Monatshefte für Chemie 136, 275–287 (2005)
DOI 10.1007/s00706-005-0284-0

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Molecular Exciton Approach to Anisotropic Absorption and Circular Dichroism II. The Partial Optic Axis and its Application in Molecular Exciton Theory

Aage E. Hansen[*,#]

Department of Chemistry, H. C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark

Received October 7, 2004; accepted (revised) December 21, 2004

Summary. The first part of the present communication develops the general theory of the partial optic axis, which is an excitation specific structural feature first proposed as an aid to the choice of chromophoric reference points in a molecular exciton approach to optical rotatory power, and discusses its applicability to symmetry analyses in the light of the distinction between the three categories for anisotropic optical rotatory power, *i.e.* chiral, achiral optically active, and achiral optically inactive molecular structures. The second part of the communication discusses the special role played by the concept of the partial optic axis in the evaluation of the anisotropic chromophoric intensity contributions in a molecular exciton approach, in particular in relation to the use of the chromophoric symmetry for the systematic selection and characterization of the intensity contributions.

Keywords. Molecular exciton theory; Exciton chirality; Partial optic axis; Anisotropic circular dichroism; Point group symmetry.

Introduction

Anisotropic and isotropic molecular optical rotatory power differ in the multipolar nature of the theoretical intensity expressions for the two phenomena, and in their structural requirements. For anisotropic chiroptical intensities, electric dipole – magnetic dipole and electric dipole – electric quadrupole contributions enter on an equal footing in the intensity expressions, see Refs. [1–4] and references therein. In addition, an analysis of the requirements for anisotropic optical rotatory power leads to a classification in three categories: chiral, achiral optically active, and achiral optically inactive structures [4, 5]. In contrast, it is of course well established that only electric dipole – magnetic dipole terms contribute under

---

[*] E-mail: aage@gene.ki.ku.dk
[#] Permanent address, Holmebjerg 5, DK-2950 Vedbæk, Denmark

isotropic conditions [6], and that the categories chiral and achiral suffice for structural classifications. This difference provides the language of point group symmetry [7, 8] with a more prominent role in the discussion of the anisotropic properties. In symmetry terms, chiral molecular structures belong to the pure rotation groups C_n, D_n, T, and O, and achiral optically active molecular structures belong to the point group D_{2d} or to one of its achiral subgroups, *i.e.* $C_s = C_h$, C_{2v}, and S_4 [4, 5, 7], the remaining point groups accounting for the achiral optically inactive structures.

The threefold structural classification is important for the treatment of the chromophoric contributions in an exciton approach to anisotropic molecular chiroptical properties [5], and is coupled to seemingly rather technical problems relating to the translational properties of the theoretical intensity expressions and to the choice of appropriate locations for the chromophoric reference points required for evaluation or estimate of the exciton intensities. The importance of the latter two problems was first pointed out by *Moffitt* [9] in his pioneering work on the application of a molecular exciton approach to polymer chiroptical properties. As a remedy, *Moffitt* suggested the application of a construct called a partial optic axis as a basis for the choice of chromophoric reference points, and provided a brief discussion of the symmetry aspects in the context of isotropic optical rotatory power. In the following section, we develop the theory of the partial optic axis in more detail for anisotropic chiroptical properties in general, and discuss its application to a molecular symmetry based analysis of the multipolar anisotropic intensity contributions. In the subsequent section, we summarize the molecular exciton expressions for anisotropic chiroptical intensities presented in Ref. [5], and discuss the special role played by the concept of the partial optic axis in the evaluation of the anisotropic chromophoric intensity contributions, in particular in relation to the use of the chromophoric symmetry for the systematic selection and characterization of the intensity contributions. The final section contains concluding summary and remarks.

The Partial Optic Axis

Chiroptical Intensity Quantities

We shall be concerned with the following intensity quantities, the dipole strength tensor (Eq. (1)) governing the anisotropic ordinary absorption intensity of excitation $q \leftarrow o$, and the rotatory strength tensor (Eq. (2)) governing the anisotropic circular dichroism of this excitation in the socalled small molecule limit [4, 5]. The molecular wavefunctions are assumed purely real throughout. $\underline{r}_j$ and $\underline{p}_j$ are the position and momentum vectors for electron j, and the electric dipole transition moment for the excitation $q \leftarrow o$ is given by Eq. (3) where $\omega_q = (E_q - E_o)/\hbar$ is the angular resonance frequency. See the appendix in Ref. [5] for the vector and tensor notation used in Eqs. (1) and (2).

$$\boldsymbol{D}_q = (3/2)[\langle o|\underline{\mu}_e|q\rangle \cdot \langle q|\underline{\mu}_e|o\rangle \mathbf{I} - \langle o|\underline{\mu}_e|q\rangle : \langle q|\underline{\mu}_e|o\rangle] \tag{1}$$

$$\boldsymbol{R}_q = \frac{3e^2}{4m^2\omega_q}\left[\left\langle o\left|\sum_j \underline{r}_j : \underline{p}_j\right|q\right\rangle \times \left\langle q\left|\sum_j \underline{p}_j\right|o\right\rangle - \left\langle o\left|\sum_j \underline{p}_j\right|q\right\rangle \times \left\langle q\left|\sum_j \underline{p}_j : \underline{r}_j\right|o\right\rangle\right] \tag{2}$$

$$\langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle = -e\left\langle q\left|\sum_j \underline{\mathrm{r}}_j\right|\mathrm{o}\right\rangle = \mathrm{i}e\left\langle q\left|\sum_j \underline{\mathrm{p}}_j\right|\mathrm{o}\right\rangle \Big/ m\omega_{\mathrm{q}} \tag{3}$$

Alternatively, the rotatory strength tensor can be separated into multipolar components [4, 5] (Eq. (4)) where the electric dipole – magnetic dipole contribution is given by Eq. (5) and the electric dipole – electric quadrupole contribution is shown in Eq. (6).

$$\boldsymbol{R}_{\mathrm{q}} = \boldsymbol{R}(\mathrm{M})_{\mathrm{q}} + \boldsymbol{R}(\mathrm{Q})_{\mathrm{q}} \tag{4}$$

$$\begin{aligned}\boldsymbol{R}(\mathrm{M})_{\mathrm{q}} = {} & (3/4)Im[2\langle \mathrm{o}|\underline{\mu}_{\mathrm{e}}|\mathrm{q}\rangle \cdot \langle \mathrm{q}|\underline{\mu}_{\mathrm{m}}|\mathrm{o}\rangle \mathbf{I} - \langle \mathrm{o}|\underline{\mu}_{\mathrm{e}}|\mathrm{q}\rangle : \langle \mathrm{q}|\underline{\mu}_{\mathrm{m}}|\mathrm{o}\rangle \\ & + \langle \mathrm{o}|\underline{\mu}_{\mathrm{m}}|\mathrm{q}\rangle : \langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle]\end{aligned} \tag{5}$$

$$\boldsymbol{R}(\mathrm{Q})_{\mathrm{q}} = (3\omega_{\mathrm{q}}/8)[\langle \mathrm{o}|\mathbf{q}_{\mathrm{e}}|\mathrm{q}\rangle \times \langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle - \langle \mathrm{o}|\underline{\mu}_{\mathrm{e}}|\mathrm{q}\rangle \times \langle \mathrm{q}|\mathbf{q}_{\mathrm{e}}|\mathrm{o}\rangle] \tag{6}$$

The magnetic dipole and electric quadrupole transitions moments are given by Eqs. (7) and (8).

$$\langle \mathrm{q}|\mathbf{q}_{\mathrm{e}}|\mathrm{o}\rangle = -e\left\langle \mathrm{q}\left|\sum_j \underline{\mathrm{r}}_j : \underline{\mathrm{r}}_j\right|\mathrm{o}\right\rangle = \mathrm{i}e\left\langle \mathrm{q}\left|\sum_j (\underline{\mathrm{r}}_j : \underline{\mathrm{p}}_j + \underline{\mathrm{p}}_j : \underline{\mathrm{r}}_j)\right|\mathrm{o}\right\rangle \Big/ m\omega_{\mathrm{q}} \tag{7}$$

$$\langle \mathrm{q}|\underline{\mu}_{\mathrm{m}}|\mathrm{o}\rangle = -(e/2m)\left\langle \mathrm{q}\left|\sum_j \underline{\mathrm{r}}_j \times \underline{\mathrm{p}}_j\right|\mathrm{o}\right\rangle \tag{8}$$

The tensor in Eq. (1) is symmetric in the *Cartesian* indices as written, and Eqs. (2), (5), and (6) retain the *Cartesian* symmetrization as derived in Ref. [4]; *cf.* Eq. (13) of Ref. [5]. The isotropic absorption and CD intensities are governed by the dipole strength (Eq. (9)) and the rotatory strength (Eq. (10)), the tensor $\boldsymbol{R}(\mathrm{Q})_{\mathrm{q}}$, Eq. (6), being traceless.

$$D_{\mathrm{q}} = (1/3)\mathrm{tr}\{\boldsymbol{D}_{\mathrm{q}}\} = |\langle \mathrm{o}|\underline{\mu}_{\mathrm{e}}|\mathrm{q}\rangle|^2 \tag{9}$$

$$R_{\mathrm{q}} = (1/3)\mathrm{tr}\{\boldsymbol{R}_{\mathrm{q}}\} = (1/3)\mathrm{tr}\{\boldsymbol{R}(\mathrm{M})_{\mathrm{q}}\} = Im[\langle \mathrm{o}|\underline{\mu}_{\mathrm{e}}|\mathrm{q}\rangle \cdot \langle \mathrm{q}|\underline{\mu}_{\mathrm{m}}|\mathrm{o}\rangle] \tag{10}$$

Translational Properties

The essential feature behind the introduction of a partial optic axis is the behaviour of the multipolar electronic transition moments, and hence the chiroptical intensity expressions, with respect to translation of the molecular coordinate origin. Under translation of the origin along a vector $\underline{\mathrm{a}}$ relative to the molecular frame, the position and momentum vectors for electron j transform as $\underline{\mathrm{r}}_j \to \underline{\mathrm{r}}_j - \underline{\mathrm{a}}$ and $\underline{\mathrm{p}}_j \to \underline{\mathrm{p}}_j$. For the electric dipole transition moment, Eq. (3), the translation leaves the momentum version, $\langle \mathrm{o}|\sum_j \underline{\mathrm{p}}_j|\mathrm{q}\rangle$, strictly invariant, while orthogonality of the states o and q ensures invariance of the length version of the electric dipole transition moment (Eq. (11)), i.e.

$$\langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}(\underline{\mathrm{a}})|\mathrm{o}\rangle = -e\left\langle \mathrm{q}\left|\sum_j (\underline{\mathrm{r}}_j - \underline{\mathrm{a}})\right|\mathrm{o}\right\rangle = \langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle \tag{11}$$

For the magnetic dipole and electric quadrupole transitions moments, Eqs. (7) and (8), translation implies the transformations shown by Eqs. (12) and (13) where Eq. (12) assumes orthogonality of the states o and q, and Eq. (13) assumes Eq. (3) for the introduction of the length version of the electric dipole transition moment.

$$\begin{aligned}\langle \mathrm{q}|\mathbf{q}_{\mathrm{e}}(\underline{\mathrm{a}})|\mathrm{o}\rangle &= -e\left\langle \mathrm{q}\left|\sum_j\{(\underline{\mathrm{r}}_j-\underline{\mathrm{a}}):(\underline{\mathrm{r}}_j-\underline{\mathrm{a}})\}\right|\mathrm{o}\right\rangle \\ &= \langle \mathrm{q}|\mathbf{q}_{\mathrm{e}}|\mathrm{o}\rangle - \underline{\mathrm{a}}:\langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle - \langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle:\underline{\mathrm{a}} \end{aligned} \tag{12}$$

$$\begin{aligned}\langle \mathrm{q}|\underline{\mu}_{\mathrm{m}}(\underline{\mathrm{a}})|\mathrm{o}\rangle &= -(e/2m)\left\langle \mathrm{q}\left|\sum_j\{(\underline{\mathrm{r}}_j-\underline{\mathrm{a}})\times\underline{\mathrm{p}}_j\}\right|\mathrm{o}\right\rangle \\ &= \langle \mathrm{q}|\underline{\mu}_{\mathrm{m}}|\mathrm{o}\rangle - (\mathrm{i}\omega_q/2)\underline{\mathrm{a}}\times\langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle \end{aligned} \tag{13}$$

The dipole strength tensor and its isotropic component, Eqs. (1) and (9), are trivially invariant to origin translation, and for the rotatory strength tensor, Eq. (2), we find Eq. (14), ensuring the translational invariance of the rotatory strength tensor, since the cross product $\langle \mathrm{o}|\sum_j \underline{\mathrm{p}}_j|\mathrm{q}\times\langle \mathrm{q}|\sum_j \underline{\mathrm{p}}_j|\mathrm{o}\rangle$ vanishes for real wavefunctions. Equation (14) implies the corresponding invariance relation for the rotatory strength, Eq. (10) as given by Eq. (15).

$$\begin{aligned}\boldsymbol{R}(\underline{\mathrm{a}})_{\mathrm{q}} &= \frac{3e^2}{4m^2\omega_{\mathrm{q}}}\left[\left\langle \mathrm{o}\left|\sum_j(\underline{\mathrm{r}}_j-\underline{\mathrm{a}}):\underline{\mathrm{p}}_j\right|\mathrm{q}\right\rangle\times\left\langle \mathrm{q}\left|\sum_j\underline{\mathrm{p}}_j\right|\mathrm{o}\right\rangle\right. \\ &\qquad \left.-\left\langle \mathrm{o}\left|\sum_j\underline{\mathrm{p}}_j\right|\mathrm{q}\right\rangle\times\left\langle \mathrm{q}\left|\sum_j\underline{\mathrm{p}}_j:(\underline{\mathrm{r}}_j-\underline{\mathrm{a}})\right|\mathrm{o}\right\rangle\right] \\ &= \boldsymbol{R}_{\mathrm{q}} - \frac{3e^2}{4m^2\omega_{\mathrm{q}}}\left[\underline{\mathrm{a}}:\left\langle \mathrm{o}\left|\sum_j\underline{\mathrm{p}}_j\right|\mathrm{q}\right\rangle\times\left\langle \mathrm{q}\left|\sum_j\underline{\mathrm{p}}_j\right|\mathrm{o}\right\rangle\right. \\ &\qquad \left.-\left\langle \mathrm{o}\left|\sum_j\underline{\mathrm{p}}_j\right|\mathrm{q}\right\rangle\times\left\langle \mathrm{q}\left|\sum_j\underline{\mathrm{p}}_j\right|\mathrm{o}\right\rangle:\underline{\mathrm{a}}\right] \end{aligned} \tag{14}$$

$$R(\underline{\mathrm{a}})_{\mathrm{q}} = (1/3)\mathrm{tr}\{\boldsymbol{R}(\underline{\mathrm{a}})_{\mathrm{q}}\} = (1/3)\mathrm{tr}\{\boldsymbol{R}_{\mathrm{q}}\} = R_{\mathrm{q}} \tag{15}$$

The rotatory strength tensor and its isotropic component are therefore invariant to origin displacements [1–3, 10], whereas the translational properties of the magnetic dipole and electric quadrupole transitions moments, Eqs. (12) and (13), imply that the tensors $\boldsymbol{R}(\mathrm{M})_{\mathrm{q}}$ and $\boldsymbol{R}(\mathrm{Q})_{\mathrm{q}}$, Eqs. (5) and (6), in general change by numerically equal but oppositely signed amounts [2, 3]. Hence computed results for the elements of these two tensors will depend on the choice of molecular reference coordinate system, regardless of computational approach. See Refs. [2, 23] for a discussion of the experimental perspective on the separation of the rotatory tensor into multipolar components, and see Refs. [3, 4] for discussions of the computational problems relating to translational invariance.

The Partial Optic Axis

Equation (13) allows the determination of a set of excitation specific reference locations $\{\underline{\mathrm{a}}_{\mathrm{q}}\}$ for an electric dipole allowed excitation q ← o such that the magnetic dipole transition moment vanishes identically or is strictly parallel to the electric dipole transition moment for this excitation as shown by Eq. (16), where $\underline{\alpha}_{\mathrm{q}}$ (Eq. (17)) is a real quantity or zero. The general solution of Eq. (16) is given by Eq. (18) parametrized in terms of the real quantity β. The line given by Eq. (18) is the partial optic axis as defined by *Moffitt* [9]. We shall use $\underline{\mathrm{a}}_{\mathrm{q}}$ to denote a specific reference point on the axis.

$$\langle \mathrm{q}|\underline{\mu}_{\mathrm{m}}(\underline{\mathrm{a}}_{\mathrm{q}})|\mathrm{o}\rangle = \langle \mathrm{q}|\underline{\mu}_{\mathrm{m}}|\mathrm{o}\rangle - (\mathrm{i}\omega_{\mathrm{q}}/2)\underline{\mathrm{a}}_{\mathrm{q}} \times \langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle = \mathrm{i}\alpha_{\mathrm{q}}\langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle \qquad (16)$$

$$\alpha_{\mathrm{q}} = -\mathrm{i}\langle \mathrm{o}|\underline{\mu}_{\mathrm{e}}|\mathrm{q}\rangle \cdot \langle \mathrm{q}|\underline{\mu}_{\mathrm{m}}|\mathrm{o}\rangle / |\langle \mathrm{o}|\underline{\mu}_{\mathrm{e}}|\mathrm{q}\rangle|^2 = R_{\mathrm{q}}/D_{\mathrm{q}} \qquad (17)$$

$$\underline{\mathrm{a}}_{\mathrm{q}}(\beta) = (2/D_{\mathrm{q}}\omega_{\mathrm{q}})\mathrm{Im}\{\langle \mathrm{o}|\underline{\mu}_{\mathrm{e}}|\mathrm{q}\rangle \times \langle \mathrm{q}|\underline{\mu}_{\mathrm{m}}|\mathrm{o}\rangle\} + \beta\langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle \qquad (18)$$

From Eqs. (16) and (17) the resulting magnetic dipole transition moment referred to a point on the corresponding partial optic axis is given by Eq. (19) allowing the electric dipole – magnetic dipole rotatory strength tensor referred to a point on the partial optic axis to be expressed by Eq. (20) from Eqs. (1), (5), and (19). The electric dipole – magnetic dipole rotatory strength tensor referred to a point on the partial optic axis is accordingly proportional to the dipole strength tensor $\boldsymbol{D}_{\mathrm{q}}$, Eq. (1), the proportionality factor being the ratio of the rotatory strength R_{q}, Eq. (10), and the dipole strength D_{q}, Eq. (9). Relative to a point on the partial optic axis, the electric dipole – electric quadrupole rotatory strength tensor is expressed by Eq. (21), *cf.* Eq. (6). An alternative expression for $\boldsymbol{R}(\mathrm{Q}, \underline{\mathrm{a}}_{\mathrm{q}})_{\mathrm{q}}$ can be obtained by utilizing that the total rotatory strength tensor is invariant under translation, *cf.* Eq. (14), and Eqs. (20) and (22) then provide Eq. (23) for the electric dipole – electric quadrupole tensor referred to the partial optic axis.

$$\langle \mathrm{q}|\underline{\mu}_{\mathrm{m}}(\underline{\mathrm{a}}_{\mathrm{q}})|\mathrm{o}\rangle = \mathrm{i}(R_{\mathrm{q}}/D_{\mathrm{q}})\langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle \qquad (19)$$

$$\begin{aligned}\boldsymbol{R}(\mathrm{M}, \underline{\mathrm{a}}_{\mathrm{q}})_{\mathrm{q}} &= (3R_{\mathrm{q}}/2D_{\mathrm{q}})\{\langle \mathrm{o}|\underline{\mu}_{\mathrm{e}}|\mathrm{q}\rangle \cdot \langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle\mathbf{I} - \langle \mathrm{o}|\underline{\mu}_{\mathrm{e}}|\mathrm{q}\rangle : \langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle\} \\ &= (R_{\mathrm{q}}/D_{\mathrm{q}})\boldsymbol{D}_{\mathrm{q}} \end{aligned} \qquad (20)$$

$$\boldsymbol{R}(\mathrm{Q}, \underline{\mathrm{a}}_{\mathrm{q}})_{\mathrm{q}} = (3\omega_{\mathrm{q}}/8)\{\langle \mathrm{o}|\mathbf{q}_{\mathrm{e}}(\underline{\mathrm{a}}_{\mathrm{q}})|\mathrm{q}\rangle \times \langle \mathrm{q}|\underline{\mu}_{\mathrm{e}}|\mathrm{o}\rangle - \langle \mathrm{o}|\underline{\mu}_{\mathrm{e}}|\mathrm{q}\rangle \times \langle \mathrm{q}|\mathbf{q}_{\mathrm{e}}(\underline{\mathrm{a}}_{\mathrm{q}})|\mathrm{o}\rangle\} \qquad (21)$$

$$\boldsymbol{R}(\underline{\mathrm{a}}_{\mathrm{q}})_{\mathrm{q}} = \boldsymbol{R}(\mathrm{M}, \underline{\mathrm{a}}_{\mathrm{q}})_{\mathrm{q}} + \boldsymbol{R}(\mathrm{Q}, \underline{\mathrm{a}}_{\mathrm{q}})_{\mathrm{q}} = \boldsymbol{R}_{\mathrm{q}} \qquad (22)$$

$$\boldsymbol{R}(\mathrm{Q}, \underline{\mathrm{a}}_{\mathrm{q}})_{\mathrm{q}} = \boldsymbol{R}_{\mathrm{q}} - (R_{\mathrm{q}}/D_{\mathrm{q}})\boldsymbol{D}_{\mathrm{q}} \qquad (23)$$

Equations (20) and (23) suggest the determination of electric dipole – magnetic dipole and electric dipole – electric quadrupole rotatory strength tensors referred to a point on the partial optic axis from the (at least in principle) observable quantities $\boldsymbol{R}_{\mathrm{q}}$ and $\boldsymbol{D}_{\mathrm{q}}$, and can hence be viewed as a basis for a physically meaningful multipolar interpretation of ACD, in contrast to the in general arbitrary decomposition expressed by Eqs. (4)–(6).

Discussion of Symmetry Aspects

For molecular systems devoid of symmetry, *i.e.* point group symmetry C_1 [8], the determination of a reference point on the partial optic axis for a particular excitation requires solution of Eq. (18) and a judicious choice of the parameter

β, while symmetry may assist the determination of the partial optic axis for an excitation in a system with one or more symmetry elements. For centrosymmetric molecular systems, defined as systems for which all symmetry elements intersect in a single point, *Moffitt* [9] noted that all the partial optic axes intersect at the molecular center. Here the term centrosymmetric is not restricted to molecules containing a center of inversion, and the improper reflection plane implied in the S_n operation is counted as a symmetry element. For uniaxial molecules belonging to the chiral point groups C_n or to the achiral point groups C_{nv}, the partial optic axis for an excitation polarized along the symmetry axis will coincide with the axis, while the partial optic axis for an excitation polarized perpendicular to the symmetry axis intersects the axis at a point determined by evaluation of Eq. (18). For molecules belonging to the achiral point group $C_s = C_h$ having a single symmetry plane, the partial optic axis for an excitation polarized in the molecular symmetry plane will lie in the plane, whereas the partial optic axis for an excitation polarized perpendicular to the symmetry plane will intersect the plane at a point determined by evaluation of Eq. (18). In the cases where the partial optic axis intersects one or more symmetry elements, the point of intersection, as determined by symmetry or by Eq. (18), becomes a natural choice for a reference point, whereas coincidence of the partial optic axis and a symmetry axis requires a choice of reference location on the axis. Finally, specification of a reference point when the partial optic axis lies in a symmetry plane requires solution of Eq. (18) and a choice of the parameter β.

In the context of optical rotatory power, we note that for chiral molecular systems, where the rotatory strength, the total rotatory strength tensor, and its multipolar components are non-vanishing for all electric dipole allowed excitations, the use of reference points or coordinate origins based on the partial optic axis for a particular excitation, ensures the numerically smallest value for the magnetic dipole transition moment [9], and at the same time allows a physically meaningful representation of the electric dipole – magnetic dipole and electric dipole – electric quadrupole rotatory strength tensors for this excitation, if the argument advocated towards the end of the preceeding subsection is accepted. For achiral optically active molecular systems, the rotatory strength vanishes identically for all excitations, and Eqs. (19) and (20) then imply that the above choices of reference points make the magnetic dipole transition moments and the electric dipole – magnetic dipole rotatory strength tensor vanish identically for all electric dipole allowed excitations, contrary to expectations based on standard character table selection rules [8], leaving non-vanishing electric quadrupole transition moments and electric dipole – electric quadrupole rotatory strength tensors for electric dipole allowed excitations, in accord with character table selection rules. For molecular systems belonging to one of the achiral optically inactive point groups, the rotatory strength and the total rotatory strength tensor now vanish identically, and the above choices of reference points ensure that the electric dipole – magnetic dipole and electric dipole – electric quadrupole rotatory strength tensors also vanish identically for all excitations in these systems. For the achiral optically inactive point groups C_{nv} ($n \geq 3$), C_{3h}, D_{3h}, and T_d, the selection rules in the character tables suggest non-zero elements for the rotatory strength tensor, while the symmetrization of the tensors in Eqs. (2), (5), and (6), *cf.* Eq. (13) of Ref. [5], ensures the vanishing of the resulting rotatory strength tensor and its components also for these point groups, *cf.* Ref. [7].

We note that the selection rules outlined in the above paragraph, conversely speaking, imply that choices of reference points or equivalently molecular coordinate origins not coinciding with a point on the partial optic axis for a given electric dipole allowed excitation may lead to unphysical contributions to the magnetic dipole and electric quadrupole transition moments for electric dipole allowed excitations, and hence to unphysical, but mutually cancelling, contributions to the electric dipole – magnetic dipole and electric dipole – electric quadrupole rotatory strength tensors. Explicit examples of the unphysical electric dipole – magnetic dipole and electric dipole – electric quadrupole rotatory strength tensors generated by a reference choice not respecting molecular symmetry are given in Ref. [3].

Application to the Molecular Exciton Theory of Circular Dichroism

Summary of Molecular Exciton Intensity Quantities

In molecular exciton theory [5, 9, 11], the basic assumption is that the overall molecular system consists of identical subunits or chromophores arranged in a regular structure, and that the local chromophoric electric dipole transition moment (Eq. (24))

$$(\alpha,1|{}^{\alpha}\underline{\mu}_{\mathrm{e}}|\alpha,\mathrm{o}) = -e\left(\alpha,1\middle|{}^{\alpha}\sum_{j}(\underline{r}_j-\underline{R}_{\alpha})\middle|\alpha,\mathrm{o}\right) \tag{24}$$

is non-vanishing. In Eq. (24), $\underline{R}_{\alpha}$ is the position vector for a local reference point in chromophore α [12], the reference points being assigned the same relative position in all chromophores. ${}^{\alpha}\sum_{j}$ indicates summation over the electrons in this chromophore. The corresponding local magnetic dipole and electric quadrupole transition moments are given by Eqs. (25) and (26) expressed relative to the local reference points, *cf.* Eqs. (12) and (13). The energetic interactions between the chromophoric excitations are governed by the term shown by Eq. (27) representing the interaction between the local transition densities $\varphi_{\alpha,1}\varphi_{\alpha,\mathrm{o}}$ and $\varphi_{\beta,1}\varphi_{\beta,\mathrm{o}}$, most often expressed as the electric dipole – electric dipole interaction in Eq. (32) of Ref. [5].

$$(\alpha,1|{}^{\alpha}\underline{\mu}_{\mathrm{m}}|\alpha,\mathrm{o}) = -\frac{e}{2m}\left(\alpha,1\middle|{}^{\alpha}\sum_{j}\{(\underline{r}_j-\underline{R}_{\alpha})\times\underline{p}_j\middle|\alpha,\mathrm{o}\right) \tag{25}$$

$$(\alpha,1|{}^{\alpha}\mathbf{q}_{\mathrm{e}}|\alpha,\mathrm{o}) = -e\left(\alpha,1\middle|{}^{\alpha}\sum_{j}(\underline{r}_j-\underline{R}_{\alpha}):(\underline{r}_j-\underline{R}_{\alpha})\middle|\alpha,\mathrm{o}\right) \tag{26}$$

$$\mathrm{V}_{\alpha,1:\beta,1} = (\varphi_{\alpha,1}\varphi_{\beta,\mathrm{o}}|\mathrm{V}_{\alpha,\beta}|\varphi_{\alpha,\mathrm{o}}\varphi_{\beta,1}) \tag{27}$$

$$\begin{aligned}\mathit{\Delta}_{\alpha,1;\beta,1} &= m^2\omega_1{}^2\{(\alpha,\mathrm{o}|{}^{\alpha}\underline{\mu}_{\mathrm{e}}|\alpha,1)\cdot(\beta,1|{}^{\beta}\underline{\mu}_{\mathrm{e}}|\beta,\mathrm{o})\mathbf{I}\\ &\quad-(\alpha,\mathrm{o}|{}^{\alpha}\underline{\mu}_{\mathrm{e}}|\alpha,1):(\beta,1|{}^{\beta}\underline{\mu}_{\mathrm{e}}|\beta,\mathrm{o})\}\end{aligned} \tag{28}$$

The resulting absorption intensities are governed by the absorption strength coupling tensor (Eq. (28)) and the CD intensities are governed by three coupling terms, the electric dipole – electric dipole coupling tensor (Eq. (29)) the electric dipole – magnetic dipole coupling tensor (Eq. (30)) and the electric dipole – electric quadrupole coupling tensor (Eq. (31)).

$$ {}^{dip}\boldsymbol{\Gamma}_{\alpha,1;\beta,1} = m^2\omega_1{}^2\{(\underline{\mathrm{R}}_\alpha - \underline{\mathrm{R}}_\beta) : [(\alpha,\mathrm{o}|{}^\alpha\underline{\mu}_\mathrm{e}|\alpha,1)\times(\beta,1|{}^\beta\underline{\mu}_\mathrm{e}|\beta,\mathrm{o})]\} \tag{29} $$

$$ \begin{aligned} {}^{inh}\boldsymbol{\Gamma}(\mathrm{M})_{\alpha,1;\beta,1} = m^2\omega_1\{&\mathit{Im}[(\alpha,\mathrm{o}|{}^\alpha\underline{\mu}_\mathrm{e}|\alpha,1)\cdot(\beta,1|{}^\beta\underline{\mu}_\mathrm{m}|\beta,\mathrm{o})\mathbf{I} \\ &-(\alpha,\mathrm{o}|{}^\alpha\underline{\mu}_\mathrm{e}|\alpha,1):(\beta,1|{}^\beta\underline{\mu}_\mathrm{m}|\beta,\mathrm{o})] \\ &+\mathit{Im}[(\beta,\mathrm{o}|{}^\beta\underline{\mu}_\mathrm{e}|\beta,1)\cdot(\alpha,1|{}^\alpha\underline{\mu}_\mathrm{m}|\alpha,\mathrm{o})\mathbf{I} \\ &-(\beta,\mathrm{o}|{}^\beta\underline{\mu}_\mathrm{e}|\beta,1):(\alpha,1|{}^\alpha\underline{\mu}_\mathrm{m}|\alpha,\mathrm{o})]\} \end{aligned} \tag{30} $$

$$ \begin{aligned} {}^{inh}\boldsymbol{\Gamma}(\mathrm{Q})_{\alpha,1;\beta,1} = (1/2)m^2\omega_1^2\{&(\alpha,\mathrm{o}|{}^\alpha\mathbf{q}_\mathrm{e}|\alpha,1)\times(\beta,1|{}^\beta\underline{\mu}_\mathrm{e}|\beta,\mathrm{o}) \\ &+(\beta,\mathrm{o}|{}^\beta\mathbf{q}_\mathrm{e}|\beta,1)\times(\alpha,1|{}^\alpha\underline{\mu}_\mathrm{e}|\alpha,\mathrm{o})\} \end{aligned} \tag{31} $$

The terms labelled *inh* account for contributions from inherent optical rotatory power of the chromophores. In accord with the discussion in Ref. [5], the tensors in Eqs. (28)–(31) are symmetric in the chromophore indices, but are not symmetric in the *Cartesian* indices.

In Ref. [5], expressions are given for the partial absorption and CD intensities, *i.e.* the intensities for the individual exciton excitations, and for the corresponding total band intensities, obtained by summing over the partial intensities. The structural and chiral information extracted from the two sets of intensities is essentially the same. Here we focus on the band intensities, and refer to Ref. [5] for details of the derivations. For anisotropic absorption, the directional band intensity can be written as shown by Eq. (32) where $\underline{\mathrm{u}}$ is a unit vector in the direction of propagation of a light beam of angular frequency ω, $\mathrm{N_o}$ is the number of molecules per unit volume, ω_1 is the angular resonance frequency for the chromophoric excitation $1 \leftarrow \mathrm{o}$, and $\rho(\omega - \omega_1 - \mathrm{d}_\kappa(\underline{\mathrm{u}}))$ is the nomalized line shape function for the chromophoric excitation $1 \leftarrow \mathrm{o}$, shifted by the parameter $\mathrm{d}_\kappa(\underline{\mathrm{u}})$. $\mathrm{d}_\kappa(\underline{\mathrm{u}})$ is a function of the direction of the light beam relative to the molecule, and depends on interchromophoric interactions and intensity couplings. This line shift parameter, and the corresponding line shift parameters in the expressions for CD band intensities below, are not central in the present context, see Ref. [5] for detailed expressions for these quantities. The dipole strength tensor for excitation $1 \leftarrow \mathrm{o}$ in chromophore α can be expressed by Eq. (33) where $\mathit{\Delta}_{\alpha,1;\alpha,1}$ is the diagonal block of the absorption strength coupling tensor, Eq. (28). The corresponding isotropic band intensity becomes Eq. (34) where N is the number of chromophores, and $D_1 = D_{\alpha,1} = |(\alpha,\mathrm{o}|{}^\alpha\underline{\mu}_\mathrm{e}|\alpha,1)|^2$ is the dipole strength for the chromohoric excitation $1 \leftarrow \mathrm{o}$. The dipole strength $D_{\alpha,1}$ is independent of chromophore index by the assumption of identical chromophoric units, while the dipole strength tensors $\boldsymbol{D}_{\alpha,1}$, Eq. (33), are identical for the individual chromophores except for the rotations following the relative orientation of the chromophores in the overall structure of the exciton system.

$$ \kappa(\underline{\mathrm{u}},\omega) = \frac{\pi \mathrm{N_o}\omega_1{}^2}{3\epsilon_\mathrm{o}\hbar\omega\mathrm{c}}\rho(\omega - \omega_1 - \mathrm{d}_\kappa(\mathrm{u}))\sum_\alpha\{\underline{\mathrm{u}}\cdot\boldsymbol{D}_{\alpha,1}\cdot\underline{\mathrm{u}}\} \tag{32} $$

$$ \boldsymbol{D}_{\alpha,1} = \frac{3}{2m^2\omega_1{}^2}\mathit{\Delta}_{\alpha,1;\alpha,1} \tag{33} $$

$$ \kappa(\omega) = \frac{\pi \mathrm{N_o N}}{3\epsilon_\mathrm{o}\hbar\omega\mathrm{c}}\omega_1{}^2\rho(\omega - \omega_1 - \mathrm{d}_\kappa)D_1 \tag{34} $$

For anisotropic CD, the band intensity is divided into two contributions (Eq. (35)) where the electric dipole – electric dipole contribution is given by Eq. (36) expressed in terms of the coupling tensor in Eq. (29). $\rho'(\omega-\omega_1-{}^{dip}\mathrm{g}_{\Delta\kappa}(\underline{\mathrm{u}}))$ is the first derivative of the line shape function for the chromophoric excitation $1\leftarrow\mathrm{o}$, shifted by the parameter ${}^{dip}\mathrm{g}_{\Delta\kappa}(\underline{\mathrm{u}})$, and the explicit expression for the corresponding isotropic band intensity becomes Eq. (37).

$$\Delta\kappa(\underline{\mathrm{u}},\omega) = {}^{dip}\Delta\kappa(\underline{\mathrm{u}},\omega) + {}^{inh}\Delta\kappa(\underline{\mathrm{u}},\omega) \tag{35}$$

$$\begin{aligned}{}^{dip}\Delta\kappa(\underline{\mathrm{u}},\omega) = &-\frac{\pi\mathrm{N_o}}{\epsilon_\mathrm{o}\hbar m^2\mathrm{c}^2}\rho'(\omega-\omega_1-{}^{dip}\mathrm{g}_{\Delta\kappa}(\underline{\mathrm{u}}))\\ &\times\sum_{\alpha,\beta}\mathrm{V}_{\alpha,1;\beta,1}\{\underline{\mathrm{u}}\cdot{}^{dip}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}\end{aligned} \tag{36}$$

$$\begin{aligned}{}^{dip}\Delta\kappa(\omega) = &-\frac{\pi\mathrm{N_o}}{3\epsilon_\mathrm{o}\hbar\mathrm{c}^2}{\omega_1}^2\rho'(\omega-\omega_1-{}^{dip}\mathrm{g}_{\Delta\kappa})\\ &\times\sum_{\alpha,\beta}\mathrm{V}_{\alpha,1;\beta,1}\{(\underline{\mathrm{R}}_\alpha-\underline{\mathrm{R}}_\beta)\cdot[(\alpha,\mathrm{o}|^\alpha\underline{\mu}_\mathrm{e}|\alpha,1)\times(\beta,1|^\beta\underline{\mu}_\mathrm{e}|\alpha,\mathrm{o})]\}\end{aligned} \tag{37}$$

The contribution ${}^{inh}\Delta\kappa(\underline{\mathrm{u}},\omega)$ is given by Eq. (38) where $\boldsymbol{R}_{\alpha,1}$ (Eq. (39)) is the rotatory strength tensor for excitation $1\leftarrow\mathrm{o}$ in chromophore α, expressed in terms of the diagonal block of the coupling tensors in Eqs. (30) and (31), and ${}^{inh}\mathrm{g}_{\Delta\kappa}(\underline{\mathrm{u}})$ is the line shift parameter. The corresponding isotropic band intensity is then given by Eq. (40).

$$\begin{aligned}{}^{inh}\Delta\kappa(\underline{\mathrm{u}},\omega) = \frac{\pi\mathrm{N_o}}{\epsilon_\mathrm{o}\hbar m^2\mathrm{c}^2}\Bigg\{&\frac{4\mathrm{m}^2\omega_1}{3}\rho(\omega-\omega_1)\sum_\alpha\{\underline{\mathrm{u}}\cdot\boldsymbol{R}_{\alpha,1}\cdot\underline{\mathrm{u}}\}\\ &-\rho'(\omega-\omega_1-{}^{inh}\mathrm{g}_{\Delta\kappa}(\underline{\mathrm{u}}))\sum_{\alpha,\beta}\mathrm{V}_{\alpha,1;\beta,1}\{\underline{\mathrm{u}}\cdot{}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}\Bigg\}\end{aligned} \tag{38}$$

$$\begin{aligned}\boldsymbol{R}_{\alpha,1} &= \frac{3}{4m^2\omega_1}{}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\alpha,1} = \frac{3}{4m^2\omega_1}\{{}^{inh}\boldsymbol{\Gamma}(\mathrm{M})_{\alpha,1;\alpha,1}+{}^{inh}\boldsymbol{\Gamma}(\mathrm{Q})_{\alpha,1;\alpha,1}\}\\ &= \boldsymbol{R}_{\alpha,1}(\mathrm{M})+\boldsymbol{R}_{\alpha,1}(\mathrm{Q})\end{aligned} \tag{39}$$

$$\begin{aligned}{}^{inh}\Delta\kappa(\omega) = \frac{4\pi\mathrm{N_o}}{3\epsilon_\mathrm{o}\hbar\mathrm{c}^2}\omega_1\Bigg\{&\mathrm{N}\rho(\omega-\omega_1)R_1-\rho'(\omega-\omega_1-{}^{inh}\mathrm{g}_{\Delta\kappa})\\ &\times\sum_{\alpha,\beta}\mathrm{V}_{\alpha,1;\beta,1}\{\mathit{Im}[(\varphi_{\alpha,\mathrm{o}}|^\alpha\underline{\mu}_\mathrm{e}|\varphi_{\alpha,1})\cdot(\varphi_{\beta,1}|^\beta\underline{\mu}_\mathrm{m}|\varphi_{\beta,\mathrm{o}})]\}\Bigg\}\end{aligned} \tag{40}$$

The isotropic part of the electric dipole – electric quadrupole coupling tensor, Eq. (31), vanishes identically, *cf.* Eq. (10), and the rotatory strength for the chromohoric excitation $1\leftarrow\mathrm{o}$, $R_1=R_{\alpha,1}=\mathit{Im}[(\alpha,\mathrm{o}|^\alpha\underline{\mu}_\mathrm{e}|\alpha,1)\cdot(\alpha,1|^\alpha\underline{\mu}_\mathrm{m}|\alpha,\mathrm{o})]$, *cf.* Eq. (10), is independent of chromophore index by the assumption of identical chromophoric units, while the rotatory strength tensors $\boldsymbol{R}_{\alpha,1}$, Eq. (39), are identical for the individual chromophores except for the rotations following the relative orientation of the chromophores in the overall structure of the exciton system. We note that Eq. (37) forms the basis for the exciton chirality method developed by *Harada*, *Nakanishi*, and *Berova* [13–15].

Application of the Partial Optic Axis

An immediate consequence of identifying the general chromophoric reference point $\underline{\mathrm{R}}_\alpha$, introduced in Eq. (24), with a reference point $\underline{\mathrm{a}}_\alpha$ on the partial optic axis for excitation $1 \leftarrow \mathrm{o}$ in chromophore α, chosen according to the discussion in the preceeding section, is that Eqs. (19), (28), and (30) combine to yield Eq. (41) for the electric dipole – magnetic dipole contribution to the inherent CD coupling tensor, using POA to label intensity quantities evaluated relative to reference points located on the partial optic axis for the excitations coupled in the tensor. R_1 and D_1 are the rotatory strength and dipole strength for the chromophoric $1 \leftarrow \mathrm{o}$ excitation, and $\boldsymbol{\Delta}_{\alpha,1;\beta,1}$ is the absorption strength coupling tensor, Eq. (28). The diagonal block of Eq. (41) combines with Eqs. (33) and (39) to reproduce Eq. (20). The electric dipole – electric quadrupole coupling tensor, Eq. (31), referenced to the respective partial optic axis is shown by Eq. (42).

$$ {}^{inh}\boldsymbol{\Gamma}(\mathrm{M},\mathrm{POA})_{\alpha,1;\beta,1} = \frac{2R_1}{\omega_1 D_1}\boldsymbol{\Delta}_{\alpha,1;\beta,1} \tag{41} $$

$$ \begin{aligned} {}^{inh}\boldsymbol{\Gamma}(\mathrm{Q},\mathrm{POA})_{\alpha,1;\beta,1} = {} & (1/2)m^2\omega_1{}^2\{(\alpha,\mathrm{o}|{}^{\alpha}\mathbf{q}_\mathrm{e}(\underline{\mathrm{a}}_\mathrm{q})|\alpha,1)\times(\beta,1|{}^{\beta}\underline{\mu}_\mathrm{e}|\beta,\mathrm{o}) \\ & + (\beta,\mathrm{o}|{}^{\beta}\mathbf{q}_\mathrm{e}(\underline{\mathrm{a}}_\mathrm{q})|\beta,1)\times(\alpha,1|{}^{\alpha}\underline{\mu}_\mathrm{e}|\alpha,\mathrm{o})\} \end{aligned} \tag{42} $$

The introduction of reference points located on the chromophoric partial optic axes implies that the factors of $(\underline{\mathrm{R}}_\alpha - \underline{\mathrm{R}}_\beta)$ in the interaction term $\mathrm{V}_{\alpha,1;\beta,1}$, Eq. (27), when evaluated according to Eq. (32) of Ref. [5], are replaced by $(\underline{\mathrm{a}}_\alpha - \underline{\mathrm{a}}_\beta)$. The absorption band intensities in Eqs. (32) and (34) are unaffected by the choice of chromophoric reference points, except for the evaluation of the line shift parameters, *cf.* Eq. (61) of Ref. [5].

Following the discussion in the preceeding section, the essential function of the choice of reference points anchored on the partial optic axes is to allow full advantage of symmetry considerations for the individual chromophores coupled with a systematic procedure for the determination of the reference points in cases where symmetry does not suffice for the determination. For identical chromophores, the determination of partial optic axis reference points requires analysis of a single, representative chromophore. With these reference points at hand, the partial optic axes evaluation of the electric dipole – electric dipole CD intensities in Eqs. (29), (36), and (37) is mandatory for all chromophore structures, and for anisotropic as well as isotropic intensities. For chiral chromophores all terms in Eqs. (38) and (40) must also be evaluated. In this case perhaps the most important consequence of a partial optic axis approach is the simplification offered by the use of Eq. (41) for the electric dipole – magnetic dipole tensor, ${}^{inh}\boldsymbol{\Gamma}(\mathrm{M},\mathrm{POA})_{\alpha,1;\beta,1}$, in place of the general expression in Eq. (30). For achiral optically active chromophores, the chromophoric rotatory strength R_1 and hence the electric dipole – magnetic dipole tensor ${}^{inh}\boldsymbol{\Gamma}(\mathrm{M},\mathrm{POA})_{\alpha,1;\beta,1}$, Eq. (41), vanish identically, leaving the electric dipole – electric quadrupole rotatory strength tensor $\boldsymbol{R}_{\alpha,1}(\mathrm{Q},\ \mathrm{POA})$, Eq. (39), and the coupling tensor ${}^{inh}\boldsymbol{\Gamma}(\mathrm{Q},\mathrm{POA})_{\alpha,1;\beta,1}$, Eq. (42), as the only surviving contributions in the anisotropic intensities expressions in Eq. (38). For achiral optically inactive chromophores, the chromophoric rotatory strength R_1 and hence the electric dipole – magnetic dipole tensor ${}^{inh}\boldsymbol{\Gamma}(\mathrm{M},\mathrm{POA})_{\alpha,1;\beta,1}$, Eq. (41), as well as the electric dipole – electric quadrupole tensor ${}^{inh}\boldsymbol{\Gamma}(\mathrm{Q},\mathrm{POA})_{\alpha,1;\beta,1}$, Eq. (42), vanish identically as a consequence of the selection rules discussed in the preceeding section, making the electric dipole – electric dipole CD intensity in Eqs. (29), (36), and (37) the only surviving intensity mechanism for anisotropic CD for these chromophores. Electric dipole – electric quadrupole terms do not contribute to isotropic CD, leaving Eq. (37) as the only surviving isotropic CD intensity mechanism for all achiral chromophoric systems.

Discussion

A partial optic axis approach can hence lead to a significant reduction or simplification of the terms required for the evaluation of the chiroptical properties in a molecular exciton context, and can provide a well defined multipolar interpretation of the surviving contributions. By contrast, approaches based on general choices of reference points require the evaluation of all terms in the intensity expressions. The author is not aware of studies of exciton coupled chiral chromophores, but apologizes in advance for any oversights. On the other hand, in the reported exciton studies, *cf.* Refs. [13, 16] and references therein, achiral optically active systems of $C_{\mathrm{s}} = C_{\mathrm{h}}$ and $C_{2\mathrm{v}}$ are quite common, alongside a wide selection of achiral optically inactive chromophores; see also Refs. [22, 23]. All of these systems qualify for the application of the analysis given in the above subsection, as can be illustrated for achiral optically inactive chromophores by the interplay between electric dipole – electric dipole band intensity in Eqs. (36) and (37) and the inherent band intensity in Eqs. (38) and (40). For dimeric systems the line shift parameters in these intensity expressions vanish identically [17], and the two sets of intensity terms therefore exhibit identical derivative line shapes, their relative signs and magnitudes being governed by the chromophoric interaction and the optical coupling tensors. These tensors are in turn governed by the choice of reference points, implying in particular that parts or all of the inherent contributions represented by Eqs. (38) and (40) can be neglected with impunity only for a partial optic axis based approach. The importance of this point can be exemplified by the erroneous assignment of the absolute configurations of molecular systems containing exciton coupled achiral chromophores based on the dimeric version of the isotropic electric dipole – electric dipole CD expression in Eq. (37) reported in Ref. [18]. The error was subsequently traced [19] to the neglect of the contributions from inherent electric dipole – magnetic dipole terms in Eq. (40), which were required for the particular choice of reference points used for the assignments. It should be added that *Kirkwood*'s neglect of a term corresponding to Eq. (40) in his development of a polarizability theory for optical rotation [12], was part of the motivation for *Moffitt*'s introduction of the partial optic axis [9]; see also Ref. [20].

Concluding Remarks

The material in this communication focuses on the application of the concept of the partial optic axis for analysis and selection of anisotropic chiroptical intensity contributions for general molecular systems and for molecular exciton coupled systems. For isotropic chiroptical properties of exciton coupled systems, experimental results and structural analyses abound, *cf.* Refs. [13–16] and references therein, and the discussion of the results in Refs. [18, 19] in the preceeding subsection, illustrate the applicability of the present formalism in the context of isotropic intensities. For anisotropic chiroptical properties of exciton coupled systems, which would be the acid test of the applicability of the formalism, practical results are quite sparse at present; see Refs. [21–23] and references therein. In a separate publication [24], we report the first ab-initio calculations and molecular exciton analyses of the anisotropic chiroptical spectra for exciton coupled molecular systems, *in casu* two dimeric molecular systems containing chromophores of C_{2v} and $C_s = C_h$ symmetry, respectively.

Acknowledgement

The author is grateful to Professor *D. A. Lightner*, Department of Chemistry, University of Nevada at Reno, for hospitality and support during a visit in January, 2003, where parts of this work were performed, and to Professor *K. V. Mikkelsen*, Danish Center for Scientific Computing at the Department of Chemistry, University of Copenhagen, Denmark, for kindly providing working accommodation and support after my retirement.

References

[1] Snir J, Schellman JA (1973) J Phys Chem **77**: 1653
[2] Kuball H-G, Sieber G, Neubrech S, Schultheis B, Schönhofer A (1993) Chem Phys **169**: 335
[3] Pedersen TB, Hansen AaE (1995) Chem Phys Lett **246**: 1
[4] Hansen AaE, Bak KL (2000) J Phys Chem A **104**: 11362
[5] Hansen AaE (2005) Monatsh Chem **136**: 253
[6] Condon EU (1937) Rev Mod Phys **9**: 432
[7] Nye JF (1957) Physical Properties of Crystals. Oxford University Press, Oxford
[8] Atkins PW, Child MS, Phillips CSG (1970) Tables for Group Theory. Oxford University Press, Oxford
[9] Moffitt W (1956) J Chem Phys **25**: 467
[10] Moscowitz A (1965) In: Sinanoglu O (ed) Modern Quantum Chemistry, vol 3. Academic Press, New York
[11] Davydov AS (1962) Theory of Molecular Excitons (translated by Kasha M, Oppenheimer M). McGraw-Hill, New York
[12] Kirkwood JG (1937) J Chem Phys **5**: 479
[13] Harada N, Nakanishi K (1983) Circular Dichroic Spectroscopy. Mill Valley, California (University Science Books)
[14] Berova N, Nakanishi K (2000) In: Berova N, Nakanishi K, Woody RW (eds) (2000) Circular Dichroism. Wiley-VCH, New York
[15] Berova N (2005) Monatsh Chem **136**: 367
[16] Lightner DA, Gurst JE (2000) Organic Conformational Analysis and Stereochemistry from Circular Dichroism Spectroscopy. Wiley-VCH, New York
[17] Hansen AaE (to be published)
[18] Tanaka J, Katayama C, Ogura F, Tatemitsu H, Nagakawa M (1973) J Chem Soc Chem Commun 21
[19] Hezemans AMF, Groenewege MP (1973) Tetrahedron **29**: 1223
[10] Stiles PJ (1971) Mol Phys **22**: 731
[21] Mandel R, Holzwarth G (1972) J Chem Phys **57**: 3469

[22] Kuball H-G, Schönhofer A (1988) In: Samori B, Thulstrup EW (eds) Polarized Spectroscopy of Ordered Systems. Dordrecht, Kluwer
[23] Kuball H-G (2005) Monatsh Chem **136**: 289
[24] Hansen AaE, Sauer SPA (to be published)