have symmetries $(G^{(i)}, G^{(j)})$ such as (C_s, C_s), (C_s, C_{nv}), (C_{nh}, C_{mv}). The results correspond with symmetry rules for static-coupling effects given by Schellman [13].

The dynamic-coupling term $H_2^{(ij)}$ is transformed with the aid of (5a) into the expression

$$\begin{aligned} H_2^{(ij)} &= H_{21}^{(ij)} + H_{22}^{(ij)}, \\ H_{21}^{(ij)} &= -S_{ij} \sum_{\rho,\sigma,\rho',\sigma'} \alpha_{\rho\sigma}^{(i)} \gamma_{\rho'\sigma'}^{(j)} (\boldsymbol{R}^{(j)})(\boldsymbol{e}_\rho^{(i)} \cdot \boldsymbol{e}_{\sigma'}^{(j)})(\boldsymbol{e}_\sigma^{(i)} \cdot \boldsymbol{T}^{(ij)} \cdot \boldsymbol{e}_{\rho'}^{(j)}), \\ H_{22}^{(ij)} &= \frac{\pi}{c} \sum_{\rho,\sigma,\rho',\sigma'} \alpha_{\rho\sigma}^{(i)} \alpha_{\rho'\sigma'}^{(j)} [\boldsymbol{R}^{(j)} - \boldsymbol{R}^{(i)}, \boldsymbol{e}_\rho^{(i)} \times \boldsymbol{e}_{\sigma'}^{(j)}](\boldsymbol{e}_\sigma^{(i)} \cdot \boldsymbol{T}^{(ij)} \cdot \boldsymbol{e}_{\rho'}^{(j)}), \end{aligned} \tag{7}$$

where $[\boldsymbol{a}, \boldsymbol{b} \times \boldsymbol{c}]$ is the scalar triple vector product. Examples for $G^{(i)}$ and $G^{(j)}$ are given, for which $H_{21}^{(ij)}$ vanishes:

$$\begin{aligned} H_{21}^{(ij)} = 0 \quad &\text{if } G^{(k)} \neq C_s, C_{nv}, S_4, D_{2d}, \ k = i, j \\ &\text{or } G^{(k)} \supset C_n, \ n \geq 3, \ k = i, j, \text{ axes coplanar.} \end{aligned} \tag{8}$$

The second condition is proven as follows: the $\boldsymbol{\alpha}$- and $\boldsymbol{\gamma}$-tensor for a system with a threefold or higher order rotation axis can be written in the form of

$$\boldsymbol{\alpha} = \alpha_{11}\mathbf{1} + \Delta\alpha \boldsymbol{e}_3 \boldsymbol{e}_3, \qquad \mathbf{1} = \sum_\rho \boldsymbol{e}_\rho \boldsymbol{e}_\rho, \qquad \Delta\alpha = \alpha_{33} - \alpha_{11},$$

$$\boldsymbol{\gamma} = \gamma_{12}(\boldsymbol{e}_1 \boldsymbol{e}_2 - \boldsymbol{e}_2 \boldsymbol{e}_1);$$

insertion into the expression for $H_{21}^{(ij)}$ yields

$$H_{21}^{(ij)} = S_{ij} \Delta\alpha^{(i)} \gamma_{12}^{(j)} (\boldsymbol{e}_3^{(i)} \cdot (\boldsymbol{e}_1^{(j)} \boldsymbol{e}_2^{(j)} - \boldsymbol{e}_2^{(j)} \boldsymbol{e}_1^{(j)}) \cdot \boldsymbol{T}^{(ji)} \cdot \boldsymbol{e}_3^{(i)});$$

this term vanishes if the axes are coplanar, i.e. if $\boldsymbol{e}_3^{(i)}$ and $\boldsymbol{e}_3^{(j)}$ are coplanar, since then the vectors $\boldsymbol{e}_1^{(j)}$ and $\boldsymbol{e}_2^{(j)}$ can be chosen so that $(\boldsymbol{e}_3^{(i)} \cdot \boldsymbol{e}_1^{(j)}) = (\boldsymbol{e}_3^{(i)} \cdot \boldsymbol{e}_2^{(j)})$, $(\boldsymbol{e}_1^{(j)} \cdot \boldsymbol{R}^{(ij)}) = (\boldsymbol{e}_2^{(j)} \cdot \boldsymbol{R}^{(ij)})$ and *vice versa* for $i \leftrightarrow j$.

The term $H_{22}^{(ij)}$ depends on polarizabilities $\boldsymbol{\alpha}^{(k)}$, $k = i, j$ and on geometrical parameters. It vanishes if one of the subunits, say l_i, is isotropically polarizable, since by using principal axes for $\boldsymbol{\alpha}^{(j)}$

$$\begin{aligned} H_{22}^{(ij)} &= \alpha_{11}^{(i)} \sum_{\rho,\sigma} \alpha_{\sigma\sigma}^{(j)} [\boldsymbol{R}^{(ij)}, \boldsymbol{e}_\rho^{(i)} \times \boldsymbol{e}_\sigma^{(j)}](\boldsymbol{e}_\rho^{(i)} \cdot \boldsymbol{T}^{(ij)} \cdot \boldsymbol{e}_\sigma^{(j)}) \\ &= -\alpha_{11}^{(i)} \sum_\sigma \alpha_{\sigma\sigma}^{(j)} [\boldsymbol{R}^{(ij)}, \boldsymbol{e}_\sigma^{(j)} \times \boldsymbol{T}^{(ij)} \cdot \boldsymbol{e}_\sigma^{(j)}] = 0. \end{aligned}$$

$H_{22}^{(ij)}$ vanishes as well if both subunits have a threefold or higher order axis and if these axes are coplanar. The reason: for such subunits the tensor $\boldsymbol{\alpha}$ has cylinder symmetrical transformation behavior, and a pair of $C_{\infty v}$-subunits with coplanar axes is achiral. Thus

$$\begin{aligned} H_{22}^{(ij)} = 0 \quad &\text{if } G^{(i)} \text{ is cubic} \\ &\text{or } G^{(k)} \supset C_n \text{ or } S_n, \ n \geq 3, \ k = i, j, \text{ axes coplanar.} \end{aligned} \tag{9}$$

It is thus shown: depending on the symmetry of subunits, the contribution to the optical rotatory power by a chiral pair (l_i, l_j) in first order dipole–dipole approximation vanishes, or it is described by one or both of the dynamic-coupling terms

Table 2. Simple examples showing the dependence of $H_n^{(ij)}$ on subunit symmetries $G^{(i)}$, $G^{(j)}$ [a]

$H_1^{(ij)}$	$H_{21}^{(ij)}$	$H_{22}^{(ij)}$	if $G^{(i)}$	$G^{(j)}$	and if
0	0	0	C_{nv}	C_{mv}	$n, m \geq 3$, axes coplanar
0	●	●	C_{nv}	C_{mv}	axes not coplanar for $n, m \geq 3$
0	0	●	C_{nh}	C_{mh}	axes not coplanar for $n, m \geq 3$
0	●	0	cubic	C_s, C_{2v}, D_{2d}	
●	0	0	C_{nh}	C_{mv}	$n, m \geq 3$, axes coplanar
●	●	●	C_s	C_s, C_{nv}	

[a] Apart from exceptions, terms ● cannot be excluded for reasons of symmetry.

$H_{21}^{(ij)}$, $H_{22}^{(ij)}$ or by the static-coupling term $H_1^{(ij)}$, or it is generated by both of the coupling mechanisms. Some examples are given in Table 2. If the subunits are interpreted as ligands coupled to an archiral molecular skeleton, their symmetry groups permitted are only C_s, C_{nv}.

4. γ-Centers and Kirkwood's approximate formula

The γ-components referred to the coordinate systems introduced above do not vanish in the case of C_s, C_{nv}, S_4, and D_{2d}. However, they might also vanish if referred to other origins. For determining such origins, the vectors $\boldsymbol{\gamma}_\rho$ and $\boldsymbol{\alpha}_\rho$ are introduced,

$$\boldsymbol{\gamma}_\rho = \sum_\sigma \gamma_{\rho\sigma} \boldsymbol{e}_\sigma, \qquad \boldsymbol{\alpha}_\rho = \sum_\sigma \alpha_{\rho\sigma} \boldsymbol{e}_\sigma, \qquad \rho = 1, 2, 3$$

and the transformation equation (5a) is written as follows

$$\boldsymbol{\gamma}_\rho(\boldsymbol{r}) = \boldsymbol{\gamma}_\rho(\boldsymbol{R}) + \frac{\pi}{c} \boldsymbol{\alpha}_\rho \times (\boldsymbol{r} - \boldsymbol{R}). \tag{10a}$$

For achiral systems, $\boldsymbol{\gamma}_\rho(\boldsymbol{R})$ and $\boldsymbol{\alpha}_\rho$ are orthogonal to each other for all ρ or can at least be chosen to be so. Therefore, origins $\boldsymbol{r}$ exist where $|\boldsymbol{\gamma}_\rho(\boldsymbol{r})| = 0$. The set of these points is denoted by $\boldsymbol{L}_\rho$. (10a) yields

$$|\boldsymbol{\gamma}_\rho(\boldsymbol{L}_\rho)| = 0, \qquad \rho = 1, 2, 3$$

where

$$\boldsymbol{L}_\rho = \boldsymbol{R} + \boldsymbol{u}_\rho(\boldsymbol{R}) + \kappa \boldsymbol{\alpha}_\rho, \qquad \boldsymbol{u}_\rho(\boldsymbol{R}) = \frac{c}{\pi} \frac{\boldsymbol{\alpha}_\rho \times \boldsymbol{\gamma}_\rho(\boldsymbol{R})}{|\boldsymbol{\alpha}_\rho|^2} \tag{10b}$$

and with κ being an arbitrary real constant. $\boldsymbol{L}_\rho$ defines a straight line which is independent of the special choice of origin $\boldsymbol{R}$. For $\kappa = 0$, it is

$$|\boldsymbol{\gamma}_\rho(\boldsymbol{Z}_\rho)| = 0 \quad \text{with } \boldsymbol{Z}_\rho = \boldsymbol{R} + \boldsymbol{u}_\rho(\boldsymbol{R}).$$

The results are summarized:

a) In the case of C_s, the vectors $\boldsymbol{Z}_\rho$ are directed to different points of the plane. The lines $\boldsymbol{L}_1$ and $\boldsymbol{L}_2$ lie in the plane, $\boldsymbol{L}_3$ is perpendicular to the plane. Apart from

exceptions, $\boldsymbol{L}_1$ and $\boldsymbol{L}_2$ have an intersection point; there, the $\boldsymbol{\gamma}$-components vanish except for γ_{31} and γ_{32}. Correspondingly, at the intersection of $\boldsymbol{L}_3$ and the mirror plane, the $\boldsymbol{\gamma}$-components vanish except for γ_{13} and γ_{23}.
b) In the case of C_{nv}, $\boldsymbol{Z}_1$, $\boldsymbol{Z}_2$ are vectors to points of the axis, and $\boldsymbol{Z}_3 = \boldsymbol{R}$. If $n = 2$, $\boldsymbol{Z}_1$ and $\boldsymbol{Z}_2$ do not coincide. If $n \geq 3$, however, $\boldsymbol{Z}_1 = \boldsymbol{Z}_2$, i.e. there is but one origin at the axis where all components $\gamma_{\rho\sigma}$ vanish.
c) In the case of D_{2d}, the vectors $\boldsymbol{u}_\rho(\boldsymbol{R})$, $\rho = 1, 2$ with $\boldsymbol{u}_1 = -\boldsymbol{u}_2$ are parallel to the axis of subsymmetry C_{2v}; $|\boldsymbol{u}_3(\boldsymbol{R})| = 0$. $\boldsymbol{Z}_1 = \boldsymbol{R} + \boldsymbol{u}_1(\boldsymbol{R}), \boldsymbol{Z}_2 = \boldsymbol{R} - \boldsymbol{u}_1(\boldsymbol{R}), \boldsymbol{Z}_3 = \boldsymbol{R}$ are vectors to points of the axis. $\boldsymbol{R}$ is the point of intersection of the three C_2-axes where $\gamma_{12} = \gamma_{21}$.
d) In the case of S_4, a coordinate system exists referred to which the diagonal tensor components $\gamma_{\rho\rho}$ vanish. The components γ_{12} and γ_{21} vanish at points of the axis on opposite sides of $\boldsymbol{R}$ as in the case of D_{2d}.
e) In the other cases of achiral systems, $|\boldsymbol{u}_\rho(\boldsymbol{R})| = 0$, $\forall \rho$ and the lines $\boldsymbol{L}_\rho$ intersect at the geometric center $\boldsymbol{R} = \boldsymbol{Z}_\rho$, $\forall \rho$ where $\boldsymbol{\gamma} = \boldsymbol{0}$.

The points $\boldsymbol{Z}_\rho = \boldsymbol{R} + \boldsymbol{u}_\rho(\boldsymbol{R})$, $\rho = 1, 2, 3$ shall be called $\boldsymbol{\gamma}$-centers. In the cases of symmetry C_s, C_{nv}, D_{2d}, S_4, their position in the mirror plane or, respectively, at the axis is defined in terms of dynamic polarizabilities and thus depends on the frequency of light used; its dependence on the nuclear masses is negligible[1]. For any other achiral system, only one $\boldsymbol{\gamma}$-center exists which coincides with the center of mass.

If the $\boldsymbol{\gamma}$-centers are used as origins for the corresponding $\boldsymbol{\gamma}$-components, the term $H_2^{(ij)}$ can be written as an expression depending on polarizabilities $\boldsymbol{\alpha}^{(i)}$, $\boldsymbol{\alpha}^{(j)}$ as well as on geometrical parameters, but not explicitly on $\boldsymbol{\gamma}^{(i)}$- and $\boldsymbol{\gamma}^{(j)}$-components. From Eqs. (4), (5a), and (10b)

$$H_2^{(ij)} = \frac{\pi}{c} \sum_{\rho,\sigma,\rho',\sigma'} \alpha_{\rho\sigma}^{(i)} \alpha_{\rho'\sigma'}^{(j)} [\boldsymbol{Z}_{\rho'}^{(j)} - \boldsymbol{Z}_\sigma^{(i)}, \boldsymbol{e}_\rho^{(i)} \times \boldsymbol{e}_{\sigma'}^{(j)}] (\boldsymbol{e}_\sigma^{(i)} \cdot \boldsymbol{T}^{(ij)} \cdot \boldsymbol{e}_{\rho'}^{(j)}) \tag{11}$$

where

$$\boldsymbol{Z}_\rho^{(k)} = \boldsymbol{R}^{(k)} + \boldsymbol{u}_\rho^{(k)}(\boldsymbol{R}^{(k)}), \qquad k = i, j.$$

$H_2^{(ij)}$ does not depend on the additive term $\kappa \boldsymbol{\alpha}_\rho$ of $\boldsymbol{L}_\rho$, as expected. This formulation of $H_2^{(ij)}$ is comparable with that of $H_{22}^{(ij)}$ according to Eq. (7). In (11), however, two types of geometrical parameters occur: distances between multipole expansion points as well as distances between $\boldsymbol{\gamma}$-centers.

In his approach to the theory of natural optical activity, Kirkwood used exclusively the term $H_{22}^{(ij)}$ to describe the contribution to the rotatory parameter by a chiral pair of molecular achiral subunits. The limits of this description follow from a comparison of $H_{22}^{(ij)}$ with $H_2^{(ij)}$.

i) If none of the achiral subunits l_i, l_j has pure symmetry C_s, C_{nv}, D_{2d}, or S_4, it is $H_{22}^{(ij)} = H_2^{(ij)}$ as well as $H_1^{(ij)} = 0$.

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[1] Buckingham and Longuet-Higgins [19] mentioned corresponding properties of the "effective quadrupole centres" of dipolar molecules.

ii) If at least one of the subunits l_i, l_j has symmetry C_s, C_{nv}, D_{2d}, or S_4 and if $H_{22}^{(ij)}$ does not vanish, the relative magnitude of $H_2^{(ij)}$ and $H_{22}^{(ij)}$ is of the order

$$|H_2^{(ij)}/H_{22}^{(ij)}| \approx \overline{|\boldsymbol{Z}_\rho^{(j)} - \boldsymbol{Z}_\sigma^{(i)}|}/|\boldsymbol{R}^{(j)} - \boldsymbol{R}^{(i)}|$$

where $\overline{|\boldsymbol{Z}_\rho^{(j)} - \boldsymbol{Z}_\sigma^{(i)}|}$ is a mean distance between the $\boldsymbol{\gamma}$-centers of l_i, l_j and normally different from the distance $|\boldsymbol{R}^{(ij)}|$. Their ratio, however, is the less different from 1 the larger $|\boldsymbol{R}^{(ij)}|$ as compared to the separation of charges within the subunits. This is exactly the condition for the validity of truncating the multipole expansion after the dipole–dipole term. In this approximation it is, therefore, valid to neglect the difference between $H_{22}^{(ij)}$ and $H_2^{(ij)}$. A comment of this type was first given by Moffitt [21].

Thus, the Kirkwood term $H_{22}^{(ij)}$ describes the contribution to the optical rotatory parameter $\mathrm{tr}\,\boldsymbol{\gamma}$ by the subunit pair (l_i, l_j) if the inter-subunit potential is the dipole–dipole potential and if the subunit symmetries are such that the static-coupling term $H_1^{(ij)}$ vanishes, but $H_{22}^{(ij)}$ does not. Examples were discussed above. When adding, however, further terms of the multipole expansion series, $H_{22}^{(ij)}$ must be replaced by $H_2^{(ij)}$, that is: if the conditions of case ii) are fulfilled, the term $H_{21}^{(ij)}$ has to be taken into account or, respectively, the $\boldsymbol{\gamma}$-centers and the multipole expansion points have to be distinguished from each other.

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