Optical activity of electronically delocalized molecular aggregates: Nonlocal response formulation

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A unified description of circular dichroism and optical rotation in small optically active molecules, larger conjugated molecules, and molecular aggregates is developed using spatially nonlocal electric and magnetic optical response tensors $\boldsymbol{\chi}(\mathbf{r},\mathbf{r}',\omega)$. Making use of the time dependent Hartree Fock equations, we express these tensors in terms of delocalized electronic oscillators. We avoid the commonly-used long wavelength (dipole) approximation $\mathbf{k}\cdot\mathbf{r}\ll 1$ and include the full multipolar form of the molecule–field interaction. The response of molecular aggregates is expressed in terms of monomer response functions. Intermolecular Coulomb interactions are rigorously taken into account thus eliminating the necessity to resort to the local field approximation or to a perturbative calculation of the aggregate wave functions. Applications to naphthalene dimers and trimers show significant corrections to the standard interacting point dipoles treatment.
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I. INTRODUCTION

Circular dichroism (CD), i.e., the difference in absorption of right and left circularly polarized light has long been used in the investigation of structural properties of extended chiral molecules or aggregates. This technique exploits the spatial variation of the electromagnetic field across the molecule and yields valuable structural information, which is missed by the ordinary linear absorption (LA). It has been used in the investigation of a variety of systems including polythiophenes,[1] polynucleotides,[2,3] helical polymers,[4–6] molecular crystals,[7,8] and antenna systems and the reaction center of photosynthesis.[9–12] Also commonly used are other related signatures of optical activity (OA), i.e., optical rotation (OR) and ellipticity.

A molecular theory for optical activity was first formulated by Born,[13] and almost simultaneously by Oseen.[14] Born attributed the origin of optical activity to the spatial variation of the electromagnetic field over the system under investigation. Rosenfeld reformulated these ideas in terms of the quantum-mechanical theory of dispersion.[15] These results were later derived as scattering problems in quantum field theory.[16] The next step was the development of polarizability theories, which express the optical rotatory power (ORP) of a molecule in terms of the configuration and polarizabilities of its constituent groups.[17–20] In transparent spectral regions, Kirkwood achieved this goal by applying Borns' theory to a molecule which he separated into smaller units, and perturbatively calculating the wavefunctions modified by the interaction of these subunits. Moffitt and Moscowitz also studied absorptive spectral regions. By using complex polarizabilities they worked out a unified description of dispersive (refraction, optical rotation) and absorptive (linear absorption, circular dichroism) properties.[21] They established Kramers–Kronig relations between OR and CD and further discussed the effects of vibrational degrees of freedom on these observables.

De Voe approached this many-body problem by applying the local field approximation (LFA) which accounts for intermolecular electrostatic interactions via a local field which—at a point like molecule in an aggregate—is the superposition of the external field and the field induced by the surrounding molecules modeled as point dipoles. He thus expressed LA and OR of unaggregated monomers, aggregates in solution, and molecular crystals in terms of the aggregate geometry and the complex polarizabilities of the constituent monomers. Using this method, Applequist calculated the polarizabilities of halomethanes,[22] and presented a normal mode analysis of polarizabilities and OR.[23,24] When dealing with solvated molecules or aggregates, the local field should also include the contribution from the solvent.[25,26]

In all models discussed since then, the spatial variation of the field with wavevector $\mathbf{k}$ was accounted for by the expansion $e^{i\mathbf{kr}} \approx 1 + i\mathbf{kr} + \cdots$. Usually the series is truncated after the second (dipole) or third (quadrupole) term. The molecule itself is modeled by an electric and a magnetic transition dipole moment. Larger molecules or aggregates are regarded as an assembly of point-like units, each having an electric and a magnetic transition dipole moment. Charge transfer between units is neglected and their mutual coupling is given by the dipole–dipole interaction. De Voe also improved the description of the interaction between units, replacing the dipole–dipole interaction term T_{ij} by the intermolecular interaction of all point-charges (point monopole approximation) contained in units i and j.[25] This correction is essential when the dimensions of the units are comparable to their separation, as is the case in typical aggregates of polynucleotides.[2,3]

The purpose of this paper is to develop a computationally feasible procedure for the investigation of OA which avoids the commonly used multipolar expansion and replaces the LFA by a rigorous treatment of intermolecular electrostatic interactions. To set the stage, we shall briefly review the conventional theory of OA using the notation of Moffitt and Moscowitz.[21] It is based on the observation, that

the induced electric dipole moment is not only proportional to the electric field, but also to the magnetic field and its time derivative. Analogously, the induced magnetic dipole moment is proportional to the magnetic field, as well as to the electric field and its time derivative

$$\boldsymbol{\mu}_\omega = \alpha(\omega)\mathbf{E}_\omega + \gamma(\omega)\mathbf{H}_\omega - \beta(\omega)\frac{\partial \mathbf{H}_\omega}{\partial t}, \tag{1}$$

$$\boldsymbol{m}_\omega = \chi(\omega)\mathbf{H}_\omega + \gamma(\omega)\mathbf{E}_\omega - \beta(\omega)\frac{\partial \mathbf{E}_\omega}{\partial t}, \tag{2}$$

where α, κ are the polarizability and magnetizability of the molecule and $\mathbf{E}_\omega, \mathbf{H}_\omega$ are monochromatic fields with frequency ω. The coefficient γ has no effect on OA, and β which is responsible for OA, can be separated into real and imaginary parts according to

$$\beta = \beta_1 + i\beta_2, \tag{3}$$

which are related to each other via the Kramers Krönig relations [Eq. (52) in Ref. 21]. For transparent regions one obtains

$$\beta_1 = \frac{4\pi c}{33\hbar}\sum_i \frac{R_{i0}}{\omega_{i0}^2 - \omega^2}, \tag{4}$$

where the central quantities describing optical activity are the rotational strengths R_{i0} for transitions from the ground state $|0\rangle$ to an excited state $|i\rangle$ with transition frequency ω_{i0}. For systems much smaller than the optical wavelength they are given by

$$R_{0i} = \mathrm{Im}(\langle 0|\hat{\boldsymbol{\mu}}|i\rangle \cdot \langle i|\hat{\mathbf{m}}|0\rangle), \tag{5}$$

where $\hat{\boldsymbol{\mu}}$, $\hat{\mathbf{m}}$ denote the electric, and magnetic dipole moment operators of the entire system.

In an optically active medium, left and right circularly polarized light propagate with different speeds and are absorbed differently. In transparent regions the polarization vector of linearly polarized light is rotated by an angle which is proportional to the propagation distance. The optical rotation in radians per unit length is given by[21]

$$\phi = N\frac{n_0^2+2}{3}\frac{4\pi\omega^2}{c}\beta_1, \tag{6}$$

where N is the number density of molecules, and a correction factor for the surrounding medium with refraction index n_0 has been added. In absorptive regions linearly polarized light turns into elliptically polarized light after propagating through the medium, and ϕ denotes the angle between the long axis of the ellipse and the direction of polarization of the incident linearly polarized wave. The ellipticity Θ per unit length is given by[21]

$$\Theta = N\frac{n_0^2+2}{3}\frac{4\pi\omega^2}{c}\beta_2. \tag{7}$$

It is directly proportional to the difference in absorption of right and left circularly polarized light $\Delta\epsilon$, i.e., the CD signal

$$\Delta\epsilon = 33\Theta. \tag{8}$$

An early yet very instructive review on theories of optical rotatory power was written by Condon.[27] A clear discussion of CD at a minimum level of complexity (time dependent perturbation theory with simple electric and magnetic dipole interaction) can be found in Ref. 28. Finally there are numerous textbooks covering theory and experiment exhaustively.[29–32]

In order to develop a unified microscopic approach to OA which applies to a broad class of molecular systems we shall employ nonlocal response tensors, which relate the induced linear polarization $\tilde{\mathbf{P}}(\mathbf{r},\omega)$ and magnetization $\tilde{\mathbf{M}}(\mathbf{r},\omega)$ to the driving electric and magnetic fields $\mathbf{E}_{\mathrm{ext}}(\mathbf{r},\omega), \mathbf{H}_{\mathrm{ext}}(\mathbf{r},\omega)$ via the linearized relationships

$$\tilde{\mathbf{P}}(\mathbf{r},\omega) = \int d\mathbf{r}' \,[\boldsymbol{\alpha}(\mathbf{r},\mathbf{r}';\omega)\cdot\mathbf{E}_{\mathrm{ext}}(\mathbf{r}',\omega) + \boldsymbol{\beta}(\mathbf{r},\mathbf{r}';\omega)\cdot\mathbf{H}_{\mathrm{ext}}(\mathbf{r}',\omega)], \tag{9}$$

$$\tilde{\mathbf{M}}(\mathbf{r},\omega) = \int d\mathbf{r}' \,[\boldsymbol{\gamma}(\mathbf{r},\mathbf{r}';\omega)\cdot\mathbf{E}_{\mathrm{ext}}(\mathbf{r}',\omega) + \boldsymbol{\kappa}(\mathbf{r},\mathbf{r}';\omega)\cdot\mathbf{H}_{\mathrm{ext}}(\mathbf{r}',\omega)]. \tag{10}$$

In this nonlocal response formulation (NLRF), the tensors $\boldsymbol{\chi}(\mathbf{r},\mathbf{r}';\omega), \boldsymbol{\chi} = \boldsymbol{\alpha},\boldsymbol{\beta},\boldsymbol{\gamma},\boldsymbol{\kappa}$ are intrinsic molecular properties that describe all linear optical phenomena. Structural and chemical details of different systems enter through their effects on these tensors. By using *nonlocal* response tensors we completely avoid the commonly employed multipolar expansion, which uses the induced electric and magnetic dipole, quadrupole, octopole, etc. moments. If so desired, the latter can be calculated by integrating Eqs. (9,10) over $\mathbf{r}$ and expanding the driving electric and magnetic fields around a reference point of the molecule. By formulating the problem this way we can defer the introduction of details to the final stage of the calculation. This enables us to unify many of the treatments in the literature that are restricted to specific models (e.g., aggregates of point dipoles, etc.).

We already employed the nonlocal polarizability tensor $\boldsymbol{\alpha}(\mathbf{r},\mathbf{r}',\omega)$ for investigating the anisotropy of the linear absorption, and for gaining insight into the role of intramolecular coherences.[33–36] When magnetic interactions contribute to the linear response, the magnetizability $\boldsymbol{\kappa}(\mathbf{r},\mathbf{r}',\omega)$ and the cross response tensors $\boldsymbol{\beta}(\mathbf{r},\mathbf{r}',\omega)$, $\boldsymbol{\gamma}(\mathbf{r},\mathbf{r}',\omega)$ enter the picture as well. We will show that these tensors fully determine the CD signal, so that the level of rigor is determined by the approximations applied for their calculation. By using the multipolar Hamiltonian and the time dependent Hartree Fock (TDHF) procedure we derive general formulas for these response tensors which contain the full multipolar expansion, thus avoiding the dipole approximation ($\mathbf{kr} \ll 1$). When investigating molecular aggregates we will go beyond the commonly used local field approximation [LFA, see Eqs. (65, 67) below] and rigorously express the nonlocal response tensors in terms of those of the monomers. Using this method, intermolecular interactions are fully incorporated, and the need for a perturbative expansion of the aggregate

wavefunctions is eliminated, providing a clear advantage over the commonly used point dipole or point monopole approximations.

In Sec. II we derive an expression for the CD signal of a spatially extended molecular system using the electric and magnetic nonlocal response tensors. We next calculate the latter in Sec. III using the TDHF equations. In Sec. IV we express the aggregate response in terms of the response functions of its constituent monomers. Applying the point dipole and local field approximations we retrieve Tinoccos' formulas for the rotational strengths in Sec. V. We then apply these results to naphthalene dimers and trimers in Sec. VI, and summarize in Sec. VII.

II. NONLOCAL RESPONSE FORMULATION OF CIRCULAR DICHROISM

The multipolar Hamiltonian describing a molecular system interacting with a classical electromagnetic field is given by[32,37]

$$\hat{H}^{sc}=\hat{H}_m+\hat{V}_{\text{inter}}+\hat{H}' - \int d\mathbf{r}[\hat{\mathbf{P}}(\mathbf{r})\cdot\mathbf{E}^{\perp}(\mathbf{r})+\hat{\mathbf{M}}(\mathbf{r})\cdot\mathbf{H}^{\perp}(\mathbf{r})].$$

Here H_m denotes the molecular Hamiltonian, and

$$\hat{V}_{\text{inter}}=\sum_{s<t}\int d\mathbf{r}\int d\mathbf{r}'[\hat{\mathbf{P}}_s\mathbf{T}(\mathbf{r}-\mathbf{r}')\hat{\mathbf{P}}_t+\hat{\mathbf{M}}_s\mathbf{T}(\mathbf{r}-\mathbf{r}')\hat{\mathbf{M}}_t],$$

describes the interaction between the electric and magnetic dipole densities of the electrons, defined as

$$\hat{\mathbf{P}}_s(\mathbf{r})=-e(\hat{\mathbf{r}}_s-\mathbf{R})\int_0^1 d\lambda\ \delta(\mathbf{r}-\mathbf{R}-\lambda(\hat{\mathbf{r}}_s-\mathbf{R})), \tag{11}$$

$$\hat{\mathbf{M}}_s(\mathbf{r})=-e(\hat{\mathbf{r}}_s-\mathbf{R})\times\hat{\mathbf{p}}_s\int_0^1 d\lambda\ \lambda\,\delta(\mathbf{r}-\mathbf{R}-\lambda(\hat{\mathbf{r}}_s-\mathbf{R})), \tag{12}$$

where $\mathbf{R}$ is an arbitrary reference point, $-e$ is the electron charge, $\hat{\mathbf{r}}_s$ denote the position operators of the charges labeled by s, and $\hat{\mathbf{p}}_s$ is the corresponding canonical momentum. The polarization $\mathbf{P}(\mathbf{r},t)=\langle\psi(t)|\hat{\mathbf{P}}(\mathbf{r})|\psi(t)\rangle$ is given by the expectation value of the microscopic polarization operator[32]

$$\hat{\mathbf{P}}(\mathbf{r})=\sum_s\ \hat{\mathbf{P}}_s(\mathbf{r}), \tag{13}$$

where $|\psi(t)\rangle$ is the electronic wavefunction. The magnetization $\mathbf{M}(\mathbf{r},t)=\langle\psi(t)|\hat{\mathbf{M}}(\mathbf{r})|\psi(t)\rangle$ is similarly defined as the expectation value of the microscopic magnetization operator[32]

$$\hat{\mathbf{M}}(\mathbf{r})=\sum_s\ \hat{\mathbf{M}}_s(\mathbf{r}), \tag{14}$$

and $\mathbf{F}^{\perp}$ denotes the transverse part of a vector field $\mathbf{F}$, defined by

$$\mathbf{F}^{\perp}(\mathbf{r})=\int d\mathbf{r}'\,\boldsymbol{\delta}^{\perp}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{F}(\mathbf{r}'),$$

with the transverse δ-function

$$\boldsymbol{\delta}^{\perp}(\mathbf{r})=\frac{2}{3}\mathbf{1}\delta(\mathbf{r})-\frac{1}{4\pi r^3}(\mathbf{1}-3\hat{\mathbf{r}}\hat{\mathbf{r}}).$$

Here we use a dyadic notation for the tensor product $\hat{\mathbf{r}}\hat{\mathbf{r}}$.

Both polarization and magnetization depend on the reference point $\mathbf{R}$, but their transverse parts entering Maxwells' equations for the observable fields (see below), do not. This follows from the gauge invariance of the observable transverse fields.

The third term in the Hamiltonian

$$H'=\sum_s\int d\mathbf{r}\,|\mathbf{m}_s^{\perp}(\mathbf{r})|^2+\frac{2}{3}{\sum_{s,t}}'\int d\mathbf{r}\ \mathbf{m}_s(\mathbf{r})\cdot\mathbf{m}_t(\mathbf{r}),$$

is quadratic in the magnetization densities $\hat{\mathbf{m}}_s$, and we have omitted terms quadratic in the magnetic field, as they do not contribute to the linear response. Finally, the last term in the Hamiltonian represents the coupling of the system to the external transverse electric and magnetic fields.

We start our analysis with the microscopic Maxwell equations for the electric and magnetic fields $\mathbf{E}(\mathbf{r},t)$ and $\mathbf{H}(\mathbf{r},t)$ (Ref. 32)

$$\nabla\times\mathbf{E}^{\perp}(\mathbf{r},t)=-\frac{1}{c}\frac{\partial}{\partial t}[\mathbf{H}(\mathbf{r},t)+4\pi\mathbf{M}(\mathbf{r},t)]^{\perp}, \tag{15}$$

$$\nabla\times\mathbf{H}(\mathbf{r},t)=\frac{1}{c}\frac{\partial}{\partial t}[\mathbf{E}(\mathbf{r},t)+4\pi\mathbf{P}(\mathbf{r},t)]^{\perp}. \tag{16}$$

Here c is the vacuum speed of light. The rhs of Eqs. (15, 16) are transverse, as $\nabla\cdot\mathbf{D}=\nabla\cdot\mathbf{B}=0$ with $\mathbf{D}\equiv\mathbf{E}+4\pi\mathbf{P}$ and $\mathbf{B}\equiv\mathbf{H}+4\pi\mathbf{M}$. However, for the sake of clarity we add the symbol $\perp$ explicitly in the derivation below.

We shall switch to the frequency domain by the Fourier transform

$$\tilde{f}(\omega)=\int_{-\infty}^{\infty}dt\ e^{i\omega t}f(t),$$

$$f(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\ e^{-\omega t}\tilde{f}(\omega).$$

The induced electric and magnetic dipole moment densities can be expanded in a power series in the driving fields. For linear absorption, the first terms Eq. (9, 10) in these expansions are needed. $\boldsymbol{\alpha}(\mathbf{r},\mathbf{r}';\omega)$ denotes the nonlocal electric polarizability tensor, $\boldsymbol{\kappa}(\mathbf{r},\mathbf{r}';\omega)$ the nonlocal magnetizability tensor, and the remaining cross response tensors describe the effects of the magnetic (electric) field on the polarization (magnetization). They have the symmetries

$$\alpha^{ij}(\mathbf{r},\mathbf{r}';\omega)=\alpha^{ji}(\mathbf{r}',\mathbf{r};\omega), \tag{17}$$

$$\kappa^{ij}(\mathbf{r},\mathbf{r}';\omega)=\kappa^{ji}(\mathbf{r}',\mathbf{r};\omega), \tag{18}$$

$$\beta^{ij}(\mathbf{r},\mathbf{r}';\omega)=-\gamma^{ji}(\mathbf{r}',\mathbf{r};\omega), \tag{19}$$

where the indices i, j denote Cartesian components. Note that we have defined these tensors with respect to the external fields $\mathbf{E}_{\rm ext}$, $\mathbf{H}_{\rm ext}$ [Eqs. (9, 10)].

The absorption cross section σ_A of an arbitrary system can be calculated by integrating the Poynting vector of the electromagnetic field over a closed surface encompassing it. For a monochromatic field with frequency $\omega=2\pi/T$ we find (see Appendix)

$$\sigma_A=\frac{1}{\Phi_{\rm in}}\frac{1}{T}\int_0^T dt\int_V d\mathbf{r}\left[\mathbf{E}^{\perp}(\mathbf{r},t)\cdot\frac{\partial\mathbf{P}(\mathbf{r},t)}{\partial t}+\mathbf{H}^{\perp}(\mathbf{r},t)\cdot\frac{\partial\mathbf{M}(\mathbf{r},t)}{\partial t}\right], \tag{20}$$

where $\Phi_{\rm in}=(1/T)\int dt(c/4\pi)|\mathbf{E}_{\rm ext}\times\mathbf{H}_{\rm ext}|$ is the time-averaged incident energy flux. The solution of the coupled Maxwell equations Eqs. (15, 16) can be written in the form (see Appendix)

$$\mathbf{E}^{\perp}=\mathbf{E}_{\rm ext}+\mathbf{E}',$$

$$\mathbf{H}^{\perp}=\mathbf{H}_{\rm ext}+\mathbf{H}',$$

where $\mathbf{E}'$, $\mathbf{H}'$ are the solutions of the inhomogeneous part of the wave equations and can be expressed in terms of the retarded Greens' function. Consequently the absorption cross section can be written as (see Appendix)

$$\sigma_A=\sigma_A^{(0)}+\sigma_A^{(1)}. \tag{21}$$

The first term

$$\sigma_A^{(0)}=\frac{1}{\Phi_{\rm in}}\frac{1}{T}\int_0^T dt\int_V d\mathbf{r}\left[\mathbf{E}_{\rm ext}(\mathbf{r},t)\cdot\frac{\partial\mathbf{P}(\mathbf{r},t)}{\partial t}+\mathbf{H}_{\rm ext}(\mathbf{r},t)\cdot\frac{\partial\mathbf{M}(\mathbf{r},t)}{\partial t}\right] \tag{22}$$

is obtained from Eq. (20) by replacing the transverse Maxwell field by the external field. $\sigma_A^{(1)}$ which is given in Eq. (A15) contains the effects of multiple scattering in the sample. It becomes important when scattering phenomena of large particles such as proteins or DNA strands have to be accounted for. Hereafter we shall only consider $\sigma_A^{(0)}$. To establish the connection with macroscopic observables we assume a sample with ρ_N noninteracting aggregates per unit volume. The change of intensity I with the penetration depth l is given by $dI=-I\rho_N\sigma_A dl$, resulting in

$$I(l)=I_0e^{-\rho_N\sigma_A l}.$$

Substituting a linearly polarized incident plane wave propagating in the z direction

$$\mathbf{E}_{\rm ext}(\mathbf{r},t)=\frac{E_0}{\sqrt{2}}\mathbf{e}_x(e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}+e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}),$$

$$\mathbf{H}_{\rm ext}(\mathbf{r},t)=\frac{H_0}{\sqrt{2}}\mathbf{e}_y(e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}+e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}),$$

with $H_0=nE_0$, and $\mathbf{e}_y=\mathbf{e}_z\times\mathbf{e}_x$ into Eq. (22), yields the absorption cross section for a molecule embedded in a medium with refractive index n

$$\sigma_A^{(0)}(\omega)=\frac{4\pi\omega}{nc}{\rm Im}\int d\mathbf{r}\int d\mathbf{r}'\ e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\left[\frac{\alpha^{xx}(\mathbf{r},\mathbf{r}',\omega)}{n}+n\kappa^{yy}(\mathbf{r},\mathbf{r}',\omega)+\gamma^{yx}(\mathbf{r},\mathbf{r}',\omega)+\beta^{xy}(\mathbf{r},\mathbf{r}',\omega)\right]. \tag{23}$$

Here $\alpha^{ij}\equiv\mathbf{e}_i\cdot\boldsymbol{\alpha}\cdot\mathbf{e}_j$, etc. denote the tensor components. In the long wavelength approximation $e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\approx1$ the cross terms β,γ cancel each other because of the symmetry Eq. (19) and we obtain the familiar result[38,37]

$$\lim_{k\to0}\sigma_A^{(0)}(\omega)=\frac{4\pi\omega}{c}{\rm Im}\left[\frac{\alpha^{\rm tot}(\omega)}{n}+\kappa^{tot}n\right],$$

with $\alpha^{\rm tot}(\omega)=\int d\mathbf{r}\int d\mathbf{r}'\mathbf{e}_1\cdot\boldsymbol{\alpha}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{e}_1$, $\kappa^{\rm tot}(\omega)=\int d\mathbf{r}\int d\mathbf{r}'\mathbf{e}_2\cdot\boldsymbol{\kappa}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{e}_2$.

By specializing to circularly polarized plane waves we can express the CD signal in terms of the nonlocal electric and magnetic response functions. A right $(+)$ or left $(-)$ circularly polarized plane wave propagating in z direction $[\mathbf{k}=(n\omega/c)\mathbf{e}_z,\ k=(2\pi/\lambda)]$ can be represented in the form

$$\mathbf{E}_{\rm ext}^{\pm}(\mathbf{r},t)=E_0[\mathbf{e}_x\cos(\mathbf{k}\cdot\mathbf{r}-\omega t)\pm\mathbf{e}_y\sin(\mathbf{k}\cdot\mathbf{r}-\omega t)], \tag{24}$$

$$\mathbf{H}_{\rm ext}^{\pm}(\mathbf{r},t)=H_0[\mp\mathbf{e}_x\sin(\mathbf{k}\cdot\mathbf{r}-\omega t)+\mathbf{e}_y\cos(\mathbf{k}\cdot\mathbf{r}-\omega t)]. \tag{25}$$

It is customary to use the separation

$$\sigma_{A\pm}=\overline{\sigma_A}\pm\Delta\sigma_A, \tag{26}$$

with

$$\overline{\sigma_A}=\frac{\sigma_{A+}+\sigma_{A-}}{2},$$

$$\Delta\sigma_A=\frac{\sigma_{A+}-\sigma_{A-}}{2}.$$

Here $\overline{\sigma_A}$ denotes the average absorption, and $\Delta\sigma_A$ is the CD signal. When substituting these fields into Eq. (22) we find (see Appendix)

$$\overline{\sigma_A^{(0)}}(\omega)=\frac{4\pi\omega}{c}{\rm Re}\int d\mathbf{r}\int d\mathbf{r}'e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\times\left\{\frac{\alpha^{xx}(\mathbf{r},\mathbf{r}',\omega)+\alpha^{yy}(\mathbf{r},\mathbf{r}',\omega)}{n}+[\kappa^{xx}(\mathbf{r},\mathbf{r}',\omega)-\kappa^{yy}(\mathbf{r},\mathbf{r}',\omega)]n-[\beta^{yx}(\mathbf{r},\mathbf{r}',\omega)-\beta^{xy}(\mathbf{r},\mathbf{r}',\omega)-\gamma^{yx}(\mathbf{r},\mathbf{r}',\omega)+\gamma^{xy}(\mathbf{r},\mathbf{r}',\omega)]\right\}. \tag{27}$$

$$\Delta\sigma_A^{(0)}(\omega)=\frac{4\pi\omega}{c}\mathrm{Re}\int d\mathbf{r}\int d\mathbf{r}'\,e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\times\Bigg\{\frac{\alpha^{yx}(\mathbf{r},\mathbf{r}',\omega)-\alpha^{xy}(\mathbf{r},\mathbf{r}',\omega)}{n}+[\kappa^{yx}(\mathbf{r},\mathbf{r}',\omega)-\kappa^{xy}(\mathbf{r},\mathbf{r}',\omega)]n-[\beta^{xx}(\mathbf{r},\mathbf{r}',\omega)+\beta^{yy}(\mathbf{r},\mathbf{r}',\omega)-\gamma^{xx}(\mathbf{r},\mathbf{r}',\omega)-\gamma^{yy}(\mathbf{r},\mathbf{r}',\omega)]\Bigg\}. \tag{28}$$

This exact expression which relates the CD signal of an arbitrary molecular system to its nonlocal electric and magnetic response tensors [defined by Eqs. (9, 10)] forms the basis for our subsequent analysis. Equation (28) is not restricted to a specific order of the widely used multipolar expansion. The latter is completely avoided by using *nonlocal* response tensors, which implicitly include *all* multipoles. The problem of the unphysical origin dependence connected with the electric quadrupole and higher moments, discussed e.g., in Refs. 39,40, is naturally resolved with our approach. As can be seen from Eq. (22), our result does not depend on the origin. The scalar product with the external fields $\mathbf{E}_{\mathrm{ext}},\mathbf{H}_{\mathrm{ext}}$ which are intrinsically transverse, ensures, that only the transverse part of the polarization $\mathbf{P}$ and the magnetization $\mathbf{M}$, respectively enter the absorption cross section, and—as indicated earlier—they do not depend on $\mathbf{R}$. No specific model of the system has been assumed yet (for example, these expressions hold whether the molecular states are localized or delocalized), and no assumptions were made on the system-size in comparison with the optical wavelength. All approximations will enter through the different levels of rigor used in modeling the nonlocal response tensors.

In the long wavelength limit $\mathbf{k}(\mathbf{r}-\mathbf{r}')=0$ the CD signal vanishes, which follows from Eqs. (17–19) and interchanging the integration variables $\mathbf{r}\leftrightarrow\mathbf{r}'$. This is to be expected since a finite spatial extent of the system (compared with the optical wavelength) is necessary in order to observe chirality. The leading term in a multipolar expansion is thus obtained assuming $e^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')}\approx 1-i\mathbf{k}(\mathbf{r}-\mathbf{r}')$ which will lead to the celebrated Tinoco formulae.[29,41]

III. CALCULATION OF THE NONLOCAL RESPONSE TENSORS USING THE TIME DEPENDENT HARTREE FOCK EQUATIONS

Consider an N-electron system (a molecule or an aggregate) which we describe using single electron basis functions $\psi_m, m=1,\ldots,N$. We define $\hat{c}_m^\dagger$ ($\hat{c}_m$) as the creation (annihilation) operators of an electron at site m. We further introduce the reduced single electron density matrix ρ with matrix elements $\rho_{mn}\equiv\langle\hat{c}_m^\dagger\hat{c}_n\rangle$. Since the polarization and magnetization are single-electron operators, their expectation values can be expanded using the density matrix

$$\mathbf{P}(\mathbf{r},\omega)=\sum_{mn}\rho_{mn}(\omega)\mathscr{P}_{mn}(\mathbf{r}), \tag{29}$$

where

$$\mathscr{P}_{mn}(\mathbf{r})=\langle\psi_m|\hat{\mathbf{P}}|\psi_n\rangle, \tag{30}$$

are the matrix elements of the polarization operator Eq. (13). Similarly, the expectation value of the magnetization is given by

$$\mathbf{M}(\mathbf{r},\omega)=\sum_{mn}\rho_{mn}(\omega)\mathscr{M}_{mn}(\mathbf{r}), \tag{31}$$

where the matrix elements of the magnetization operator are defined by

$$\mathscr{M}_{mn}(\mathbf{r})=\langle\psi_m|\hat{\mathbf{M}}|\psi_n\rangle. \tag{32}$$

To calculate the linear optical response we expand the density matrix to first order in the driving fields setting $\rho_{mn}(\omega)=\overline{\rho_{mn}}(\omega)+\delta\rho_{mn}^{(1)}(\omega)$. Here $\overline{\rho_{mn}}$ is the reduced one electron ground state density matrix obtained by iterative diagonalization.[42] The dynamics of the linear response $\delta\rho_{mn}^{(1)}(\omega)$ in Liouville space will be calculated using the time dependent Hartree Fock (TDHF) procedure, resulting in the equation of motion[35,36,42,43]

$$\hbar\omega\,\delta\rho_{mn}^{(1)}(\omega)-\sum_{kl}A_{mn,kl}\delta\rho_{kl}^{(1)}(\omega)+i\sum_{kl}\Gamma_{mn,kl}\delta\rho_{kl}^{(1)}(\omega)=F_{mn}(\omega). \tag{33}$$

The source F_{mn} is given by

$$F_{mn}(\omega)=[\overline{\rho},V(\omega)]_{mn}, \tag{34}$$

with

$$V_{mn}(\omega)=\int d\mathbf{r}[\mathscr{P}_{mn}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r},\omega)+\mathscr{M}_{mn}(\mathbf{r})\cdot\mathbf{H}(\mathbf{r},\omega)], \tag{35}$$

and the matrices A,Γ are defined in Ref. 43. Terms quadratic in the magnetic field have been neglected in Eq. (33), as we are interested in linear absorption. Equation (33) generalizes the results of Refs. 35, 36, 43 to include the magnetic interaction $\mathbf{M}\cdot\mathbf{H}$ as well as off-diagonal matrix elements $\mathscr{P}_{mn}$ in F_{mn}. The TDHF procedure deals with physically relevant quantities (charges ρ_{nn} and electronic coherences ρ_{mn}), and a dominant mode picture can be developed which greatly reduces computational cost.[44] By using position-dependent electric and magnetic dipole densities which can be calculated from the electronic basis set we avoid the long wavelength approximation and the following expressions for the polarizabilities hold for arbitrary system size.

The solution of this TDHF equation can be written in the form

$$\delta\rho_{mn}^{(1)}(\omega)=\sum_{kl}\tilde{\alpha}_{mn,kl}(\omega)V_{kl}(\omega), \tag{36}$$

with the nonlocal response matrix

$$\tilde{\alpha}_{mn,kl}(\omega)=\sum_{\nu}\sum_{t}\frac{S_{mn,\nu}[S^{-1}_{\nu,tl}\overline{\rho_{tk}}-S^{-1}_{\nu,kt}\overline{\rho_{lt}}]}{\omega-\omega_\nu+i\gamma_\nu}. \tag{37}$$

Here $S_{mn,\nu}$ diagonalizes the matrix $A_{mn,kl}$ according to

$$\sum_{mnkl} S^{-1}_{\nu,mn} A_{mn,kl} S_{kl,\nu'} = \hbar\omega_\nu \delta_{\nu,\nu'}, \tag{38}$$

and γ_ν are radiative damping constants. The expectation values of Eqs. (29, 31) then satisfy Eqs. (9, 10), with

$$\boldsymbol{\alpha}(\mathbf{r},\mathbf{r}',\omega) = \sum_{mn,kl} \tilde{\alpha}_{mn,kl}(\omega) \mathscr{P}_{mn}(\mathbf{r}) \mathscr{P}_{kl}(\mathbf{r}'), \tag{39}$$

$$\boldsymbol{\beta}(\mathbf{r},\mathbf{r}',\omega) = \sum_{mn,kl} \tilde{\alpha}_{mn,kl}(\omega) \mathscr{P}_{mn}(\mathbf{r}) . \mathscr{M}_{kl}(\mathbf{r}'), \tag{40}$$

$$\boldsymbol{\gamma}(\mathbf{r},\mathbf{r}',\omega) = \sum_{mn,kl} \tilde{\alpha}_{mn,kl}(\omega) . \mathscr{M}_{mn}(\mathbf{r}) \mathscr{P}_{kl}(\mathbf{r}'), \tag{41}$$

$$\boldsymbol{\kappa}(\mathbf{r},\mathbf{r}',\omega) = \sum_{mn,kl} \tilde{\alpha}_{mn,kl}(\omega) . \mathscr{M}_{mn}(\mathbf{r}) . \mathscr{M}_{kl}(\mathbf{r}'). \tag{42}$$

All response tensors factorize into the discrete nonlocal response matrix Eq. (37) and position-dependent tensor products of electric and magnetic dipole densities such as $\mathscr{P}_{mn}(\mathbf{r})\mathscr{P}_{kl}(\mathbf{r}')$. In practice these expressions are limited to small systems, as the required memory scales with the fourth power of the basis set size. This problem can be remedied by the coupled electronic oscillator (CEO) picture.[35,36,42–44] The matrix $S_{kl,\nu}$ can be regarded as a transformation matrix from the site representation to a nonlocal mode representation. Since A is not symmetric, S is in general a complex matrix. However, one can show that all eigenvalues ω_ν are real and come in pairs ω_ν, $\omega_{\bar{\nu}} = -\omega_\nu$.[43] Moreover, in applications to conjugated polymers the S matrix is real.[35,36] The transformations of the electric and magnetic transition dipole moment densities to this representation are given by

$$\boldsymbol{\mu}_\nu(\mathbf{r}) = \sum_{mn} \mathscr{P}_{mn}(\mathbf{r}) S_{mn,\nu}, \tag{43}$$

$$\mathbf{m}_\nu(\mathbf{r}) = \sum_{mn} \mathscr{M}_{mn}(\mathbf{r}) S_{mn,\nu}. \tag{44}$$

Without loss of generality we can choose the basis functions ψ_n to be real. The polarization densities $\mathscr{P}_{mn}(\mathbf{r})$ are then purely real, and the magnetization densities $\mathscr{M}_{mn}(\mathbf{r})$ are zero for $m=n$, and purely imaginary for $m \neq n$. Consequently the electric transition dipole moments $\boldsymbol{\mu}_\nu(\mathbf{r})$ are real and the magnetic transition dipole moments $\mathbf{m}_\nu(\mathbf{r})$ are imaginary.

One can therefore follow similar steps as in Ref. 43, which finally yields

$$\boldsymbol{\alpha}(\mathbf{r},\mathbf{r}';\omega) = \frac{2}{\hbar}\sum_\nu \frac{\omega_\nu \boldsymbol{\mu}_\nu(\mathbf{r}) \boldsymbol{\mu}^*_\nu(\mathbf{r}')}{(\omega + i\gamma_\nu)^2 - \omega_\nu^2}, \tag{45}$$

$$\boldsymbol{\beta}(\mathbf{r},\mathbf{r}';\omega) = \frac{2}{\hbar}\sum_\nu \frac{(\omega + i\gamma_\nu) \boldsymbol{\mu}_\nu(\mathbf{r}) \mathbf{m}^*_\nu(\mathbf{r}')}{(\omega + i\gamma_\nu)^2 - \omega_\nu^2}, \tag{46}$$

$$\boldsymbol{\gamma}(\mathbf{r},\mathbf{r}';\omega) = \frac{2}{\hbar}\sum_\nu \frac{(\omega + i\gamma_\nu) \mathbf{m}_\nu(\mathbf{r}) \boldsymbol{\mu}^*_\nu(\mathbf{r}')}{(\omega + i\gamma_\nu)^2 - \omega_\nu^2}, \tag{47}$$

$$\boldsymbol{\kappa}(\mathbf{r},\mathbf{r}';\omega) = \frac{2}{\hbar}\sum_\nu \frac{\omega_\nu \mathbf{m}_\nu(\mathbf{r}) \mathbf{m}^*_\nu(\mathbf{r}')}{(\omega + i\gamma_\nu)^2 - \omega_\nu^2}. \tag{48}$$

Here the ν summation runs over particle-hole oscillators with frequency $\omega_\nu > 0$. The advantage of this picture is that typically very few oscillators contribute to the optical response,[42,44] leading to a drastic reduction in the number of terms compared with the (mn) summation in the site representation. Note that this form immediately yields the symmetry Eq. (19).

IV. NONLOCAL POLARIZABILITIES OF SPATIALLY EXTENDED AGGREGATES

We consider molecular aggregates with electrostatic intermolecular forces (no intermolecular charge exchange). In this case it is possible to rigorously express the global nonlocal response tensors in terms of nonlocal response tensors of the constituent monomers. These expressions greatly reduce computational cost and simplify the theoretical analysis. Usually molecular aggregates are treated within the LFA (Refs. 20, 25, 26, 22) which assume the individual molecules as point dipoles. The nonlocal expressions derived here using the TDHF equations are exact and provide a concrete means for modeling aggregates when molecular sizes are comparable to their separation so that the point dipole approximation is not expected to hold.

Consider an aggregate made out of M molecules labeled $a,b,c,\ldots$, each described by a basis set of N_a, N_b,... orbitals indicated by subscripts $a_i, b_j, \ldots$. We have shown earlier,[36] that all intermolecular coherences vanish ($\overline{\rho_{a_i b_j}} = \delta\rho^{(1)}_{a_i b_j} = 0$) when charge exchange is negligible. Eqs. (35, 29, 31, 36) lead to

$$\boldsymbol{\alpha}(\mathbf{r},\mathbf{r}',\omega) = \sum_{a,b} \sum_{i,j,k,l} \tilde{\alpha}_{a_i a_j, b_k b_l}(\omega) \mathscr{P}_{a_i a_j}(\mathbf{r}) \mathscr{P}_{b_k b_l}(\mathbf{r}'), \tag{49}$$

$$\boldsymbol{\beta}(\mathbf{r},\mathbf{r}',\omega) = \sum_{a,b} \sum_{i,j,k,l} \tilde{\alpha}_{a_i a_j, b_k b_l}(\omega) \mathscr{P}_{a_i a_j}(\mathbf{r}) . \mathscr{M}_{b_k b_l}(\mathbf{r}'), \tag{50}$$

$$\boldsymbol{\gamma}(\mathbf{r},\mathbf{r}',\omega) = \sum_{a,b} \sum_{i,j,k,l} \tilde{\alpha}_{a_i a_j, b_k b_l}(\omega) . \mathscr{M}_{a_i a_j}(\mathbf{r}) \mathscr{P}_{b_k b_l}(\mathbf{r}'), \tag{51}$$

$$\boldsymbol{\kappa}(\mathbf{r},\mathbf{r}',\omega) = \sum_{a,b} \sum_{i,j,k,l} \tilde{\alpha}_{a_i a_j, b_k b_l}(\omega) . \mathscr{M}_{a_i a_j}(\mathbf{r}) . \mathscr{M}_{b_k b_l}(\mathbf{r}'), \tag{52}$$

where intermolecular components $\mathscr{P}_{a_i b_j}, \mathscr{M}_{a_i b_j}$ were neglected. Following similar steps as used in Ref. 36 we first derive a closed EOM in the space of molecule a

$$\hbar\omega\,\delta\rho^{(1)}_{a_i a_j} - \sum_{kl} \overline{A}_{a_i a_j, a_k a_l} \delta\rho^{(1)}_{a_k a_l} = \sum_l \overline{\rho}_{a_i a_l} V^{loc}_{a_l a_j} - V^{loc}_{a_i a_l} \overline{\rho}_{a_l a_j}, \tag{53}$$

where the generalized local potential is defined as

$$V^{\mathrm{loc}}_{a_i b_j} = V_{a_i b_j} - 2\,\delta_{a_i b_j} \sum_{c\neq a,l} U_{a_i c_l}\delta\rho_{c_l c_l}. \tag{54}$$

The difference from Ref. 36 is that we now include nondiagonal matrix elements $V_{a_i b_j}$. The EOM is modified by the ground state charge distribution of the surrounding molecules according to

$$\overline{A}_{a_i a_j, a_k a_l} = A_{a_i a_j, a_k a_l} + \delta_{ik}\delta_{jl} \sum_{c\neq a,l} (U_{a_i c_l} - U_{a_j c_l})(2\overline{\rho}_{c_l c_l} - 1), \tag{55}$$

where $U_{a_i c_l}$ denotes the Coulomb interaction between orbitals a_i and c_l. The solution of Eq. (53) can then be expressed in terms of the molecular response matrices $\overline{\alpha}_{a_i a_j, a_r a_s}$

$$\delta\rho^{(1)}_{a_i a_j}(\omega) = \sum_{rs} \overline{\alpha}_{a_i a_j, a_r a_s} V^{\mathrm{loc}}_{a_r a_s}. \tag{56}$$

Here $\overline{\alpha}$ is defined in analogy to Eq. (37), with S replaced by the matrix S which diagonalizes A according to

$$\sum_{ijkl} \overline{S^{-1}}_{a_\nu, a_i a_j} \overline{A}_{a_i a_j, a_k a_l} \overline{S}_{a_k a_l, a_{\nu'}} = \hbar\omega_{a_\nu}\delta_{\nu,\nu'}. \tag{57}$$

Inserting the definition of the local field Eq. (54), equating to Eq. (36), and assuming further, that $V_{a_i b_j}$ is negligible for $a \neq b$ yields an equation for $\tilde{\alpha}$, whose solution is

$$\tilde{\alpha}_{a_i a_j, b_k b_l}(\omega) = \sum_{nm} \mathscr{S}_{a_i a_j, b_n b_m}(\omega)\overline{\alpha}_{b_n b_m, b_k b_l}(\omega), \tag{58}$$

with

$$\mathscr{S}^{-1}_{a_i a_j, b_k b_l}(\omega) = \delta_{a_i b_k}\delta_{a_j b_l} + 2(1-\delta_{ab}) \times \sum_m \overline{\alpha}_{a_i a_j, a_m a_m} U_{a_m b_k}\delta_{kl}. \tag{59}$$

This exact result (provided intermolecular charge exchange as well as $V_{a_i b_j}$ are negligible), together with Eq. (49) allows the calculation of aggregate response tensors using the monomer response tensors. Since off diagonal (intramolecular) matrix elements $\mathscr{S}_{a_m a_n}, \mathscr{M}_{a_m a_n}$ are included, the number of indices in α and V doubled.

Switching to the CEO representation leads to

$$\tilde{\alpha}_{a_\nu, b_{\nu'}}(\omega) = \sum_{\nu''} S_{a_\nu, b_{\nu''}}(\omega)\overline{\alpha}_{b_{\nu''}, b_{\nu'}}(\omega),$$
$$\mathscr{S}^{-1}_{a_\nu, b_{\nu'}}(\omega) = \overline{S^{-1}}_{a_\nu, a_i a_j}\mathscr{S}^{-1}_{a_i a_j, b_k b_l}(\omega)\overline{S}_{b_k b_l, b_\nu}, \tag{60}$$

where a_ν denotes the ν-th oscillator of molecule a (note that a_i denotes the i-th site in molecule a). The nonlocal response tensors finally assume the form

$$\boldsymbol{\alpha}(\mathbf{r},\mathbf{r}',\omega) = \sum_{a,b}\sum_{\nu,\nu'} \tilde{\alpha}_{a_\nu, b_{\nu'}}(\omega)\boldsymbol{\mu}_{a_\nu}(\mathbf{r})\boldsymbol{\mu}_{b_{\nu'}}(\mathbf{r}'),$$
$$\boldsymbol{\beta}(\mathbf{r},\mathbf{r}',\omega) = \sum_{a,b}\sum_{\nu,\nu'} \tilde{\alpha}_{a_\nu, b_{\nu'}}(\omega)\boldsymbol{\mu}_{a_\nu}(\mathbf{r})\mathbf{m}_{b_{\nu'}}(\mathbf{r}'), \tag{61}$$

$$\boldsymbol{\gamma}(\mathbf{r},\mathbf{r}',\omega) = \sum_{a,b}\sum_{\nu,\nu'} \tilde{\alpha}_{a_\nu, b_{\nu'}}(\omega)\mathbf{m}_{a_\nu}(\mathbf{r})\boldsymbol{\mu}_{b_{\nu'}}(\mathbf{r}'),$$
$$\boldsymbol{\kappa}(\mathbf{r},\mathbf{r}',\omega) = \sum_{a,b}\sum_{\nu,\nu'} \tilde{\alpha}_{a_\nu, b_{\nu'}}(\omega)\mathbf{m}_{a_\nu}(\mathbf{r})\mathbf{m}_{b_{\nu'}}(\mathbf{r}'). \tag{62}$$

The CEO representation greatly reduces computational effort, as the number of dominant oscillators is generally much smaller than the square of the basis set dimensionality. Moreover, the matrix $\tilde{\alpha}_{a_\nu, b_{\nu'}}$ provides information regarding the coupling between electronic oscillators of different molecules.

V. OPTICAL ACTIVITY IN THE POINT DIPOLE APPROXIMATION

So far we have formulated optical activity in terms of nonlocal response functions, completely avoiding the multipolar expansion. We also paved the way for computational applications by rigorously expressing aggregate response functions in terms of monomer response functions, provided that exchange interactions between the monomers are negligible. In order to establish the connection to commonly employed approximations in the investigation of optical activity we now specialize to the lowest order in the multipolar expansion of the polarization and magnetization densities $\mathscr{P}$, $\mathscr{M}$. This amounts to keeping only the lowest order term in the δ functions appearing in Eqs. (13, 14), resulting in

$$\mathscr{P}_{mn}(\mathbf{r}) \approx \boldsymbol{\mu}_{mn}\delta(\mathbf{r}),$$
$$\mathscr{M}_{mn}(\mathbf{r}) \approx \mathbf{m}_{mn}\delta(\mathbf{r}),$$

with

$$\boldsymbol{\mu}_{mn} = -e\int d\mathbf{r}'\,\psi^*_m(\mathbf{r}')\mathbf{r}'\psi_n(\mathbf{r}'),$$
$$\mathbf{m}_{mn} = ie\hbar\int d\mathbf{r}'\,\psi^*_m(\mathbf{r}')\mathbf{r}'\times\nabla'\psi_n(\mathbf{r}'),$$

where we have set $\mathbf{R}=\mathbf{0}$, and the dipole densities in the CEO representation Eqs. (43, 44) assume the form

$$\boldsymbol{\mu}_\nu(\mathbf{r}) = \boldsymbol{\mu}_\nu\delta(\mathbf{r}),$$
$$\mathbf{m}_\nu(\mathbf{r}) = \mathbf{m}_\nu\delta(\mathbf{r}),$$

with

$$\boldsymbol{\mu}_\nu = \sum_{mn} \boldsymbol{\mu}_{mn}S_{mn,\nu},$$
$$\mathbf{m}_\nu = \sum_{mn} \mathbf{m}_{mn}S_{mn,\nu}.$$

Under these assumptions the nonlocal polarizability Eq. (45) becomes

$$\boldsymbol{\alpha}(\mathbf{r},\mathbf{r}';\omega) = \sum_\nu \boldsymbol{\alpha}_\nu(\omega)\,\delta(\mathbf{r})\,\delta(\mathbf{r}'), \tag{63}$$

where the contribution of the ν-th oscillator to the polarizability tensor (labeled by Greek subscripts) is

$$\boldsymbol{\alpha}_\nu(\omega)=\frac{2\omega_\nu}{\hbar}\frac{\boldsymbol{\mu}_\nu\boldsymbol{\mu}_\nu}{(\omega+i\gamma_\nu)^2-\omega_\nu^2}. \tag{64}$$

Analogous expressions hold for the other response tensors $\boldsymbol{\beta},\gamma$, and $\boldsymbol{\kappa}$.

We now consider an aggregate made of N point-like molecules located at $\mathbf{r}_a,\mathbf{r}_b,\ldots$ which are characterized by their linear response tensors $\overline{\boldsymbol{\chi}_a},\overline{\boldsymbol{\chi}_b},\ldots$ with $\chi=\alpha,\beta,\gamma,\kappa$. The label ν in Eq. (64) is then replaced by the double index $a\nu$ denoting the contribution from the ν-th oscillator of molecule a. Intermolecular charge transfer is neglected, so that dipole-dipole coupling is the only interaction. The polarization and magnetization can then be written as

$$\mathbf{P}(\mathbf{r})=\sum_a \mathbf{P}_a\delta(\mathbf{r}-\mathbf{r}_a),$$

$$\mathbf{M}(\mathbf{r})=\sum_a \mathbf{M}_a\delta(\mathbf{r}-\mathbf{r}_a).$$

The induced electric and magnetic dipole moments at the a-th molecule can be calculated from the molecular response functions by employing the LFA

$$\mathbf{P}_a=\overline{\boldsymbol{\alpha}_a}\cdot\mathbf{E}_a^{\mathrm{loc}}+\overline{\boldsymbol{\beta}_a}\cdot\mathbf{H}_a^{\mathrm{loc}}, \tag{65}$$

$$\mathbf{M}_a=\overline{\boldsymbol{\kappa}_a}\cdot\mathbf{H}_a^{\mathrm{loc}}+\overline{\boldsymbol{\gamma}_a}\cdot\mathbf{E}_a^{\mathrm{loc}}, \tag{66}$$

where the local electric and magnetic fields are given by the sum of the external fields and the fields induced by the surrounding molecules

$$\mathbf{E}_a^{\mathrm{loc}}=\mathbf{E}_a+\sum_b \mathbf{T}_{ab}\cdot\mathbf{P}_b, \tag{67}$$

$$\mathbf{H}_a^{\mathrm{loc}}=\mathbf{H}_a+\sum_b \mathbf{T}_{ab}\cdot\mathbf{M}_b. \tag{68}$$

Here $\mathbf{T}_{ab}$ is given by

$$\mathbf{T}_{ab}=(1-\delta_{ab})\frac{3\mathbf{e}_{ab}\mathbf{e}_{ab}-\mathbf{1}}{|\mathbf{R}_{ab}|^3}.$$

Substitution of Eqs. (67, 68) into Eqs. (65, 66) yields a linear system of equations for $\mathbf{P}_a$ and $\mathbf{M}_a$, whose solution is

$$\mathbf{P}_a=\sum_d (\boldsymbol{\alpha}_{ad}\cdot\mathbf{E}_d+\boldsymbol{\beta}_{ad}\cdot\mathbf{H}_d), \tag{69}$$

$$\mathbf{M}_a=\sum_d (\boldsymbol{\gamma}_{ad}\cdot\mathbf{E}_d+\boldsymbol{\kappa}_{ad}\cdot\mathbf{H}_d), \tag{70}$$

with the nonlocal response matrices

$$\boldsymbol{\alpha}_{ad}=\sum_{be}\mathbf{X}_{ae}\cdot\mathbf{S}_{eb}(\overline{\alpha})\cdot\left[\delta_{bd}\overline{\boldsymbol{\alpha}_d}+\sum_c\overline{\boldsymbol{\beta}_b}\cdot\mathbf{T}_{bc}\cdot\mathbf{S}_{cd}(\overline{\kappa})\cdot\overline{\boldsymbol{\gamma}_d}\right], \tag{71}$$

$$\boldsymbol{\beta}_{ad}=\sum_{be}\mathbf{X}_{ae}\cdot\mathbf{S}_{eb}(\overline{\alpha})\cdot\left[\delta_{bd}\overline{\boldsymbol{\beta}_d}+\sum_c\overline{\boldsymbol{\beta}_b}\cdot\mathbf{T}_{bc}\cdot\mathbf{S}_{cd}(\overline{\kappa})\cdot\overline{\boldsymbol{\kappa}_d}\right], \tag{72}$$

$$\boldsymbol{\gamma}_{ad}=\sum_{be}\mathbf{Y}_{ae}\cdot\mathbf{S}_{eb}(\overline{\kappa})\cdot\left[\delta_{bd}\overline{\boldsymbol{\gamma}_d}+\sum_c\overline{\boldsymbol{\gamma}_b}\cdot\mathbf{T}_{bc}\cdot\mathbf{S}_{cd}(\overline{\alpha})\cdot\overline{\boldsymbol{\alpha}_d}\right], \tag{73}$$

$$\boldsymbol{\kappa}_{ad}=\sum_{be}\mathbf{Y}_{ae}\cdot\mathbf{S}_{eb}(\overline{\kappa})\cdot\left[\delta_{bd}\overline{\boldsymbol{\kappa}_d}+\sum_c\overline{\boldsymbol{\gamma}_b}\cdot\mathbf{T}_{bc}\cdot\mathbf{S}_{cd}(\overline{\alpha})\cdot\overline{\boldsymbol{\beta}_d}\right]. \tag{74}$$

The various tensors appearing in these equations are defined as follows:

$$\mathbf{S}_{ab}^{-1}(\overline{\chi})=\mathbf{1}\delta_{ab}-\overline{\boldsymbol{\chi}_a}\cdot\mathbf{T}_{ab},\quad \chi=\alpha,\kappa,$$

$$\mathbf{X}_{ae}^{-1}=\mathbf{1}\delta_{ae}-\sum_{bcd}\mathbf{S}_{ab}(\overline{\alpha})\cdot\overline{\boldsymbol{\beta}_b}\cdot\mathbf{T}_{bc}\cdot\mathbf{S}_{cd}(\overline{\kappa})\cdot\overline{\boldsymbol{\gamma}_d}\cdot\mathbf{T}_{de}$$

$$\mathbf{Y}_{ae}^{-1}=\mathbf{1}\delta_{ae}-\sum_{bcd}\mathbf{S}_{ab}(\overline{\kappa})\cdot\overline{\boldsymbol{\gamma}_b}\cdot\mathbf{T}_{bc}\cdot\mathbf{S}_{cd}(\overline{\alpha})\cdot\overline{\boldsymbol{\beta}_d}\cdot\mathbf{T}_{de},$$

where $\mathbf{R}_{ab}=\mathbf{r}_a-\mathbf{r}_b$, $\mathbf{e}_{ab}=\mathbf{R}_{ab}/|\mathbf{R}_{ab}|$. By comparing Eqs. (69, 70) with Eqs. (9, 10) we obtain the nonlocal response tensors for this model

$$\boldsymbol{\chi}(\mathbf{r}.\mathbf{r}';\omega)=\sum_{ab}\delta(\mathbf{r}-\mathbf{r}_a)\delta(\mathbf{r}'-\mathbf{r}_b)\boldsymbol{\chi}_{ab}(\omega),$$

$$\chi=\alpha,\beta,\gamma,\kappa,$$

so that the difference in absorption cross section for right and left circularly polarized light Eq. (28) becomes

$$\Delta\sigma_A^{(0)}(\omega)=\frac{4\pi\omega}{c}\mathrm{Re}\sum_{ab}e^{-i\mathbf{k}\cdot\mathbf{R_{ab}}}\left\{\frac{\alpha_{ab}^{yx}(\omega)-\alpha_{ab}^{xy}(\omega)}{n}+[\kappa_{ab}^{yx}(\omega)-\kappa_{ab}^{xy}(\omega)]n-[\beta_{ab}^{xx}(\omega)+\beta_{ab}^{yy}(\omega)-\gamma_{ab}^{xx}(\omega)-\gamma_{ab}^{yy}(\omega)]\right\}. \tag{75}$$

The response tensors $\chi_{ab},\chi=\alpha,\beta,\gamma,\kappa$ can be computed by numerical inversion of $3N\times3N$ matrices, where N is the basis set dimensionality. However, this expression is simplified by expanding the matrices **S,X,Y** to first order in **T** and neglecting terms of the order $|\mathbf{m}|^2$, which results in

$$\boldsymbol{\alpha}_{ab}=\delta_{ab}\overline{\boldsymbol{\alpha}_a}+\overline{\boldsymbol{\alpha}_a}\cdot\mathbf{T}_{ab}\cdot\overline{\boldsymbol{\alpha}_b}, \tag{76}$$

$$\boldsymbol{\beta}_{ab}=\delta_{ab}\overline{\boldsymbol{\beta}_a}+\overline{\boldsymbol{\alpha}_a}\cdot\mathbf{T}_{ab}\cdot\overline{\boldsymbol{\beta}_b}, \tag{77}$$

$$\boldsymbol{\gamma}_{ab}=\delta_{ab}\overline{\boldsymbol{\gamma}_a}+\overline{\boldsymbol{\gamma}_a}\cdot\mathbf{T}_{ab}\cdot\overline{\boldsymbol{\alpha}_b}, \tag{78}$$

$$\boldsymbol{\kappa}_{ab}=0. \tag{79}$$

Setting $e^{-i\mathbf{k}\cdot\mathbf{r}}\approx1-i\mathbf{k}\cdot\mathbf{r}$, performing orientational averaging $\langle(\mathbf{A}\cdot\hat{\mathbf{k}})(\mathbf{B}\cdot\hat{\mathbf{k}})\rangle_{\hat{\mathbf{k}}}=\frac{1}{3}\mathbf{A}\cdot\mathbf{B}$, and using $\beta_{ab}^{ij}=-\gamma_{ba}^{ji}$ gives

$$\Delta\sigma_A^{(0)}=\frac{32\omega^3}{3nc}\sum_a\sum_\nu\frac{R_{a\nu}\gamma_{a\nu}}{[\omega^2-\omega_{a\nu}^2-\gamma_{a\nu}^2]^2+4\gamma_{a\nu}^2\omega_{a\nu}^2}, \tag{80}$$

where we have defined the *rotational strength* $R_{a\nu}$ for the ν-th transition of molecule a

$$R_{a\nu}=\sum_a \mathrm{Im}(\boldsymbol{\mu}_{a\nu}\cdot\mathbf{m}_{a\nu})$$

$$-2\sum_{b\neq a}\sum_{\nu\neq\nu'}\frac{\mathrm{Im}[V_{ab}^{\nu\nu'}(\omega_a\boldsymbol{\mu}_{a\nu}\cdot\mathbf{m}_{b\nu'}+\omega_b\boldsymbol{\mu}_{b\nu'}\cdot\mathbf{m}_{a\nu})]}{\omega_{a\nu}^2-\omega_{b\nu'}^2}$$

$$-\frac{2\pi}{c}\sum_{b\neq a}\sum_{\nu'\neq\nu}\frac{\omega_{a\nu}\omega_{b\nu'}V_{ab}^{\nu\nu'}\boldsymbol{\mu}_{a\nu}\times\boldsymbol{\mu}_{b\nu'}\cdot\mathbf{R}_{ab}}{[\omega_{a\nu}^2-\omega_{b\nu'}^2]}, \tag{81}$$

with

$$V_{ab}^{\nu\nu'}=\boldsymbol{\mu}_{a\nu}\cdot\mathbf{T}_{ab}\cdot\boldsymbol{\mu}_{b\nu'}. \tag{82}$$

The CD-signal vanishes as the damping rates go to zero, and it scales as ω^{-1} for large frequencies. The first term in the rotational strengths, describing the intrinsic CD of the individual molecules stems from the diagonal terms in Eqs. (77, 78). The second term in Eq. (81) is due to the mixed terms in Eqs. (77, 78), and the third term comes from the second term in Eq. (76). Terms including molecular magnetic transition dipole moments are finite even when setting $e^{-i\mathbf{kr}}\approx 1$, whereas the last term in Eq. (81) requires $e^{-i\mathbf{kr}}\approx 1-i\mathbf{kr}$. This last term can also be identified with Kirkwoods polarizability approximation[20]

$$\Delta\sigma_A\approx\frac{4\pi\omega}{nc}\mathrm{Im}\sum_{ab,ij}[\overline{\alpha_a^{yi}}T_{ab}^{ij}\overline{\alpha_b^{jx}}-\overline{\alpha_a^{xi}}T_{ab}^{ij}\overline{\alpha_b^{jy}}]\mathbf{k}\cdot\mathbf{R}_{ab},$$

$$=\frac{8\pi\omega}{nc}\mathrm{Im}\sum_{ab,ij}\overline{\alpha_a^{yi}}T_{ab}^{ij}\overline{\alpha_b^{jx}}\mathbf{k}\cdot\mathbf{R}_{ab}.$$

The celebrated Tinocco formulas[29,41] for the rotation of the polarization plane of linearly polarized incident light per unit length ϕ are readily obtained using the Kramers Krönig relation

$$\phi(\omega)=\frac{2\omega^2}{\pi}\mathscr{P}\int_0^\infty d\omega'\,\frac{\sigma_A(\omega')}{\omega'(\omega'^2-\omega^2)},$$

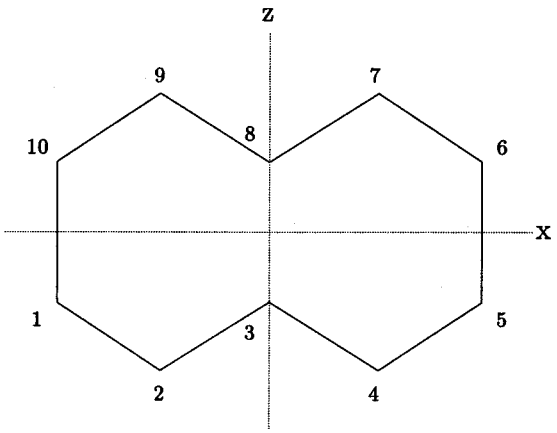

FIG. 1. Orientation of the monomer in the $x-z$ plane and labeling of the atom, used in Fig. 3.

where $\mathscr{P}$ denotes the principal part of the integral. Neglecting damping ($\gamma_\nu\to 0$) results in the familiar expression for OR in transparent regions of the aggregate

$$\phi(\omega)=\frac{16\omega^2}{3nc}\sum_a\sum_\nu\frac{R_{a\nu}}{\omega^2-\omega_{a\nu}^2}.$$

The remaining two terms in Tinoccos' result (see e.g., p. 70 in Ref. 29) representing interactions with the ground state charge distribution are included implicitly in Eq. (81), as we use molecular response tensors $\boldsymbol{\chi}_a,\chi=\alpha,\beta,\gamma,\kappa$ modified by the ground state charge distribution of the neighboring molecules.[36] They can be retrieved by a perturbative expansion of $\boldsymbol{\chi}_a$ in the interaction Hamiltonian.

VI. CD SPECTROSCOPY OF NAPHTHALENE CLUSTERS

We have applied the present nonlocal formalism to calculate the CD spectrum of naphthalene dimers and trimers. Comparison with the standard (local) formulation shows significant differences, which illustrates the need for a nonlocal formulation. Small naphthalene clusters have been investigated by studying isotopically mixed crystals[45] and by supersonic molecular beam techniques[46] revealing insight into their geometry. Although CD spectra of these systems are not available, they were chosen for their simplicity. They also serve as models for more complex conjugated systems that appear in biological aggregates.[4–6,9–12]

We assume circularly polarized light propagating in z-direction and investigate the trimer geometry suggested in Fig. 7 of Ref. 46. Using the SPARTAN package for a HF *ab initio* calculation with geometry optimization in an STG6-11* basis set yields the monomer geometry. The dimer is constructed from a monomer in the xz-plane shown in Fig. 1 by a 60° rotation around the z-axis and a translation of 3.7 Å in the z-direction. The trimer is obtained by adding one more molecule rotated by 120° around the z-axis and translated by 7.4 Å in the z-direction relative to the first molecule. Instead of the absorption cross section, we switch to the absorption coefficient via the relation[37]

$$\sigma_A=\frac{4\pi\omega}{c}\epsilon,$$

so that Eq. (26) becomes

$$\epsilon_\pm=\overline{\epsilon}\pm\Delta\epsilon. \tag{83}$$

In the NLRF calculation we have considered only the polarization term $\boldsymbol{\alpha}$ in Eq. (28) and neglected the magnetic terms $\boldsymbol{\beta},\boldsymbol{\gamma},\boldsymbol{\kappa}$. Neglecting further nondiagonal matrix elements $\mathscr{P}_{a_ia_j}$, setting $n=1$, and substituting Eq. (49) into Eq. (28) leads to

$$\overline{\epsilon}^{(0)}(\omega)=\mathrm{Im}\sum_{ab,ij}\tilde{\alpha}_{a_ia_i,b_jb_j}(\omega)[\mathscr{P}^x_{a_ia_i}(\mathbf{k})\mathscr{P}^x_{b_jb_j}(-\mathbf{k})$$

$$+\mathscr{P}^y_{a_ia_i}(\mathbf{k})\mathscr{P}^y_{b_jb_j}(-\mathbf{k})],$$

$$\Delta\epsilon^{(0)}(\omega) = -\mathrm{Re}\sum_{ab,ij} \tilde{\alpha}_{a_i a_i, b_j b_j}(\omega)\ \mathscr{P}_{a_i a_i}(\mathbf{k}) \times \mathscr{P}_{b_j b_j}(-\mathbf{k})\cdot \mathbf{e}_{\mathbf{k}},$$

where we have defined the Fourier transform of the polarization densities

$$\mathscr{P}_{a_i a_j}(\mathbf{k}) = \int d\mathbf{r}'\, e^{-i\mathbf{k}\cdot\mathbf{r}} \mathscr{P}_{a_i a_j}(\mathbf{r}).$$

Assuming point charges $\psi^2_{a_i}(\mathbf{r}) = \delta(\mathbf{r}-\mathbf{r}_{a_i})$ results in

$$\mathscr{P}_{a_i a_i}(\mathbf{k}) = -e\mathbf{r}_{a_i} \frac{\sin\frac{\mathbf{k}\cdot\mathbf{r}_{a_i}}{2}}{\frac{\mathbf{k}\cdot\mathbf{r}_{a_i}}{2}} e^{-i\frac{\mathbf{k}\cdot\mathbf{r}_{a_i}}{2}},$$

and the matrix $\tilde{\alpha}$ is calculated using Eq. (58). This point-monopole approximation is widely used for the calculation of intermolecular interactions.[3,4,25,26] However, here we also keep the full matter-field interaction to all orders in the multipolar expansion by using nonlocal response functions, which have a non-trivial $\mathbf{r}$ or $\mathbf{k}$ dependence.

Since Tinoccos' formulae Eqs. (80–82) (which are derived using the approximative matrix inversion $(\mathbf{1}-\boldsymbol{\alpha}\mathbf{S})^{-1} \approx \mathbf{1}+\boldsymbol{\alpha}\mathbf{S}$) are not applicable for the small intermolecular distances of the investigated aggregates, we resort to the more accurate precursor, Eq. (75) for an oriented sample as a comparison. Neglecting again magnetic contributions ($\mathbf{m}_{a\nu}=0$) results in $\boldsymbol{\beta}=\boldsymbol{\gamma}=\boldsymbol{\kappa}=0$, and $\mathbf{X}_{ae}=\mathbf{1}\delta_{ae}$, so that

$$\overline{\epsilon^{\mathrm{LFA}}}(\omega) \approx \mathrm{Im}\sum_{ab} e^{-i\mathbf{k}\cdot\mathbf{R}_{ab}}[\alpha^{xx}_{ab}(\omega)+\alpha^{yy}_{ab}(\omega)],$$

$$\Delta\epsilon^{\mathrm{LFA}}(\omega) \approx -\mathrm{Re}\sum_{ab} e^{-i\mathbf{k}\cdot\mathbf{R}_{ab}}[\alpha^{xy}_{ab}(\omega)-\alpha^{yx}_{ab}(\omega)],$$

with

$$\boldsymbol{\alpha}_{ad} = \mathbf{S}_{ad}(\alpha)\boldsymbol{\alpha}_d,$$

$$\mathbf{S}^{-1}_{ad}(\alpha) = \mathbf{1}\delta_{ad} - \boldsymbol{\alpha}_a\cdot\mathbf{T}_{ad}.$$

In Fig. 2 we display the average absorption coefficient $\overline{\epsilon(\omega)}$ [see Eq. (26)] for the naphthalene monomer (top panel), the dimer (middle panel), and the trimer (bottom panel) calculated via the NLRF approach (solid lines). For the dimer and trimer we also show the LFA results for comparison (dashed lines). We only show the region of the lowest absorption band. Other bands are smaller by a factor of > 20. We further choose a small damping $\gamma = 0.001$ eV. The monomer has one absorption peak at 5.58 eV. In case of the dimer the exact calculation yields four peaks. Approximating the monomers by point dipoles leads to two absorption peaks. Their separation exceeds the absorption range as obtained by the NLRF. For the trimer the NLRF calculation also yields four peaks, and the LFA results in three. The LFA results can be understood with a simple two or three dimensional model Hamiltonian. For the dimer the monomer peak splits into two peaks which are symmetrically positioned around the monomer peak. Assuming

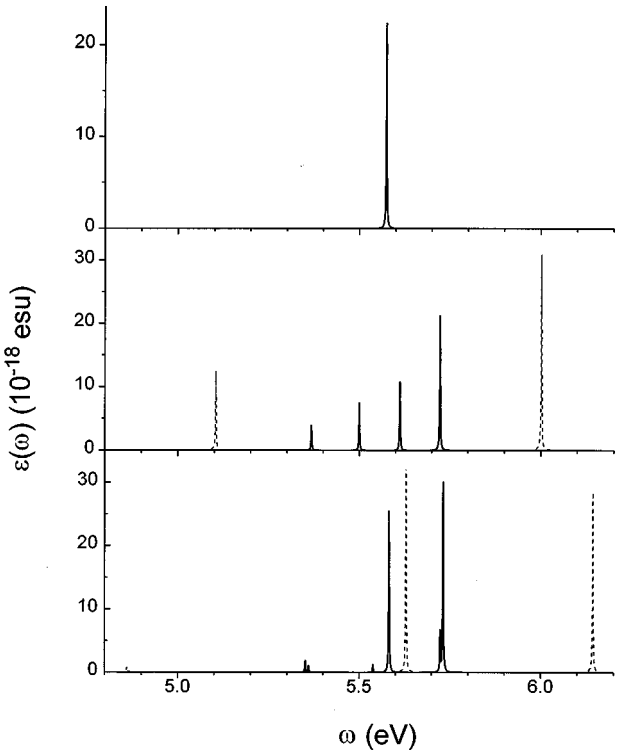

FIG. 2. Absorption spectrum $\overline{\epsilon(\omega)}$ of a naphthalene monomer (top panel), the dimer (middle panel) and the trimer (bottom panel). The solid lines show the NLRF calculations, and dashed lines depict the LFA results for the dimer and trimer. $\gamma = 0.001$ eV, and for the other parameters see the text.

$$H_t = \begin{pmatrix} E_M & a & b \\ a & E_M & a \\ b & a & E_M \end{pmatrix}$$

for the trimer yields the eigenvalues

$$\lambda_1 = E_M + b, \tag{84}$$

$$\lambda_{2,3} = E_M + \frac{-b \pm \sqrt{8a^2+b^2}}{2}, \tag{85}$$

which explains the position of the peaks observed in Fig. 2. The additional peaks in the NLRF reflect the fact that this calculation fully accounts for the intermolecular interactions, whereas the LFA result retains only the leading dipole-dipole interaction.

In order to study inter and intramolecular coherences, we depict the nonlocal response matrix $\tilde{\alpha}$ at the frequencies of the four peaks of the NLRF in Fig. 3. The real part (left panel) is naturally considerable smaller than the imaginary part (right panel) near resonances. Resorting to Fig. 1 for the labeling of the atoms we find that the second and third transitions predominantly correlate the closest sites of each monomer, whereas the first and fourth transitions correlate the most distant ones.

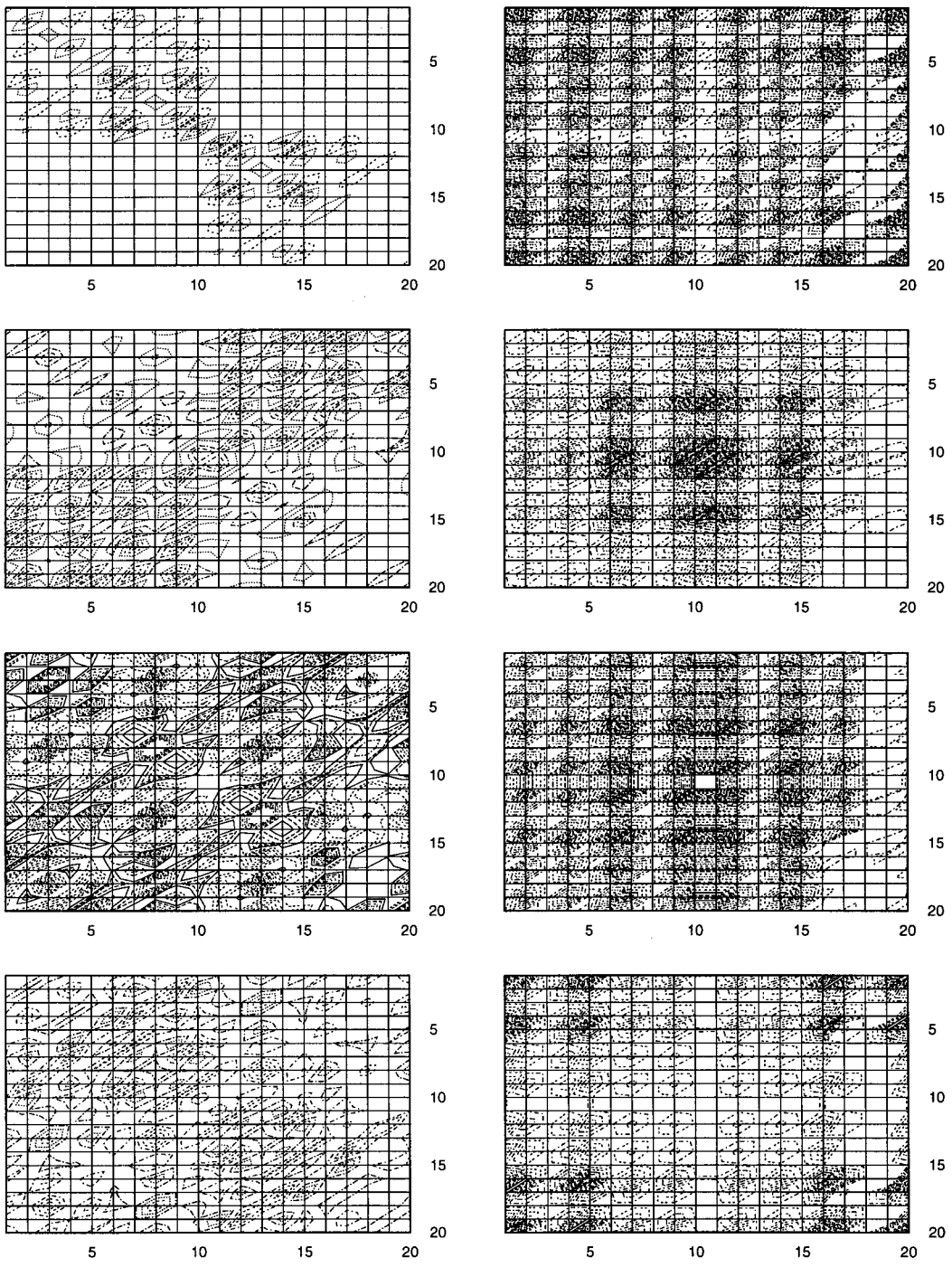

FIG. 3. Real (left) and imaginary (right) part of the nonlocal response matrix $\tilde{\alpha}(\omega)$ of a naphthalene dimer for the four peaks shown in Fig. 2 from top to bottom ($\omega = 5.37, 5.50, 5.61, 5.72$ eV). Atoms 1–10, 11–20, 21–30 correspond to the three monomers (see Fig. 1). For aggregate geometry see the text.

Figure 4 shows CD of the dimer (left panel) and the trimer (right panel) calculated in the NLRF (solid lines) and the LFA (dashed lines). Each absorption peak leads to a distinct peak in the CD signal, whose amplitude reflects the rotational strength of the optical transition. Apart from the magnitude of these peaks, their sign carries important information, reflecting the handedness of the molecule. In Fig. 5 we used a larger damping $\gamma = 0.08$ eV which yielded reasonable absorption line shapes for PPV oligomers.[35,36] The top panels show the absorption coefficient $\bar{\epsilon}$ of the dimer (left) and the trimer (right), calculated using the NLRF (solid) and the LFA (dashed). The bottom panels display the CD signal $\Delta\epsilon(\omega)$. The absorption coefficients for both systems are now characterized by a single peak with internal structure. In order to show the transitions involved we also plot the results for small damping. In case of the dimer the zero of the CD

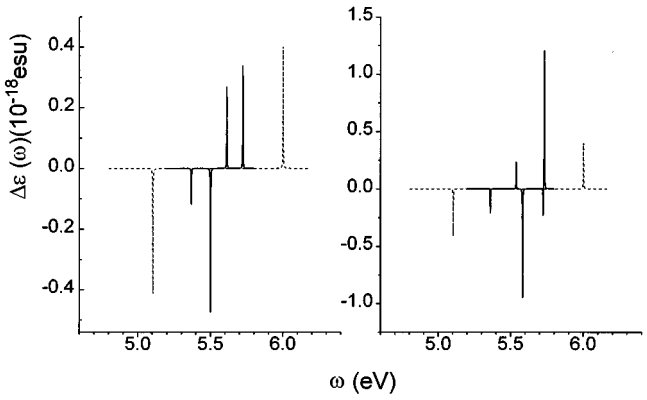

FIG. 4. CD signal $\Delta\epsilon(\omega)$ calculated with the NLRF of the naphthalene dimer (left) and trimer (right) for a damping rate of $\gamma=0.001$ eV.

signal coincides with the monomer frequency ω_M. In the LFA the two rotational strengths are equal in magnitude and opposite in sign, so that the signal for finite damping is symmetric with respect to ω_M. For the trimer such a relation does not hold, because of the form of the transition frequencies Eqs. (84, 85).

Due to the small intermolecular separation (smaller than the monomer size) the LFA gives markedly different results compared to the LFA. However, as shown in Fig. 6 the LFA convergences towards the NLRF results with increasing intermolecular separation. This series clearly demonstrates the breakdown of the LFA, as the intermolecular separation approaches molecular dimensions. The NLRF must be employed for distances smaller than 10 Å.

Since we used Ohnos' formula

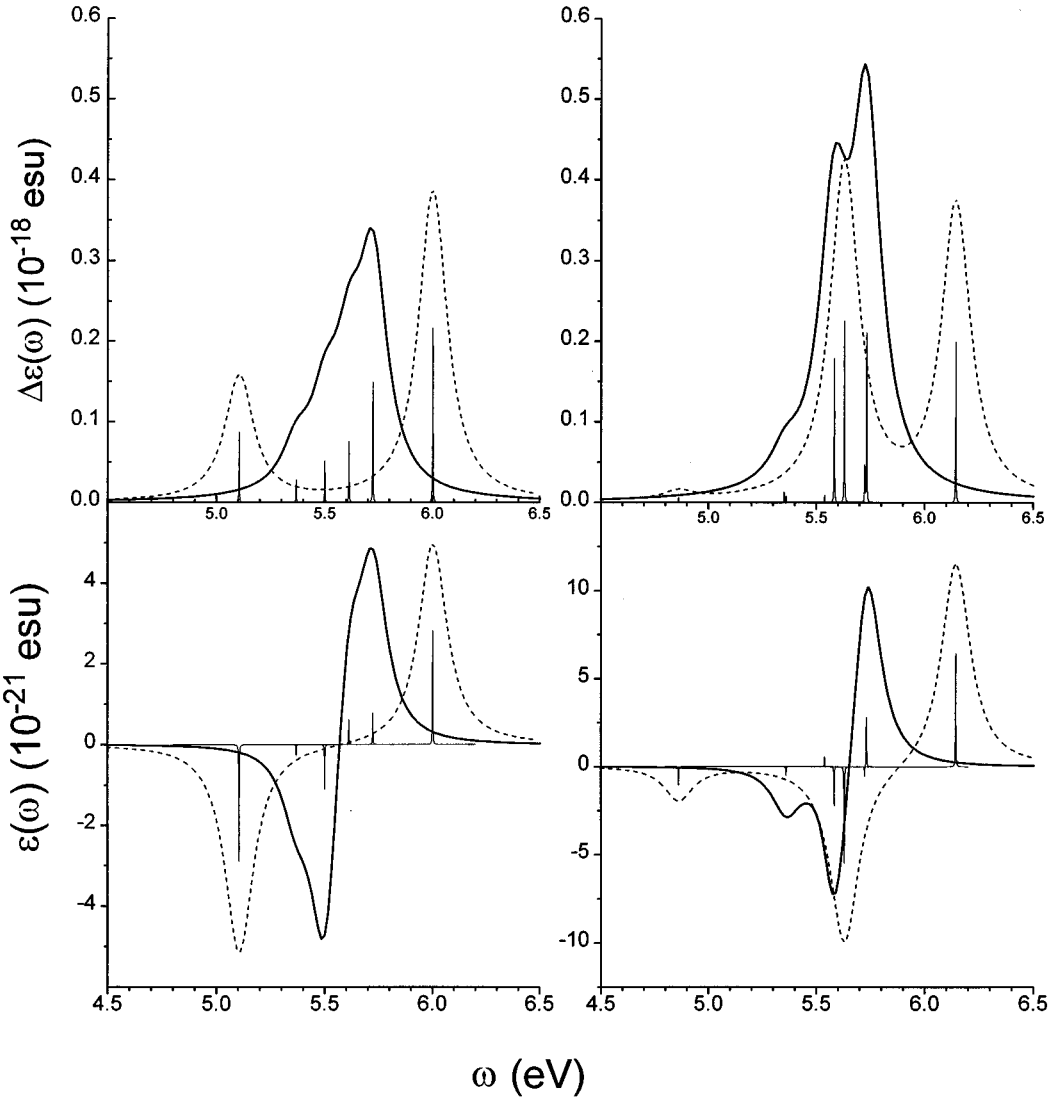

FIG. 5. Comparison of linear absorption $\overline{\epsilon(\omega)}$ (top panels) and CD $\Delta\epsilon(\omega)$ (bottom panels) calculated with the NLRF (solid line) and the LFA (dashed line) of a naphthalene dimer (left panels) and trimer (right panels) for a damping rate $\gamma=0.08$ eV. The vertical lines show the small damping results.

$$U_{mn}=\frac{U'}{\sqrt{1+(r_{mn}/a_0)^2}} \tag{86}$$

with $UI' = 7.4200$ eV, $a_0 = 1.2935$ Å for the electrostatic interactions in the PPP Hamiltonian,[35] the long distance behaviour is k/r with $k=9.5977$ eV Å. Considering the approximation $(\mathbf{1+B})^{-1}\approx\mathbf{1-B}$ (which applies at large separations and is necessary to obtain Tinoccos' formula), the CD signal is determined to first order by the second term in Eq. (59), so that k enters the CD signal as an overall scaling factor. In order to obtain agreement with the LFA results (which assume $1/r_{mn}$ for the Coulomb interaction) for large intermolecular separation we divided the NLRFs result by k.

Naphthalene molecules do not have a permanent dipole moment and the ground state charges are identical for all sites ($\overline{\rho_{nn}}=0.5$). Therefore the modifications of the molecular response functions by the ground state charge distribution of the surrounding molecules cancel [see Eq. (55)], and the response matrix $\underline{\alpha}$ coincides with that of isolated molecules. This is not expected to be the case for donor acceptor substituted molecules, in which the ground state charge distribution is nonuniform.

VII. SUMMARY

The conventional approach to the description of optical activity is based on the multipolar expansion. Circular dichroism or optical rotation are calculated term by term for systems much smaller than the optical wavelength. The present theory is based on the concept of nonlocal response tensors and completely avoids these approximations.

We first calculated circular dichroism (CD) defined as the difference in absorption cross section for right and left circularly polarized light. Eq. (20) contains the polarization $\mathbf{P(r)}$, the magnetization $\mathbf{M(r)}$ and the electric and magnetic fields $\mathbf{E(r)}$, $\mathbf{H(r)}$. Utilizing the linearized relationships $\mathbf{P(E,H)}$, $\mathbf{M(E,H)}$ Eqs. (9, 10) lead to our final expression Eq. (28) which holds for arbitrary wavelengths and system sizes. With this result the theory of optical activity (OA) is fully captured through four nonlocal response tensors $\boldsymbol{\alpha}(\mathbf{r},\mathbf{r}',\omega)$, $\boldsymbol{\beta}(\mathbf{r},\mathbf{r}',\omega)$, $\boldsymbol{\gamma}(\mathbf{r},\mathbf{r}',\omega)$, $\boldsymbol{\kappa}(\mathbf{r},\mathbf{r}',\omega)$ which relate polarization and magnetization to the driving external fields. It is formally exact; approximations necessary for practical computations enter in the calculation of the response tensors $\boldsymbol{\chi}$.

We then focused on electronically delocalized conjugated systems described by a Pariser–Parr–Pople Hamiltonian. Using the time dependent Hartree Fock equations and the multipolar form of the interaction Hamiltonian we derived the expressions Eqs. (39–42) for the response tensors. They factorize into a central, nonlocal response matrix $\underline{\tilde{\alpha}}$ and dyadics $\mathscr{P}(\mathbf{r})\mathscr{P}(\mathbf{r})$, $\mathscr{P}(\mathbf{r})\mathscr{M}(\mathbf{r})$, etc. Once a convenient electronic basis set has been chosen, the polarization and magnetization densities $\mathscr{P}(\mathbf{r}),\mathscr{M}(\mathbf{r})$ can be calculated without any further approximations. In particular, our final expression Eq. (28) implicitly includes *all* multipolar moments, such as electric and magnetic dipole, quadrupole, octopole, etc. Moreover we could show easily the independence of the absorption cross section, and hence of the CD-signal of the choice of origin.

A considerable reduction of computational cost in the investigation of spatially extended molecular aggregates is possible if intermolecular charge exchange is negligible. In this case, intermolecular electronic coherences, i.e., off-diagonal elements of the single electron density matrix between basis functions located at different monomers, vanish identically. This makes it possible to rigorously express the aggregate response in terms of monomer response tensors. The exact relationship Eq. (58) derived in this article eliminates the need for the commonly used local field approximation which completely neglects the molecular internal structure. The calculation was carried out by deriving molecular equations of motion for the reduced one electron density matrix in Liouville space, which fully account for intermolecular Coulomb interactions. This way we completely avoided a perturbative calculation of aggregate wavefunctions. To account for exchange interactions and charge transfer, intermolecular electronic coherences need to be included in the calculation of the nonlocal response tensors. Note that the nonlocal response tensors $\boldsymbol{\chi}(\mathbf{r},\mathbf{r}',\omega)$, where $\mathbf{r}$ and $\mathbf{r}'$ are at different monomers imply the existence of *excitonic* coherences, whereby electron–hole pairs can hop among monomers retaining their phase. *Electronic* coherences on the other hand imply coherent motion of electrons between monomers and reflects a phase between an electron at one

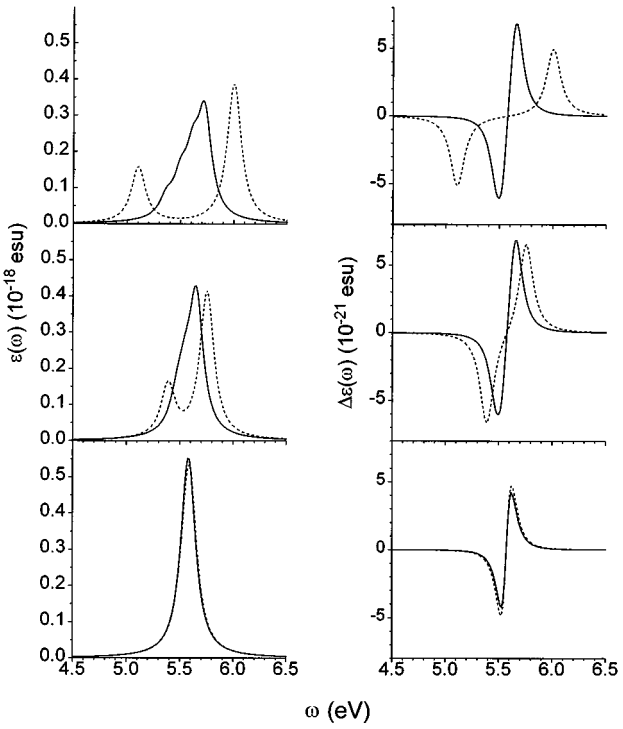

FIG. 6. Convergence of the LFA (dashed) towards the NLRF (solid) with increasing intermolecular distance (3.7,5,10 Å from top to bottom) for a naphthalene dimer. Shown are the absorption coefficient $\overline{\epsilon}$ (left panels) and the CD signal $\Delta\epsilon$ (right panels).

monomer and a hole at another. Electronic coherence is not required to attain excitonic coherence which can arise from purely electrostatic interactions. However, the presence of intermolecular charge exchange does affect the excitonic coherence and the optical response.[35,36]

We have further formulated the response functions using the coupled electronic oscillator representation [see Eqs. (45–48, 61–62)]. As demonstrated in Refs. 42, 44 only very few oscillators contribute significantly to the optical response which leads to a drastic reduction in computational cost, as can be inferred from the dimension of the matrices $\tilde{\alpha}_{a_i a_j, b_k b_l}$ and $\tilde{\alpha}_{a_\nu, b_{\nu'}}$. Moreover, the latter quantities carry information about the coupling between oscillators of different molecules and thus provide most valuable insight into intermolecular interactions.

The well known Tinocco formula Eq. (81) for the rotational strengths was recovered by introducing the local field approximation, the long wavelength approximation, and an approximative matrix inversion $(\mathbf{1}-\boldsymbol{\alpha}\mathbf{T})^{-1}\approx\mathbf{1}+\boldsymbol{\alpha}\mathbf{T}$ to our general result for $\Delta\sigma_A^{(0)}(\omega)$.

Finally we compared our results with those obtained from Tinoccos' formulae by application to naphthalene dimers and trimers. The aggregate geometries were taken from Ref. 46, and we first chose a damping rate small enough to reveal the involved electronic transitions. The resulting spectra then reflect the structure of the oscillator and rotational strengths. For the monomer, the average frequency dependent absorption coefficient $\overline{\epsilon}$ of circularly polarized light is characterized by one absorption peak at 5.58 eV [see Fig. 2]. This peak splits up into two (three) peaks for the dimer (trimer) when calculated with the LFA, which can be understood with a simple two (three) dimensional exciton Hamiltonian. The exact NLRF yields four absorption peaks for the dimer and the trimer, which are not as much separated as the LFA indicates. Each absorption peak has a corresponding peak in the CD spectrum (Fig. 4). This figure also contains the sign information of the rotational strengths, which is essential for differentiating between right or left handed geometries. The increased number of transitions reflects the corrections due to nonlocal interactions between spatially extended molecules. We finally demonstrated the breakdown of the LFA for intermolecular separations comparable to molecular dimensions in Fig. 6. For intermolecular distances smaller than 10 Å the NLRF has to be employed.

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APPENDIX: THE ABSORPTION CROSS SECTION OF AN AGGREGATE

The energy flux density of an electromagnetic wave in a dielectric is given by the pointing vector (see Sec. 61 in Ref. 38)

$$\mathbf{S}(\mathbf{r},\omega)=\frac{c}{4\pi}\mathbf{E}(\mathbf{r},\omega)\times\mathbf{H}(\mathbf{r},\omega). \tag{A1}$$

Integrating $\nabla\mathbf{S}=(c/4\pi)(\mathbf{H}\cdot\nabla\times\mathbf{E}-\mathbf{E}\cdot\nabla\times\mathbf{H})$ over a volume V with surface $\mathcal{O}$ and making use of Maxwells' equations (15, 16) leads to

$$-\oint_{\mathcal{O}} d\mathcal{F}\cdot\mathbf{S}=\frac{1}{8\pi}\frac{d}{dt}\int_V d\mathbf{r}[(\mathbf{H}^\perp)^2+(\mathbf{E}^\perp)^2] + \int_V d\mathbf{r}\left[\mathbf{E}\cdot\frac{\partial\mathbf{P}^\perp}{\partial t}+\mathbf{H}\cdot\frac{\partial\mathbf{M}^\perp}{\partial t}\right]. \tag{A2}$$

In this energy balance equation the left-hand side is the decrease of energy per unit time, due to the flux through the surface $\mathcal{O}$, and the right hand side has been separated into the time derivative of the energy of the fields $\mathbf{E}$, $\mathbf{H}$, and a dissipation term due to the induced electric and magnetic dipoles. We now assume V to be the entire space, and apply this result to an isolated aggregate. The absorbed energy per unit time is then given by the time average of Eq. (A2). Dividing by the time averaged incident energy flux

$$\Phi_{in}=\frac{1}{T}\int_0^T dt\,\frac{c}{4\pi}|\mathbf{E}_{\text{ext}}\times\mathbf{H}_{\text{ext}}| \tag{A3}$$

yields the effective absorption cross section σ_A. For monochromatic fields with frequency $\omega=2\pi/T$ the time average of the first term on the rhs of Eq. (A2) vanishes (as the fields have the same values at $t=0$ and $t=T$), and using $\int d\mathbf{r}\,\mathbf{f}(\mathbf{r})\cdot\mathbf{g}^\perp(\mathbf{r})=\int d\mathbf{r}\,\mathbf{f}^\perp(\mathbf{r})\cdot\mathbf{g}(\mathbf{r})$ we arrive at

$$\sigma_A=\frac{1}{\Phi_{\text{in}}}\frac{1}{T}\int_0^T dt\int_V d\mathbf{r}\left[\mathbf{E}^\perp\cdot\frac{\partial\mathbf{P}}{\partial t}+\mathbf{H}^\perp\cdot\frac{\partial\mathbf{M}}{\partial t}\right]. \tag{A4}$$

The transverse electric and magnetic Maxwell fields $\mathbf{E}^\perp$ and $\mathbf{H}^\perp$ are solutions of the wave equations

$$\Delta\mathbf{E}^\perp-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{E}^\perp=\frac{4\pi}{c^2}\frac{\partial}{\partial t}\left[\frac{\partial}{\partial t}\mathbf{P}^\perp+c\nabla\times\mathbf{M}\right], \tag{A5}$$

$$\Delta\mathbf{H}^\perp-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{H}^\perp=-\frac{4\pi}{c^2}\frac{\partial}{\partial t}\left[c\nabla\times\mathbf{P}-\frac{\partial}{\partial t}\mathbf{M}^\perp\right], \tag{A6}$$

which follow from the Maxwell Eqs. (15, 16). These linear equations can be solved using Greens' functions. The Maxwell fields are given to lowest order by the external fields $\mathbf{E}_{\text{ext}}(\mathbf{r},t),\mathbf{H}_{\text{ext}}(\mathbf{r},t)$, and corrections are due to multiple scattering of the incoming wave by the charge distribution:

$$\mathbf{E}^\perp(\mathbf{r},t)=\mathbf{E}_{\text{ext}}(\mathbf{r},t)+\mathbf{E}'(\mathbf{r},t), \tag{A7}$$

$$\mathbf{H}^\perp(\mathbf{r},t)=\mathbf{H}_{\text{ext}}(\mathbf{r},t)+\mathbf{H}'(\mathbf{r},t). \tag{A8}$$

The primed fields can be obtained from Eqs. (A5, A6) after transforming to $\mathbf{k},\omega$ space via

$$f(\mathbf{k},\omega)=\int d\mathbf{r}\int dt\ f(\mathbf{r},t)e^{-i(\mathbf{kr}-\omega t)}, \tag{A9}$$

resulting in

$$\mathbf{E}'(\mathbf{k},\omega)=\frac{-4\pi\omega^2}{\omega^2-k^2c^2}[\mathbf{P}^{\perp}(\mathbf{k},\omega)-\hat{\mathbf{k}}\times\mathbf{M}(\mathbf{k},\omega)], \tag{A10}$$

$$\mathbf{H}'(\mathbf{k},\omega)=\frac{-4\pi\omega^2}{\omega^2-k^2c^2}[\hat{\mathbf{k}}\times\mathbf{P}(\mathbf{k},\omega)+\mathbf{M}^{\perp}(\mathbf{k},\omega)], \tag{A11}$$

where $\hat{\mathbf{k}}=\mathbf{k}/|\mathbf{k}|$. Equations (9, 10) become

$$\tilde{\mathbf{P}}(\mathbf{k},\omega)=\frac{1}{(2\pi)^3}\int d\mathbf{k}'[\boldsymbol{\alpha}(\mathbf{k},-\mathbf{k}';\omega)\cdot\mathbf{E}_{\mathrm{ext}}(\mathbf{k}',\omega)+\boldsymbol{\beta}(\mathbf{k},-\mathbf{k}';\omega)\cdot\mathbf{H}_{\mathrm{ext}}(\mathbf{k}',\omega)], \tag{A12}$$

$$\tilde{\mathbf{M}}(\mathbf{k},\omega)=\frac{1}{(2\pi)^3}\int d\mathbf{k}'[\boldsymbol{\gamma}(\mathbf{k},-\mathbf{k}';\omega)\cdot\mathbf{E}_{\mathrm{ext}}(\mathbf{k}',\omega)+\boldsymbol{\kappa}(\mathbf{k},-\mathbf{k}';\omega)\cdot\mathbf{H}_{\mathrm{ext}}(\mathbf{k}',\omega)], \tag{A13}$$

and the transverse vector components in $\mathbf{k}$–space are obtained by multiplication with the projector $(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})$. Substituting Eqs. (A7, A8) into Eq. (A4) yields to the separation Eq. (21)

$$\sigma_A=\sigma_A^{(0)}+\sigma_A^{(1)}, \tag{A14}$$

where $\sigma_A^{(0)}$ is given by Eq. (22), and

$$\sigma_A^{(1)}=\frac{1}{\Phi_{in}}\frac{1}{T}\int_0^T dt\int d\mathbf{k}\left[\mathbf{E}'(\mathbf{k},t)\cdot\frac{\partial\mathbf{P}(-\mathbf{k},t)}{\partial t}+\mathbf{H}'(\mathbf{k},t)\cdot\frac{\partial\mathbf{M}(-\mathbf{k},t)}{\partial t}\right]. \tag{A15}$$

A linearly polarized plane wave with wavevector $\mathbf{k}=(n\omega/c)\,\mathbf{e}_{\mathbf{k}}$ and polarization direction $\mathbf{e}_1$ perpendicular to $\mathbf{e}_{\mathbf{k}}$ can be represented by

$$\mathbf{E}_{\mathrm{ext}}(\mathbf{r},t)=\frac{E_0}{\sqrt{2}}\mathbf{e}_1(e^{i(\mathbf{kr}-\omega t)}+e^{-i(\mathbf{kr}-\omega t)}), \tag{A16}$$

$$\mathbf{H}_{\mathrm{ext}}(\mathbf{r},t)=\frac{H_0}{\sqrt{2}}\mathbf{e}_2(e^{i(\mathbf{kr}-\omega t)}+e^{-i(\mathbf{kr}-\omega t)}), \tag{A17}$$

with $H_0=nE_0$, and $\mathbf{e}_2=\mathbf{e}_{\mathbf{k}}\times\mathbf{e}_1$. Upon substitution into Eq. (20) we find $\Phi_{\mathrm{in}}=(cE_0H_0/4\pi)$, which results in Eq. (23) Choosing $\mathbf{e_1}=\mathbf{e_x}$ and $\hat{\mathbf{k}}=\mathbf{e_z}$, this assumes the form

$$\sigma_A^{(0)}(\omega)=\frac{4\pi\omega}{nc}\mathrm{Im}\int d\mathbf{r}\int d\mathbf{r}'\ e^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')} \tag{A18}$$

$$\times\left[\frac{1}{n}\alpha^{xx}(\mathbf{r},\mathbf{r}',\omega)+n\kappa^{yy}(\mathbf{r},\mathbf{r}',\omega)+\gamma^{yx}(\mathbf{r},\mathbf{r}',\omega)+\beta^{xy}(\mathbf{r},\mathbf{r}',\omega)\right]. \tag{A19}$$

Circularly polarized fields can be written as

$$\mathbf{E}_{\mathrm{ext}}^{\pm}(\mathbf{r},t)=\frac{E_0}{\sqrt{2}}(\mathbf{e}_{\pm}e^{i(\mathbf{kr}-\omega t)}+\mathbf{e}_{\mp}e^{-i(\mathbf{kr}-\omega t)}), \tag{A20}$$

$$\mathbf{H}_{\mathrm{ext}}^{\pm}(\mathbf{r},t)=\pm i\frac{H_0}{\sqrt{2}}(\mathbf{e}_{\pm}e^{i(\mathbf{kr}-\omega t)}-\mathbf{e}_{\mp}e^{-i(\mathbf{kr}-\omega t)}), \tag{A21}$$

where the complex unit vectors are defined as[32]

$$\mathbf{e}_+=\frac{\mathbf{e}_x-i\mathbf{e}_y}{\sqrt{2}}, \tag{A22}$$

$$\mathbf{e}_-=\frac{\mathbf{e}_x+i\mathbf{e}_y}{\sqrt{2}}. \tag{A23}$$

We find again $\Phi_{\mathrm{in}}=(c/4\pi)E_0H_0$ and the difference in absorption cross sections for right and left circularly polarized light Eq. (22) becomes

$$\Delta\sigma_A^{(0)}(\omega)=\sigma_{A+}^{(0)}-\sigma_{A-}^{(0)} \tag{A24}$$

$$=\frac{8\pi\omega}{nc}\mathrm{Im}\int d\mathbf{r}\int d\mathbf{r}'(\mathbf{e}_+^*\cdot\boldsymbol{\alpha}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{e}_+-\mathbf{e}_-^*\cdot\boldsymbol{\alpha}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{e}_-)e^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')}+\frac{8\pi\omega}{c}\mathrm{Re}\int d\mathbf{r}\int d\mathbf{r}'$$

$$\times(\mathbf{e}_+^*\cdot\boldsymbol{\beta}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{e}_++\mathbf{e}_-^*\cdot\boldsymbol{\beta}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{e}_-)e^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')}-\frac{8\pi\omega}{c}\mathrm{Re}\int d\mathbf{r}\int d\mathbf{r}'(\mathbf{e}_+^*\cdot\boldsymbol{\gamma}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{e}_++\mathbf{e}_-^*$$

$$\cdot\boldsymbol{\gamma}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{e}_-)e^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')}+\frac{8\pi\omega n}{c}\mathrm{Im}\int d\mathbf{r}\int d\mathbf{r}'(\mathbf{e}_+^*\cdot\boldsymbol{\kappa}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{e}_+-\mathbf{e}_-^*\cdot\boldsymbol{\kappa}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{e}_-)e^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')}. \tag{A25}$$

Switching back to the real basis vectors $\mathbf{e}_x,\mathbf{e}_y$ we recover Eq. (28).

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