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# Applications of group-theoretical statistical mechanics: Interaction of electromagnetic fields with molecular ensembles

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The techniques of group-theoretical statistical mechanics (GTSM) are applied to various aspects of the interaction of electromagnetic radiation with molecular ensembles. Six nonlinear optical effects are examined in terms of the three principles of GTSM, using a classical series expansion of the induced electric dipole moment in terms of the electric and magnetic components of the electromagnetic field. Classical-quantum equivalence relations are derived at each stage. Symmetry arguments are applied to the chiral properties of some of the new nonlinear optical effects using the third principle of GTSM. A careful distinction is made between natural and magnetic optical activity, and our analysis attempts to resolve some recent disagreements in the literature.

## I. INTRODUCTION

The three principles of group-theoretical statistical mechanics (GTSM) have recently been developed[1–4] following the guidelines provided by equilibrium and nonequilibrium computer simulation of the dynamics of molecular ensembles. The first two principles deal with the field-free dynamics, and the third with the interaction of external fields with atomic and molecular ensembles. Using these principles, advances have been made in microrheology,[5–8] light scattering,[9] and shear-induced dielectric relaxation for atomic and molecular ensembles, and for liquid crystals.[10–12]

In this paper, we extend the range of applicability of the three principles to nonlinear optics, chirality, and parity violation in the interaction of molecular matter with electromagnetic radiation. In Sec. II the interaction of radiation with ensemble is described in a classical expansion of the induced-dipole moment in terms of field-susceptibility tensor products which are used to define the classical equivalents of six nonlinear optical effects: (1) the electromagnetic **EB** effect; (2) the **BB** magnetochiral birefringence; (3) the inverse Faraday effect; (4) the inverse magnetochiral birefringence (the Wagnière effect); (5) second-order electric rectification; and (6) second-order magnetic rectification. In each case the third principle of group-theoretical statistical mechanics is used to describe the new ensemble averages expected from the various field-molecule interactions. This extends consideration of these effects to ensembles of molecules, as opposed to isolated molecules. The latter is usually the basis for the accepted quantum-mechanical perturbation theory[13–20] but the third principle allows definition of new field-induced ensemble averages for each term in the field multipole expansion of the induced-dipole moment. Thus, each term has its own set of field-dependent Langevin functions of appropriate order, and time correlation functions of relevant molecular dynamical variables. These are ensemble averages accessible in principle to computer simulation.[21–25]

Having established the classical basis of the various nonlinear optical effects, Sec. III describes their chiral properties in terms of natural and magnetic optical activity. The latter are defined with irreducible representations of appropriate ensemble point groups, i.e., the rotation or reflection group of achiral ensembles, or the rotation group of chiral ensembles, both in the laboratory frame $(X,Y,Z)$.

Principle (3) anticipates possible parity-violating configurations in the interaction of electromagnetic radiation with molecular ensembles. The complete $C$, $P$, $T$, and $D$ symmetries or force fields must be imparted to atomic and molecular ensembles, i.e., it is a generally applicable cause-and-effect principle. Parity inversion symmetry is part of the complete field symmetry, and parity violation is deemed to occur when an observable does not conserve the complete symmetry according to principle (3).

Section IV is a discussion of possible applications, in these areas, of computer simulation.

## II. SYMMETRIES OF NONLINEAR OPTICAL EFFECTS

Principle (3) in this context deals with the interaction of electromagnetic radiation with molecular matter. In general the interaction results in the appearance of new field-induced observables, for example nonvanishing ensemble averages over molecular electric and magnetic dipole moments, respectively termed "polarization" and "magnetization." The electromagnetic radiation field in general has electric and magnetic components which can generate sum and difference frequencies.[26-28] The symmetry of the observable is in general obtained from a product of a susceptibility term and a field term. Principle (3) asserts that the relevant set of *C*, *P*, *T*, and *D* symmetries of this product are imparted to the observable in the absence of parity-violating effects. The observable is a thermodynamic ensemble average with this *C*, *P*, *T*, and *D* symmetry. This can be a thermodynamic average over a sum of induced and permanent molecular dipole moments, from which Langevin functions may be constructed[21-25] as a function of field strength; or time correlation functions describing the dynamical response of the complete ensemble. Principle (3) isolates the correlation functions that can respond to the field from those which must vanish by symmetry.

### A. Symmetry definitions

*C*, *P*, and *T* are operators signifying respectively the symmetries of charge reversal, parity inversion, and time reversal in standard literature definitions.[29,30] The *D* symmetries are irreducible representations of the point groups of molecular ensembles. For ensembles of structurally achiral molecules they are irreducible representations of the point group $R_h(3)$ of all rotations and reflections, denoted by $D_g^{(0)}, \ldots, D_g^{(n)}$ or $D_u^{(0)}, \ldots, D_u^{(n)}$. The superscripts denote order of spherical harmonics, and subscripts denote whether a quantity is positive ($g$) or negative ($u$) to $P$. The *D* symmetry of a scalar (such as mass) is $D_g^{(0)}$, that of a polar vector such as velocity is $D_u^{(1)}$. A traceless, symmetric, tensor quantity of second rank is $D_g^{(2)}$; an axial vector or pseudovector, is $D_g^{(1)}$. Higher-order tensor quantities may be generated from those of lower order using the Clebsch-Gordan theorem, which in general is

$$\begin{gathered} D^{(n)}D^{(m)}=D^{n+m}+\cdots+D^{|n-m|} , \\ g\times g=u\times u=g , \\ g\times u=u\times g=u . \end{gathered} \tag{1}$$

The point group of isotropic ensembles of structurally chiral molecules is denoted $R(3)$, and is the point group of all rotations. Its irreducible representations are the *D* symbols without subscripts, because *P* in this case takes the ensemble to its enantiomer, a physically different entity. Thus the complete representation of a quantity such as $\nabla\mathbf{E}$ in $R(3)$ is constructed from the complete product of those of $\nabla$ and $\mathbf{E}$. Here $\mathbf{E}$ represents the electric field and $\nabla$ the del operator. The Clebsch-Gordan theorem gives

$$\Gamma(\nabla\mathbf{E})=D^{(0)}+D^{(1)}+D^{(2)} , \tag{2}$$

a sum of three parts. Note that this sum is an expression of the fact that the second rank tensor $A_{ij}$ is in general the sum

$$A_{ij}=\tfrac{1}{3}A\delta_{ij}+C_k+S_{ij} . \tag{3}$$

TABLE I. Principle (3) of GTSM applied to six nonlinear optical effects.

| Effect | Susceptibility elements | | | Field elements | | Observable |
|---|---|---|---|---|---|---|
| 1 | **m** | $\mu$ | $\mu$ | $\mathbf{B}_+$ | $\mathbf{E}_-$ | **p** |
| *P* | + | − | − | + | − | − |
| *T* | − | + | + | − | + | + |
| 2 | **m** | **m** | $\mu$ | $\mathbf{B}_+$ | $\mathbf{B}_-$ | **p** |
| *P* | + | + | − | + | + | − |
| *T* | − | − | + | − | − | + |
| 3 | $\mu$ | $\mu$ | **m** | $\mathbf{E}_-$ | $\mathbf{E}_+$ | **M** |
| *P* | − | − | + | − | − | + |
| *T* | + | + | − | + | + | − |
| 4 | $\mu$ | **m** | **m** | $\mathbf{E}_-$ | $\mathbf{B}_+$ | **M** |
| *P* | − | + | + | − | + | + |
| *T* | + | − | − | + | − | − |
| 5 | $\mu$ | $\mu$ | $\mu$ | $\mathbf{E}_-$ | $\mathbf{E}_+$ | **p** |
| *P* | − | − | − | − | − | − |
| *T* | + | + | + | + | + | + |
| 6 | **m** | **m** | **m** | $\mathbf{B}_-$ | $\mathbf{B}_+$ | **M** |
| *P* | + | + | + | + | + | + |
| *T* | − | − | − | − | − | − |

$A/3$ is the trace, denoted by $D^{(0)}$. Here $\delta_{ij}$ is the Kronecker $\delta$ function. $C_k = B_{ij} = \frac{1}{2}(A_{ij} - A_{ji})$ is the antisymmetric part, equivalent to a pseudovector through the relation $C_k = \frac{1}{2}\epsilon_{ijk} B_{ij}$ where $\epsilon_{ijk}$ is the Levi-Civita symbol. This part is denoted $D^{(1)}$. The third part $D^{(2)}$ is the irreducible, traceless, symmetric, second-rank tensor $\frac{1}{2}(A_{ij} + A_{ji}) - \frac{1}{3} A \delta_{ij}$. The quantities $A$, $C_k$, and $S_{ij}$ form spherical tensors of rank 0, 1, and 2, transforming as the spherical harmonics $Y_L^M$ for $L=0$, 1, and 2.

The principle (3) (Refs. 1–4) of group theoretical statistical mechanics (GTSM) applied to the interaction of electromagnetic radiation with molecular ensembles asserts that the $C$, $P$, $T$, and $D$ symmetries of the field-induced observable is in general all or part of the complete product of the symmetry representation of the field with that of the susceptibility of the ensemble.

Examples of the principle at work in the perturbation theory[26–28] of six nonlinear optical effects are given in Table I. These are (1) the second-order electromagnetic **BE** effect; (2) **BB** magnetochiral birefringence (a type of Wagnière-Meier effect); (3) the inverse Faraday effect; (4) inverse magnetochiral birefringence (the Wagnière effect); (5) electric rectification; and (6) magnetic rectification.

In Table I the $\boldsymbol{\mu}$ symbols denote matrix elements[26–28] of the field-induced molecular electric dipole moment. The **m** symbols denote the magnetic equivalents. A complete description of the susceptibility and field parts of the field–single-molecule interaction in perturbation theory is available in Refs. 31 and 32. The field and susceptibility parts factorize[31,32] after isotropic averaging. In Table I $\mathbf{B}_\pm$ denotes in general the magnetic component of the electromagnetic field and $\mathbf{E}_\pm$ the electric component. Finally, **p** denotes polarization and **M** magnetization. It can be seen that for each of the six nonlinear optical effects the product of $P$ and $T$ symmetries of the three susceptibility and two field components are the same as the $P$ and $T$ symmetries of the observable, i.e., magnetization or polarization as the case may be. The $D$ symmetries of the observables are obtained from the appropriate components of the complete product of $D$ symmetries of field and susceptibility.

This illustrates the use of principle (3) in the single-molecule quantum-mechanical perturbation theory[26–28,31,32] of which Table I is a summary.

Principle (3) may be used to extend this analysis to the nonlinear interaction of electromagnetic radiation with ensembles of molecules. We use the classical equivalent of the quantum theory to bring the interaction components into forms suitable for computer simulation, which is still largely classical.[21–25] This has the great advantage of allowing the detailed investigation by computer simulation of Langevin functions and time correlation functions (the Fourier transforms of spectral functions) produced by the appropriate field-ensemble interaction operator for each nonlinear optical effect.

### B. Electromagnetic field equations

In nonlinear optical effects complex-conjugate sum and difference frequencies occur[31,32] and in Table I these are classified by the + or − subscripts. The electromagnetic field in general is left or right circularly polarized. In order to be clear about the meaning of these subscripts, the complete set of field equations is given below:

$$\mathbf{E}_-^{(L)} = E_0(\mathbf{i} + i\mathbf{j})e^{-i\theta_L}, \quad \mathbf{E}_-^{(R)} = E_0(\mathbf{i} - i\mathbf{j})e^{-i\theta_R},$$

$$\mathbf{E}_+^{(L)} = E_0(\mathbf{i} - i\mathbf{j})e^{i\theta_L}, \quad \mathbf{E}_+^{(R)} = E_0(\mathbf{i} + i\mathbf{j})e^{i\theta_R},$$

$$\mathbf{B}_-^{(L)} = B_0(\mathbf{j} - i\mathbf{i})e^{-i\theta_L}, \quad \mathbf{B}_-^{(R)} = B_0(\mathbf{j} + i\mathbf{i})e^{-i\theta_R},$$

$$\mathbf{B}_+^{(L)} = B_0(\mathbf{j} + i\mathbf{i})e^{i\theta_L}, \quad \mathbf{B}_+^{(R)} = B_0(\mathbf{j} - i\mathbf{i})e^{i\theta_R},$$

$$\theta_L = \omega t - \mathbf{K}_L \cdot \mathbf{r}, \quad \theta_R = \omega t - \mathbf{K}_R \cdot \mathbf{r} .$$

These equations describe electromagnetic radiation propagating in the $Z$ axis of the laboratory frame with unit vector **i** in $X$, unit vector **j** in $Y$. Here $i$ denotes $(-1)^{1/2}$. The phase factors $\theta_L$ and $\theta_R$ are in IUPAC convention.

### C. Classical expansion of the induced electric and magnetic molecular dipole moments

With these definitions of symmetry and electromagnetic field the radiation induced molecular electric and magnetic dipole moments can be written in a series expansion involving term-by-term products of molecular property tensors with field components. These classical tensors have quantum equivalents which are exemplified at low order in the expansion.

For each molecule in the ensemble, the total molecular electric dipole moment at an instant $t$ is expanded as[33]

$$\langle \boldsymbol{\mu} \rangle_i = \langle \boldsymbol{\mu}_0 \rangle_i + \langle \boldsymbol{\alpha}_{ij} \rangle \mathbf{E}_j + \langle \boldsymbol{\beta}_{ijk} \rangle \mathbf{E}_j \mathbf{E}_k + \langle \boldsymbol{\alpha}_{1ij} \rangle \dot{\mathbf{B}}_j + \langle \boldsymbol{\beta}_{1ijk} \rangle \dot{\mathbf{B}}_j \dot{\mathbf{B}}_k + \langle \beta_{2ijk} \rangle \mathbf{E}_j \dot{\mathbf{B}}_k + \cdots . \tag{4}$$

The right-hand side of this equation is written in standard tensor notation, where summation over repeated indices is implied.

The complete dipole moment is the sum of a permanent molecular dipole moment $\boldsymbol{\mu}_0$ and field-induced components proportional to powers of **E** and **B** through classical molecular property tensors. For example, $\langle \boldsymbol{\alpha} \rangle$ is the molecular electric polarizability, of symmetry $D_g^{(0)} + D_g^{(2)}$; $\langle \boldsymbol{\beta} \rangle$ is the molecular electric hyperpolarizability of symmetry $D_u^{(1)} + D_u^{(3)}$. In chiral ensembles[33] the less-well-known molecular tensors $\langle \boldsymbol{\alpha}_1 \rangle$, $\langle \boldsymbol{\beta}_1 \rangle$, and $\langle \boldsymbol{\beta}_2 \rangle$ are nonzero. The molecular tensor $\langle \boldsymbol{\alpha}_1 \rangle$ is the foundation of the Rosenfeld equation[33] for optical rotation strength, and being − to $P$, can survive ensemble averaging only in chiral ensembles, where there are no parity subscripts to the $D$ representations.

Similarly, the total molecular magnetic dipole moment is expressed classically as the sum of a permanent magnetic dipole moment $\mathbf{m}_0$ and field-induced components, products of molecular property tensors of appropriate $D$ symmetry, and field terms,

$$\langle \mathbf{m} \rangle_i = \langle \mathbf{m}_0 \rangle_i + \langle \mathbf{a}_{ij} \rangle \mathbf{B}_j + \langle \mathbf{b}_{ijk} \rangle \mathbf{B}_j \mathbf{B}_k + \langle \mathbf{a}_{1ij} \rangle \dot{\mathbf{E}}_j + \langle b_{1ijk} \rangle \dot{\mathbf{E}}_j \dot{\mathbf{E}}_k + \langle b_{2ijk} \rangle \mathbf{B}_j \dot{\mathbf{E}}_k + \cdots . \tag{5}$$

The complete $D$ symmetries of the terms in Eqs. (4) and (5) are summarized in Table II for point groups $R_h(3)$

TABLE II. Irreducible $D$ representations of terms in Eqs. (4) and (5).

| Quantity | $P$ | $T$ | $R_h(3)$ | $R(3)$ |
|---|---|---|---|---|
| $\mathbf{E}$ | − | + | $D_u^{(1)}$ | $D^{(1)}$ |
| $\mathbf{EE}$ | + | + | $D_g^{(0)}+D_g^{(1)}+D_g^{(2)}$ | $D^{(0)}+D^{(1)}+D^{(2)}$ |
| $\dot{\mathbf{B}}$ | + | + | $D_g^{(1)}$ | $D^{(1)}$ |
| $\dot{\mathbf{B}}\dot{\mathbf{B}}$ | + | + | $D_g^{(0)}+D_g^{(1)}+D_g^{(2)}$ | $D^{(0)}+D^{(1)}+D^{(2)}$ |
| $\mathbf{E}\dot{\mathbf{B}}$ | − | + | $D_u^{(0)}+D_u^{(1)}+D_u^{(2)}$ | $D^{(0)}+D^{(1)}+D^{(2)}$ |
| $\langle \boldsymbol{\mu}_0 \rangle$ | − | + | $D_u^{(1)}$ | $D^{(1)}$ |
| $\langle \boldsymbol{\alpha} \rangle$ | + | + | $D_g^{(0)}+D_g^{(2)}$ | $D^{(0)}+D^{(2)}$ |
| $\langle \boldsymbol{\beta} \rangle$ | − | + | $D_u^{(1)}+D_u^{(3)}$ | $D^{(1)}+D^{(3)}$ |
| $\langle \boldsymbol{\alpha}_1 \rangle$ | − | + | $D_u^{(0)}+D_u^{(2)}$ | $D^{(0)}+D^{(2)}$ |
| $\langle \boldsymbol{\beta}_1 \rangle$ | − | + | $D_u^{(1)}+D_u^{(3)}$ | $D^{(1)}+D^{(3)}$ |
| $\langle \boldsymbol{\beta}_2 \rangle$ | + | + | $D_g^{(1)}+D_g^{(3)}$ | $D^{(1)}+D^{(3)}$ |
| $\mathbf{B}$ | + | − | $D_g^{(1)}$ | $D^{(1)}$ |
| $\mathbf{BB}$ | + | + | $D_g^{(0)}+D_g^{(1)}+D_g^{(2)}$ | $D^{(0)}+D^{(1)}+D^{(2)}$ |
| $\dot{\mathbf{E}}$ | − | − | $D_u^{(1)}$ | $D^{(1)}$ |
| $\dot{\mathbf{E}}\dot{\mathbf{E}}$ | + | + | $D_g^{(0)}+D_g^{(1)}+D_g^{(2)}$ | $D^{(0)}+D^{(1)}+D^{(2)}$ |
| $\mathbf{B}\dot{\mathbf{E}}$ | − | + | $D_u^{(0)}+D_u^{(1)}+D_u^{(2)}$ | $D^{(0)}+D^{(1)}+D^{(2)}$ |
| $\langle \mathbf{m} \rangle$ | + | − | $D_g^{(1)}$ | $D^{(1)}$ |
| $\langle \mathbf{a} \rangle$ | + | + | $D_g^{(0)}+D_g^{(2)}$ | $D^{(0)}+D^{(2)}$ |
| $\langle \mathbf{b} \rangle$ | + | − | $D_g^{(1)}+D_g^{(3)}$ | $D^{(1)}+D^{(3)}$ |
| $\langle \mathbf{a}_1 \rangle$ | − | + | $D_u^{(0)}+D_u^{(2)}$ | $D^{(0)}+D^{(2)}$ |
| $\langle \mathbf{b}_1 \rangle$ | + | − | $D_g^{(1)}+D_g^{(3)}$ | $D^{(1)}+D^{(3)}$ |
| $\langle \mathbf{b}_2 \rangle$ | − | − | $D_u^{(1)}+D_u^{(3)}$ | $D^{(1)}+D^{(3)}$ |

and $R(3)$.

Applying principle (3), terms on the right-hand side of either equation contribute to the ensemble average over the observable on the left-hand side if the product of $D$ representations contains the $D$ representation of the left-hand side at least once. Taking the linear effect as a first example, this is produced classically[33] by truncating Eq. (1) to terms linear in $\mathbf{E}$ and $\dot{\mathbf{B}}$, i.e., $\langle \alpha_{ij} \rangle \mathbf{E}_j$ and $\langle \alpha_{1ij} \rangle \dot{\mathbf{B}}_j$. The ensemble averaged quantity $\langle \alpha_1 \rangle$ is negative to $P$ because it multiplies a quantity $\dot{\mathbf{B}}$ which is positive to $P$, the proportionality arising directly from the Maxwell equations.[33] The two constants can be obtained quantum mechanically[33] by first-order perturbation theory, giving

$$\langle \alpha_{ij} \rangle \mathbf{E}_j = \frac{2}{\hbar} \sum_n{}' \left[ \frac{\omega_{n0}}{\omega_{n0}^2 - \omega^2} \right] \mu_{0ni} \mu_{n0j} \mathbf{E}_j \; , \tag{6}$$

$$\langle \alpha_{1ij} \rangle \dot{\mathbf{B}}_j = \frac{2}{\hbar} \operatorname{Im} \sum_n{}' \left[ \frac{1}{\omega_{n0}^2 - \omega^2} \right] \mu_{0ni} \mu_{n0j} \dot{\mathbf{B}}_j \; . \tag{7}$$

The $P$, $T$, and $D$ symmetries in these classical-quantum expressions are the same on the left- and right-hand sides.

The complete $D$ symmetry of the product

$$\begin{aligned} \Gamma(\langle \alpha_{ij} \rangle E_j) &= (D_g^{(0)} + D_g^{(2)}) D_u^{(1)} \\ &= D_u^{(3)} + 2D_u^{(1)} + D_u^{(2)} \end{aligned} \tag{8}$$

contains the $D_u^{(1)}$ symmetry of the observable $\langle \mu_i \rangle$ two times, and these two products contribute to the observable. Similarly in general for the product $\langle \alpha_{1ij} \rangle \dot{\mathbf{B}}_j$. They arise from the diagonal and symmetric off-diagonal parts of the molecular tensors $\langle \alpha_{ij} \rangle$ and $\langle \alpha_{1ij} \rangle$. In order to prepare these terms for a computer simulation[21–25] it is necessary to transform the molecular quantity from the molecule fixed frame $(x,y,z)$, in which it is usually and conveniently expressed, to the laboratory frame $(X,Y,Z)$. The details of this transformation for tensor molecular quantities are given in the Appendix.

## III. CHIRALITY OF NONLINEAR FIELD EFFECTS

The symmetry and chirality of field-induced natural and magnetic optical activity can be investigated with principle (3) of GTSM. In this context an observable is defined by the symmetry of field multiplied by susceptibility. Tables I and II provide a summary of the $P$ and $T$ symmetries of the quantum and classical susceptibility and field components of the six nonlinear effects described in this paper. The $P$ symmetries of the various susceptibilities are sometimes positive both in quantum and classical representations, and sometimes negative. In the quantum-mechanical treatment the susceptibility symmetry is the product of individual, isotropic averaged dipole matrix element symmetries as in Table I. In the classical treatment the susceptibility symmetry is that of a molecular property tensor, such as the molecular polarizability, hyperpolarizability, magnetizability, hypermagnetizability, and mixed property tensors such as $\langle \boldsymbol{\alpha}_1 \rangle$, $\langle \boldsymbol{\beta}_1 \rangle$, $\langle \mathbf{a}_1 \rangle$, and so on. The ensemble averages over these quantities in the laboratory frame $(X,Y,Z)$ have either positive or negative $P$ symmetries. By principle (1) of GTSM an ensemble average in $R_h(3)$ which does not contain $D_g^{(0)}$ must vanish. Therefore, at field free equilibrium, molecular property tensors with $u$ (negative $P$) symmetry always vanish in ensembles of structurally achiral molecules, because the tensor symmetry cannot include $D_g^{(0)}$. An applied electromagnetic field brings the ensemble to field-on equilibrium and the property tensors multiply into the field terms as shown in Eqs. (4) and (5). The number of induced dipole components is given by the number of times the dipole symmetry appears in the total product. Some details of this procedure are given in the Appendix, and Table III summarizes the various torques to be associated with each of the nonlinear effects considered in this paper. These torques are generated as nonvanishing ensemble averages by the interaction of the electromagnetic field with the ensemble.

In this context it is important to have a working definition of chirality. Barron has proposed a definition of chirality[34] which has been implemented in a preliminary investigation of the symmetry of the Wagnière-Meier effect by the present author.[35] Natural optical activity is defined as a chiral phenomenon of pseudoscalar symmetry, negative to $P$ and positive to $T$. Magnetic optical activity is defined by Barron as a phenomenon of $D_g^{(1)}$ symmetry, positive to $P$ and negative to $T$. It is regarded as achiral because the $P$ and $T$ symmetries are opposite to those of natural optical activity.

In this context we can define the Wagnière-Meier and Wagnière effects through the appropriate product of molecular property tensor $\langle \boldsymbol{\beta}_1 \rangle$ and $\langle \mathbf{b}_2 \rangle$ with the field terms. In the Wagnière-Meier effect the observable is electric polarization, with product negative to $P$ and positive to $T$. In the Wagnière effect the observable is magne-

TABLE III. Torques in the electromagnetic-field–molecule interaction: third-order effects.

| Effect | | Field tensor symmetry | |
|---|---|---|---|
| | $D^{(0)}$ | $D^{(1)}$ | $D^{(2)}$ |
| Electric rectification | $(\boldsymbol{\beta}\mathbf{E}_+\cdot\mathbf{E}_-)\times\mathbf{E}_\pm$ | $(\boldsymbol{\beta}\mathbf{E}_+\times\mathbf{E}_-)\times\mathbf{E}_\pm$ | $(\boldsymbol{\beta}\mathbf{E}_+\mathbf{E}_-^T)\times\mathbf{E}_\pm$ |
| Magnetic rectification | $(\mathbf{b}\mathbf{B}_+\cdot\mathbf{B}_-)\times\mathbf{B}_\pm$ | $(\mathbf{b}\mathbf{B}_+\times\mathbf{B}_-)\times\mathbf{B}_\pm$ | $(\mathbf{b}\mathbf{B}_+\mathbf{B}_-^T)\times\mathbf{B}_\pm$ |
| Electromagnetic *EB* effect | $(\boldsymbol{\beta}_2\mathbf{E}_-\cdot\dot{\mathbf{B}}_+)\times\mathbf{E}_\pm$ | $(\boldsymbol{\beta}_2\mathbf{E}_-\times\dot{\mathbf{B}}_+)\times\mathbf{E}_\pm$ | $(\boldsymbol{\beta}_2\mathbf{E}_-\dot{\mathbf{B}}_+^T)\times\mathbf{E}_\pm$ |
| Magnetochiral effect (cf. Wagnière-Meier effect) | $(\boldsymbol{\beta}_1\dot{\mathbf{B}}_+\cdot\dot{\mathbf{B}}_-)\times\mathbf{E}_\pm$ | $(\boldsymbol{\beta}_1\dot{\mathbf{B}}_+\times\dot{\mathbf{B}}_-)\times\mathbf{E}_\pm$ | $(\boldsymbol{\beta}_1\dot{\mathbf{B}}_+\dot{\mathbf{B}}_-^T)\times\mathbf{E}_\pm$ |
| Inverse magnetochiral (Wagnière) effect | $(\mathbf{b}_2\dot{\mathbf{E}}_-\cdot\mathbf{B}_+)\times\mathbf{B}_\pm$ | $(\mathbf{b}_2\dot{\mathbf{E}}_1\times\mathbf{B}_+)\times\mathbf{B}_\pm$ | $(\mathbf{b}_2\dot{\mathbf{E}}_-\mathbf{B}_+^T)\times\mathbf{B}_\pm$ |
| Inverse Faraday effect | $(\mathbf{b}_1\dot{\mathbf{E}}_-\cdot\dot{\mathbf{E}}_+)\times\mathbf{B}_\pm$ | $(\mathbf{b}_1\dot{\mathbf{E}}_-\times\dot{\mathbf{E}}_+)\times\mathbf{B}_\pm$ | $(\mathbf{b}_1\dot{\mathbf{E}}_-\dot{\mathbf{E}}_+^T)\times\mathbf{B}_\pm$ |

tization, with product symmetry positive to $P$ and negative to $T$. Both effects come from a combination of the electric and magnetic sum and difference components of the electromagnetic field, and both occur only in chiral ensembles. In both cases principle (3) of GTSM asserts that the *complete* symmetry of the relevant field-susceptibility products (1) $\langle\beta_{1ijk}\rangle\dot{\mathbf{B}}_j\dot{\mathbf{B}}_k$ and (2) $\langle\mathbf{b}_{2ijk}\rangle\mathbf{B}_j\dot{\mathbf{E}}_k$ may be imparted to the ensemble. If the complete product contains the symmetry $D^{(0)}$, optical rotation may be observed. However, for the Wagnière-Meier effect this must be $T$ positive, and for the Wagnière effect $T$ negative. Both effects can be observed with a plane-polarized laser, and the presence of optical rotation of $D$ symmetry can be observed through the rotation of this plane.

Note that effects 1 and 2 of Table I are both caused by sum and difference frequencies of the *electromagnetic* field. The Wagnière-Meier effect (similar to effect 2) is conventionally caused by a static magnetic field combining with the magnetic component of a separate, unpolarized electromagnetic field. The literature Wagnière-Meier effect causes the refractive index to become different according to whether the static magnetic field and probe laser propagation vector are parallel or antiparallel. Effect 2, in contrast, is *circular* birefringence caused by and measured with a plane-polarized laser, i.e., a combination of right and left circularly polarized components. It is electric polarization caused by $\langle\beta_{1ijk}\rangle\dot{\mathbf{B}}_j\dot{\mathbf{B}}_k$.

## IV. DISCUSSION

The principles of group-theoretical statistical mechanics have been used to define the symmetries of various nonlinear optical phenomena. The list of six treated in this paper is by no means exhaustive, but the Appendix is a guide to the definition of torques generated between the electromagnetic field and the molecules of an ensemble, using a classical approach in terms of molecular property tensors. These torques can be coded into a conventional, classical, molecular-dynamics simulation algorithm to generate a variety of information. The latter includes rise transients, Langevin functions, correlation functions and distribution functions in the field-on steady state, and finally fall transients after the field is switched off. There are many codes available[36] which are suitable for the incorporation of the extra torques in the forces loop. This will be the subject of future work in a variety of chiral and achiral ensembles, providing detailed simulations of the nonlinear optical effects, for example thermodynamic and spectral data.

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## APPENDIX: DETAILS OF TORQUE TERMS IN THE CLASSICAL NONLINEAR INTERACTION OF ELECTROMAGNETIC FIELDS AND MOLECULAR ENSEMBLES

### 1. Second order in *E*

Taking as a first example the second-order interaction of the electric field with the induced dipole moment $\langle\alpha\rangle\mathbf{E}$ the torque $-\langle\alpha\rangle\mathbf{E}\times\mathbf{E}$ is coded into the simulation algorithm at the appropriate point in the forces loop. In general $\mathbf{E}$ is any electric sum or difference component of a right or left circularly polarized electromagnetic field. The first step is to use tensor algebra to isolate the possible vector parts of the complete product $\langle\alpha\rangle\mathbf{E}$ and to evaluate the torque in the frame $(x,y,z)$ of the principal molecular moments of inertia. Therefore, $\mathbf{E}$ is transformed from $(X,Y,Z)$ to $(x,y,z)$ using a transformation matrix of unit vectors in the axes $x$, $y$, and $z$, whose components are defined with respect to frame $(X,Y,Z)$

$$\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = \begin{bmatrix} e_{xX} & e_{xY} & e_{xZ} \\ e_{yX} & e_{yY} & e_{yZ} \\ e_{zX} & e_{zY} & e_{zZ} \end{bmatrix} \begin{bmatrix} E_X \\ E_Y \\ 0 \end{bmatrix} . \tag{A1}$$

The assumption is then made that the molecular polarizability is diagonal in $(x,y,z)$, in general an approximation because molecular polarizability is not necessarily diagonal in the same frame as the molecular principal moments of inertia. The diagonal components of the polarizability can be evaluated in principle by *ab initio* computation. Rarely are they known experimentally. With this assumption

$$(\langle\alpha\rangle\mathbf{E})_{x,y,z}=\left\langle\begin{bmatrix}\alpha_{xx}E_x\\ \alpha_{yy}E_y\\ \alpha_{zz}E_z\end{bmatrix}\right\rangle , \tag{A2}$$

giving the torque

$$\left\langle\begin{bmatrix}T_x\\ T_y\\ T_z\end{bmatrix}\right\rangle=\left\langle\begin{bmatrix}\alpha_{yy}E_yE_x-\alpha_{zz}E_zE_y\\ \alpha_{zz}E_zE_x-\alpha_{xx}E_xE_z\\ \alpha_{xx}E_xE_y-\alpha_{yy}E_yE_x\end{bmatrix}\right\rangle , \tag{A3}$$

which is back transformed finally to frame $(X,Y,Z)$,

$$\left\langle\begin{bmatrix}T_X\\ T_Y\\ T_Z\end{bmatrix}\right\rangle=\left\langle\begin{bmatrix}e_{xX} & e_{yX} & e_{zX}\\ e_{xY} & e_{yY} & e_{zY}\\ e_{xZ} & e_{yZ} & e_{zZ}\end{bmatrix}\begin{bmatrix}T_x\\ T_y\\ T_z\end{bmatrix}\right\rangle \tag{A4}$$

and coded into the forces loop of the molecular-dynamics algorithm. Some preliminary results of this nature are available in the literature for the achiral molecular dichloromethane.[23] These show the development of second-order Langevin functions (Kielich functions), and time correlation functions of the dynamical response of the system to the second-order torque.

The nonlinear effects discussed in this paper are to order 3 in the field, giving a much richer variety of effects with different contributing $D$ symmetries. Some of the torques are exemplified here, and those contributing to the six effects of the text are tabulated.

### 2. Third order in the field

Taking the classical treatment of electric rectification as an example, the general form of the third-order torque is

$$\langle\mathbf{T}\rangle=\langle\beta\rangle\mathbf{EE}\times\mathbf{E} , \tag{A5}$$

where $\beta$ is the molecular hyperpolarizability, a third-rank tensor. The complete product $\beta$**EE** reduces to a vector (rank-one tensor) through the relation

$$C_i=A_{ijk}B_{jk}\equiv\sum_j\sum_k A_{ijk}B_{jk} \tag{A6}$$

of tensor algebra. This is worked out in frame $(x,y,z)$ and in general the vector part $V$ of the complete product $\beta$**EE** is

$$V(\beta\mathbf{EE})=\begin{bmatrix}C_x\\ C_y\\ C_z\end{bmatrix} \tag{A7}$$

where

$$\begin{aligned}C_x=&\beta_{xxx}E_{xx}+\beta_{xxy}E_{xy}+\beta_{xxz}E_{xz}+\beta_{xyx}E_{yx}+\beta_{xyy}E_{yy}\\ &+\beta_{xyz}E_{yz}+\beta_{xzx}E_{zx}+\beta_{xzy}E_{zy}+\beta_{xzz}E_{zz} ,\\ C_y=&\beta_{yxx}E_{xx}+\beta_{yxy}E_{xy}+\beta_{yxz}E_{xz}+\beta_{yyx}E_{yx}+\beta_{yyy}E_{yy}\\ &+\beta_{yyz}E_{yz}+\beta_{yzx}E_{zx}+\beta_{yzy}E_{zy}+\beta_{yzz}E_{zz} ,\\ C_z=&\beta_{zxx}E_{xx}+\beta_{zxy}E_{xy}+\beta_{zxz}E_{xz}+\beta_{zyx}E_{yx}+\beta_{zyy}E_{yy}\\ &+\beta_{zyz}E_{yz}+\beta_{zzx}E_{zx}+\beta_{zzy}E_{zy}+\beta_{zzz}E_{zz} .\end{aligned}$$

This can be reduced to a simpler form by assuming that the hyperpolarizability is diagonal in frame $(x,y,z)$. This is equivalent to

$$\beta_{xxx}\neq\beta_{yyy}\neq\beta_{zzz}\neq\beta_{xyy}\neq\beta_{xzz}\neq\beta_{yxx}\neq\beta_{yzz}\neq\beta_{zyy}\neq\beta_{zxx} , \tag{A8}$$

all other components being assumed to be zero in frame $(x,y,z)$. *Ab initio* computation might be available to test the validity of this assumption.

In general the **EE** part of this expression is a complete product, a second-rank of symmetry $D_g^{(0)}+D_g^{(1)}+D_g^{(2)}$. We take each $D$ symmetry in turn. The $D_g^{(0)}$ part of **EE** is a dot product such as

$$\mathbf{E}_-^{(L)}\cdot\mathbf{E}_+^{(L)}=\mathbf{E}_-^{(R)}\cdot\mathbf{E}_+^{(R)}=2E_0^2 , \tag{A9}$$

so that

$$(\beta\mathbf{E}_+\cdot\mathbf{E}_-)_{x,y,z}=\begin{bmatrix}E_0^2(\beta_{xxx}+\beta_{xyy}+\beta_{xzz})\\ E_0^2(\beta_{yxx}+\beta_{yyy}+\beta_{yzz})\\ E_0^2(\beta_{zxx}+\beta_{zyy}+\beta_{zzz})\end{bmatrix} . \tag{A10}$$

Two possible torques in $(x,y,z)$ are then

$$\begin{aligned}&(\beta\mathbf{E}_+\cdot\mathbf{E}_-)\times\mathbf{E}_+ ,\\ &(\beta\mathbf{E}_+\cdot\mathbf{E}_-)\times\mathbf{E}_- ,\end{aligned} \tag{A11}$$

which are finally back transformed into $(X,Y,Z)$ and coded into the forces loop of the simulation algorithm, which then provides third-order Langevin functions and dynamical and structural data.[21–25] This is a classical description of *ensemble* response due to one part of the electric rectification phenomenon.

The $D_g^{(1)}$ part of **EE** is a cross product such as

$$\mathbf{E}_-^{(L)}\times\mathbf{E}_+^{(L)}=2E_0^2 i\mathbf{k}=(E_{-X}^{(L)}E_{+Y}^{(L)}-E_{-Y}^{(L)}E_{+X}^{(L)})\mathbf{k} \tag{A12}$$

(for left circularly polarized radiation). This is an antisymmetric, traceless, second-rank tensor through the general relation

$$C_i=\tfrac{1}{2}\epsilon_{ijk}C_{jk} , \tag{A13}$$

where $\epsilon_{ijk}$ is the Levi-Civita symbol.

The $D_g^{(2)}$ part of **EE** is the symmetric counterpart of (A13), one part of which is

$$\mathbf{E}_-^{(L)}\mathbf{E}_+^{(L)T}=\begin{bmatrix}0 & E_{-X}^{(L)}E_{+Y}^{(L)} & 0\\ E_{-Y}^{(L)}E_{+X}^{(L)} & 0 & 0\\ 0 & 0 & 0\end{bmatrix} . \tag{A14}$$

Both $D_g^{(1)}$ and $D_g^{(2)}$ parts of **EE** are purely imaginary tensor quantities. However, torques such as

$$(\boldsymbol{\beta}_-\mathbf{E}_-\times\mathbf{E}_+)\times\mathbf{E}_+,\quad(\boldsymbol{\beta}\mathbf{E}_-\mathbf{E}_+^T)\times\mathbf{E}_+\ ,$$

$$(\boldsymbol{\beta}\mathbf{E}_-\times\mathbf{E}_+)\times\mathbf{E}_-,\quad(\boldsymbol{\beta}\mathbf{E}_-\mathbf{E}_+^T)\times\mathbf{E}_-\ ,$$

have real parts due to the product with the imaginary part of the field terms outside the brackets. Taking the torque $(\beta_-\mathbf{E}_-^{(L)}\times\mathbf{E}_+^{(L)})\times\mathbf{E}_+^{(L)}$ as an example, we first rotate $\mathbf{E}_-^{(L)}\times\mathbf{E}_+^{(L)}$ into frame $(x,y,z)$,

$$(\mathbf{E}_-^{(L)}\times\mathbf{E}_+^{(L)})_{x,y,z}=\begin{bmatrix}-e_{xX}E_{-X}^{(L)}E_{+Y}^{(L)} & e_{xY}E_{-X}^{(L)}E_{+Y}^{(L)} & 0\\ -e_{yY}E_{-X}^{(L)}E_{+Y}^{(L)} & e_{yX}E_{-X}^{(L)}E_{+Y}^{(L)} & 0\\ -e_{zY}E_{-X}^{(L)}E_{+Y}^{(L)} & e_{zX}E_{-X}^{(L)}E_{+Y}^{(L)} & 0\end{bmatrix}, \tag{A15}$$

and use this matrix to work out the complete torque in this frame, then finally back transforming into $(X,Y,Z)$. The molecular-dynamics method then works out transients, autocorrelation functions, cross correlation functions, and thermodynamic quantities at the steady state in response to this torque.

Similarly, the thermodynamic, structural, transient and molecular-dynamical response of torques appropriate to all six nonlinear effects can be explored for any molecular symmetry, including chiral symmetry. The various torque components are tabulated as follows for the $D^{(0)}$, $D^{(1)}$, and $D^{(2)}$ components of **EE**, **BB**, and other appropriate field tensors of the polarizability-field expansion of the induced molecular dipole moment used in the text.

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