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Molecular Exciton Approach to Anisotropic Absorption and Circular Dichroism I. General Formulation

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Summary. The history of the molecular exciton approach and its application to optical rotatory power is outlined, followed by a summary of the general theory of electronic anisotropic chiroptical spectroscopy. The summary includes intensity expressions that are valid regardless of molecular dimensions as well as expressions valid only in the socalled small molecule limit, and presents the multipolar representation of the intensity expressions in the later case, emphasizing the importance of including electric dipole–magnetic dipole and electric dipole–electric quadrupole optical coupling terms on an equal footing in the description of anisotropic optical rotatory power. Expressions for isotropic chiroptical intensities are also included, and the difference in structural and point group symmetry requirements for anisotropic and isotropic optical rotatory power is discussed. On this basis, we present the molecular exciton approach for anisotropic chiroptical spectra, including interchromophoric electric dipole–electric dipole couplings and inter- and intra-chromophoric higher multipole couplings, allowing for the explicit treatment of coupling between achiral as well as chiral chromophores. Expressions are developed both for the partial intensities of the individual excitonic excitations and for the effective band shapes resulting from summation over all excitations within the exciton band. We discuss the importance of the choice of the reference points required for the description of the relative locations of the chromophoric units and for the definition of the local chromophoric multipolar transition moments, and we discuss the limitations of the present formulation. An appendix outlines the basic rules for the dyadic tensor notations utilized in the theoretical intensity formulations.

Keywords. Molecular exciton theory; Exciton chirality; Anisotropic absorption spectra; Anisotropic circular dichroism; Point group symmetry.

Introduction

The exciton concept was introduced in solid state physics in the 1930s [1] in attempts to understand how purely insulating crystals absorb visible or ultraviolet

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light, and it was developed into a variety of approaches differing in the range, or delocalization, of the assumed elementary excitation processes [2]. In the socalled tight-binding *Frenkel* exciton approach [1, 2], which leads directly into the *Davydov* molecular exciton approach [3–6], a molecular crystal or an extended molecular system is divided into identical or closely similar subunits or chromophores [7]. A localized electric dipole allowed electronic excitation within a subunit or chromophore represents the elementary excitation process, and the term exciton denotes the collective excitation reflecting the interactions between the chromophores. Within the field of ordinary molecular electronic spectroscopy, the application of the *Davydov* molecular exciton approach was initiated by *McClure* [3], *Kasha* [4, 5], and *Craig* [6] around 1960.

In the field of natural molecular optical rotatory power [8], models based on interactions between localized excitations came as no surprise in view of the central role played by the coupled oscillator approaches [8–11] in the history of this field, and starting in the mid-1950s molecular exciton theory proper was applied to molecular optical rotatory power in the work of *Moffitt et al.* [12, 13], *Tinoco et al.* [14–16], and *Schellman et al.* [17, 18] for biopolymers, and by *Mason et al.* [19, 20] and *Bosnich* [21] for organic and inorganic systems, see also Refs. [22–24]. Subsequently, molecular exciton approaches have been developed into powerful methods for the study of molecular structure problems based on natural optical rotatory power, see Refs. [25–29] for surveys and discussion of these developments. For certain classes of molecular systems the ''Exciton Chirality'' model proposed by *Harada* and *Nakanishi* [23, 26, 30, 31] has been successful in the assignment of absolute molecular configurations. The overwhelming majority of experimental and theoretical structural studies based on natural optical rotatory power, including studies applying molecular exciton theory, have been concerned with systems characterized by isotropic conditions, as witnessed by the observation that out of the 29 chapters in the almost encyclopedic volume on circular dichroism edited by *Berova*, *Nakanishi*, and *Woody* [28], only two chapters address the theory and measurement of circular dichroism under anisotropic conditions [32, 33].

The basic theme of the present account is the molecular exciton approach to natural anisotropic ordinary absorption and circular dichroism, *i.e.* chiroptical spectroscopy of oriented molecules in the absence of static magnetic fields; see Refs. [34, 35] for discussions of exciton approaches to magnetically induced optical activity. A theory of anisotropic natural molecular optical rotatory power, was first formulated by *Tinoco* and *Hammerle* [36], and a number of alternative derivations and formulations have been presented over the years [18, 37–44], see Refs. [32, 33, 46–49] for experimental aspects and results. An obvious difference between isotropic and anisotropic optical rotatory power is that the three-dimensional nature of the anisotropic optical sampling provides additional spectroscopic and structural information relative to isotropic data. In addition, in the theoretical treatment of anisotropic optical rotatory power the electric dipole–magnetic dipole and the electric dipole–electric quadrupole interactions appear on an equal footing [18, 25, 36, 39–44], whereas isotropic optical rotatory power is governed entirely by the electric dipole–magnetic dipole interaction [8]. An important structural difference between anisotropic and isotropic optical activity is that certain classes of achiral molecular structures may exhibit natural optical rotatory power under anisotropic conditions [44, 50–54], referred to as non-enantiomeric optical rotatory power, whereas chirality (enantiomerism) of course is a *sine qua non* for isotropic optical rotatory power. Non-enantiomeric optical rotatory power is well-established in crystal optics [52–54]. For molecules, the condition for non-enantiomeric natural optical rotatory power is that the molecule belongs to the achiral point group D_{2d} or to one of its achiral subgroups, *i.e.* $C_s = C_h$, C_{2v}, and S_4 [44, 52, 55]. This feature of anisotropic molecular optical rotatory power is important in an exciton context, since a number of chromophoric units in fact belong to the achiral point groups $C_s = C_h$ and C_{2v}; see the accompanying communication [56].

As background for the discussion of the exciton approach, the following section outlines the general theory of natural anisotropic ordinary absorption and circular dichroism, emphasizing the transition from theoretical intensity expressions that are valid regardless of molecular dimensions, to the socalled small molecule limit appropriate for molecules that are small relative to the wavelength of light in the optical region. The former set of expressions form convenient points of departure for intensity approaches for extended molecular structures, such as the molecular exciton approximation, whereas the latter set of expressions are deployed in the treatment of the intensity contributions from the individual chromophoric units in the present context. The subsequent section presents the molecular exciton approach for anisotropic chiroptical properties with two specific aims in mind, namely the inclusion of contributions from local magnetic dipole and electric quadrupole transition moments, and the explicit treatment of both partial intensities, *i.e.* the intensities for the individual excitations within the exciton band, and overall band intensities with special emphasis on the parameters determining the spectral shifts in the band maxima. The presentation in the two sections is focussed on the basic theory of the chiroptical anisotropic intensities utilizing a consistent tensorial formulation, the use of a tensorial formulation being necessitated by the three dimensional nature of the anisotropic spectral response [18, 40, 42, 43]. The socalled dyadic tensor formulation [43, 44, 57] used here may be somewhat unfamiliar, and the notation and pertinent rules for the manipulation of dyadic tensors are outlined in the Appendix.

The fact that the contributions from electric quadrupole and magnetic dipole transition moments are equally important for the anisotropic intensities is intimately coupled to the existence of the non-enantiomeric optical rotatory power alluded to above. This feature, in turn, makes the choice of chromophoric centers or reference points for the formulation of the anisotropic intensity expressions in the exciton model particularly crucial, and we show in the accompanying communication [56] that the concept of a partial optic axis, introduced by *Moffitt* [12], provides a convenient basis for the choice of chromoporic centers and for classification and analysis of the intensity contributions.

Theory of Anisotropic Absorption Spectra and Circular Dichroism

General Expressions

For a beam of unpolarized light of angular frequency ω, the anisotropic partial absorption coefficient for the electronic excitation $q \leftarrow o$ in a collection of non-interacting molecules with identical spatial orientation can be written as shown in

Eq. (1) expressed in S.I. units [25]. N_o is the number of molecules per unit volume, $\rho_q(\omega)$ is a normalized line shape, and we have introduced the directional absorption intensity $A_q(\underline{u},\omega)$ (Eq. (2)) where $\underline{u}$ is a unit vector in the direction of light propagation, and where the transition moment is defined in Eq. (3) in terms of the position and momentum operators, $\underline{r}_j$ and $\underline{p}_j$, for electron j. $\mathbf{I}$ is a second rank unit tensor, and the symbol $\mathbf{:}$ denotes a dyadic vector product making the quantity $\underline{\eta}_q(\underline{u},\omega)^* \mathbf{:} \underline{\eta}_q(\underline{u},\omega)$ a second rank tensor; see the Appendix for vector and dyadic tensor notation, and for the notation used for the complex quantities, and see Refs. [39, 40, 42] for tensorial formulations of chiroptical properties in terms of explicit index summations.

$$\kappa_q(\underline{u},\omega) = \frac{\pi N_o}{2\epsilon_o \hbar m^2 \omega c}\rho_q(\omega) A_q(\underline{u},\omega) \tag{1}$$

$$A_q(\underline{u},\omega) = Re\{\underline{u}\cdot[\underline{\eta}_q(\underline{u},\omega)^* \cdot \underline{\eta}_q(\underline{u},\omega)\mathbf{I} - \underline{\eta}_q(\underline{u},\omega)^* \mathbf{:} \underline{\eta}_q(\underline{u},\omega)]\cdot\underline{u}\} \tag{2}$$

$$\underline{\eta}_q(\underline{u},\omega) = -e\left\langle q\left|\sum_j \underline{p}_j \exp[i(\omega/c)\underline{u}\cdot\underline{r}_j]\right|o\right\rangle \tag{3}$$

The corresponding anisotropic circular dichroism (ACD), expressed in terms of the partial absorption coefficients for left (ℓ) and right (r) circularly polarized light [8, 29], is shown in Eq. (4) [18, 25, 39, 41, 43, 44]. Here the directional ACD intensity is defined in Eq. (5) and the electronic excitation q ← o is assigned identical line shapes for absorption and ACD [58].

$$\Delta\kappa_q(\underline{u},\omega) = \kappa_q^{\ell}(\underline{u},\omega) - \kappa_q^{r}(\underline{u},\omega) = \frac{\pi N_o}{\epsilon_o \hbar m^2 \omega c}\rho_q(\omega) B_q(\underline{u},\omega) \tag{4}$$

$$B_q(\underline{u},\omega) = -Im\{\underline{u}\cdot[\underline{\eta}_q(\underline{u},\omega)^* \times \underline{\eta}_q(\underline{u},\omega)]\} \tag{5}$$

Equations (2) and (5) include the full spatial variation of the electromagnetic field through the exponential factor $\exp[i(\omega/c)\underline{u}\cdot\underline{r}_j]$ in the transition moment in Eq. (3), and can be referred to as fully retarded [41]. These expressions are valid regardless of molecular dimensions, and form convenient points of departure for the treatment of extended molecular structures, making them particularly appropriate for the formulation of molecular exciton approaches. The formulation in Eqs. (2) and (5) allows the use of complex molecular wavefunctions, although the use of real wavefunctions can be assumed with impunity in the absence of a static magnetic field. Formulations in terms of complex wavefunctions may come into play in the treatment of the chiroptical properties of molecular systems allowing degenerate excited states [50], the selection rules for α-helical polymers being a case in point, see Refs. [25, 35, 59] and references therein.

Small Molecule Limits

For the description of the chiroptical properties of molecules that are small relative to the wavelength of light in the optical region, the socalled small molecule limit of

Eqs. (2) and (5) obtains by expansion to second order in the wave vector $\underline{\mathrm{k}} = (\omega/\mathrm{c})\underline{\mathrm{u}} = (2\pi/\lambda)\underline{\mathrm{u}}$, where λ is the wavelength of the light beam. Assuming purely real wavefunctions for the description of the molecular states in this limit, expansion of Eq. (2) yields Eq. (6) [25].

$$\begin{aligned}\mathrm{A_q}(\underline{\mathrm{u}},\omega) &= e^2\left\{\underline{\mathrm{u}}\cdot\left[\left\langle \mathrm{o}\middle|\sum_j \underline{\mathrm{p}}_j\middle|\mathrm{q}\right\rangle\cdot\left\langle \mathrm{q}\middle|\sum_j \underline{\mathrm{p}}_j\middle|\mathrm{o}\right\rangle\mathbf{I} - \left\langle \mathrm{o}\middle|\sum_j \underline{\mathrm{p}}_j\middle|\mathrm{q}\right\rangle : \left\langle \mathrm{q}\middle|\sum_j \underline{\mathrm{p}}_j\middle|\mathrm{o}\right\rangle\right]\cdot\underline{\mathrm{u}}\right\} \\ &= \frac{2m^2}{3}\omega_\mathrm{q}^2\{\underline{\mathrm{u}}\cdot\boldsymbol{D}_\mathrm{q}\cdot\underline{\mathrm{u}}\}\end{aligned} \tag{6}$$

Here $\omega_\mathrm{q} = (\mathrm{E_q} - \mathrm{E_o})/\hbar$ is the angular resonance frequency, and D_q (Eq. (7)) is the dipole strength tensor. The electric dipole transition moment is given in Eq. (8), and the assumption of real wavefunctions in the small molecule limit makes Eq. (7) symmetric in the *Cartesian* indices, *i.e.* $[\boldsymbol{D}_\mathrm{q}]_{\alpha\beta} = [\boldsymbol{D}_\mathrm{q}]_{\beta\alpha}$, *cf.* Eq. (A.8).

$$\boldsymbol{D}_\mathrm{q} = (3/2)[\langle \mathrm{o}|\underline{\mu}_\mathrm{e}|\mathrm{q}\rangle\cdot\langle \mathrm{q}|\underline{\mu}_\mathrm{e}|\mathrm{o}\rangle\mathbf{I} - \langle \mathrm{o}|\underline{\mu}_\mathrm{e}|\mathrm{q}\rangle : \langle \mathrm{q}|\underline{\mu}_\mathrm{e}|\mathrm{o}\rangle] \tag{7}$$

$$\langle \mathrm{q}|\underline{\mu}_\mathrm{e}|\mathrm{o}\rangle = -e\left\langle \mathrm{q}\middle|\sum_j \underline{\mathrm{r}}_j\middle|\mathrm{o}\right\rangle = \mathrm{i}e\left\langle \mathrm{q}\middle|\sum_j \underline{\mathrm{p}}_j\middle|\mathrm{o}\right\rangle\Big/ m\omega_\mathrm{q} \tag{8}$$

In the same limit the expansion of Eq. (5) yields Eq. (9) [44].

$$\begin{aligned}\mathrm{B_q}(\underline{\mathrm{u}},\omega) = {}&-e^2 Im\left\{\underline{\mathrm{u}}\cdot\left[\left\langle \mathrm{o}\middle|\sum_j \underline{\mathrm{p}}_j\middle|\mathrm{q}\right\rangle\times\left\langle \mathrm{q}\middle|\sum_j \underline{\mathrm{p}}_j\middle|\mathrm{o}\right\rangle\right]\right. + \frac{e^2\omega}{\mathrm{c}} Re\left\{\underline{\mathrm{u}}\cdot\left[\left\langle \mathrm{o}\middle|\sum_j \underline{\mathrm{r}}_j : \mathrm{p}_j\middle|\mathrm{q}\right\rangle\right.\right. \\ &\left.\left.\times\left\langle \mathrm{q}\middle|\sum_j \underline{\mathrm{p}}_j\middle|\mathrm{o}\right\rangle - \left\langle \mathrm{o}\middle|\sum_j \underline{\mathrm{p}}_j\middle|\mathrm{q}\right\rangle\times\left\langle \mathrm{q}\middle|\sum_j \underline{\mathrm{p}}_j : \underline{\mathrm{r}}_j)\middle|\mathrm{o}\right\rangle\right]\cdot\underline{\mathrm{u}}\right\}\end{aligned} \tag{9}$$

For real wavefunctions the first term in Eq. (9) vanishes identically, the prefix *Re* on the second term becomes superfluous, and Eq. (9) can be written as shown in Eq. (10) where R_q (Eq. (11)) is the rotatory strength tensor [18, 40–44]. From Eqs. (A.4) and (A.9), the explicit expressions for the transition moment products in Eq. (11) become as given in Eq. (12) utilizing the alternating character of $\epsilon_{\beta\delta\gamma}$, and under the assumption of real wavefunctions. The tensor in Eq. (11) is hence symmetric in the *Cartesian* indices.

$$\mathrm{B_q}(\underline{\mathrm{u}},\omega) = \frac{4m^2\omega}{3\mathrm{c}}\omega_\mathrm{q}\{\underline{\mathrm{u}}\cdot\boldsymbol{R}_\mathrm{q}\cdot\underline{\mathrm{u}}\} \tag{10}$$

$$\boldsymbol{R}_\mathrm{q} = \frac{3e^2}{4m^2\omega_\mathrm{q}}\left[\left\langle \mathrm{o}\middle|\sum_j \underline{\mathrm{r}}_j : \mathrm{p}_j\middle|\mathrm{q}\right\rangle\times\left\langle \mathrm{q}\middle|\sum_j \underline{\mathrm{p}}_j\middle|\mathrm{o}\right\rangle - \left\langle \mathrm{o}\middle|\sum_j \underline{\mathrm{p}}_j\middle|\mathrm{q}\right\rangle\times\left\langle \mathrm{q}\middle|\sum_j \underline{\mathrm{p}}_j : \underline{\mathrm{r}}_j)\middle|\mathrm{o}\right\rangle\right] \tag{11}$$

$$\begin{aligned}[\langle \mathrm{o}|\underline{\mathrm{r}} : \underline{\mathrm{p}}|\mathrm{q}\rangle\times\langle \mathrm{q}|\underline{\mathrm{p}}|\mathrm{o}\rangle]_{\alpha\beta} &= \sum_\gamma\sum_\delta\langle \mathrm{o}|r_\alpha \mathrm{p}_\gamma|\mathrm{q}\rangle\langle \mathrm{q}|\mathrm{p}_\delta|\mathrm{o}\rangle\epsilon_{\gamma\delta\beta} \\ &= -[\langle \mathrm{o}|\underline{\mathrm{r}} : \underline{\mathrm{p}}|\mathrm{q}\rangle\times\langle \mathrm{q}|\underline{\mathrm{p}}|\mathrm{o}\rangle]_{\alpha\beta}\end{aligned} \tag{12}$$

We note in passing that the quantities $\{\underline{\mathrm{u}} \cdot \boldsymbol{D}_\mathrm{q} \cdot \underline{\mathrm{u}}\}$ and $\{\underline{\mathrm{u}} \cdot \boldsymbol{R}_\mathrm{q} \cdot \underline{\mathrm{u}}\}$ entering in the expressions for the directional absorption and ACD intensities in Eqs. (6) and (10) can be expressed in the more general form given in Eq. (13) [60].

$$\begin{aligned}\Omega(\underline{\mathrm{u}}) = \{\underline{\mathrm{u}} \cdot \boldsymbol{\Omega} \cdot \underline{\mathrm{u}}\} = {} & \sin^2\theta\cos^2\phi\,\Omega_{11} + \sin^2\theta\sin^2\phi\,\Omega_{22} + \cos^2\theta\,\Omega_{33} \\ & + \sin^2\theta\sin\phi\cos\phi\,[\Omega_{12} + \Omega_{21}] \\ & + \sin\theta\cos\theta\,\{\cos\phi\,[\Omega_{13} + \Omega_{31}] + \sin\phi\,[\Omega_{23} + \Omega_{32}]\} \qquad (13)\end{aligned}$$

Here θ and φ are the spherical polar coordinates of the directional unit vector $\mathbf{u}$ relative to the molecular coordinate system, and $\boldsymbol{\Omega}$ is a second rank tensor with the *Cartesian* elements Ω_{ij}, *cf.* Eq. (A.7). For absorption and ACD spectra, Eq. (13) shows explicitly how the tensor elements govern the way the anisotropic intensities vary with the direction of the light beam, as illustrated in Refs. [44, 61]; see Ref. [60] for discussion and display of related directional molecular properties. Note that the projection represented by the expression $\{\underline{\mathrm{u}} \cdot \boldsymbol{\Omega} \cdot \underline{\mathrm{u}}\}$ only samples the symmetric tensor component with the elements $1/2[\Omega_{ij} + \Omega_{ji}]$. The use of symmetrized response tensors in Eq. (11) and in Eqs. (15) and (16) below, as derived in Ref. [44], can therefore be seen as a notational redundancy; see Ref. [44] for a discussion of this aspect.

Multipolar Representations

Separation of the dyadic transition moment operator $\sum_j \underline{\mathrm{r}}_j : \underline{\mathrm{p}}_j$ in Eq. (11) into its symmetric and antisymmetric components, *cf.* Eqs. (A.13)–(A.15), yields Eq. (14) [44, 45], where $\boldsymbol{R}(\mathrm{M})_\mathrm{q}$ is the electric dipole–magnetic dipole contribution and $\boldsymbol{R}(\mathrm{Q})_\mathrm{q}$ is the electric dipole–electric quadrupole contribution (Eqs. (15) and (16)). The electric dipole transition moment is given in Eq. (8), and the electric quadrupole and magnetic dipole transition moments are given in Eqs. (17) and (18).

$$\boldsymbol{R}_\mathrm{q} = \boldsymbol{R}(\mathrm{M})_\mathrm{q} + \boldsymbol{R}(\mathrm{Q})_\mathrm{q} \tag{14}$$

$$\begin{aligned}\boldsymbol{R}(\mathrm{M})_\mathrm{q} = {} & (3/4)\mathit{Im}[2\langle \mathrm{o}|\underline{\mu}_\mathrm{e}|\mathrm{q}\rangle \cdot \langle \mathrm{q}|\underline{\mu}_\mathrm{m}|\mathrm{o}\rangle \mathbf{I} - \langle \mathrm{o}|\underline{\mu}_\mathrm{e}|\mathrm{q}\rangle : \langle \mathrm{q}|\underline{\mu}_\mathrm{m}|\mathrm{o}\rangle \\ & + \langle \mathrm{o}|\underline{\mu}_\mathrm{m}|\mathrm{q}\rangle : \langle \mathrm{q}|\underline{\mu}_\mathrm{e}|\mathrm{o}\rangle]\end{aligned} \tag{15}$$

$$\boldsymbol{R}(\mathrm{Q})_\mathrm{q} = (3\omega_\mathrm{q}/8)[\langle \mathrm{o}|\mathbf{q}_\mathrm{e}|\mathrm{q}\rangle \times \langle \mathrm{q}|\underline{\mu}_\mathrm{e}|\mathrm{o}\rangle - \langle \mathrm{o}|\underline{\mu}_\mathrm{e}|\mathrm{q}\rangle \times \langle \mathrm{q}|\mathbf{q}_\mathrm{e}|\mathrm{o}\rangle] \tag{16}$$

$$\langle \mathrm{q}|\mathbf{q}_\mathrm{e}|\mathrm{o}\rangle = -e\left\langle \mathrm{q}\left|\sum_j \underline{\mathrm{r}}_j : \underline{\mathrm{r}}_j\right|\mathrm{o}\right\rangle = \mathrm{i}e\left\langle \mathrm{q}\left|\sum_j (\underline{\mathrm{r}}_j : \underline{\mathrm{p}}_\mathrm{j} + \underline{\mathrm{p}}_j : \underline{\mathrm{r}}_j)\right|\mathrm{o}\right\rangle \Big/ m\omega_\mathrm{q} \tag{17}$$

$$\langle \mathrm{q}|\underline{\mu}_\mathrm{m}|\mathrm{o}\rangle = -(e/2m)\left\langle \mathrm{q}\left|\sum_j \underline{\mathrm{r}}_j \times \underline{\mathrm{p}}_j\right|\mathrm{o}\right\rangle \tag{18}$$

The multipolar tensors in Eqs. (15) and (16) are written in a form that is symmetric in the *Cartesian* indices; *cf.* the discussion of Eq. (13).

Anisotropic versus Isotropic Intensities

The intensities expressed in Eqs. (1), (2), (6) and (4), (5), (10) for ordinary and rotatory absorption are anisotropic, *i.e.* they depend explicitly on the direction of the light beam relative to the space fixed molecular ensemble, as expressed by the propagation vector **u**. In the fully retarded expressions for the directional intensities, Eqs. (2) and (5), the propagation vector enters both as external multiplicative factor and through the phase factor in the exponential part of the operator in Eq. (3), making the formulation of explicit expressions for the directional dependence, and hence the extraction of isotropic, *i.e.* spherically averaged or directionally independent, intensities a demanding undertaking; see Refs. [50, 62]. On the other hand, in the response expression in the small molecule limit, Eq. (13), the directional dependence is contained entirely in the trigonometric factors multiplying the tensor elements, and the isotropic component is obtained as Eq. (19), [50].

$$\Omega = (1/4\pi)\int \Omega(\theta,\phi)\sin\theta \mathrm{d}\theta \mathrm{d}\phi = (1/3)\{\Omega_{11} + \Omega_{22} + \Omega_{33}\} = (1/3)tr\{\boldsymbol{\Omega}\} \qquad (19)$$

From Eqs. (7), (14)–(16), and (19) the resulting dipole strength [63] and the rotatory strength [8, 58, 64] governing ordinary rotatory intensities under isotropic conditions are shown in Eqs. (20) and (21).

$$D_{\mathrm{q}} = (1/3)\mathrm{tr}\{\boldsymbol{D}_{\mathrm{q}}\} = |\langle \mathrm{o}|\underline{\mu}_{\mathrm{e}}|\mathrm{q}\rangle|^2 \qquad (20)$$

$$R_{\mathrm{q}} = (1/3)\mathrm{tr}\{\boldsymbol{R}_{\mathrm{q}}\} = (1/3)\mathrm{tr}\{\boldsymbol{R}(\mathrm{M})_{\mathrm{q}}\} = Im[\langle \mathrm{o}|\underline{\mu}_{\mathrm{e}}|\mathrm{q}\rangle \cdot \langle \mathrm{q}|\underline{\mu}_{\mathrm{m}}|\mathrm{o}\rangle] \qquad (21)$$

The tensor $\boldsymbol{R}(\mathrm{Q})_{\mathrm{q}}$, Eq. (16), is traceless, and electric dipole–electric quadrupole terms hence do not contribute to isotropic CD [8], whereas electric dipole–magnetic dipole and electric dipole–electric quadrupole terms enter on an equal footing in the description of anisotropic ACD, Eqs. (14)–(16).

Discussion

Chirality (enantiomerism) is a well established condition for isotropic natural optical rotatory power, *i.e.* a necessary condition for non-vanishing values of the isotropic rotatory strength R_{q}, Eq. (21). In the language of point group symmetry [55], the chirality condition translates into the absence of inversion center and symmetry planes, or more generally the absence of an improper rotation axis S_{n}, so that the only chiral point groups become the pure rotation groups C_{n}, D_{n}, T, and O. As mentioned in the Introduction, certain classes of achiral (non-enantiomeric) molecular structures may exhibit natural optical rotatory power under anisotropic conditions [44, 50–54]. The condition for non-enantiomeric natural optical rotatory power is that the molecule belongs to the achiral point group $D_{2\mathrm{d}}$ or to one of its achiral subgroups, *i.e.* $C_{\mathrm{s}} = C_{\mathrm{h}}$, $C_{2\mathrm{v}}$, and S_4 [44, 52]. Calculations and graphical displays illustrating the ACD of enantiomeric and non-enantiomeric optically active molecular systems are presented in Ref. [44], while the accompanying communication [56] presents a more detailed discussion of the symmetry aspects of the rotatory strength tensors, Eqs. (14)–(16), in the perspective of the partial optic axis.

Computational aspects are not an issue here. However, we note that the relations between transition moments expressed in terms of the operator pairs $\sum_j \underline{\mathrm{p}}_j$ and $\sum_j \underline{\mathrm{r}}_j$ in Eq. (8), and $\sum_j (\underline{\mathrm{r}}_j : \underline{\mathrm{p}}_j + \underline{\mathrm{p}}_j : \underline{\mathrm{r}}_j)$ and $\sum_j \underline{\mathrm{r}}_j : \underline{\mathrm{r}}_j$ in Eq. (17), are not necessarily fulfilled in approximate calculations [12, 18, 43, 58]. See Ref. [61] for an overview of computational approaches.

Molecular Exciton Theory

Description of the Exciton States

The *Frenkel-Davidov* molecular exciton approach [1–6] assumes a partitioning of an extended part of a molecular system into identical subunits or chromophores, and neglects overlap and electron exchange between the spectroscopically active electrons in different chromophores [7, 11]. Using $\varphi_{\gamma,\mathrm{s}}$ to denote the wavefunction for the s'th electronic state of chromophore γ, the electronic ground state of the exciton system can be represented by the product function shown in Eq. (22) where N is the number of chromophores in the excitonic system. Single chromophore excited states can similarly be represented as given in Eq. (23) and the q'th electronic state of an exciton band associated with chromophore states $\varphi_{\alpha,1}$ is then given as Eq. (24).

$$|\mathrm{o}\rangle = \prod_{\gamma}^{\mathrm{N}} \varphi_{\gamma,\mathrm{o}} \tag{22}$$

$$|\lambda, \mathrm{s}\rangle = \varphi_{\lambda,\mathrm{s}} \prod_{\gamma\neq\lambda}^{\mathrm{N}} \varphi_{\gamma,\mathrm{o}} \tag{23}$$

$$|\mathrm{q}\rangle = \sum_{\alpha}^{\mathrm{N}} \mathrm{C}_{\alpha,\mathrm{q}} |\alpha, 1\rangle \tag{24}$$

We shall assume that the $1 \leftarrow \mathrm{o}$ chromophoric excitation is electric dipole allowed, *i.e.* the local electric dipole transition moment (Eq. (25)) is assumed non-vanishing. In Eq. (25), $\underline{\mathrm{R}}_{\alpha}$ is the position vector for a reference point in chromophore α [11], the reference points being assigned the same relative position in all chromophores. ${}^{\alpha}\sum_{j}$ indicates summation over the electrons in this chromophore, and ω_1 is the angular resonance frequency for the chromophoric excitation $1 \leftarrow \mathrm{o}$, *cf.* Eq. (8). The sharp bracket notation $|\rangle$ denotes matrix elements and transition moments for the product wavefunctions defined in Eqs. (22)–(24), whereas the soft bracket notation $|)$ denotes matrix elements and transition moments expressed for the chromophoric wavefunctions.

$$\begin{aligned}(\alpha, 1|{}^{\alpha}\underline{\mu}_{\mathrm{e}}|\alpha, \mathrm{o}) &= -e\left(\alpha, 1\left|{}^{\alpha}\sum_{j}(\underline{\mathrm{r}}_{j} - \underline{\mathrm{R}}_{\alpha})\right|\alpha, \mathrm{o}\right)\\ &= \frac{\mathrm{i}e}{m\omega_1}\left(\alpha, 1\left|{}^{\alpha}\sum_{j}\underline{\mathrm{p}}_{j}\right|\alpha, \mathrm{o}\right)\end{aligned} \tag{25}$$

The chromophoric wavefunctions $\varphi_{\alpha,\mathrm{s}}$ will be assumed purely real, in accord with the treatment of the small molecule limit discussed in the preceeding section, whereas the formulation of the general exciton theory in this section allows complex-valued coefficients, $\mathrm{C}_{\alpha,\mathrm{q}}$. These coefficients are determined either by symmetry considerations for the entire exciton system, or by explicit solution of the linear equations (Eq. (26)) where ω_{q} is the angular resonance frequency for the excitonic excitation q ← o, and where $V_{\lambda,s;\gamma,t}$ is the chromophoric interaction term. The coefficients determined by Eq. (26) fulfill the unitary relations (Eqs. (27)–(30)).

$$\sum_{\alpha}^{N} V_{\alpha,1;\beta,1} C_{\alpha,q} = (\omega_q - \omega_1) C_{\beta,q} \tag{26}$$

$$\sum_{\alpha}^{N} \sum_{\beta}^{N} C_{\alpha,q} V_{\alpha,1;\beta,1} C^{*}_{\beta,q} = (\omega_q - \omega_1) \tag{27}$$

$$\sum_{q}^{N} C_{\alpha,q} C^{*}_{\beta,q} = \delta_{\alpha,\beta} \tag{28}$$

$$\sum_{q}^{N} C_{\alpha,q} (\omega_q - \omega_1) C^{*}_{\beta,q} = V_{\alpha,1;\beta,1} \tag{29}$$

$$\sum_{q}^{N} C_{\alpha,q} (\omega_q - \omega_1)^2 C^{*}_{\beta,q} = \sum_{\nu} V_{\alpha,1;\nu,1} V_{\nu,1;\beta,1} \tag{30}$$

Numerical solution of Eq. (26) will generate real-valued coefficients, whereas complex-valued coefficients may result from symmetry considerations [12, 35, 50, 59]. For the interaction term we note that the neglect of overlap and electron exchange between the spectroscopically active electrons in different chromophores in the molecular exciton approach, and the concomitant use of product wavefunctions of the form given in Eqs. (22) and (23), imply that $V_{\lambda,s;\gamma,t}$ in general takes the form of multipolar interactions between localized transition densities shown in Eq. (31), representing the interaction between the transition densities $\varphi_{\lambda,s}\varphi_{\lambda,o}$ and $\varphi_{\gamma,t}\varphi_{\gamma,o}$. For electric dipole allowed excitations, as assumed here, the interaction in Eq. (31) can be truncated to the electric dipole–electric dipole level, expressed in a dyadic notation in Eq. (32), *cf.* Eq. (25). Chromophoric self-interaction is omitted by the condition defined by Eq. (33).

$$V_{\lambda,s;\gamma,t} = \langle \lambda, s | V_{\lambda,\gamma} | \gamma, t \rangle = (\varphi_{\lambda,s}\varphi_{\gamma,o} | V_{\lambda,\gamma} | \varphi_{\lambda,o}\varphi_{\gamma,t}) \tag{31}$$

$$\begin{aligned} V_{\alpha,1;\beta,1} = \frac{1}{4\pi\epsilon_o |\underline{R}_\alpha - \underline{R}_\beta|^3} \Big\{ & (\alpha, o|{}^{\alpha}\underline{\mu}_e|\alpha, 1) \cdot (\beta, 1|{}^{\beta}\underline{\mu}_e|\beta, o) - \frac{3}{|\underline{R}_\alpha - \underline{R}_\beta|^2} \\ & \times (\alpha, o|{}^{\alpha}\underline{\mu}_e|\alpha, 1) \cdot [(\underline{R}_\alpha - \underline{R}_\beta) : (\underline{R}_\alpha - \underline{R}_\beta)] \cdot (\beta, 1|{}^{\beta}\underline{\mu}_e|\beta, o) \Big\} \end{aligned} \tag{32}$$

$$V_{\alpha,1;\alpha,1} = 0 \tag{33}$$

In practice the evaluation of the interaction in Eq. (32) often proceeds *via* distributed transition densities [65].

As defined in Eq. (22), the description of the ground state omits perturbations due to doubly excited states of the form given by Eq. (34).

$$|\alpha, 1; \beta, 1\rangle = \varphi_{\alpha,1}\varphi_{\beta,1} \prod_{\kappa \neq \alpha,\beta}^{N} \varphi_{\kappa,o} \tag{34}$$

A consistent treatment of these states can be obtained in the random phase approximation (RPA) [25, 34]. However, the intensity expressions obtained from RPA and from Eqs. (22)–(33) are quite similar [25], and become essentially identical when ω_q is identified with ω_1, except when they appear in the combination $(\omega_q - \omega_1)$. In addition, we note that the description of the exciton states in Eq. (24) neglects perturbations due to higher excited chromophore states, also referred to as interband mixing; see the Discussion subsection below. For ease of notation we suppress the superscript N on products and summations in the remaining part of this section.

Partial Exciton Intensities

The localization of the spectroscopically active electrons into chromophoric regions implies that the transition moment in Eq. (3) can be written as Eq. (35) from Eqs. (23) and (24). The chromophoric reference vector $\underline{R}_\alpha$ is introduced in Eq. (25), and the local chromophoric transition moment is defined in Eq. (36).

$$\begin{aligned}\underline{\eta}_q(\underline{u},\omega) &= -e\left\langle q\left|\sum_\lambda\{\exp[i(\omega/c)\underline{u}\cdot\underline{R}_\lambda]\}^\lambda\sum_j \underline{p}_j\exp[i(\omega/c)\underline{u}\cdot(\underline{r}_j-\underline{R}_\lambda)]\right|o\right\rangle\\ &= \sum_\alpha C^*_{\alpha,q}\exp[i(\omega/c)\underline{u}\cdot\underline{R}_\alpha]\underline{\eta}_{\alpha,1}(\underline{u},\omega)\end{aligned} \tag{35}$$

$$\underline{\eta}_{\alpha,1}(\underline{u},\omega) = -e\left(\alpha,1\left|{}^\alpha\sum_j \underline{p}_j\exp[i(\omega/c)\underline{u}\cdot(\underline{r}_j-\underline{R}_\alpha)]\right|\alpha,o\right) \tag{36}$$

From Eqs. (2) and (35) the partial directional absorption intensity for the excitation q ← o in the coupled system is then given by Eq. (37) expressed in terms of the absorption strength coupling tensor (Eq. (38)).

$$A_q(\underline{u},\omega) = Re\sum_\alpha\sum_\beta C_{\alpha,q}C^*_{\beta,q}\exp[-i(\omega/c)\underline{u}\cdot(\underline{R}_\alpha-\underline{R}_\beta)]\{\underline{u}\cdot\boldsymbol{\mathit{\Delta}}_{\alpha,1;\beta,1}\cdot\underline{u}\} \tag{37}$$

$$\begin{aligned}\boldsymbol{\mathit{\Delta}}_{\alpha,1;\beta,1} = (1/2)\Big\{&[\underline{\eta}_{\alpha,1}(\underline{u},\omega)^*\cdot\underline{\eta}_{\beta,1}(\underline{u},\omega)+\underline{\eta}_{\beta,1}(\underline{u},\omega)\cdot\underline{\eta}_{\alpha,1}(\underline{u},\omega)^*]\mathbf{I}\\ &-\underline{\eta}_{\alpha,1}(\underline{u},\omega)^*:\underline{\eta}_{\beta,1}(\underline{u},\omega)-\underline{\eta}_{\beta,1}(\underline{u},\omega):\underline{\eta}_{\alpha,1}(\underline{u},\omega)^*\Big\}\end{aligned} \tag{38}$$

Since the reference point $\underline{R}_\alpha$ is located inside the chromophore, and the dimensions of the chromophores are much smaller than the resonance wavelength of the light, Eq. (38) can be truncated to the small molecule limit, *cf.* Eqs. (6) and (7), yielding Eq. (39), whose diagonal blocks are given by Eq. (40) where $\boldsymbol{D}_{\alpha,1}$ is the dipole strength tensor for excitation 1 ← o in chromophore α, *cf.* Eq. (7).

$$\begin{aligned}\boldsymbol{\mathit{\Delta}}_{\alpha,1;\beta,1} = m^2\omega_1^2\{&(\alpha,o|{}^\alpha\underline{\mu}_e|\alpha,1)\cdot(\beta,1|{}^\beta\underline{\mu}_e|\beta,o)\mathbf{I}\\ &-(\alpha,o|{}^\alpha\underline{\mu}_e|\alpha,1):(\beta,1|{}^\beta\underline{\mu}_e|\beta,o)\}\end{aligned} \tag{39}$$

$$\boldsymbol{\mathit{\Delta}}_{\alpha,1;\alpha,1} = (2/3)m^2\omega_1^2\boldsymbol{D}_{\alpha,1} \tag{40}$$

The dipole strength tensors are identical for the individual chromophores except for the rotations following the orientation of the chromophores, as consequence of the assumption of identical chromophoric units. The tensors in Eq. (39), and in

Eqs. (46), (47), and (63) below, are symmetric with respect to interchange of the chromophoric indices, but are chosen not to be symmetric with respect to the *Cartesian* indices in order to avoid notational overcrowding; as justified by the symmetric sampling of the optical coupling tensors in all the intensity expressions; *cf.* the discussion following Eq. (13).

For the partial directional ACD intensity, Eqs. (5) and (35) yield Eq. (41).

$$\begin{aligned}\mathrm{B_q}(\underline{\mathrm{u}},\omega) &= -\mathit{Im}\sum_{\alpha}\sum_{\beta}\mathrm{C}_{\alpha,\mathrm{q}}\mathrm{C}^{*}_{\beta,\mathrm{q}}\exp[-\mathrm{i}(\omega/\mathrm{c})\underline{\mathrm{u}}\cdot(\underline{\mathrm{R}}_{\alpha}-\underline{\mathrm{R}}_{\beta})]\\ &\quad\times\{\underline{\mathrm{u}}\cdot[\underline{\eta}_{\alpha,1}(\underline{\mathrm{u}},\omega)^{*}\times\underline{\eta}_{\beta,1}(\underline{\mathrm{u}},\omega)\}\end{aligned}\tag{41}$$

Expanding the transition moment terms, *mutatis mutandis* Eq. (9), Eq. (41) can be written as Eq. (42).

$$\mathrm{B_q}(\underline{\mathrm{u}},\omega) = {}^{dip}\mathrm{B_q}(\underline{\mathrm{u}},\omega) + {}^{inh}\mathrm{B_q}(\underline{\mathrm{u}},\omega)\tag{42}$$

Here ${}^{dip}\mathrm{B_q}(\underline{\mathrm{u}},\omega)$ (Eq. (43)) collects the electric dipole–electric dipole ACD contributions. The inherent ACD contributions are collected in the term ${}^{inh}\mathrm{B_q}(\underline{\mathrm{u}},\omega)$ (Eq. (44)) where we have introduced the inherent ACD strength coupling tensor ${}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}$ (Eq. (45)) with the electric dipole–magnetic dipole contribution ${}^{inh}\boldsymbol{\Gamma}(\mathrm{M})_{\alpha,1;\beta,1}$ (Eq. (46)) and the electric dipole–electric quadrupole contribution ${}^{inh}\boldsymbol{\Gamma}(\mathrm{Q})_{\alpha,1;\beta,1}$ (Eq. (47)), *cf.* Eqs. (14)–(16).

$$\begin{aligned}{}^{dip}\mathrm{B_q}(\underline{\mathrm{u}},\omega) &= -m^2\omega_1^2\mathit{Im}\sum_{\alpha}\sum_{\beta}\mathrm{C}_{\alpha,\mathrm{q}}\mathrm{C}^{*}_{\beta,\mathrm{q}}\exp[-\mathrm{i}(\omega/\mathrm{c})\underline{\mathrm{u}}\cdot(\underline{\mathrm{R}}_{\alpha}-\underline{\mathrm{R}}_{\beta})]\\ &\quad\times\{\underline{\mathrm{u}}\cdot[(\alpha,\mathrm{o}|^{\alpha}\underline{\mu}_{\mathrm{e}}|\alpha,1)\times(\beta,1|^{\beta}\underline{\mu}_{\mathrm{e}}|\beta,\mathrm{o})]\}\end{aligned}\tag{43}$$

$$\begin{aligned}{}^{inh}\mathrm{B_q}(\underline{\mathrm{u}},\omega) &= \frac{\omega}{\mathrm{c}}\mathit{Re}\sum_{\alpha}\sum_{\beta}\mathrm{C}_{\alpha,\mathrm{q}}\mathrm{C}^{*}_{\beta,\mathrm{q}}\exp[-\mathrm{i}(\omega/\mathrm{c})\underline{\mathrm{u}}\cdot(\underline{\mathrm{R}}_{\alpha}-\underline{\mathrm{R}}_{\beta})]\\ &\quad\times\{\underline{\mathrm{u}}\cdot{}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}\end{aligned}\tag{44}$$

$${}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\beta,1} = {}^{inh}\boldsymbol{\Gamma}(\mathrm{M})_{\alpha,1;\beta,1} + {}^{inh}\boldsymbol{\Gamma}(\mathrm{Q})_{\alpha,1;\beta,1}\tag{45}$$

$$\begin{aligned}{}^{inh}\boldsymbol{\Gamma}(\mathrm{M})_{\alpha,1;\beta,1} &= m^2\omega_1\{\mathit{Im}[(\alpha,\mathrm{o}|^{\alpha}\underline{\mu}_{\mathrm{e}}|\alpha,1)\cdot(\beta,1|^{\beta}\underline{\mu}_{\mathrm{m}}|\beta,\mathrm{o})\mathbf{I}\\ &\quad-(\alpha,\mathrm{o}|^{\alpha}\underline{\mu}_{\mathrm{e}}|\alpha,1):(\beta,1|^{\beta}\underline{\mu}_{\mathrm{m}}|\beta,\mathrm{o})]\\ &\quad+\mathit{Im}[(\beta,\mathrm{o}|^{\beta}\underline{\mu}_{\mathrm{e}}|\beta,1)\cdot(\alpha,1|^{\alpha}\underline{\mu}_{\mathrm{m}}|\alpha,\mathrm{o})\mathbf{I}\\ &\quad-(\beta,\mathrm{o}|^{\beta}\underline{\mu}_{\mathrm{e}}|\beta,1):(\alpha,1|^{\alpha}\underline{\mu}_{\mathrm{m}}|\alpha,\mathrm{o})]\}\end{aligned}\tag{46}$$

$$\begin{aligned}{}^{inh}\boldsymbol{\Gamma}(\mathrm{Q})_{\alpha,1;\beta,1} &= (1/2)m^2\omega_1^2\{(\alpha,\mathrm{o}|^{\alpha}\mathbf{q}_{\mathrm{e}}|\alpha,1)\times(\beta,1|^{\beta}\underline{\mu}_{\mathrm{e}}|\beta,\mathrm{o})\\ &\quad+(\beta,\mathrm{o}|^{\beta}\mathbf{q}_{\mathrm{e}}|\beta,1)\times(\alpha,1|^{\alpha}\underline{\mu}_{\mathrm{e}}|\alpha,\mathrm{o})\}\end{aligned}\tag{47}$$

The local magnetic dipole and electric quadrupole transition moments are given in Eqs. (48) and (49) and the diagonal blocks of the tensors in Eqs. (45)–(47) are given in Eqs. (50)–(52) where $\boldsymbol{R}_{\alpha,1}$, $\boldsymbol{R}(\mathrm{M})_{\alpha,1}$, and $\boldsymbol{R}(\mathrm{Q})_{\alpha,1}$ are the respective rotatory strength tensors for excitation $1\leftarrow\mathrm{o}$ in chromophore α, *cf.* Eqs. (14)–(15). These tensors are identical for the individual chromophores except for the rotations following the orientation of the chromophores, again as consequence of the assumption of identical units.

$$(\alpha,1|^{\alpha}\underline{\mu}_{\mathrm{m}}|\alpha,\mathrm{o}) = -\frac{e}{2m}\left(\alpha,1\middle|^{\alpha}\sum_{j}\{(\underline{\mathrm{r}}_j-\underline{\mathrm{R}}_{\alpha})\times\underline{\mathrm{p}}_j\middle|\alpha,\mathrm{o}\right) \tag{48}$$

$$\begin{aligned}(\alpha,1|^{\alpha}\mathbf{q}_{\mathrm{e}}|\alpha,\mathrm{o}) &= -e\left(\alpha,1\middle|^{\alpha}\sum_{j}(\underline{\mathrm{r}}_j-\underline{\mathrm{R}}_{\alpha}):(\underline{\mathrm{r}}_j-\underline{\mathrm{R}}_{\alpha})\middle|\alpha,\mathrm{o}\right)\\ &= \frac{\mathrm{i}e}{m\omega_1}\left(\alpha,1\middle|^{\alpha}\sum_{j}\{(\underline{\mathrm{r}}_j-\underline{\mathrm{R}}_{\alpha}):\underline{\mathrm{p}}_j+\underline{\mathrm{p}}_j:(\underline{\mathrm{r}}_j-\underline{\mathrm{R}}_{\alpha})\}\middle|\alpha,\mathrm{o}\right)\end{aligned} \tag{49}$$

$${}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\alpha,1} = (4/3)m^2\omega_1\boldsymbol{R}_{\alpha,1} \tag{50}$$

$${}^{inh}\boldsymbol{\Gamma}(\mathrm{M})_{\alpha,1;\alpha,1} = (4/3)m^2\omega_1\boldsymbol{R}(\mathrm{M})_{\alpha,1} \tag{51}$$

$${}^{inh}\boldsymbol{\Gamma}(\mathrm{Q})_{\alpha,1;\alpha,1} = (4/3)m^2\omega_1\boldsymbol{R}(\mathrm{Q})_{\alpha,1} \tag{52}$$

Band Intensities

In practice the experimental absorption and CD spectra often show considerable congestion, suggesting the development of expressions for the total anisotropic absorption and ACD intensities associated with the entire exciton band [35, 66–69]. Such band intensities are obtained by summing Eqs. (1) and (4) over all exciton states yielding Eqs. (53) and (54) where the two contributions to the ACD intensity are given by Eqs. (55) and (56), *cf.* Eq. (42), and where we assume identical line shape functions for the exciton transitions, *i.e.* $\rho_{\mathrm{q}}(\omega)=\rho(\omega-\omega_{\mathrm{q}})$ for all q.

$$\kappa(\underline{\mathrm{u}},\omega) = \sum_{\mathrm{q}}\kappa_{\mathrm{q}}(\underline{\mathrm{u}},\omega) = \frac{\pi\mathrm{N}_{\mathrm{o}}}{2\epsilon_{\mathrm{o}}\hbar m^2\omega\mathrm{c}}\sum_{\mathrm{q}}\rho(\omega-\omega_{\mathrm{q}})\mathrm{A}_{\mathrm{q}}(\underline{\mathrm{u}},\omega) \tag{53}$$

$$\varDelta\kappa(\underline{\mathrm{u}},\omega) = {}^{dip}\varDelta\kappa(\underline{\mathrm{u}},\omega) + {}^{inh}\varDelta\kappa(\underline{\mathrm{u}},\omega) \tag{54}$$

$${}^{dip}\varDelta\kappa(\underline{\mathrm{u}},\omega) = \frac{\pi\mathrm{N}_{\mathrm{o}}}{\epsilon_{\mathrm{o}}\hbar m^2\omega\mathrm{c}}\sum_{\mathrm{q}}\rho(\omega-\omega_{\mathrm{q}})^{dip}\mathrm{B}_{\mathrm{q}}(\underline{\mathrm{u}},\omega) \tag{55}$$

$${}^{inh}\varDelta\kappa(\underline{\mathrm{u}},\omega) = \frac{\pi\mathrm{N}_{\mathrm{o}}}{\epsilon_{\mathrm{o}}\hbar m^2\omega\mathrm{c}}\sum_{\mathrm{q}}\rho(\omega-\omega_{\mathrm{q}})^{inh}\mathrm{B}_{\mathrm{q}}(\underline{\mathrm{u}},\omega) \tag{56}$$

Inspection of Eqs. (37), (43), and (44) shows that the q dependence in the terms entering Eqs. (53), (55), and (56) is contained entirely in the factor shown in Eq. (57).

$$\begin{aligned}\sum_{\mathrm{q}}\mathrm{C}_{\alpha,\mathrm{q}}\mathrm{C}^{*}_{\beta,\mathrm{q}}\rho(\omega-\omega_{\mathrm{q}}) &= \rho(\omega-\omega_1)\sum_{\mathrm{q}}\mathrm{C}_{\alpha,\mathrm{q}}\mathrm{C}^{*}_{\beta,\mathrm{q}} - \rho'(\omega-\omega_1)\sum_{\mathrm{q}}\mathrm{C}_{\alpha,\mathrm{q}}(\omega_{\mathrm{q}}-\omega_1)\mathrm{C}^{*}_{\beta,\mathrm{q}}\\ &\quad + (1/2)\rho''(\omega-\omega_1)\sum_{\mathrm{q}}\mathrm{C}_{\alpha,\mathrm{q}}(\omega_{\mathrm{q}}-\omega_1)^2\mathrm{C}^{*}_{\beta,\mathrm{q}}\\ &= \rho(\omega-\omega_1)\delta_{\alpha,\beta} - \rho'(\omega-\omega_1)\mathrm{V}_{\alpha,1;\beta,1}\\ &\quad + (1/2)\rho''(\omega-\omega_1)\sum_{\lambda}\mathrm{V}_{\alpha,1;\lambda,1}\mathrm{V}_{\lambda,1;\beta,1}\end{aligned} \tag{57}$$

Here the lineshape function $\rho(\omega-\omega_{\mathrm{q}})$ is approximated by a *Taylor* expansion with $\rho'(\omega-\omega_1)=\partial\rho(\omega-\omega_1)/\partial\omega$ and $\rho''(\omega-\omega_1)=\partial^2\rho(\omega-\omega_1)/\partial\omega^2$, and

Eqs. (28)–(30) are invoked to close the summations over the exciton indices. In the application of Eq. (57) to Eqs. (37) and (53), (43) and (55), and (44) and (56) it is found that all terms containing the phase factor $\exp[-\mathrm{i}(\omega/\mathrm{c})\underline{\mathrm{u}}\cdot(\underline{\mathrm{R}}_\lambda-\underline{\mathrm{R}}_\gamma)]$ also contain the coupling $\mathrm{V}_{\lambda,\mathrm{s};\gamma,t}$ or the products $\mathrm{V}_{\lambda,\mathrm{s};\kappa,\mathrm{u}}\mathrm{V}_{\kappa,\mathrm{u};\gamma,\mathrm{t}}$. The coupling terms fall off so rapidly with the interchromophoric separation that the truncated expansion given by Eq. (58) can be applied with impunity [35, 68, 69].

$$\exp[-\mathrm{i}(\omega/\mathrm{c})\underline{\mathrm{u}}\cdot(\underline{\mathrm{R}}_\lambda-\underline{\mathrm{R}}_\gamma)]=1-\mathrm{i}(\omega/\mathrm{c})\underline{\mathrm{u}}\cdot(\underline{\mathrm{R}}_\lambda-\underline{\mathrm{R}}_\gamma)\tag{58}$$

Combining Eqs. (37), (53), (57), and (58) the total directional absorption intensity becomes Eq. (59).

$$\begin{aligned}\kappa(\underline{\mathrm{u}},\omega)=\frac{\pi\mathrm{N_o}}{2\epsilon_\mathrm{o}\hbar m^2\omega\mathrm{c}}\Bigg\{&\rho(\omega-\omega_1)\sum_\alpha\{\underline{\mathrm{u}}\cdot\boldsymbol{\Delta}_{\alpha,1;\alpha,1}\cdot\underline{\mathrm{u}}\}-\rho'(\omega-\omega_1)\\&\times\sum_\alpha\sum_\beta\mathrm{V}_{\alpha,1;\beta,1}\{\underline{\mathrm{u}}\cdot\boldsymbol{\Delta}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}+(1/2)\rho''(\omega-\omega_1)\\&\times\sum_\alpha\sum_\beta\sum_\lambda\mathrm{V}_{\alpha,1;\lambda,1}\mathrm{V}_{\lambda,1;\beta,1}\{\underline{\mathrm{u}}\cdot\boldsymbol{\Delta}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}\Bigg\}\end{aligned}\tag{59}$$

The second term in Eq. (58) does not contribute to the *Re* part of the terms in Eq. (37), since the coupling terms $\mathrm{V}_{\alpha,1;\beta,1}$ and $\boldsymbol{\Delta}_{\alpha,1;\beta,1}$, Eqs. (32) and (39), are purely real. In addition, the first term in Eq. (59) is non-vanishing and dominant since the local electric dipole transition moments are non-vanishing by assumption, *cf.* Eq. (25). Hence retaining only the two leading terms in Eq. (59), the application of an "inverted" *Taylor* expansion provides the contracted expression shown by Eq. (60) utilizing Eq. (40) [69]. The lineshift parameter is defined by Eq. (61).

$$\kappa(\underline{\mathrm{u}},\omega)=\frac{\pi\mathrm{N_o}\omega_1^2}{2\epsilon_\mathrm{o}\hbar\omega\mathrm{c}}\rho(\omega-\omega_1-\mathrm{d}_\kappa(\underline{\mathrm{u}}))\sum_\alpha\{\underline{\mathrm{u}}\cdot\boldsymbol{D}_{\alpha,1}\cdot\underline{\mathrm{u}}\}\tag{60}$$

$$\mathrm{d}_\kappa(\underline{\mathrm{u}})=\frac{\sum_\alpha\sum_\beta\mathrm{V}_{\alpha,1;\beta,1}\{\underline{\mathrm{u}}\cdot\boldsymbol{\Delta}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}}{\sum_\alpha\{\underline{\mathrm{u}}\cdot\boldsymbol{\Delta}_{\alpha,1;\alpha,1}\cdot\underline{\mathrm{u}}\}}\tag{61}$$

The absorption band shape for the exciton manifold therefore exhibits the same line shape as the unperturbed chromophoric excitation, shifted by the parameter defined in Eq. (61) and scaled by the directionally projected sum of the unperturbed dipole strength tensors for the individual chromophores. For a *Gaussian* line shape $\rho(\omega-\omega_1)$ of halfwidth δ, the step from Eq. (59) to Eq. (60) is valid for $|\mathrm{d}_\kappa(\underline{\mathrm{u}})|$ less than $\delta/2$ [35]. Since the intensity coupling tensors in the numerator and denominator in Eq. (61) are of the same magnitude, the lineshift parameter $\mathrm{d}_\kappa(\underline{\mathrm{u}})$ will be of the order of the chromophoric interaction terms $\mathrm{V}_{\alpha,1;\beta,1}$, making the condition for the validity of the step from Eq. (59) to Eq. (60) coincide with the condition for the validity of the *Taylor* expansion in Eq. (57). The band intensity in Eq. (60) is sensitive to the choice of chromophoric reference points only through the chromophoric interaction term, Eq. (32).

For the total directional electric dipole–electric dipole ACD intensity defined in Eq. (55), Eqs. (43), (55), (57), and (58) combine to yield Eq. (62) where we have introduced the electric dipole–electric dipole ACD coupling tensor (Eq. (63)) for which the diagonal blocks vanish identically (Eq. (64))

$$
{}^{dip}\varDelta\kappa(\underline{\mathrm{u}},\omega)=\frac{\pi\mathrm{N}_\mathrm{o}}{\epsilon_\mathrm{o}\hbar m^2\mathrm{c}^2}\Bigg\{-\rho'(\omega-\omega_1)\sum_\alpha\sum_\beta \mathrm{V}_{\alpha,1;\beta,1}\{\underline{\mathrm{u}}\cdot{}^{dip}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}
+(1/2)\rho''(\omega-\omega_1)\sum_\alpha\sum_\beta\sum_\lambda \mathrm{V}_{\alpha,1;\lambda,1}\mathrm{V}_{\lambda,1;\beta,1}\{\underline{\mathrm{u}}\cdot{}^{dip}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}\Bigg\} \tag{62}
$$

$$
{}^{dip}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}=m^2\omega_1^2\{(\underline{\mathrm{R}}_\alpha-\underline{\mathrm{R}}_\beta):[(\alpha,\mathrm{o}|{}^\alpha\underline{\mu}_\mathrm{e}|\alpha,1)\times(\beta,1|{}^\beta\underline{\mu}_\mathrm{e}|\beta,\mathrm{o})]\} \tag{63}
$$

$$
{}^{dip}\boldsymbol{\Gamma}_{\alpha,1;\alpha,1}=0 \tag{64}
$$

The line shape contribution $\rho(\omega-\omega_1)$ is absent in Eq. (62) as consequence of Eq. (64), and the contracted form of Eq. (62) becomes Eq. (65) where the lineshift parameter is defined by Eq. (66).

$$
{}^{dip}\varDelta\kappa(\underline{\mathrm{u}},\omega)=-\frac{\pi\mathrm{N}_\mathrm{o}}{\epsilon_\mathrm{o}\hbar m^2\mathrm{c}^2}\rho'(\omega-\omega_1-{}^{dip}\mathrm{g}_{\varDelta\kappa}(\underline{\mathrm{u}}))
\times\sum_\alpha\sum_\beta \mathrm{V}_{\alpha,1;\beta,1}\{\underline{\mathrm{u}}\cdot{}^{dip}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\} \tag{65}
$$

$$
{}^{dip}\mathrm{g}_{\varDelta\kappa}(\underline{\mathrm{u}})=\frac{\sum_\alpha\sum_\beta\sum_\lambda \mathrm{V}_{\alpha,1;\lambda,1}\mathrm{V}_{\lambda,1;\beta,1}\{\underline{\mathrm{u}}\cdot{}^{dip}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}}{2\sum_\alpha\sum_\beta \mathrm{V}_{\alpha,1;\beta,1}\{\underline{\mathrm{u}}\cdot{}^{dip}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}} \tag{66}
$$

The electric dipole–electric dipole ACD exciton band shape hence becomes the negative of the derivative of the line shape function, shifted by the parameter in Eq. (66) and scaled by the coupling term $\sum_\alpha\sum_\beta \mathrm{V}_{\alpha,1;\beta,1}\{\underline{\mathrm{u}}\cdot{}^{dip}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}$ [68, 69]. The intensity tensors in Eq. (66) are governed by the chromophoric electric dipole transition moments, and the condition for the validity of the contraction from Eq. (62) to Eq. (65) again coincides with the condition for the validity of the expansion in Eq. (57).

For the total directional inherent ACD intensity defined in Eq. (56), Eqs. (44), (57), and (58) combine to yield Eq. (67).

$$
{}^{inh}\varDelta\kappa(\underline{\mathrm{u}},\omega)=\frac{\pi\mathrm{N}_\mathrm{o}}{\epsilon_\mathrm{o}\hbar m^2\mathrm{c}^2}\Bigg\{\rho(\omega-\omega_1)\sum_\alpha\{\underline{\mathrm{u}}\cdot{}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\alpha,1}\cdot\underline{\mathrm{u}}\}
-\rho'(\omega-\omega_1)\sum_\alpha\sum_\beta \mathrm{V}_{\alpha,1;\beta,1}\{\underline{\mathrm{u}}\cdot{}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}
+(1/2)\rho''(\omega-\omega_1)\sum_\alpha\sum_\beta\sum_\lambda \mathrm{V}_{\alpha,1;\lambda,1}\mathrm{V}_{\lambda,1;\lambda,1}\{\underline{\mathrm{u}}\cdot{}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}\Bigg\} \tag{67}
$$

Utilizing Eq. (50), Eq. (67) can be contracted to Eq. (68) where the lineshift parameter is given by Eq. (69).

$$
{}^{inh}\varDelta\kappa(\underline{\mathrm{u}},\omega)=\frac{\pi\mathrm{N}_\mathrm{o}}{\epsilon_\mathrm{o}\hbar m^2\mathrm{c}^2}\Bigg\{\frac{4m^2\omega_1}{3}\rho(\omega-\omega_1)\sum_\alpha\{\underline{\mathrm{u}}\cdot\boldsymbol{R}_{\alpha,1}\cdot\underline{\mathrm{u}}\}
-\rho'(\omega-\omega_1-{}^{inh}\mathrm{g}_{\varDelta\kappa}(\underline{\mathrm{u}}))\sum_\alpha\sum_\beta \mathrm{V}_{\alpha,1;\beta,1}\{\underline{\mathrm{u}}\cdot{}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}\cdot\underline{\mathrm{u}}\}\Bigg\} \tag{68}
$$

$$^{inh}\mathrm{g}_{\Delta\kappa}(\underline{\mathrm{u}}) = \frac{\sum_\alpha \sum_\beta \sum_\lambda \mathrm{V}_{\alpha,1;\lambda,1}\mathrm{V}_{\lambda,1;\beta,1}\{\underline{\mathrm{u}} \cdot {}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\beta,1} \cdot \underline{\mathrm{u}}\}}{2\sum_\alpha \sum_\beta \mathrm{V}_{\alpha,1;\beta,1}\{\underline{\mathrm{u}} \cdot {}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\beta,1} \cdot \underline{\mathrm{u}}\}} \tag{69}$$

The first term in Eq. (68), which vanishes identically for achiral optically inactive chromophores, is manifestly independent of the choice of chromophoric reference points if non-vanishing, *i.e.* for chiral and achiral optically active chromophores. The second term in Eq. (68) and the expression in Eq. (65) for the electric dipole–electric dipole band intensity both represent derivative band shapes scaled and shifted by parameters determined by the intensity coupling terms $^{inh}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}$ and $^{dip}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}$ and by the interaction term, Eq. (32). The relative signs and magnitudes of these band intensity contributions hence depend on the chromophoric reference points, as discussed in more detail in the subsection on the choice of chromophoric reference points below and in Ref. [56].

Small Molecule Limits and Isotropic Intensities

Expressions for anisotropic and isotropic partial intensities applicable to molecular exciton approaches for smaller coupled systems, such as the dimeric compounds targeted by the exciton chirality method [26–31], are obtained by expansion of Eqs. (37) and (41)–(44) to second order in the wave vector; *cf.* the subsection on the small molecule limits in the preceeding section. For the partial absorption intensity, Eq. (37), the small molecule limit follows by complete neglect of the factor $\exp[-\mathrm{i}(\omega/\mathrm{c})\underline{\mathrm{u}} \cdot (\underline{\mathrm{R}}_\lambda - \underline{\mathrm{R}}_\gamma)]$, *cf.* Eqs. (2), (3), and (6). Using Eq. (6) to express the intensity in term of the dipole strength tensor, Eq. (37) then yields Eq. (70) and the explicit expression for the isotropic counterpart becomes Eq. (71) utilizing Eq. (19) to obtain the isotropic part of Eq. (39).

$$\boldsymbol{D}_\mathrm{q} = \frac{3}{2m^2{\omega_1}^2} Re \sum_\alpha \sum_\beta \mathrm{C}_{\alpha,\mathrm{q}}\mathrm{C}^*_{\beta,\mathrm{q}} \boldsymbol{\Delta}_{\alpha,1;\beta,1} \tag{70}$$

$$D_\mathrm{q} = Re \sum_\alpha \sum_\beta \mathrm{C}_{\alpha,\mathrm{q}}\mathrm{C}^*_{\beta,\mathrm{q}}[(\alpha,\mathrm{o}|^\alpha\underline{\mu}_\mathrm{e}|\alpha,1) \cdot (\beta,1|^\beta\underline{\mu}_\mathrm{e}|\beta,\mathrm{o})] \tag{71}$$

For the small molecule limit of the CD intensities, we write the rotatory strength tensor for the excitation in the form given in Eq. (72).

$$\boldsymbol{R}_\mathrm{q} = {}^{dip}\boldsymbol{R}_\mathrm{q} + {}^{inh}\boldsymbol{R}_\mathrm{q} \tag{72}$$

Application of Eqs. (58) and (63) in conjunction with Eqs. (10) and (43) then yields Eq. (73) for the rotatory strength tensor representing the electric dipole–electric dipole CD intensity, and Eqs. (19) and (63) provide the isotropic counterpart (Eq. (74)).

$$^{dip}\boldsymbol{R}_\mathrm{q} = \frac{3}{4m^2\omega_1} Re \sum_\alpha \sum_\beta \mathrm{C}_{\alpha,\mathrm{q}}\mathrm{C}^*_{\beta,\mathrm{q}} {}^{dip}\boldsymbol{\Gamma}_{\alpha,1;\beta,1} \tag{73}$$

$$^{dip}R_\mathrm{q} = \frac{\omega_1}{4} Re \sum_\alpha \sum_\beta \mathrm{C}_{\alpha,\mathrm{q}}\mathrm{C}^*_{\beta,\mathrm{q}}(\underline{\mathrm{R}}_\alpha - \underline{\mathrm{R}}_\beta) \cdot [(\alpha,\mathrm{o}|^\alpha\underline{\mu}_\mathrm{e}|\alpha,1) \times (\beta,1|^\beta\underline{\mu}_\mathrm{e}|\alpha,\mathrm{o})] \tag{74}$$

In the inherent CD intensity in Eq. (44), the term $\{\underline{u}\cdot{}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\beta,1}\cdot\underline{u}\}$ again represents the second order limit and Eqs. (10) and (44) then yield Eq. (75) for the rotatory strength tensor representing the inherent CD intensity with the isotropic counterpart (Eq. (76)) utilizing Eq. (19) to obtain the isotropic part of Eq. (46) and recalling that the isotropic part of Eq. (47) vanishes identically.

$$ {}^{inh}\boldsymbol{R}_{q} = \frac{3}{4m^2\omega_1} Re \sum_{\alpha}\sum_{\beta} C_{\alpha,q}C^{*}_{\beta,q}\,{}^{inh}\boldsymbol{\Gamma}_{\alpha,1;\beta,1} \tag{75} $$

$$ {}^{inh}R_{q} = Re \sum_{\alpha}\sum_{\beta} C_{\alpha,q}C^{*}_{\beta,q}\, Im[(\varphi_{\alpha,o}|{}^{\alpha}\underline{\mu}_{e}|\varphi_{\alpha,1})\cdot(\varphi_{\beta,1}|{}^{\beta}\underline{\mu}_{m}|\varphi_{\beta,o})] \tag{76} $$

In the anisotropic band intensities, Eqs. (60), (65), and (68), the effective coherence length of the exciton states is restricted by the short range nature of the interchromophoric coupling $V_{\lambda,s;\gamma,t}$ [70], as used to justify the application of the truncated expansion in Eq. (58). These expressions therefore represent the small molecule limit as they stand. For the corresponding isotropic band intensities, Eqs. (19) and (60) yield Eq. (77) for the absorption intensity. Here N is the number of chromophores, *cf.* Eqs. (22)–(24), d_κ is the isotropic lineshift parameter, obtained as the ratio of the isotropic parts of numerator and denominator in Eq. (61), and $D_1 = D_{\alpha,1}$ is the dipole strength for the chromohoric excitation $1 \leftarrow o$, which is independent of chromophore index by the assumption of identical chromophores and sensitive to the reference point only through the interchromophoric interaction in Eq. (32).

$$ \kappa(\omega) = (1/3)\sum_{i}\kappa(\underline{u}_i,\omega) = \frac{\pi N_o N}{3\epsilon_o\hbar\omega c}\omega_1^2\rho(\omega-\omega_1-d_\kappa)D_1 \tag{77} $$

Similarly Eqs. (19), (63), and (65) yield Eq. (78) for the isotropic electric dipole–electric dipole CD band intensity, where ${}^{dip}g_{\Delta\kappa}$ is the isotropic part of the lineshift parameter in Eq. (66). Finally, for the inherent isotropic CD band intensities, Eqs. (19), (68), and (70) combine to yield Eq. (79) where ${}^{inh}g_{\Delta\kappa}$ is the isotropic part of the lineshift parameter in Eq. (68). R_1 is the rotatory strength for the chromohoric exucitation $1 \leftarrow o$, *cf.* Eq. (21), which is independent of chromophore index by the assumption of identical chromophores, if non-vanishing. We recall that electric dipole–electric quadrupole contributions vanish for isotopic intensities, and we note that the comments at the end of the preceeding subsection concerning the reference point dependent interplay between Eq. (65) and the second term in Eq. (68) apply equally well to the isotropic counterparts in Eqs. (78) and (79).

$$ \begin{aligned} {}^{dip}\Delta\kappa(\omega) &= (1/3)\sum_{i}{}^{dip}\Delta\kappa(\underline{u}_i,\omega) = -\frac{\pi N_o}{\epsilon_o\hbar c^2}\omega_1{}^2\rho'(\omega-\omega_1-{}^{dip}g_{\Delta\kappa}) \\ &\quad\times\sum_{\alpha}\sum_{\beta}V_{\alpha,1;\beta,1}\{(\underline{R}_\alpha-\underline{R}_\beta)\cdot[(\alpha,o|{}^{\alpha}\underline{\mu}_{e}|\alpha,1)\times(\beta,1|{}^{\beta}\underline{\mu}_{e}|\alpha,o)]\} \end{aligned} \tag{78} $$

$$ \begin{aligned} {}^{inh}\Delta\kappa(\omega) &= (1/3)\sum_{i}{}^{inh}\Delta\kappa(\omega) = \frac{4\pi N_o}{3\epsilon_o\hbar c^2}\omega_1\Big\{N\rho(\omega-\omega_1)R_1-\rho'(\omega-\omega_1-{}^{inh}g_{\Delta\kappa}) \\ &\quad\times\sum_{\alpha}\sum_{\beta}V_{\alpha,1;\beta,1}\{Im[(\varphi_{\alpha,o}|{}^{\alpha}\underline{\mu}_{e}|\varphi_{\alpha,1})\cdot(\varphi_{\beta,1}|{}^{\beta}\underline{\mu}_{m}|\varphi_{\beta,o})]\}\Big\} \end{aligned} \tag{79} $$

Choice of Chromophoric Reference Points

The chromophoric reference points $\underline{R}_\alpha$ introduced in Eq. (25) were left unspecified, except for the requirement of identical relative locations within the chromophores. The partial absorption intensity in Eqs. (37)–(39) and the partial CD intensity in Eqs. (41)–(47) are invariant to the choice of reference points, whereas the relative magnitudes of the terms resulting from the separation into electric dipole–electric dipole and inherent CD contributions in Eqs. (42)–(44), and from the separation of the inherent CD contribution into multipolar terms in Eqs. (45)–(47), are sensitive to first order in the choice of reference points, in line with the general discussion of the translational properties in Ref. [56]. If all optical CD coupling tensor contributions are retained, the exciton absorption and CD spectra simulated from the partial intensity expressions using different choices of reference points will hence differ only as a consequence of the variation of the energy spectrum, Eq. (26), resulting from the reference point sensitivity of the interaction term, Eq. (32).

The reference point sensitivity of the band intensities is discussed in connection with Eqs. (60), (65), and (68), and in connection with Eqs. (77), (78), and (79). As with the spectra simulated from the partial intensity expressions, the spectra simulated from the expressions for the band intensities will differ only as a consequence of the reference point variation of the interaction term, Eq. (32), if all the optical CD tensor contributions are retained.

However, by the same token these remarks suggest that neglect of some of the optical CD tensor contributions may introduce serious errors in the predicted CD spectra, potentially compromising structure and chirality assignments. This aspect is discussed in the accompanying communication [56], in the context of the application of the concept of the partial optic axis for the choice of reference point and the exploitation of chromophore symmetry for the selection of the optical contributions.

Discussion

The material presented in this section provides a theoretical framework for analysis and computation of the anisotropic and isotropic molecular chiroptical properties generated by exciton coupling between electric dipole allowed localized excitations in a system of identical chromophoric units, and the formalism allows for the inclusion of chromophoric chiroptical contributions through retaining the local electric quadrupole and magnetic dipole chromophoric transition moments. Application of the resulting expressions for the anisotropic and isotropic partial intensities of the individual exciton transitions requires the evaluation of the interaction term in Eq. (32) and the solution of Eq. (26) for the determination of the exciton coefficients, in addition to the evaluation of the local multipolar transition moments in Eqs. (25), (48), and (49). The evaluation of the interaction term and of the multipolar transition moments in turn requires specification of the local chromophoric reference points $\underline{R}_\alpha$, as discussed in the last subsection of the preceeding section; see also Ref. [56]. The need for the explicit solution of Eq. (26) is circumvented in the expressions for the anisotropic and isotropic band intensities.

The essence of the structural and chiral information provided by the spectral simulations based on the partial intensity expressions and based on the band intensity expressions is the same. However, when applicable, structural and chiral correlations are most directly extracted from the band intensities. For the ACD and CD band intensities, the energetic and optical coupling between the chomophores reflecting the chiral nature of the secondary structure of the exciton system, *i.e.* the arrangement of the chromophores, are represented by the sign and magnitude of the ACD derivative terms in Eqs. (65) and (68) and the CD derivative terms in Eqs. (78) and (79), whereas the intensity of the unperturbed band shape term in Eqs. (68) and (79) depends entirely on the nature of the individual chromophores. For the absorption band intensity Eqs. (60) and (77), the secondary structure enters only through the line shift factors in Eq. (61), whereas the overall intensity is determined entirely by the nature of the individual chromophores, and the band shape is identical to the line shape of the individual chromophores except for the line shift.

Within the framework of an exciton approach, the essential limitations of the present formalism lie in the neglect of the doubly excited states in Eq. (22), which is counterbalanced by approximations in the energy terms, as discussed in the subsection on the description of the exciton states above, and in the neglect of higher singly excited chromophoric states (interband mixing), and of vibrational-electronic (vibronic) coupling effects. Interband mixing can play an important role in the description of the total intensities, since the intensities predicted within the exciton formalism are conservative, *i.e.* the band shape contributions proportional to the unperturbed chromophore line shape in Eqs. (60), (68), (77), and (79) integrate to the corresponding unperturbed chromophoric intensities, whereas the derivate band shape contributions in Eqs. (65), (68), (78), and (79) integrate to zero. In this context, deviations from conservative intensity patterns must therefore be ascribed to interband mixing [14, 15, 35, 69]. The neglect of vibronic effects is coupled to the present use of the socalled strong coupling exciton approach, see Refs. [6, 25, 70] for discussion and illustration of weak and strong coupling cases.

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Appendix: Mathematical Supplement

Notation for Complex Quantities

A complex quantity z can be written in the form of Eq. (A.1) where i is the imaginary unit, and the prefixes *Re* and *Im* denote the real and imaginary parts of z. By definition *Re* {z} and *Im* {z} both represent purely real quantities. Using z* to denote the complex conjugate of z, we have Eq. (A.2)

$$\mathrm{z} = Re\{\mathrm{z}\} + \mathrm{i}\, Im\{\mathrm{z}\} \tag{A.1}$$

$$Re\{\mathrm{z}\} = (1/2)\{\mathrm{z}^* + \mathrm{z}\}, \qquad Im\{\mathrm{z}\} = (\mathrm{i}/2)\{\mathrm{z}^* - \mathrm{z}\} \tag{A.2}$$

Vectors, Dyadics, and Tensors

Writing a Cartesian vector as $\underline{a} = \{a_1, a_2, a_3\}$, the dot and cross products of two vectors (Eq. (A.3)) produce a scalar quantity and a vector quantity. The components of the vector $\underline{c}$ are given by Eq. (A.4) where $\epsilon_{\alpha\beta\gamma}$ is the *Levi-Civita* symbol ($=1$ for $\alpha\beta\gamma = 123$ and cyclic permutations, $= -1$ for $\alpha\beta\gamma = 132$ and cyclic permutations, $= 0$ otherwise). In addition, two vectors can be combined in a dyadic product (Eq. (A.5)) producing a second rank *Cartesian* tensor represented by the 3×3 dimensional matrix constructed from the *Cartesian* components of the vectors $\underline{a}$ and $\underline{b}$. The dyadic product in Eq. (A.3) and the second rank unit tensor defined by Eq. (A.6) are special cases of a *Cartesian* second rank tensor with the general form of Eq. (A.7).

$$\underline{a} \cdot \underline{b} = \sum_{\alpha} a_{\alpha} b_{\alpha} = c \quad \text{and} \quad \underline{a} \times \underline{b} = \underline{c} \tag{A.3}$$

$$c_{\alpha} = \sum_{\beta} \sum_{\gamma} \epsilon_{\alpha\beta\gamma} a_{\beta} b_{\gamma} \tag{A.4}$$

$$\underline{a} : \underline{b} = \left\{ \begin{matrix} a_1 b_1 & a_1 b_2 & a_1 b_3 \\ a_2 b_1 & a_2 b_2 & a_2 b_3 \\ a_3 b_1 & a_3 b_2 & a_3 b_3 \end{matrix} \right\} \tag{A.5}$$

$$\mathbf{I} = \left\{ \begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix} \right\} \tag{A.6}$$

$$\boldsymbol{\Omega} = \left\{ \begin{matrix} \Omega_{11} & \Omega_{12} & \Omega_{13} \\ \Omega_{21} & \Omega_{22} & \Omega_{23} \\ \Omega_{31} & \Omega_{32} & \Omega_{33} \end{matrix} \right\} \tag{A.7}$$

In terms of the *Cartesian* unit vectors $\underline{e}_{\alpha}$ and $\underline{e}_{\beta}$ the tensor elements in Eq. (A.7) are given by Eq. (A.8).

$$\Omega_{\alpha\beta} = \underline{e}_{\alpha} \cdot \boldsymbol{\Omega} \cdot \underline{e}_{\beta} \tag{A.8}$$

The dyadic tensor allows two dot products (Eq. (A.9)) producing vector quantities, and two cross products (Eq. (A.10)) producing dyadic tensor quantities. Scalar quantities are obtained as shown by Eq. (A.11) and (A.12).

$$\underline{c} \cdot [\underline{a} : \underline{b}] = (\underline{c} \cdot \underline{a})\underline{b} \quad \text{and} \quad [\underline{a} : \underline{b}] \cdot \underline{c} = \underline{a}(\underline{b} \cdot \underline{c}) \tag{A.9}$$

$$[\underline{a} : \underline{b}] \times \underline{c} = \underline{a} : (\underline{b} \times \underline{c}) \quad \text{and} \quad \underline{c} \times [\underline{a} : \underline{b}] = (\underline{c} \times \underline{a}) : \underline{b} \tag{A.10}$$

$$\underline{c} \cdot [\underline{a} : \underline{b}] \cdot \underline{d} = (\underline{c} \cdot \underline{a})(\underline{b} \cdot \underline{c}) \tag{A.11}$$

$$\underline{c} \cdot \boldsymbol{\Omega} \cdot \underline{d} = \sum_{\alpha} \sum_{\beta} c_{\alpha} \Omega_{\alpha\beta} d_{\beta} \tag{A.12}$$

We note further that the dyadic tensor $\underline{a} : \underline{b}$, Eq. (A.3), is not necessarily symmetric in the *Cartesian* indices, *i.e.* $a_{\alpha} b_{\beta} \neq a_{\beta} b_{\alpha}$ in general. However, from the decomposition in Eq. (A.13) we obtain a symmetric and an antisymmetric tensor with the *Cartesian* components (Eqs. (A.14) and (A.15)), *cf.* Eq. (A.8), where the antisymmetric part contains the cross product of the two vectors.

$$\underline{a}:\underline{b} = (1/2)\{\underline{a}:\underline{b}+\underline{b}:\underline{a}\} + (1/2)\{\underline{a}:\underline{b}-\underline{b}:\underline{a}) \tag{A.13}$$

$$\underline{e}_\alpha \cdot \{\underline{a}:\underline{b}+\underline{b}:\underline{a}\} \cdot \underline{e}_\beta = \underline{e}_\beta \cdot \{\underline{a}:\underline{b}+\underline{b}:\underline{a}\} \cdot \underline{e}_\alpha \tag{A.14}$$

$$\underline{e}_\alpha \cdot \{\underline{a}:\underline{b}-\underline{b}:\underline{a}\} \cdot \underline{e}_\beta = \sum_\gamma \epsilon_{\alpha\beta\gamma}\{\underline{e}_\gamma \cdot (\underline{a}\times\underline{b})\} = -\underline{e}_\beta \cdot \{\underline{a}:\underline{b}-\underline{b}:\underline{a}\} \cdot \underline{e}_\alpha \tag{A.15}$$

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