Electro-optic rotation in isotropic media

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Abstract

A formal proof has recently been given to show that an electro-optic response of chiral molecules in isotropic media is forbidden by time reversal invariance. A claim to the contrary by Beljonne *et al.* for the occurrence of such an effect in second order, when dephasing terms are included, is examined critically using a quantum electrodynamics (QED) formulation.

1 Introduction

Optical processes in which the coherent scattering of light couples linearly with a static electric field are semiclassically considered to be mediated by a second order (three-wave) nonlinear susceptibilities which, in the dipole approximation, can only be supported by systems lacking a centre of symmetry.[1]

In isotropic liquids, this symmetry condition can be satisfied only by chiral or gyrotropic molecules, as is the case for other even order (odd-wave) interactions such as sum-frequency generation,[2] and also a newly conjectured mechanism for second harmonic generation.[3] In the context of a recent study on the signing of phenomenological damping[4] However, it is necessary to entertain other considerations to resolve the issue of whether a linear electro-optic response (EOR) is fundamentally allowed in such fluids.

Recently Beljonne et al.[5] have presented a discussion of the electro-optic response of chiral helicenes in isotropic media. In detail the process they consider involves forward Rayleigh scattering, between orthogonal linear polarisations, coupled with an external electric field. Their analysis hinges on the inclusion in their (semiclassical) susceptibility expression of phenomenological damping factors, meant to represent lifetime broadening and dephasing effects. The authors conclude that chiral molecules in isotropic media possess a significant electro-optic response (at the electric dipole level). This conclusion is in strong contrast to that of Andrews *et al.*[4] who find that electro-optic response is forbidden in fluid media. In this paper we discuss why this difference in conclusion exists, and we give an alternative formulation whose results support the results of Andrews *et al.*

Beljonne *et al.*[5] stress the basis of their inclusion of homogeneous damping as a two-particle effect. This two-particle origin has no bearing on the correctness or otherwise of their conclusions when all damping mechanisms are assimilated in one phenomenological parameter. Even had this not been so, each many-body effect must respect time-reversal invariance when the basic Hamiltonian is time-even (i.e. does not explicitly include CP violation effects). As Andrews *et al.* indicate, the mere presence of a two-particle effect cannot exonerate such an analysis from the demands of time reversal symmetry. Dephasing effects in particular are not exempt, although they certainly lead to destructive interference between the one-particle decay amplitudes contributing to observed linewidths.[5,6]

2 QED-theoretic description of EOR

2.1 Tensors

In the multipolar formulation of quantum electrodynamics, interactions which are classically termed static (longitudinal or instantaneous) are cast in terms of a coupling mediated by the radiation field (transverse photons). In the description which follows we calculate the quantum mechanical measurable corresponding to registration of the static field by a probe. In the present context, this entails the concatenation of what might classically be regarded as the 'production' of the static field by a molecule A and the 'detection' of that field as registered by a probe molecule at a site D. The probe molecule is a simplified model of a detector; if a more general and complex case is considered, the detector should be modelled as a microscopic ensemble fixed in space.

The molecules interact with the electromagnetic field by absorbing a photon of mode (k_1, λ_1) and emitting a photon of mode (k_2, λ_2). To consider the most general case, obviating any unnecessary assumptions, these two interactions can take place either in molecule A, positioned at $\mathbf{R}_A$ and free to rotate, or at the probe molecule, fixed at $\mathbf{R}_D$ — though to admit the latter is a potentially complicating feature with little practical significance. However, the fact that the probe molecule is fixed in its site restricts the final results. In what follows, the general case is considered and then, the restriction is appropriately addressed.

The complete radiation-molecular system, including the detector, can first be described by the following Hamiltonian:

$$H = \sum_A H_0^A + H_0^D + H_{rad} + H_{\text{int}} \tag{2.1}$$

where H_0^A and H_0^D are the molecular Hamiltonians, H_{rad} is the electromagnetic Hamiltonian in free space and H_{int} is the interaction term for the coupling between the molecules and the field. In the multipolar formalism, and within the electric-dipole (E1) approximation, the interaction Hamiltonian is represented by

$$H_{\text{int}} = -\frac{1}{\epsilon_o} \sum_A \boldsymbol{\mu}(A) \cdot \mathbf{d}^{\perp}(A) - \frac{1}{\epsilon_o} \boldsymbol{\mu}(D) \cdot \mathbf{d}^{\perp}(D) . \tag{2.2}$$

The electro-optic effect can be described in terms of the matrix element for the pair AD, M_{fi}^{AD} , for which the first non-zero contribution is

$$M_{fi}^{AD} = - \sum_{I,\, II,\, III} \left\{ \frac{\langle f| H_{\text{int}} |III\rangle \langle III| H_{\text{int}} |II\rangle \langle II| H_{\text{int}} |I\rangle \langle I| H_{\text{int}} |i\rangle}{\tilde{E}_{III\,i}\, \tilde{E}_{II\,i}\, \tilde{E}_{I\,i}} \right\} \tag{2.3}$$

To evaluate this matrix element it is necessary to establish the initial and final states of the system, which are cast in terms of the solutions to the Schrödinger equation when no interaction is present:

$$\begin{aligned} |i\rangle &= \prod_{\mathrm{A}} \left|E_0^{\mathrm{A}}\right\rangle \times \left|E_0^{\mathrm{D}}\right\rangle \times \left|n\left(\mathbf{k}_1, \lambda_1\right),\ n'\left(\mathbf{k}_2, \lambda_2\right)\right\rangle , \\ |f\rangle &= \prod_{\mathrm{A}} \left|E_0^{\mathrm{A}}\right\rangle \times \left|E_0^{\mathrm{D}}\right\rangle \times \left|(n-1)\left(\mathbf{k}_1, \lambda_1\right),\ (n'+1)\left(\mathbf{k}_2, \lambda_2\right)\right\rangle . \end{aligned} \tag{2.4}$$

With the initial and final states of the system properly defined the matrix element can be written as the following integration over $\mathbf{p}$ (a wave-vector for the virtual coupling of each AD pair), following similar steps to those of Craig and Thirunamachandran[7]:

$$\begin{aligned} M_{fi}^{\mathrm{AD}} &= A_{kl} \int d\mathbf{p} \left\{ p \left(-\nabla^2 \delta_{kl} + \nabla_k \nabla_l\right) \left[\frac{\exp\left(-\mathrm{i}\mathbf{p} \cdot \mathbf{R}\right)}{k-p} - \frac{\exp\left(\mathrm{i}\mathbf{p} \cdot \mathbf{R}\right)}{k+p} \right] \right\} + \\ &\quad - B_{kl} \int d\mathbf{p}\ \left\{ \left(-\nabla^2 \delta_{kl} + \nabla_k \nabla_l\right) \left[\exp\left(-\mathrm{i}\mathbf{p} \cdot \mathbf{R}\right) - \exp\left(\mathrm{i}\mathbf{p} \cdot \mathbf{R}\right)\right] \right\}\ + (\mathrm{A} \leftrightarrow \mathrm{D}) \end{aligned} \tag{2.5}$$

where the tensors A_{kl} and B_{kl} are:

$$A_{kl} = \frac{\hbar c}{(2\epsilon_o)^2}\ \frac{k\sqrt{n\,(n'+1)}}{(2\pi)^3\, V}\ \exp\left[\mathrm{i}\left(\mathbf{k}_1 \cdot \mathbf{R}_{\mathrm{A}} - \mathbf{k}_2 \cdot \mathbf{R}_{\mathrm{D}}\right)\right]\ e_i^{\lambda_1} \bar{e}_j^{\lambda_2}\ \alpha_{jk}^{00}\ (\mathrm{D})\ \ \alpha_{li}^{00}\ (\mathrm{A}) , \tag{2.6}$$

$$B_{kl} = \frac{\hbar c}{(2\epsilon_o)^2}\ \frac{k\sqrt{n\,(n'+1)}}{(2\pi)^3\, V}\ \exp\left[\mathrm{i}\left(\mathbf{k}_1 - \mathbf{k}_2\right) \cdot \mathbf{R}_A\right]\ e_i^{\lambda_1} \bar{e}_j^{\lambda_2}\ \beta_{jki}^{00}\ (\mathrm{A})\ \ \mu_l^{00}\ (\mathrm{D}) . \tag{2.7}$$

Because of the phase factor in equation (2.6), the first term of the matrix element will give a null contribution when an ensemble is considered, and therefore this term can be dropped from here onwards. Using the Cauchy Principal Value theorem we obtain the following expression for the matrix element:

$$M_{fi}^{\mathrm{AD}} = \left(\frac{\hbar c k}{2\epsilon_o V}\right) \sqrt{n\ (n'+1)}\, e_i^{\lambda_1} \bar{e}_j^{\lambda_2} \left[\beta_{jki}^{00}(A)\ \ \mu_l^{00}(D)\ \ \exp\left(\mathrm{i}\, \Delta\mathbf{k} \cdot \mathbf{R}_A\right) +\ (\mathrm{D} \leftrightarrow \mathrm{A})\right]\ V_{kl}\left(0, \mathbf{R}\right) , \tag{2.8}$$

where $V_{kl}(0,\,\mathbf{R})$ is the instantaneous electrostatic interaction potential

$$V_{kl}(0,\,R) = \frac{1}{4\pi\epsilon_o R^3}\left(\delta_{kl} - 3\hat{R}_k\hat{R}_l\right). \tag{2.9}$$

From expression (2.8) it can be seen that the second term vanishes when the rotational average over the species A is calculated. It is also important to notice that the expression found for the matrix element M_{fi}^{AD} is for the case where $\mathbf{k}_1$ and $\mathbf{k}_2$ satisfy the energy conservation condition; to satisfy wave-vector matching we have that $\mathbf{k}_1 = \mathbf{k}_2 = \mathbf{k}$. In summary the matrix element for this process can be written as:

$$M_{fi}^{\mathrm{AD}} = \left(\frac{\hbar ck}{2\epsilon_o V}\right)\sqrt{n\,(n'+1)}\;e_i^{\lambda_1}\,\bar{e}_j^{\lambda_2}\beta_{jki}^{00}\,(\mathrm{A})\,V_{kl}\,(0,\,\mathbf{R})\;\;\mu_l^{00}\,(\mathrm{D}). \tag{2.10}$$

In this simple expression the inferred static field at $\mathbf{R}_{\mathrm{A}}$ is easily identified with the factor

$$\left(-\frac{\hbar ck}{2\epsilon_o V}\right)\;\sqrt{n\,(n'+1)}\;e_i^{\lambda_1}\,\bar{e}_j^{\lambda_2}\beta_{jki}^{00}\,(\mathrm{A})\,V_{kl}\,(0,\,\mathbf{R}) = E\,(0,\,\mathbf{R})\;\;(\hat{\mathbf{e}}_s)_l\,, \tag{2.11}$$

where E is the static field at $\mathbf{R}_{\mathrm{A}}$ and $(\hat{\mathbf{e}}_s)_l$ is a component of the unit vector. In passing, it is important to note that the direction of the static field is determined by the instantaneous electrostatic interaction potential.

Equation (2.10) has been written in terms of a third-rank hyperpolarisability tensor, . This tensor can be expressed as follows in terms of the dipole moments $\boldsymbol{\mu}^{ab}$ and differences between the energy of the initial and intermediate states:

$$\begin{aligned}\beta_{jki}\,(\mathrm{A}) \;\; = \;\; & \sum_{r,s}\left\{\frac{\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}}{(E_{s0}-\hbar\omega)\,(E_{r0}-\hbar\omega)} + \frac{\mu_i^{0s}\mu_k^{sr}\mu_j^{r0}}{(E_{s0}+\hbar\omega)\,(E_{r0}+\hbar\omega)} + \frac{\mu_k^{0s}\mu_j^{sr}\mu_i^{r0}}{(E_{s0})\,(E_{r0}-\hbar\omega)}\right.\\ & \left. + \frac{\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}}{(E_{s0})\,(E_{r0}+\hbar\omega)} + \frac{\mu_j^{0s}\mu_i^{sr}\mu_k^{r0}}{(E_{s0}-\hbar\omega)\,(E_{r0})} + \frac{\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}}{(E_{s0}+\hbar\omega)\,(E_{r0})}\right\}_{(\mathrm{A})}\end{aligned} \tag{2.12}$$

where on the left the superscript 00 indicating the final and initial molecular states has been dropped for brevity.

To take into full account the resonant or near-resonant case, it is necessary to introduce at this stage damping factors Γ_s associated with the molecular excited state $|s\rangle$, through their lifetime, $2\hbar\Gamma_s^{-1}$. There are two different schools of thought on the signing of the damping factor. If the damping factor is introduced using the constant sign convention, *csc* for short (ref.[4] and references therein), the hyperpolarisability tensor is written as:

$$\begin{aligned}\beta_{jki}^{csc}\,(\mathrm{A}) \;\; = \;\; & \sum_{r,s}\left\{\frac{\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}}{(E_{s0}-\mathrm{i}\Gamma_s-\hbar\omega)\,(E_{r0}-\mathrm{i}\Gamma_r-\hbar\omega)} + \frac{\mu_i^{0s}\mu_k^{sr}\mu_j^{r0}}{(E_{s0}-\mathrm{i}\Gamma_s+\hbar\omega)\,(E_{r0}-\mathrm{i}\Gamma_r+\hbar\omega)}+\right.\\ & + \frac{\mu_k^{0s}\mu_j^{sr}\mu_i^{r0}}{(E_{s0}-\mathrm{i}\Gamma_s)\,(E_{r0}-\mathrm{i}\Gamma_r-\hbar\omega)} + \frac{\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}}{(E_{s0}-\mathrm{i}\Gamma_s)\,(E_{r0}-\mathrm{i}\Gamma_r+\hbar\omega)} +\\ & \left. + \frac{\mu_j^{0s}\mu_i^{sr}\mu_k^{r0}}{(E_{s0}-\mathrm{i}\Gamma_s-\hbar\omega)\,(E_{r0}-\mathrm{i}\Gamma_r)} + \frac{\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}}{(E_{s0}-\mathrm{i}\Gamma_s+\hbar\omega)\,(E_{r0}-\mathrm{i}\Gamma_r)}\right\}_{(\mathrm{A})}\end{aligned} \tag{2.13}$$

On the other hand, if the variable sign convention (vsc) (ref.[4] and references therein) is used the susceptibility tensor takes the form:

$$\begin{aligned}\beta_{jki}^{vsc}\,(\mathrm{A}) \;\; = \;\; & \sum_{r,s}\left\{\frac{\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}}{(E_{s0}-\mathrm{i}\Gamma_s-\hbar\omega)\,(E_{r0}-\mathrm{i}\Gamma_r-\hbar\omega)} + \frac{\mu_i^{0s}\mu_k^{sr}\mu_j^{r0}}{(E_{s0}+\mathrm{i}\Gamma_s+\hbar\omega)\,(E_{r0}+\mathrm{i}\Gamma_r+\hbar\omega)}+\right.\\ & + \frac{\mu_k^{0s}\mu_j^{sr}\mu_i^{r0}}{(E_{s0}-\mathrm{i}\Gamma_s)\,(E_{r0}-\mathrm{i}\Gamma_r-\hbar\omega)} + \frac{\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}}{(E_{s0}-\mathrm{i}\Gamma_s)\,(E_{r0}+\mathrm{i}\Gamma_r+\hbar\omega)} +\\ & \left. + \frac{\mu_j^{0s}\mu_i^{sr}\mu_k^{r0}}{(E_{s0}-\mathrm{i}\Gamma_s-\hbar\omega)\,(E_{r0}+\mathrm{i}\Gamma_r)} + \frac{\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}}{(E_{s0}+\mathrm{i}\Gamma_s+\hbar\omega)\,(E_{r0}+\mathrm{i}\Gamma_r)}\right\}_{(\mathrm{A})}\end{aligned} \tag{2.14}$$

By application of HT symmetry (the combination of the time reversal operation with hermitian conjugation)[4] to the first, second, fifth and sixth terms of equation (2.13) it can be seen that $\beta_{jki}^{csc}\,(-\omega;\,\omega,\,0)$ is symmetric under the interchange $j \leftrightarrow i$:

$$
\begin{aligned}
\beta^{csc}_{jki}\left(\mathrm{A}\right) \;=\; \sum_{r,s} \Bigg\{ & \frac{\frac{1}{2}\left(\mu^{0s}_{j}\mu^{sr}_{k}\mu^{r0}_{i}+\mu^{0s}_{i}\mu^{sr}_{k}\mu^{r0}_{j}\right)}{\left(E_{s0}-\mathrm{i}\Gamma_{s}-\hbar\omega\right)\left(E_{r0}-\mathrm{i}\Gamma_{r}-\hbar\omega\right)} + \frac{\frac{1}{2}\left(\mu^{0s}_{i}\mu^{sr}_{k}\mu^{r0}_{j}+\mu^{0s}_{j}\mu^{sr}_{k}\mu^{r0}_{i}\right)}{\left(E_{s0}-\mathrm{i}\Gamma_{s}+\hbar\omega\right)\left(E_{r0}-\mathrm{i}\Gamma_{r}+\hbar\omega\right)} + \\
& + \frac{\mu^{0s}_{k}\mu^{sr}_{j}\mu^{r0}_{i}}{\left(E_{s0}-\mathrm{i}\Gamma_{s}\right)\left(E_{r0}-\mathrm{i}\Gamma_{r}-\hbar\omega\right)} + \frac{\mu^{0s}_{k}\mu^{sr}_{i}\mu^{r0}_{j}}{\left(E_{s0}-\mathrm{i}\Gamma_{s}\right)\left(E_{r0}-\mathrm{i}\Gamma_{r}-\hbar\omega\right)} + \\
& + \frac{\mu^{0s}_{k}\mu^{sr}_{i}\mu^{r0}_{j}}{\left(E_{s0}-\mathrm{i}\Gamma_{s}\right)\left(E_{r0}-\mathrm{i}\Gamma_{r}+\hbar\omega\right)} + \frac{\mu^{0s}_{k}\mu^{sr}_{j}\mu^{r0}_{i}}{\left(E_{s0}-\mathrm{i}\Gamma_{s}\right)\left(E_{r0}-\mathrm{i}\Gamma_{r}+\hbar\omega\right)} \Bigg\}_{(\mathrm{A})} .
\end{aligned}
\tag{2.15}
$$

On the contrary, when the HT operation is applied to equivalent terms in equation (2.14) $\beta^{vsc}_{jki}\left(-\omega;\,\omega,\,0\right)$ does not present the same type of symmetry:

$$
\begin{aligned}
\beta^{vsc}_{jki}\left(\mathrm{A}\right) \;=\; \sum_{r,s} \Bigg\{ & \frac{\frac{1}{2}\left(\mu^{0s}_{j}\mu^{sr}_{k}\mu^{r0}_{i}+\mu^{0s}_{i}\mu^{sr}_{k}\mu^{r0}_{j}\right)}{\left(E_{s0}-\mathrm{i}\Gamma_{s}-\hbar\omega\right)\left(E_{r0}-\mathrm{i}\Gamma_{r}-\hbar\omega\right)} + \frac{\frac{1}{2}\left(\mu^{0s}_{i}\mu^{sr}_{k}\mu^{r0}_{j}+\mu^{0s}_{j}\mu^{sr}_{k}\mu^{r0}_{i}\right)}{\left(E_{s0}+\mathrm{i}\Gamma_{s}+\hbar\omega\right)\left(E_{r0}+\mathrm{i}\Gamma_{r}+\hbar\omega\right)} + \\
& + \frac{\mu^{0s}_{k}\mu^{sr}_{j}\mu^{r0}_{i}}{\left(E_{s0}-\mathrm{i}\Gamma_{s}\right)\left(E_{r0}-\mathrm{i}\Gamma_{r}-\hbar\omega\right)} + \frac{\mu^{0s}_{k}\mu^{sr}_{i}\mu^{r0}_{j}}{\left(E_{s0}-\mathrm{i}\Gamma_{s}\right)\left(E_{r0}+\mathrm{i}\Gamma_{r}-\hbar\omega\right)} + \\
& + \frac{\mu^{0s}_{k}\mu^{sr}_{i}\mu^{r0}_{j}}{\left(E_{s0}-\mathrm{i}\Gamma\right)_{s}\left(E_{r0}+\mathrm{i}\Gamma_{r}+\hbar\omega\right)} + \frac{\mu^{0s}_{k}\mu^{sr}_{j}\mu^{r0}_{i}}{\left(E_{s0}+\mathrm{i}\Gamma_{s}\right)\left(E_{r0}+\mathrm{i}\Gamma_{r}+\hbar\omega\right)} \Bigg\}_{(\mathrm{A})} .
\end{aligned}
\tag{2.16}
$$

2.2 Rotational Average

Through the electro-optic interaction, if allowed, the system suffers an energy shift, due to the interaction Hamiltonian H_{int}. This shift is associated, in first approximation, with the matrix element M^{AD}_{fi}, equation (2.10), through:

$$
\Delta E \;= M^{\mathrm{EOR}}_{fi} = \sum_{A=1}^{N} M^{\mathrm{AD}}_{fi}
\tag{2.17}
$$

Since all N AD pair matrix elements are equivalent to each other the rotational average of the energy shift is simply:

$$
\begin{aligned}
\left\langle \Delta E \;\right\rangle \;&=\; N\;\left\langle M^{\mathrm{AD}}_{fi}\right\rangle \\
&=\; \left(\frac{\hbar ck}{2\epsilon_{o}V}\right) N\,\sqrt{n\left(n'+1\right)}\, e^{\lambda_1}_{L_i}\,\bar{e}^{\lambda_2}_{L_j}\,\left\langle \beta^{00}_{L_jL_kL_i}\left(\mathrm{D}\right)\mu^{00}_{L_l}\left(\mathrm{A}\right)\,V_{L_kL_l}\left(0,\,\mathbf{R}\right)\right\rangle
\end{aligned}
\tag{2.18}
$$

In this expression we have denoted the sub-indices of the tensors with the subscript L to emphasise the fact that they refer to a space-frame fixed in the laboratory. The rotational average $\left\langle \beta^{00}_{L_jL_kL_i}\left(\mathrm{D}\right)\mu^{00}_{L_l}\left(\mathrm{A}\right)\,V_{L_kL_l}\left(0,\,\mathbf{R}\right)\right\rangle$ in general involves three different frame-decoupling rotational averages.[8] However in the case under scrutiny, the probe molecule D representing the detector is fixed, and consequently only one rotational average is necessary. To do so it is necessary to consider a frame fixed on molecule A:

$$
\mu^{00}_{L_l}\left(\mathrm{D}\right)\left\langle \beta_{L_jL_kL_i}\left(\mathrm{A}\right)\,V_{L_kL_l}\left(0,\,\mathbf{R}\right)\right\rangle = \mu^{00}_{L_l}\left(\mathrm{D}\right)\,I^{(3)}\,\beta_{A_jA_kA_i}\left(\mathrm{A}\right)\,V_{L_kL_l}\left(0,\,\mathbf{R}\right),
$$

where $I^{(3)} = \frac{1}{6}\epsilon_{L_jL_kL_i}\epsilon_{A_jA_kA_i}$. Therefore, the ensemble value of the energy shift can be written as:

$$
\left\langle \Delta E\right\rangle \approx \left(\frac{\hbar ck}{12\epsilon_{o}V}\right) N\;\sqrt{n\left(n'+1\right)}\;\epsilon_{L_jL_kL_i}e^{\lambda_1}_{L_i}\,\bar{e}^{\lambda_2}_{L_j}\mu_{L_l}\left(\mathrm{D}\right)\epsilon_{A_jA_kA_i}\,\beta_{A_jA_kA_i}\left(\mathrm{A}\right)\,V_{L_lL_k}\left(0,\,\mathbf{R}\right),
\tag{2.19}
$$

or simply

$$
\left\langle \Delta E\right\rangle \approx \left(\frac{\hbar ck}{6\,\epsilon_{o}V}\right) N\;\sqrt{n\left(n'+1\right)}\;\left[\left(\mathbf{e}^{\lambda_1}\times\bar{\mathbf{e}}^{\lambda_2}\right)_{k}\bar{\beta}\;\,V_{lk}\left(0,\,\mathbf{R}\right)\right]\;\;\mu_{l}\left(\mathrm{D}\right).
\tag{2.20}
$$

where the subscripts A and L have been dropped for simplicity. Equation (2.20) has been written in terms of $\bar{\beta}$, the anti-symmetric part of the tensor β, which can also be expressed as:

$$
\begin{aligned}
\bar{\beta} &= \frac{1}{2}\left(\beta_{xyz}-\beta_{zyx}\right)+\frac{1}{2}\left(\beta_{yzx}-\beta_{xzy}\right)+\frac{1}{2}\left(\beta_{zxy}-\beta_{yxz}\right) \\
&= \sum_{\substack{\{j,k,i\}=\{x,y,z\} \\ \text{cyclic}}} \frac{1}{2}\left(\beta_{jki}-\beta_{ikj}\right). \qquad (2.21)
\end{aligned}
$$

With a hyperpolarisability tensor correctly constructed by reference to the constant sign convention, β_{ijk}^{csc} in equation (2.15), it can easily be seen that the anti-symmetric part $\bar{\beta}$ is null, and the electro-optic signal disappears. On the other hand, the signal survives if the hyperpolarisability tensor β_{ijk}^{vsc} is constructed using the variable sign convention, since the anti-symmetric part is then non-zero and equal to:

$$
\beta^{vsc} = \sum_{\substack{\{j,k,i\}=\{x,y,z\} \\ \text{cyclic}}} \left\{ \sum_{s,\ r} \frac{\mathrm{i}\Gamma_s}{E_{s0}^2+\Gamma_s^2} \frac{(\hbar\omega+\mathrm{i}\Gamma_r)}{(E_{r0})^2-(\hbar\omega+\mathrm{i}\Gamma_r)^2} \left(\mu_l^{0s}\mu_j^{sr}\mu_i^{r0}-\mu_l^{0s}\mu_i^{sr}\mu_j^{r0}\right) \right\}. \qquad (2.22)
$$

In this case the effect would be of order Γ_s/E_{s0} times the amplitude. Hence, within the constant sign convention the process is forbidden in the electric-dipole approximation, whereas it would not be under the variable sign convention. This result should in principle be amenable to experimental verification.

3 Multipole considerations

To conclude matters it is necessary to account for the fact that, in the constant sign convention, the process is allowed at multipole couplings beyond the electric dipole approximation. It is therefore of some interest to estimate whether it is possible to attribute any residual observed electro-optic response in fluids to the breakdown of electric-dipole coupling, rather than take such an observation as a vindication of the use of a variable sign convention within E1. Would the latter mechanism, which we consider to be inapplicable, conceivably masquerade in inducing the effects of the former? Either, of course, could be wrongly attributed if an experiment were to give a false affirmative.

To address this question, let us compare the magnitudes of such E1-violating terms with a conjectured response based on equation (2.22). We denote the direction of the static electric field by $\mathbf{e}_s$ and denote the polarisations of the incoming and outgoing photons by $\mathbf{e}_1$ and $\mathbf{e}_2$ respectively (both with wave-vector $\mathbf{k}$). In the electric dipole approximation the rotational average[9] results in these three vectors contracting to give the scalar $(\mathbf{e}_2\times\mathbf{e}_1)\cdot\mathbf{e}_s$ as in equation (2.20), and $\mathbf{e}_s$ must therefore have a projection along $\mathbf{k}$. At the magnetic dipole and electric quadrupole level, i.e. at the level that is linear in k, the rotational average results in the three scalars

$$
(\mathbf{e}_2\cdot\mathbf{e}_1)(\mathbf{e}_s\cdot\mathbf{k}),\quad (\mathbf{e}_2\cdot\mathbf{e}_s)(\mathbf{e}_1\cdot\mathbf{k}),\quad (\mathbf{e}_1\cdot\mathbf{e}_s)(\mathbf{e}_2\cdot\mathbf{k}), \qquad (3.1)
$$

all three of which are necessarily zero. For the parts of the amplitude that are quadratic in k the rotational average results in scalars such as $(\mathbf{e}_2\times\mathbf{e}_1)\cdot\mathbf{e}_s\,(\mathbf{k}\cdot\mathbf{k})$, which are non-zero for any choice of polarisations. This verifies that the process is possible at higher orders than E1 coupling in the fixed sign prescription; in particular at the electric octopole/magnetic quadrupole level. A comparison of equation (2.15) with equation (2.22), where in the former the electric dipole interaction terms have been replaced by such higher order multipole interactions (and therefore reduced by approximately by a factor of α^2 where α is the fine structure constant) shows that the ratio of the amplitudes in the two conventions may be approximated as

$$
\frac{A_{vsc}}{A_{csc}} \approx \frac{\Gamma_r}{\alpha^2 E_{0r}} \qquad (3.2)
$$

In Beljonne *et al.*[5] the frequency-dependent material damping rates are defined as $\Gamma_{r0} = C\omega_{r0}$ where C is an empirical constant set to 0.016 (for condensed matter sub-systems). Then for $\omega_{r0} \sim 2-5$ eV , the homogeneous damping, $\hbar^{-1}\Gamma_{r0}$, is at least of order 10^{13} s $^{-1}$. Given that the transition energy[5] is of the order $\hbar^{-1}E_{r0} \approx 10^{15}$ s $^{-1}$, the ratio in equation (3.2) is approximately 10^2 . Our analysis, along with that of Andrews *et al.*[4] thus gives evidence that a relatively large EOR signal, predicted by the variable sign prescription, is spurious, and that any observed EOR in isotropic systems can arise (in accordance with the theory based on the fixed sign prescription) only from the relatively small contribution of multipoles beyond E1.

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