

# Resonance damping and optical susceptibilities

David L. Andrews, Luciana C. Dávila Romero  
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK

## ABSTRACT

In the formal development of optical response theory in terms of susceptibilities, proper representation of the optical frequency dependence necessitates modeling both the discrete linewidth and the finite signal enhancement associated with the onset of resonance. Such dispersion behavior is generally accommodated by damping factors, featured in both resonant and non-resonant susceptibility terms. For the resonant terms, the sign of such damping corrections is unequivocal; however the correct choice of sign for non-resonant terms has become a matter of debate, heightened by the discovery that entirely opposite conventions are applied in mainstream literature on Raman scattering and nonlinear optics. Where the two conventions are applied to electro-optical processes in fluids there are significant and potentially verifiable differences between the associated results. Through a full thorough quantum electrodynamical treatment the universal correctness of one convention can be ascertained and flaws in the counter-convention identified. Resolution of the central issue requires consideration of a number of fundamental questions concerning the nature of dissipation in quantum mechanical systems. It is concluded that optical susceptibilities formulated with correct signing of the damping corrections must fulfill several fundamental tests: satisfaction of a new sum rule; invariance of the associated quantum amplitudes under time-reversal symmetry, and a resilience to canonical transformation.

**Keywords:** nonlinear optics, resonance, optical susceptibility, electro-optics, Raman scattering, dispersion, time-reversal

## 1. INTRODUCTION

In the theory of light scattering and nonlinear optics, the issue of damping the frequency response in linear and nonlinear susceptibilities is a significant consideration when operating at frequencies near to resonance. Whenever materials exhibit an electronic excited state with energy closely similar to one or more of the participating photons, resonance enhancement is observed to occur. In such cases it is necessary to include damping in the description to properly account for the finite optical amplification and the detailed dispersion behavior. Apart from a few simple cases<sup>1</sup>, there are considerable difficulties in formulating a rigorous, non-phenomenological treatment of optical damping. In principle, quantum field theory will give the correct form of the transition amplitudes and susceptibilities, including the sign of the associated damping factors, through a perturbative development. However detailed calculation can be a formidable task<sup>2</sup> and commonly only a phenomenological treatment is tractable. Close to resonance or under strong pumping conditions, when electromagnetic field strengths become comparable to internal fields and perturbation theory is inappropriate, a simplified two-level model (or a multilevel extension) is invariably employed to elicit approximate results. For moderate fields, an equally pragmatic calculational option is to dispense with damping altogether<sup>3</sup> and to apply the ensuing results only to experiments conducted in frequency regions well away from resonance. Such approaches have the attraction of retaining abstract rigor, but they are not well suited to the analysis of dispersion effects.

Where optical response is meaningfully cast in susceptibility terms, various losses characterize the bulk or ensemble response. Phenomenological damping is the pragmatic means of representing the stochastic influence on any optical center of the *bath*, the latter term signifying local radiative and material surroundings. In this context, *damping* alludes to the classical concept of a resonant response tempered by dissipation – here, coupling into decay channels for excited states. In a formulation based on electronically independent optical centers, the association of an exponential decay  $\exp(-\mathbf{g}t)$  with the time-evolution factor  $\exp(-iEt/\hbar)$  for each excited level  $|r\rangle$  confers a homogeneously broadened linewidth, entering into the energy denominators of susceptibility tensors as imaginary addenda  $i\mathbf{h}\mathbf{g}$ . Close to resonance, damping accordingly delivers a physically broadened, Lorentzian lineshape to the optical response. Generally, each  $\mathbf{h}\mathbf{g}$  is several orders of magnitude smaller than the excited state energies, and the available decay channels determine the precise values. In solid-state systems, local field effects generate additional, heterogeneous

line-broadening. [In passing we note that other phenomenological damping constructs can also appear in connection with modeling a slow ‘adiabatic’ switching-on of the interaction from  $t = -\infty$  with a growth factor  $\exp(\Gamma t)$ ; here, we focus on quantum energy level damping, assuming a suitably prepared initial state for the system.] Accepting the pragmatic value of the damping concept, we are now concerned with a comparison of the signs in the resulting expressions.

In the course of resolving the central issue a host of more fundamental questions arise, not all with an obvious link. Is any optical susceptibility directly interpretable as a measurable, in the formal quantum mechanical sense? To what extent are time-reversal principles applicable to dissipative systems? Should line-broadening in fact be associated with the influence of static fields? Is the sign of any damping factor ever experimentally testable? And should damping even be applied for non-resonant amplitudes? These and other incidental issues are also explored in the following review.

## 2. DAMPING SIGN CONVENTIONS

Two conventions have been used in the literature for setting the signs of phenomenological damping factors. In the context of nonlinear optics the most common convention is to ascribe the signs of damping factors in each term of a susceptibility denominator on the basis of time-ordering<sup>4,5</sup>. In harmonic generation processes, for example, damping factors take signs chosen oppositely for interactions preceding and following the emission of the harmonic photon<sup>6,7</sup>. This variable-sign approach has been founded on a semiclassical formalism featuring the optical susceptibility via an explicit appeal to causality. However there are numerous exceptions<sup>8-10</sup> – examples of work in nonlinear optics where damping features with a constant sign. Moreover the latter, constant sign convention is consistent with the mainstream literature of Raman scattering<sup>11,12</sup>, in which damping is usually constant in each linear susceptibility (and corresponding electronic polarisability) denominator. Recently, it has emerged that the former variable-sign convention is in fact fundamentally inconsistent with a fully quantum development, and in particular with HT time-reversal symmetry<sup>13,14</sup>. It is worth noting that both conventions prescribe damping of the same sign for resonant terms in optical susceptibility expressions; it is in anti-resonant terms that they differ. Nonetheless it is surprising that no real attention seems to have been paid to the fundamental incompatibility of the two conventions latent in the literature until comparatively recently. The following account summarises present understanding.

The *ad hoc* phenomenological damping of excited states for any optical system reflects interactions with the bath – in particular the effects of higher-order perturbations including radiative and non-radiative decay. None of the eigenstates of the unperturbed molecular Hamiltonian is a stationary state, as the quantum electrodynamical (QED) representation forcefully emphasizes. It is for this reason that wavefunction time-evolution factors acquire dissipative corrections which, although formally imaginary in frequency or energy space, are physically associated with exponential decay<sup>15</sup>. We note that it is perfectly legitimate to require time-reversal symmetry in the fundamental quantum amplitudes when a subsystem is damped through contact with a thermal reservoir. The requirement for temporal symmetry remains valid, despite *de facto* violation of time-reversal invariance by the system itself (through interactions with the bath and ensuing state decay) via explicit accommodation of the imaginary damping factors. The necessary equality of amplitudes for time-reversed processes was proved in detail in earlier work<sup>13</sup>; the invariance is honored by the constant-sign rule but not by the variable-sign convention. To prove this we observe the following relation, writing the time-evolution operator for the full system as  $U = \exp(-i\hbar^{-1} \int H dt)$ ;

$$\langle F|U|I\rangle = \langle I|\exp(i\hbar^{-1} \int H dt)|F\rangle^* , \quad (1)$$

by Hermitian conjugation. Since the operator within the Dirac bracket on the right of equation (1) is not equal to  $U$ , the associated matrix element is not physically meaningful as a time-forward transition amplitude<sup>16</sup>. Hence a reciprocity relation of the form  $\langle F|U|I\rangle = \langle I|U|F\rangle$  does not hold in general. Berger has indeed shown that there is no special call to satisfy such a reciprocity relation<sup>17</sup>. When damping is neglected, the Fermi golden rule delivers expressions that satisfy reciprocity – but this is an exceptional case, not a generally enforceable rule. The variable-sign convention does nonetheless enforce such a symmetry. When developed into optical susceptibility form, variable signing leads to a relationship which for linear response is<sup>18</sup>:

$$\mathbf{c}_{ij}^{(1)}(-\mathbf{w}, \mathbf{w}) = \mathbf{c}_{ij}^{(1)*}(\mathbf{w}, -\mathbf{w}), \quad (2)$$

with corresponding expressions of similar form for higher orders. For example the susceptibility tensor for second harmonic generation,  $\mathbf{c}_{ijk}^{(2)}(-2\mathbf{w}; \mathbf{w}, \mathbf{w})$ , is thereby supposed to equate with the complex conjugate of the tensor for degenerate down-conversion,  $\mathbf{c}_{ijk}^{(2)}(2\mathbf{w}; -\mathbf{w}, -\mathbf{w})$ . In passing we also note that although, in terms of elementary dimensional analysis, frequencies are time-odd, they are not time-directed quantities any more than the speed of light,  $c$ . Thus susceptibility relations such as that given above, concerned with the effect of systematically changing the sign of all frequency arguments, are specifically not time-reversal principles.

To elaborate on the detail of the two sign conventions it is helpful to further pursue the simplest case, the linear optical susceptibility. Cast in molecular terms, and introducing a signing parameter  $\mathbf{s}$  which we shall use to highlight the issue throughout the following analysis, this tensor correlates with the electronic polarisability which, for a system in a state  $|s\rangle$ , is expressible as<sup>19</sup>;

$$\mathbf{a}_{ij}^{ss}(\mathbf{s}) = \sum_r \left[ \frac{\langle s | \mathbf{m}_i | r \rangle \langle r | \mathbf{m}_j | s \rangle}{E_r - E_s - \hbar \mathbf{w} - i \hbar \mathbf{g}_{rs}} + \frac{\langle s | \mathbf{m}_j | r \rangle \langle r | \mathbf{m}_i | s \rangle}{E_r - E_s + \hbar \mathbf{w} - i \mathbf{s} \hbar \mathbf{g}_{rs}} \right], \quad (3)$$

where the circular frequency of the input radiation (implicit on the left) is  $\mathbf{w}$ ,  $\mathbf{g}_{rs} = \mathbf{g}_r - \mathbf{g}_s$  and other symbols have their usual meaning. For the constant-sign convention  $\mathbf{s} = +1$ , while under the variable-sign convention,  $\mathbf{s} = -1$ . Note that the terms ‘constant sign convention’ (*csc*) and ‘variable sign convention’ (*vsc*) signify a similarity or difference of sign for the damping correction in the two energy denominators. Constancy or variability is manifest in the sign of  $i \hbar \mathbf{g}$ . with respect to the energy  $E_r$ . The *csc* approach signifies consistent modification of the energy,  $\tilde{E}_r = E_r - i \hbar \mathbf{g}_r$ ; there is a unique relationship between a particular energy level  $E_r$  and its corresponding damping constant<sup>1</sup>. On the other hand with *vsc*, the sign of the damping factor follows the sign of the radiation frequency<sup>5,6</sup>. It is crucially important to note that the polarisabilities delivered by the two different conventions are not proportional, nor do they stand in a complex conjugate relationship. Therefore, the alternative formulations lead to intensity expressions that in principle are physically distinguishable – a point we shall return to later. It is also notable that, whatever the sign of  $\mathbf{s}$ , the polarisability is never a real quantity. This is neither a surprise nor a problem; in quantum mechanics this tensor is not a measurable. However the complex character of the tensor serves as an alert to the fact that there are limitations to the conditions that can be imposed upon it, or expressions such as signal amplitudes in which it is linearly cast. It is interesting to observe that only a *vsc* result for the polarisability can satisfy reciprocity. More significantly, only the *csc* result is resilient under time-reversal.

### 3. PROBLEMS WITH VARIABLE SIGNING

In earlier work the inconsistency of *vsc* with the fundamental principles of time-reversal symmetry has been thoroughly enunciated, including a proof of the time-even character of damping constants<sup>13,15</sup>. In the following we resolve a number of further issues connected with susceptibility and polarisability applications, a number of which arise in connection with processes involving static electric fields. First we note the self-evident logic that *vsc* requires, for any electro-optical process, that any interactions with which static fields are associated should carry no damping. This follows from the observation that this convention leads to a damping factor that follows the sign of the radiation frequency. In a three-wave mixing susceptibility  $\mathbf{c}_{ijk}^{(3)}(-\mathbf{w}_1, f \mathbf{w}_0, \mathbf{w}_0)$  associated with a signal frequency  $\mathbf{w}_1 = (1+f) \mathbf{w}_0$ , *vsc* gives a discontinuity at  $f = 0$ . Here positive  $f$  denotes sum-frequency generation; negative  $f$ , difference-frequency generation;  $f = 0$ , a linear electro-optical effect (to which we return later). No such discontinuity arises with *csc*. However from a quantum field viewpoint, it is relatively obvious that static perturbations must induce damping; the case of a static field is no different in type from a time-varying field – except that, whilst causality is of course satisfied, explicit retardation features disappear. Hence the damping associated with any excited state, whose wavefunction contributes to the perturbed state vector of the system, must be vulnerable to damping, irrespective of the frequency of the field responsible for the perturbation. Damping factors are not frequency-dependent in this sense; each excited state has a damping of characteristic magnitude, irrespective of the frequency of the perturbation with which it is associated.

From a semiclassical perspective, it has been affirmed by adherents of the *vsc* sign convention that the retention of damping for electrostatic fields leads to other incongruities<sup>18,20</sup>. Again returning to a simple linear response case, consider an argument based on the case of an electric dipole induced by a static electric field  $\mathbf{F}$ . That argument concerns the correct form of polarisability to use in the defining formula for the induced dipole moment,  $\mathbf{m}_i = \mathbf{a}_{ij}^{ss} F_j$ , using the usual Einstein summation convention for repeated indices, where the salient polarisability is as given above with  $\mathbf{w} = 0$  (retaining a generalisation to the static polarisability of a system in an arbitrary state, not necessarily the ground state);

$$\begin{aligned} \mathbf{a}_{ij}^{ss}(\mathbf{s}) &= \sum_r \left[ \frac{\langle s | \mathbf{m}_i | r \rangle \langle r | \mathbf{m}_j | s \rangle}{E_r - E_s - i\hbar \mathbf{g}_{rs}} + \frac{\langle s | \mathbf{m}_j | r \rangle \langle r | \mathbf{m}_i | s \rangle}{E_r - E_s - i\mathbf{s} \hbar \mathbf{g}_{rs}} \right] \\ &\equiv \sum_r \frac{2(E_r - E_s) \text{Re} \left[ \langle s | \mathbf{m}_i | r \rangle \langle r | \mathbf{m}_j | s \rangle \right] + (-i\hbar \mathbf{g}_{rs}) \left[ \mathbf{s} \langle s | \mathbf{m}_i | r \rangle \langle r | \mathbf{m}_j | s \rangle + \langle s | \mathbf{m}_j | r \rangle \langle r | \mathbf{m}_i | s \rangle \right]}{(E_r - E_s - i\hbar \mathbf{g}_{rs})(E_r - E_s - i\mathbf{s} \hbar \mathbf{g}_{rs})} \end{aligned} \quad (4)$$

One has to be very guarded about the semiclassical interpretation of this equation, since it suggests that a real electric field can induce a complex induced dipole moment – but it is to be emphasized that such a construct is not a quantum observable<sup>19</sup>. Moreover in any such application it has to be borne in mind that the Cartesian indices  $i$  and  $j$  have a different status, because in constructing any observable one of them is invariably to be contracted with the static field index. Despite claims to the contrary, it is not possible to draw any physical inferences from the result of interchanging  $i$  and  $j$ . The disturbing possibility of a static field inducing a non-collinear dipole in a spherically symmetric system never arises.

#### 4. SUSCEPTIBILITY SUM RULES

In the theory of linear and nonlinear optical response, a common expedient for calculational and interpretive simplicity is the adoption of a two-level approximation, in which it is assumed that any material of interest has only one significant electronic excited state in the relevant frequency range. It has been known for some time that this approximation leads to an excited state polarisability that is the exact negative of the ground state polarisability, and the same proves true for the ground and excited state first hyperpolarisability<sup>15</sup>. Results of similar form also apply to the bulk susceptibilities. Recently, it has also been shown that these relationships retain validity even when resonance damping is entertained, provided the correct choice (*csc*) is made for the sign of the damping corrections, as exacted by the principles of time-reversal invariance<sup>19</sup>. Furthermore in the case of the electronic polarisability it is easily shown that a more general sum rule is satisfied,

$$\sum_s \mathbf{a}_{ij}^{ss} = 0 \quad , \quad (5)$$

where the sum is taken over all energy levels of the system. By interchange of the state labels  $r$  and  $s$  (which it is legitimate to interchange because both are summed) the polarisability as given in expression (3) can easily be seen to satisfy the summation rule when the damping factors are null, but also more generally when  $\mathbf{s} = +1$  (*csc*). Specifically, the sum given by equation (5) is:

$$\sum_s \mathbf{a}_{ij}^{ss}(\mathbf{s}) = \sum_{sr} \left[ \frac{\langle s | \mathbf{m}_i | r \rangle \langle r | \mathbf{m}_j | s \rangle}{E_{rs} - \hbar \mathbf{w} - i\hbar \mathbf{g}_{rs}} + \frac{\langle s | \mathbf{m}_j | r \rangle \langle r | \mathbf{m}_i | s \rangle}{E_{rs} + \hbar \mathbf{w} - i\mathbf{s} \hbar \mathbf{g}_{rs}} \right] \quad (6)$$

By interchanging the dummy variables  $r \leftrightarrow s$  in the second term it follows that;

$$\sum_s \mathbf{a}_{ij}^{ss} = (\mathbf{s} - 1) \sum_{sr} \langle s | \mathbf{m}_i | r \rangle \langle r | \mathbf{m}_j | s \rangle \frac{i\hbar \mathbf{g}_{rs}}{(E_{rs} - \hbar \mathbf{w} - i\hbar \mathbf{g}_{rs})(E_{sr} + \hbar \mathbf{w} - i\mathbf{s} \hbar \mathbf{g}_{sr})} \quad (7)$$

Clearly, with  $\mathbf{s} = -1$  (*vsc*) then

$$\sum_s \mathbf{a}_{ij}^{ss} = 2 \sum_{sr} \langle s | \mathbf{m} | r \rangle \langle r | \mathbf{m} | s \rangle \frac{i \hbar \mathbf{g}_{rs}}{\left( (E_{rs} - \hbar \omega)^2 + (\hbar \mathbf{g}_{rs})^2 \right)} \quad (8)$$

and the relation (5) is violated. Hence the sum rule is consistent only with constant-sign damping. A more general theory which considers multi-level systems and higher-order optical processes, such as degenerate and non-degenerate four-wave mixing, has recently been developed. Results from this work verify that there exist equivalent sum rules for all higher-order susceptibility tensors – but that these rules invariably hold true only with the provision of *csc* resonance damping.

## 5. FLUCTUATION DIPOLES IN NONLINEAR OPTICS

In the description of optical parametric processes, use of the electric dipole approximation in deriving the susceptibilities leads to expressions involving products of transition dipole moments along a connected route beginning and ending in the same (usually ground) state. The term ‘transition moment’ (used in this connection as a distinction from permanent moments) needs qualifying, however. Each such transition moment embedded *en route* in an optical susceptibility tensor connects two states, at least one of which will be a virtual state. In the perturbative sum over such states, at least one route must generate a diagonal matrix element corresponding to a permanent moment. In this sense, permanent electric dipole moments are particular instances of the transition moments, and it is now recognized that these are significantly involved in the structure of any nonlinear susceptibility<sup>21-23</sup>. In the semiclassical formulation, the role of permanent moments emerges through calculations based on a transformed electric dipole interaction, by employment of a *fluctuation dipole* operator<sup>22</sup> given by;

$$H'_{\text{int}} = -[\boldsymbol{\mu} - \boldsymbol{\mu}^{00}] \cdot \mathbf{e}^\perp, \quad (9)$$

in which the subtracted moment is the permanent dipole of the initial molecular state – usually the ground state; the absence of state superscripts on  $\boldsymbol{\mu}$  in the above expression serves as a reminder of its status as an operator on molecular wavefunctions.

Much of the work that is conducted in pursuit of two-level materials with high efficiencies for laser frequency conversion center on ‘push-pull’ systems, in which permanent dipole effects are enhanced by a juxtaposition of strongly electron-donating and electron-withdrawing functional groups. For polar molecules with an optical response strongly dominated by one electronic excited state, it proves that a singular role is played by the vector *difference* or *displacement* between the excited state (*u*) and ground state dipole moments, traditionally given the symbol  $\mathbf{d}$ . In effect only this displacement from the ground state value, rather than the absolute value of the upper state dipole, enters into the final results<sup>24-28</sup>. In such cases, it proves that the materials with the largest optical susceptibilities are commonly those associated with large  $\mathbf{d}$  values. To directly elicit the details of this connection, we have previously demonstrated an expedient algorithm for calculation of the nonlinear optical susceptibilities for such systems<sup>29</sup>, based on the coupled transformations;

$$\boldsymbol{\mu}^{uu} \rightarrow \boldsymbol{\mu}^{uu} - \boldsymbol{\mu}^{00} = \mathbf{d}; \quad \boldsymbol{\mu}^{00} \rightarrow 0 \quad (10)$$

whilst the transition dipoles remain unchanged. When the various time-orderings for any optical processes of interest are drawn up, application of this rule enables expressions involving any connected route that entails the ground state permanent dipole  $\boldsymbol{\mu}^{00}$  to be discarded, so long as those entailing the excited state dipole  $\boldsymbol{\mu}^{uu}$  are re-interpreted to invoke  $\mathbf{d}$ . By quantum electrodynamical methods this procedure has been explicitly validated for all parametric and non-parametric processes, both degenerate and fully non-degenerate. In almost every case its implementation leads in a matter of lines to results identical to those previously established by substantially more laborious means. Once again it transpires that the algorithm retains validity only with the correct (*csc*) convention for resonance damping, ensuring that results exhibit proper symmetry with respect to time reversal.

Consider for example the very simple case of second harmonic generation, mediated by a second order susceptibility  $\mathbf{c}(-2\omega; \omega, \omega)$  and associated with a ground state molecular hyperpolarisability tensor  $\mathbf{b}_{ijk}^{\text{SHG}}$ . The properly index

symmetrized hyperpolarisability emerges from the usual time-ordered perturbation theory derivation as the following expression;

$$\mathbf{b}_{ijk}^{\text{SHG}}(\mathbf{s}) = \sum_{r=0,u} \sum_{s=0,u} \left\{ \frac{\mathbf{m}_i^{0s} \mathbf{m}_j^{sr} \mathbf{m}_k^{r0}}{(E_{s0} - 2\hbar\omega - i\hbar\mathbf{g}_s)(E_{r0} - \hbar\omega - i\hbar\mathbf{g}_r)} + \frac{\mathbf{m}_j^{0s} \mathbf{m}_i^{sr} \mathbf{m}_k^{r0}}{(E_{s0} + \hbar\omega - i\hbar\mathbf{g}_s)(E_{r0} - \hbar\omega - i\hbar\mathbf{g}_r)} \right. \\ \left. + \frac{\mathbf{m}_j^{0s} \mathbf{m}_k^{sr} \mathbf{m}_i^{r0}}{(E_{s0} + \hbar\omega - i\hbar\mathbf{g}_s)(E_{r0} + 2\hbar\omega - i\hbar\mathbf{g}_r)} + \frac{\mathbf{m}_i^{0s} \mathbf{m}_k^{sr} \mathbf{m}_j^{r0}}{(E_{s0} - 2\hbar\omega - i\hbar\mathbf{g}_s)(E_{r0} - \hbar\omega - i\hbar\mathbf{g}_r)} \right. \\ \left. + \frac{\mathbf{m}_k^{0s} \mathbf{m}_i^{sr} \mathbf{m}_j^{r0}}{(E_{s0} + \hbar\omega - i\hbar\mathbf{g}_s)(E_{r0} - \hbar\omega - i\hbar\mathbf{g}_r)} + \frac{\mathbf{m}_k^{0s} \mathbf{m}_j^{sr} \mathbf{m}_i^{r0}}{(E_{s0} + \hbar\omega - i\hbar\mathbf{g}_s)(E_{r0} + 2\hbar\omega - i\hbar\mathbf{g}_r)} \right\} \quad (11)$$

Here transition moment components are written in shorthand form as  $\mathbf{m}_i^{sr} = \langle s | \mathbf{m}_i | r \rangle$ , energy differences  $E_{s0} = (E_s - E_0)$ , and we apply a two-level restriction to the sum over states; as always, the ground state damping is zero. However, adoption of the two-level algorithm requires that, in the transition sequence  $0 \rightarrow s \rightarrow r \rightarrow 0$ , only the specific sequence  $0 \rightarrow u \rightarrow u \rightarrow 0$  need be considered, with the corresponding transition moments reinterpreted accordingly. Thus the hyperpolarisability emerges in the following simpler form;

$$\tilde{\mathbf{b}}_{ijk}^{\text{SHG}}(\mathbf{s}) = \frac{\mathbf{m}_i^{0u} d_j \mathbf{m}_k^{u0}}{(E_{s0} - 2\hbar\omega - i\hbar\mathbf{g}_s)(E_{r0} - \hbar\omega - i\hbar\mathbf{g}_r)} + \frac{\mathbf{m}_j^{0u} d_i \mathbf{m}_k^{u0}}{(E_{s0} + \hbar\omega - i\hbar\mathbf{g}_s)(E_{r0} - \hbar\omega - i\hbar\mathbf{g}_r)} \\ + \frac{\mathbf{m}_j^{0u} d_k \mathbf{m}_i^{u0}}{(E_{s0} + \hbar\omega - i\hbar\mathbf{g}_s)(E_{r0} + 2\hbar\omega - i\hbar\mathbf{g}_r)} + \frac{\mathbf{m}_i^{0u} d_k \mathbf{m}_j^{u0}}{(E_{s0} - 2\hbar\omega - i\hbar\mathbf{g}_s)(E_{r0} - \hbar\omega - i\hbar\mathbf{g}_r)} \\ + \frac{\mathbf{m}_k^{0u} d_i \mathbf{m}_j^{u0}}{(E_{s0} + \hbar\omega - i\hbar\mathbf{g}_s)(E_{r0} - \hbar\omega - i\hbar\mathbf{g}_r)} + \frac{\mathbf{m}_k^{0u} d_j \mathbf{m}_i^{u0}}{(E_{s0} + \hbar\omega - i\hbar\mathbf{g}_s)(E_{r0} + 2\hbar\omega - i\hbar\mathbf{g}_r)} \quad (12)$$

It is readily shown that the equality  $\mathbf{b}_{ijk}^{\text{SHG}}(\mathbf{s}) = \tilde{\mathbf{b}}_{ijk}^{\text{SHG}}(\mathbf{s})$  holds exactly only for  $\mathbf{s} = +1$ , as in the constant sign convention; the relationship fails with *vsc*.

In a fully quantum theoretical treatment, the validity of the calculational algorithm was originally verified by a highly intricate proof. Recently we have shown that a canonical transformation method entirely circumvents such an approach; it also affords new insights into the formulation of quantum field interactions<sup>30</sup>. In detail, the transformation effects a subtraction from the transverse electric field  $\mathbf{e}^\perp$  of the transverse part of the polarization field due to the ground-state dipoles,  $\boldsymbol{\mu}^0$ . The radiation-molecule coupling is then correctly represented in terms of the fluctuation dipole operator (9). What also emerges from the QED formulation is that an additional instantaneous intermolecular interaction appears in the transformed Hamiltonian, representing perturbations of the molecular eigenstates and corresponding energies due to the surrounding polar medium. The emergence of instantaneous intermolecular coupling is a direct consequence of eliminating, in the field-mediated molecule-molecule coupling, the permanent ground-state dipoles in favor of dipole shifts. The QED method is directly amenable to the inclusion of higher rank multipole moments; furthermore it extends previous work in permitting application to molecules with an arbitrary number of molecular states. This allows the proper representation of non-resonant optical processes, and is fully consistent with *csc* damping.

## 6. LINEAR ELECTRO-OPTIC EFFECT

Damping issues come very much to the fore in connection with a controversy over the linear electro-optic effect, in which the coherent scattering of light couples linearly with a static electric field. Once again the involvement of a static field must be treated as a perturbation – otherwise there would be no possibility of finding a transition rate associated with an electro-optic response as such. It is a reminder that even a static field must limit the lifetime of the unperturbed material states. In the context of a damping formalism, once this field is switched on and its physical effects are

incorporated in the formalism, these states are no longer eigenstates of the unperturbed Hamiltonian; their algebraic expression is modified and they acquire a correspondingly finite lifetime.

Mediated by a second order nonlinear susceptibility  $\mathbf{c}(-\mathbf{w}, 0, \mathbf{w})$ , linear electro-optic or circular photovoltaic effects are supportable only in systems lacking a centre of symmetry, in the dipole approximation<sup>31</sup>. In isotropic liquids, this symmetry condition can only be satisfied by chiral or gyrotropic molecules (those lacking inversion or any axis of improper rotational symmetry), as is the case for other even-order susceptibility processes such as sum-frequency generation. In the context of phenomenological damping, however, it is necessary to entertain other considerations to resolve the issue of whether such a linear electro-optic response is fundamentally allowed in the bulk of an isotropic system. Beljonne *et al.*<sup>32</sup> first presented a discussion of the electro-optic response of chiral liquids. In detail the process they considered involves forward Rayleigh scattering, between orthogonal linear polarisations, coupled with a static electric field. That analysis concluded that chiral molecules in isotropic media possess a significant electro-optic response, at the electric dipole level.

In detail, the molecular tensor for such a process takes the following form, as delivered by the usual time-dependent perturbation theory:

$$\mathbf{b}_{jki}^{00} = \sum_{r,s} \left\{ \frac{\mathbf{m}_j^{0s} \mathbf{m}_k^{sr} \mathbf{m}_i^{r0}}{(E_{s0} - \hbar\mathbf{w} - i\hbar\mathbf{g}_s)(E_{r0} - \hbar\mathbf{w} - i\hbar\mathbf{g}_r)} + \frac{\mathbf{m}_i^{0s} \mathbf{m}_k^{sr} \mathbf{m}_j^{r0}}{(E_{s0} + \hbar\mathbf{w} - i\mathbf{s}\hbar\mathbf{g}_s)(E_{r0} + \hbar\mathbf{w} - i\mathbf{s}\hbar\mathbf{g}_r)} + \frac{\mathbf{m}_k^{0s} \mathbf{m}_j^{sr} \mathbf{m}_i^{r0}}{(E_{s0} - i\hbar\mathbf{g}_s)(E_{r0} - \hbar\mathbf{w} - i\hbar\mathbf{g}_r)} + \frac{\mathbf{m}_k^{0s} \mathbf{m}_i^{sr} \mathbf{m}_j^{r0}}{(E_{s0} - i\hbar\mathbf{g}_s)(E_{r0} + \hbar\mathbf{w} - i\mathbf{s}\hbar\mathbf{g}_r)} + \frac{\mathbf{m}_i^{0s} \mathbf{m}_k^{sr} \mathbf{m}_j^{r0}}{(E_{s0} - \hbar\mathbf{w} - i\hbar\mathbf{g}_s)(E_{r0} - i\hbar\mathbf{g}_r)} + \frac{\mathbf{m}_i^{0s} \mathbf{m}_j^{sr} \mathbf{m}_k^{r0}}{(E_{s0} + \hbar\mathbf{w} - i\mathbf{s}\hbar\mathbf{g}_s)(E_{r0} - i\hbar\mathbf{g}_r)} \right\} \quad (13)$$

which is indeed supported only by achiral species. We note that application of HT symmetry (the combination of the time reversal operation with hermitian conjugation) to equation (13) proves that the tensor is  $(i,j)$ -symmetric *only* for  $\mathbf{s} = +1$  (*csc*) – otherwise such index symmetry holds only if damping is specifically excluded. This becomes of crucial importance when the bulk response is considered because, for an isotropic fluid, the effective susceptibility of the medium is obtained by performing a rotational average of the molecular tensor. For a rank-three tensor this is effected on contraction with the isotropic tensor of rank three<sup>33</sup>, which is the Levi-Civita antisymmetric tensor  $\mathbf{e}_{ijk}$ . Index symmetry considerations thus dictate that the result is zero; the electro-optic is not allowed in an isotropic fluid. On the other hand, the signal survives if the hyperpolarisability tensor is constructed using the variable sign convention, since the anti-symmetric part is then non-zero and equal to:

$$\mathbf{b}^{00}(\mathbf{s} = -1) = \sum_{\substack{\{j,k,i\} = \{x,y,z\} \\ \text{cyclic}}} \left\{ \sum_{s,r} \frac{i\hbar\mathbf{g}_s}{E_{s0}^2 + \hbar^2\mathbf{g}_s^2} \frac{(\hbar\mathbf{w} + i\hbar\mathbf{g}_r)}{(E_{r0})^2 - (\hbar\mathbf{w} + i\hbar\mathbf{g}_r)^2} (\mathbf{m}_i^{0s} \mathbf{m}_j^{sr} \mathbf{m}_k^{r0} - \mathbf{m}_i^{0s} \mathbf{m}_r^{sr} \mathbf{m}_j^{r0}) \right\} \quad (14)$$

Hence, under *csc* the process is forbidden in the electric-dipole approximation, whereas it would not be under *vsc*<sup>34</sup>. This result might in principle be amenable to experimental verification – but first it is necessary to account for the fact that, with *csc*, the process becomes allowed at multipole couplings beyond the electric dipole approximation.

It is 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 *vsc*. Either possibility could be wrongly attributed if an experiment were to give a positive result. To address this question, we briefly consider the form of such multipolar terms. Let us 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 results in these three vectors contracting to give the scalar  $(\mathbf{e}_2 \times \mathbf{e}_1) \cdot \mathbf{e}_s$  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  $\mathbf{k}$ , the rotational average results in the three scalars:  $(\mathbf{e}_2 \cdot \mathbf{e}_1)(\mathbf{e}_s \cdot \mathbf{k})$ ,  $(\mathbf{e}_2 \cdot \mathbf{e}_s)(\mathbf{e}_1 \cdot \mathbf{k})$ ,  $(\mathbf{e}_1 \cdot \mathbf{e}_s)(\mathbf{e}_2 \cdot \mathbf{k})$ , all of which are necessarily zero. For the parts of the amplitude that are quadratic in  $\mathbf{k}$  the rotational average results in scalars derived from fifth rank isotropic tensors, such as  $(\mathbf{e}_2 \times \mathbf{e}_1) \cdot \mathbf{e}_s (\mathbf{k} \cdot \mathbf{k})$  – and these are non-zero for any choice of polarisations. This verifies that the process is permissible at higher orders under *csc*; but only at the electric octopole/magnetic quadrupole level. Most recently, through an analysis based on a dissipative harmonic oscillator model, Agarwal and Boyd have also concluded that radiative damping alone cannot lead to a non-vanishing linear electro-optic effect in a chiral isotropic medium<sup>35</sup>. The possibility of induction through the effects of *collisional* damping are also discounted as giving unobservably small signals.

## 7. CONCLUSION

The principles validated by the above analysis operate with equal force across the whole of nonlinear optics and electro-optics, the given examples being used as simple illustrations. However, it has become clear that one would need to surmount considerable difficulties in any attempt to secure experimental verification of one or other approach to the inclusion of phenomenological damping. In considering possible avenues for possible verification (of either damping convention) it is worth emphasizing that for any optical process, differences between predictions of the two theories are apparent only through ‘anti-resonant’ terms. In most cases, such terms cannot dominate the optical response; they become, at most, marginally significant in regions very far removed from resonance. Optimally one might look for a system with optical properties dominated by one very low-lying excited state, well below the energy of photons involved. From lengthy but straightforward calculations it emerges that the order of magnitude of fractional rate corrections typically lies in the region of  $g^2/E_{\text{mol}}^2$ . Even then, only if all other electronic states were very significantly higher in energy than the photons involved could an anti-resonant feature be considered amenable to experimental identification. No such truly two-level systems exist; always, higher energy states play some part in the summation over states entailed in the polarisability. Moreover, whereas attempts to determine an absolute damping sign might be expedited in a system with large damping constants, these parameters are largest for systems with a high density of electronic levels – and any vibrational structure would certainly obscure the sought features through its role in the sum over states.

A pragmatic solution to the whole controversy might be to neglect damping in anti-resonant terms and only include it in potentially resonant terms – where it does have significant impact and there is agreement over the correct sign. Indeed, recent work by Agarwal and Boyd<sup>35</sup> has concluded that it is only close to resonance that such damping has legitimacy. A proper perspective on the subject comes on recollection that phenomenological damping is at best only an approximate device designed to model a Lorentzian lineshape – and that, whereas there is always a leading order or perturbation theory contributing to the signal, other higher orders exist and also contribute marginally to observations. Ultimately the signing controversy we have addressed is significant primarily for its exposure of fundamental issues concerning dissipation in quantum systems.

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