Limitations and improvements upon the two-level approximation for molecular nonlinear optics

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ABSTRACT

When parametric nonlinear processes are employed in the cause of efficient optical frequency conversion, the media involved are generally subjected to substantially off-resonant input radiation. As such, it is usually only electronic ground states of the conversion material that are significantly populated; higher levels are engaged only in the capacity of virtual states, and it is frequently assumed that just one such state dominates in determining the response. Calculating the nonlinear optical susceptibilities of molecules on this basis, excluding all but the ground and one excited state in a sum-over-states formulation, signifies the adoption of a two-level model, a technique that is widely deployed in the calculation and analysis of nonlinear optical properties. The two-level model offers tractable and physically simple representations of molecular response, including wavelength dependence; it is also the origin of the widely applied 'push-pull' approach to designing optically nonlinear chromophores. By contrast, direct *ab initio* calculations of optical susceptibility are commonly frustrated by a complete failure to determine such dispersion features. However, caution is required; the two-level model can deliver potentially misleading results if it is applied without regard to the criteria for its validity, especially when molecular excited states are significantly populated. On the basis of a precise, quantum electrodynamical basis for the theory, we explore in detail why there are grounds for questioning the general validity of two-level calculations in nonlinear optics; we assess the criteria for high frequency conversion efficiency and provide a new graphical method to assist in determining the applicability of a two-level model for hyperpolarizability calculations. Lastly, this paper also explores the applicability and detailed conditions for the two-level model for electronically excited molecules, identifying problematic results and providing tractable methods for improving the accuracy of calculations on real molecule-photon interactions.

Keywords: nonlinear optics; nonlinear susceptibility; two-level systems; molecular optics; electronic excited states; resonance; calculational methods; quantum electrodynamics

1. Introduction

In the development of theory to address the interactions of light and matter, one of the most widely deployed models is the two-level approximation. Usually applied to electronic states in systems with discrete energy levels, it is a theoretical model that is deeply embedded in a wide range of material representations, extending from those of atoms[1,2] and more recently quantum dots[3,4] through to a formalism applicable to molecules and chromophores of significant structural complexity.[5] To the extent that any such systems are amenable to a two-level representation, the advantages are obvious; relative calculational simplicity, and results cast in formulae that entail a sufficiently small set of parameters for their experimental determination to be realistic. Moreover the theoretical constructs of a two-level system have a certain appeal, offering the potential to exploit congruence with the dynamics of a spin-½ system and its associated Pauli matrices.

In the course of developing the received theory of nonlinear optics, the two-level approach has also been very widely used. With the typical intensity levels of pulsed laser light, there arises a significant probability for two or more photons to interact simultaneously (within the limits of quantum uncertainty) with each optically distinct center. This alone suggests a need for caution in applying any model where the available electromagnetic energy can span the gap between states other than those close to the single photon energy quantum. Moreover, the materials that are most effective for the utilization of nonlinear optical effects in frequency conversion (especially in the case of second harmonic generation, forbidden in an isotropic gas) are those whose energy level structures are significantly more complex than atoms.

Nonetheless, the two-level model has received wide application in such a context;[6-22] it not only delivers results of a relatively simple form, it also relates well to long-established concepts of chemical structure. In particular, a wealth of synthetic studies[23-33] have been based upon the anticipated and oft-proven connection between 'push-pull' chromophore structures[34-40] (these facilitating intramolecular electron transfer) and an enhanced second harmonic response. The devising of simple structural rules, ultimately derived from the two-level model, has undoubtedly assisted the laboratory development of many high-efficiency nonlinear optical materials. However, the direct *ab initio* calculations of optical susceptibility are frequently frustrated by a complete failure to determine dispersion characteristics.[41-47]

When parametric nonlinear processes are employed in the cause of efficient optical frequency conversion, the media involved are generally subjected to substantially off-resonant input radiation. As such, it is usually only the electronic ground state of the conversion material that is significantly populated; higher levels are engaged only in the capacity of virtual states. Thus, in considering phenomena that involve optical frequencies comparable to the positioning of one specific level – often the lowest electronic excited state – it is tempting to cast the theory, for simplicity, in terms of a two-level system. However, caution is required; the two-level model can deliver potentially misleading results if applied without regard to the criteria for its validity – more especially when molecular excited states are indeed populated. On the basis of a precise, quantum electrodynamical framework for the theory, this paper explores the applicability and detailed conditions for the two-level model, identifying problematic results and providing tractable methods for improving the accuracy of calculations on molecule-photon interactions.

2. Basis of two-level perturbation theory

For the systems discussed in this paper, it is sufficiently accurate to develop theory in terms of non-relativistic QED. As a result, since intramolecular Coulomb binding energies are much greater than the coupling to radiation, molecule-photon interactions are treated by perturbation methods.[48] The following Hamiltonian for non-relativistic QED is directly amenable to multipolar development:

$$H = H_{\text{rad}} + H_{\text{mol}} + H_{\text{int}} \quad . \tag{1}$$

Eq. (1) comprises: (i) the radiation Hamiltonian, H_{rad}; (ii) the molecular Hamiltonian, H_{mol} and; (iii) the interaction Hamiltonian, H_{int}. The rate, Γ, of any optical interaction is found from Fermi's Rule;[49]

$$\Gamma = \frac{2\pi}{\hbar}\left|M_{FI}\right|^2 \rho_F \quad . \tag{2}$$

where ρ_F is the density of the states, and M_{FI} is the quantum amplitude coupling the initial and final states. Time-dependent perturbation theory is required to determine M_{FI}, the expression corresponding to which is generated from the following infinite series;[50]

$$\begin{aligned} M_{FI} &= \sum_{p=0}^{\infty} \left\langle F \left| H_{\text{int}} \left(T_0 H_{\text{int}} \right)^p \right| I \right\rangle \\ &= \left\langle F \left| H_{\text{int}} + H_{\text{int}} T_0 H_{\text{int}} + H_{\text{int}} T_0 H_{\text{int}} T_0 H_{\text{int}} + H_{\text{int}} T_0 H_{\text{int}} T_0 H_{\text{int}} T_0 H_{\text{int}} + ... \right| I \right\rangle \quad , \end{aligned} \tag{3}$$

where $|I\rangle$ and $|F\rangle$ represent the respective initial and final states of the system; namely, states that are composed of molecular and radiation parts, with the operator H_{int} acting upon both. Moreover, $T_0 \approx \left(E_I - H_0\right)^{-1}$ in which $H_0 = H_{\text{rad}} + H_{\text{mol}}$ is the unperturbed Hamiltonian and E_I is the energy of the initial state. The next step involves the implementation of the completeness relation $\sum_n |n\rangle\langle n| = 1$, so that Eq. (3) is recast as;

$$M_{FI} = \langle F|H_{\text{int}}|I\rangle + \sum_R \frac{\langle F|H_{\text{int}}|R\rangle\langle R|H_{\text{int}}|I\rangle}{(E_I - E_R)} + \sum_{R,S} \frac{\langle F|H_{\text{int}}|S\rangle\langle S|H_{\text{int}}|R\rangle\langle R|H_{\text{int}}|I\rangle}{(E_I - E_R)(E_I - E_S)}$$
$$+ \sum_{R,S,T} \frac{\langle F|H_{\text{int}}|T\rangle\langle T|H_{\text{int}}|S\rangle\langle S|H_{\text{int}}|R\rangle\langle R|H_{\text{int}}|I\rangle}{(E_I - E_R)(E_I - E_S)(E_I - E_T)} + \ldots \quad , \tag{4}$$

where the virtual system states are denoted by $|R\rangle$, $|S\rangle$, $|T\rangle$.... upon which H_0 operates, and E_n is the energy of a state denoted by its subscript. In the two-level model, where the virtual states are limited to either a ground state $|0\rangle$ or a single excited state $|u\rangle$, the completeness relation is an approximation since other residual states $n \geq 2$ are not applied; namely, $|0\rangle\langle 0| + |1\rangle\langle 1| = 1$ in the two-level model.

It is interesting to observe that, on application of the two-level approximation, if the expectation value determined from an operator $\hat{A}$ for a ground-state molecule is equal to the expectation value in an excited state, then the ground and the excited state expectation values for any positive integer power of that operator, $\hat{A}^n$, are again equal. That is, if $\langle 0|\hat{A}|0\rangle = \langle 1|\hat{A}|1\rangle$, the approximation implies $\langle 0|\hat{A}^n|0\rangle = \langle 1|\hat{A}^n|1\rangle$ (proven elsewhere, ref. 51). A clear flaw in applying the two-level approximation is apparent for the case where the ground and excited state energy levels have the same expectation value for distance and momentum, resulting in the expectation value for the squares of the distance and momentum to be the same for both energy levels. Since we can express the total energy of such a two-level system in terms of the latter factors, it implies that the two states are degenerate. This may readily be shown in the explicit case of the expectation value for the Hamiltonian of a harmonic oscillator:

$$E_n \equiv \hat{H}_{nn} = \frac{1}{2m}\hat{p}_{nn}^2 + \frac{1}{2}m\omega^2\hat{x}_{nn}^2. \tag{5}$$

from which it would be inferred that $E_0 = E_1$, as detailed in the above text, if $\hat{p}_{00} = \hat{p}_{11}$ and $\hat{x}_{00} = \hat{x}_{11}$. The implication is that the two-level approximation is unusable for treating two energy levels of a harmonic oscillator as a complete basis set; whereas this is an unlikely choice, there are many other systems where the same logic would apply less glaringly.

3. Two-level model for elastic scattering and second harmonic generation

3.1 Success of the two-level model

The aim of this section is to discuss the validity of the two-level model through an examination of calculations relating to elastic (Rayleigh) scattering. Returning to Eq. (4), it is clear that successive terms of the perturbation theory relate to processes of progressively higher photonic order; for our present purposes, a description of the two-photon event of Rayleigh scattering and three-photon event of second harmonic generation (SHG) are determined from the second and third terms on the right-hand side of the expression, respectively. Note, these two scattering processes are chosen for their calculational ease; higher-order optical mechanisms will follow the same pattern. An expression for the polarizability tensor α_{ij}^{00} is thus found from Eq. (4) – which is *minus* the molecular part of the quantum amplitude of Rayleigh scattering – and is given by;[52]

$$\alpha_{ij}^{00}(-\omega;\omega) = \sum_r \left(\frac{\mu_i^{0r}\mu_j^{r0}}{\tilde{E}_{r0} - \hbar\omega} + \frac{\mu_j^{0r}\mu_i^{r0}}{\tilde{E}_{r0} + \hbar\omega} \right) \quad . \tag{6}$$

Here, the index *i* is assigned to emission and *j* to absorption (since the input and output photons are identical the tensor α_{ij}^{00} is *i*, *j*-symmetric), $\boldsymbol{\mu}^{0r} \equiv \langle 0|\boldsymbol{\mu}|r\rangle$ denotes a transition dipole moment, and $\hbar\omega$ is the energy of an input photon;

$\tilde{E}_{r0} \equiv \tilde{E}_r - \tilde{E}_0$, in which r represents the virtual matter state. Moreover, the tildes denote the inclusion of a damping term $\frac{\mathrm{i}}{2}\gamma$, where γ is the FWHM linewidth, and the implied summation convention for repeated Cartesian tensor indices is employed. This summation over the virtual states, which denote electronically excited energy levels, is the vital aspect of the following discussion. Next, determining the hyperpolarizability, β_{ijk}^{00}, of second harmonic generation results in the summation;

$$\beta_{ijk}^{00}(-2\omega;\omega,\omega) = \sum_{r,s}\left(\frac{\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}}{\left(\tilde{E}_{s0}-2\hbar\omega\right)\left(\tilde{E}_{r0}-\hbar\omega\right)} + \frac{\mu_j^{0s}\mu_i^{sr}\mu_k^{r0}}{\left(\tilde{E}_{s0}+\hbar\omega\right)\left(\tilde{E}_{r0}-\hbar\omega\right)} + \frac{\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}}{\left(\tilde{E}_{s0}+\hbar\omega\right)\left(\tilde{E}_{r0}+2\hbar\omega\right)} \right) \quad , \tag{7}$$

where s denotes a second virtual state and the subscript k is assigned to an emission photon. In the case of second harmonic generation, and indeed n-harmonic generation, the input photons are indistinguishable, thus the indices associated with them are freely interchangeable. Therefore the following equation can be used in this instance to form a fully j, k symmetric tensor: $\beta_{i(jk)} = \frac{1}{2}\left[\beta_{ijk} + \beta_{ikj}\right]$.

Following from these general expressions, we now compare the two-level approximation (TLA) against a multi-level model, where the latter incorporates background contributions (BG) that are omitted in the TLA. For simplicity, the subsequently presented results are to be limited to three levels. By taking account of this comparison, Eq. (6) is now written as follows;

$$\begin{aligned} \alpha_{ij}^{00} &= \alpha_{ij}^{\mathrm{TLA}} + \alpha_{ij}^{\mathrm{BG}} \\ &= \left(\frac{\mu_i^{0u}\mu_j^{0u}}{\tilde{E}_{u0}-\hbar\omega} + \frac{\mu_i^{0u}\mu_j^{0u}}{\tilde{E}_{u0}+\hbar\omega} \right) + \frac{\mu_i^{0u'}\mu_j^{0u'}}{\tilde{E}_{u'0}-\hbar\omega} + \frac{\mu_i^{0u'}\mu_j^{0u'}}{\tilde{E}_{u'0}+\hbar\omega} + \ldots \quad , \end{aligned} \tag{8}$$

where the frequency dependence on the tensors is here and henceforth suppressed, $|u'\rangle$ is a third level, $\boldsymbol{\mu}^{0u} \equiv \boldsymbol{\mu}^{u0}$ and $\boldsymbol{\mu}^{0u'} \equiv \boldsymbol{\mu}^{u'0}$ – i.e. the transition dipole moments are assumed real (as is always possible, given a suitable choice of basis set for the molecular wavefunctions) – and the terms within brackets correspond to the TLA. It is noteworthy that, in the case where the intermediate state is $|0\rangle$, the terms involving μ_i^{00} and μ_j^{00} cancel each other out. This feature, i.e. that terms involving ground state static dipoles can be discarded, forms a basis for the algorithmic method[50,53-55] now to be deployed for the more complex (nonlinear) mechanism of SHG.

The algorithmic method, for this case, involves the restriction of both intermediate states featured within Eq. (7) to just $|0\rangle$ and $|u\rangle$, and only four unique routes describe transitions starting and finishing in the ground molecular state progressing through both r and s; explicitly the $0 \to r \to s \to 0$ sequences are expressible as 0000, $0u00$, $00u0$ and $0uu0$. Each sequence generates a combination of both transition dipole moments, either $\boldsymbol{\mu}^{0u}$ or $\boldsymbol{\mu}^{u0}$, as well as the static dipole moments of the ground and excited energy levels, $\boldsymbol{\mu}^{00}$ and $\boldsymbol{\mu}^{uu}$, respectively. Detailed analysis of nonlinear optical susceptibilities shows that the dependence on static moments emerges only in terms of their vector difference, $\mathbf{d} = \boldsymbol{\mu}^{uu} - \boldsymbol{\mu}^{00}$, and with the benefit of the algorithmic method, the following prescription is adopted:

$$\boldsymbol{\mu}^{uu} \to \boldsymbol{\mu}^{uu} - \boldsymbol{\mu}^{00} = \mathbf{d} \;;\; \boldsymbol{\mu}^{00} \to 0. \tag{9}$$

Applying this procedure requires application of an associated rule: any mechanism that connects the initial and final system states through any ground state static dipole is to be discarded, and hence only one of the originally proposed four sequences, namely $0uu0$, persists. Applying the algorithm to Eq. (7), the two-level hyperpolarizability tensor is obtained. After performing a similar analysis, when the intermediate states are restricted to the three-levels, $|0\rangle$, $|u\rangle$ and $|u'\rangle$, it is then clear that the hyperpolarizability tensor becomes;

$$\beta_{ijk}^{00} = \beta_{ijk}^{\mathrm{TLA}} + \beta_{ijk}^{\mathrm{BG}}$$
$$= \left(\frac{\mu_i^{0u} d_j \mu_k^{0u}}{\left(\tilde{E}_{u0} - 2\hbar\omega\right)\left(\tilde{E}_{u0} - \hbar\omega\right)} + \frac{\mu_j^{0u} d_i \mu_k^{0u}}{\left(\tilde{E}_{u0} + \hbar\omega\right)\left(\tilde{E}_{u0} - \hbar\omega\right)} + \frac{\mu_j^{0u} d_k \mu_i^{0u}}{\left(\tilde{E}_{u0} + \hbar\omega\right)\left(\tilde{E}_{u0} + 2\hbar\omega\right)} \right)$$
$$+ \frac{\mu_i^{0u'} d'_j \mu_k^{0u'}}{\left(\tilde{E}_{u'0} - 2\hbar\omega\right)\left(\tilde{E}_{u'0} - \hbar\omega\right)} + \frac{\mu_j^{0u'} d'_i \mu_k^{0u'}}{\left(\tilde{E}_{u'0} + \hbar\omega\right)\left(\tilde{E}_{u'0} - \hbar\omega\right)} + \frac{\mu_j^{0u'} d'_k \mu_i^{0u'}}{\left(\tilde{E}_{u'0} + \hbar\omega\right)\left(\tilde{E}_{u'0} + 2\hbar\omega\right)}$$
$$+ \frac{\mu_i^{0u} \mu_j^{uu'} \mu_k^{0u'}}{\left(\tilde{E}_{u0} - 2\hbar\omega\right)\left(\tilde{E}_{u'0} - \hbar\omega\right)} + \frac{\mu_j^{0u} \mu_i^{uu'} \mu_k^{0u'}}{\left(\tilde{E}_{u0} + \hbar\omega\right)\left(\tilde{E}_{u'0} - \hbar\omega\right)} + \frac{\mu_j^{0u} \mu_k^{uu'} \mu_i^{0u'}}{\left(\tilde{E}_{u0} + \hbar\omega\right)\left(\tilde{E}_{u'0} + 2\hbar\omega\right)}$$
$$+ \frac{\mu_i^{0u'} \mu_j^{u'u} \mu_k^{0u}}{\left(\tilde{E}_{u'0} - 2\hbar\omega\right)\left(\tilde{E}_{u0} - \hbar\omega\right)} + \frac{\mu_j^{0u'} \mu_i^{u'u} \mu_k^{0u}}{\left(\tilde{E}_{u'0} + \hbar\omega\right)\left(\tilde{E}_{u0} - \hbar\omega\right)} + \frac{\mu_j^{0u'} \mu_k^{u'u} \mu_i^{0u}}{\left(\tilde{E}_{u'0} + \hbar\omega\right)\left(\tilde{E}_{u0} + 2\hbar\omega\right)} + \ldots \quad , \qquad (10)$$

where $\mathbf{d}' = \boldsymbol{\mu}^{u'u'} - \boldsymbol{\mu}^{00}$. A justification for the two-level model is that the bracketed terms of Eqs (8) and (10) are likely to dominate over the others (as the denominator is smaller). Higher energy levels will always result in the production of larger denominators in the first term and, hence, a smaller contribution.

3.2 Failure of the two-level model

Under certain configurations, it is clear that the two-level model is likely to fail. An example of this may be illustrated by redefining the earlier expression of (10) in terms of the following variables, whose significance is apparent from Fig. 1: $\Delta\tilde{E}_1 = \tilde{E}_{u0} - \hbar\omega$, $-\Delta\tilde{E}_2 = 2\hbar\omega - \tilde{E}_{u0}$, $\Delta\tilde{E}'_1 = \tilde{E}_{u'0} - \hbar\omega$, and $\Delta\tilde{E}'_2 = \tilde{E}_{u'0} - 2\hbar\omega$ (Fig. 1). Clearly there are linear relationships between these quantities, and for casting the hyperpolarizability tensor in terms of them we shall select two that are linearly independent, namely $\Delta\tilde{E}_1$ and $\Delta\tilde{E}'_1$. In terms of these variables we have $\Delta\tilde{E}_2 = \Delta\tilde{E}_1 - \hbar\omega$ and $\Delta\tilde{E}'_2 = \Delta\tilde{E}'_1 - \hbar\omega$.

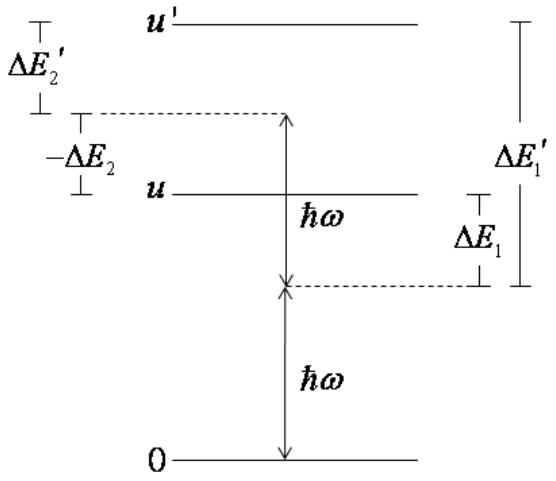

Fig. 1. Three-level energy diagram, where $\hbar\omega$ is the energy of the input beam and *u*, *u'* denote the first and second excited levels; $\Delta\tilde{E}_1$, $\Delta\tilde{E}_2$, $\Delta\tilde{E}'_1$, $\Delta\tilde{E}'_2$ are defined in the text.

Therefore, Eq. (10) now becomes;

$$\begin{aligned}\beta_{ijk}^{00} &= \beta_{ijk}^{\mathrm{TLA}} + \beta_{ijk}^{\mathrm{BG}} \\ &= \left(-\frac{\mu_i^{0u} d_j \mu_k^{0u}}{\Delta\tilde{E}_1\left(\Delta\tilde{E}_1 - \hbar\omega\right)} + \frac{\mu_j^{0u} d_i \mu_k^{0u}}{\Delta\tilde{E}_1\left(\Delta\tilde{E}_1 + 2\hbar\omega\right)} + \frac{\mu_j^{0u} d_k \mu_i^{0u}}{\left(\Delta\tilde{E}_1 + 3\hbar\omega\right)\left(\Delta\tilde{E}_1 + 2\hbar\omega\right)} \right) \\ &\quad - \frac{\mu_i^{0u'} d_j' \mu_k^{0u'}}{\Delta\tilde{E}_1'\left(\Delta\tilde{E}_1' - \hbar\omega\right)} + \frac{\mu_j^{0u'} d_i' \mu_k^{0u'}}{\Delta\tilde{E}_1'\left(\Delta\tilde{E}_1' + 2\hbar\omega\right)} + \frac{\mu_j^{0u'} d_k' \mu_i^{0u'}}{\left(\Delta\tilde{E}_1' + 2\hbar\omega\right)\left(\Delta\tilde{E}_1' + 2\hbar\omega\right)} \\ &\quad - \frac{\mu_i^{0u} \mu_j^{uu'} \mu_k^{0u'}}{\Delta\tilde{E}_1'\left(\Delta\tilde{E}_1 - \hbar\omega\right)} + \frac{\mu_j^{0u} \mu_i^{uu'} \mu_k^{0u'}}{\Delta\tilde{E}_1'\left(\Delta\tilde{E}_1 + 2\hbar\omega\right)} + \frac{\mu_j^{0u} \mu_k^{uu'} \mu_i^{0u'}}{\Delta\tilde{E}_1'\left(\Delta\tilde{E}_1 + 3\hbar\omega\right)} \\ &\quad - \frac{\mu_i^{0u'} \mu_j^{u'u} \mu_k^{0u}}{\Delta\tilde{E}_1\left(\Delta\tilde{E}_1' - \hbar\omega\right)} + \frac{\mu_j^{0u'} \mu_i^{u'u} \mu_k^{0u}}{\Delta\tilde{E}_1'\left(\Delta\tilde{E}_1' + 2\hbar\omega\right)} + \frac{\mu_j^{0u'} \mu_k^{u'u} \mu_i^{0u}}{\left(\Delta\tilde{E}_1' + 3\hbar\omega\right)\left(\Delta\tilde{E}_1 + 2\hbar\omega\right)} + \ldots \quad . \end{aligned} \tag{11}$$

From this expression it is clear that the 10th term is the most significant under conditions that generate the smallest values of the $\Delta\tilde{E}$'s, namely energy values well below that of a typical electronic transition. This is because all the terms except 1, 4, 7 and 10 will have a large denominator, and it is only in the 10th term that both denominator factors may be diminished (*i.e.* small $\Delta\tilde{E}_1$ and $\Delta\tilde{E}_2'$).

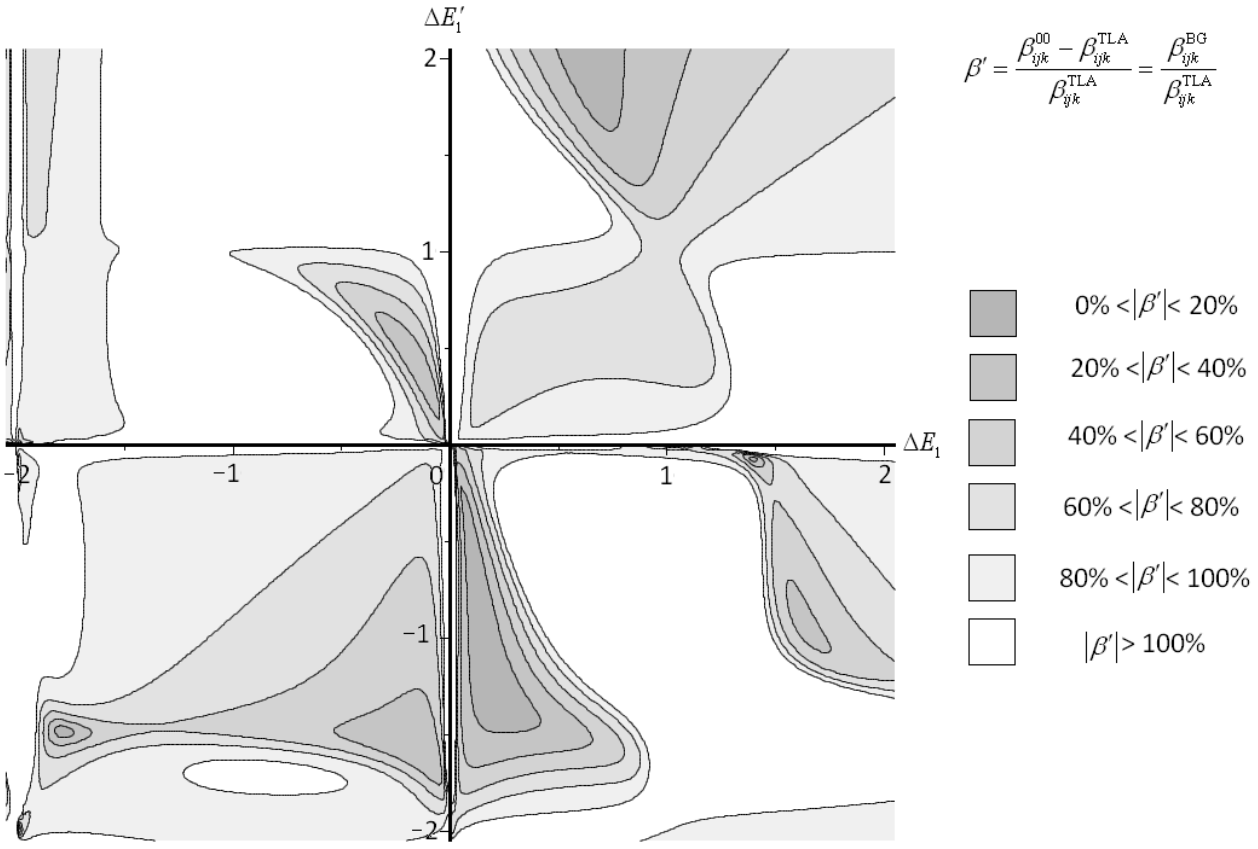

Fig. 2. A landscape illustrating the relative magnitude of the two-level denominators compared to the denominators corresponding to a third level in the SHG hyperpolarizability, β_{ijk}^{00}, where the scale is in units of $\hbar\omega$.

In order to visualize the scale of correction represented by the additional inclusion of terms involving the third level *u'*, it is expedient to devise a plot based on the magnitudes of the various tensor terms, under the simplifying assumption that all of the transition (and static) electric dipole moments have a broadly similar value. As an indicator of the difference which inclusion of the third level introduces, we now define a parameter β', a ratio of the addendum 'background' β^{BG} to the two-level result β^{TLA}. The results, exhibited in the contour map of Fig. 2, show how this parameter varies as a function of the two energy offset values $\Delta\tilde{E}_1$ and $\Delta\tilde{E}_1'$. The inclusion of an arbitrary damping factor assuages the cuts in this figure that would otherwise reflect exact resonance conditions, where perturbation theory technically fails; thus, the axes show the real energy values (in multiples of $\hbar\omega$) and the imaginary part of each complex energy is assimilated into the graph, using a representative damping factor value $\gamma \sim 0.1\ \hbar\omega$. Regions in such a map that are devoid of detail essentially represent conditions under which use of the two-level approximation generates almost useless results, since even the introduction of a third level changes the results by more than 100% – and it could only be supposed that the inclusion of higher levels would add further corrections. However the islands of increasing color density represent conditions where the two-level approach is more defensible, producing results whose error falls into a more acceptable range approaching 20% or less. For systems that satisfy these conditions, the two-level results for hyperpolarizability would be little improved by the complication of introducing a third level into the calculations. The further analysis of such criteria is the subject of ongoing research.

To complete the picture, it is worth bearing in mind the transition dipole moments of each numerator which, although for simplicity previously assumed to be of similar magnitude, may in certain systems display a very different behavior. If the lowest excited state is accessible from the ground state by a weak or forbidden transition (as denoted by a small magnitude for $\boldsymbol{\mu}^{0u}$), a single higher energy level involving a strong transition may be substituted for the lowest state in the two-level model. If other states, of similar energy magnitude, also involve strong transitions then the two-level model will again fail – as, for example, where there is significant thermal excitation.

4. Optical harmonics in electronically excited media

On application of a strongly, resonantly pumped laser to the system, the parametric optical response due to elastic scattering is partly determined by the response mediated by the excited molecule, *i.e.* whose initial and final states are defined by $|u\rangle$ in the two-level model. Within this model, it is known that the excited state polarizability is the exact negative of the ground state polarizability, as is easily shown from Eqs (6) and (8):

$$\alpha_{ij}^{uu} = \mu_i^{0u}\mu_j^{0u}\left(\frac{1}{\tilde{E}_{0u}-\hbar\omega}+\frac{1}{\tilde{E}_{0u}+\hbar\omega}\right) = -\mu_i^{0u}\mu_j^{0u}\left(\frac{1}{\tilde{E}_{u0}+\hbar\omega}+\frac{1}{\tilde{E}_{u0}-\hbar\omega}\right) = -\alpha_{ij}^{00} \quad . \tag{11}$$

It is now shown that analogous identities are obtainable for systems where the two-level model is not applied. Upon a summation over all molecular states ζ, the following expressions may be determined for the polarization from Eq. (6);

$$\begin{aligned}\sum_{\zeta}\alpha_{ij}^{\zeta\zeta} &= \sum_{\zeta}\sum_{r}\left(\frac{\mu_i^{\zeta r}\mu_j^{r\zeta}}{\tilde{E}_{r\zeta}-\hbar\omega}+\frac{\mu_j^{\zeta r}\mu_i^{r\zeta}}{\tilde{E}_{r\zeta}+\hbar\omega}\right)\\ &= -\sum_{r}\sum_{\zeta}\left(\frac{\mu_i^{r\zeta}\mu_j^{\zeta r}}{\tilde{E}_{r\zeta}+\hbar\omega}+\frac{\mu_j^{r\zeta}\mu_i^{\zeta r}}{\tilde{E}_{r\zeta}-\hbar\omega}\right)\\ &= -\sum_{\zeta}\alpha_{ij}^{\zeta\zeta} \quad ,\end{aligned} \tag{12}$$

from which the identity $\sum_{\zeta}\alpha_{ij}^{\zeta\zeta} = 0$ is formed. In the two-level model, this outcome shows that α_{ij}^{00} equates to $-\alpha_{ij}^{uu}$ minus other background contributions and, thus, reinforces Eq. (11).

Moreover, in the two-level model, an analogous 'mirror' identity will arise between the ground and excited state hyperpolarizability. To prove this we determine β_{ijk}^{uu} from an algorithmic method modified from earlier, which is achieved by simply interchanging the labels 0 and *u*, resulting in the prescription:[54]

$$\boldsymbol{\mu}^{00} \to \boldsymbol{\mu}^{00} - \boldsymbol{\mu}^{uu} = -\mathbf{d} \; ; \; \boldsymbol{\mu}^{uu} \to 0 \quad . \tag{13}$$

Therefore, by again restricting both intermediate states of Eq. (6) to just $|0\rangle$ and $|u\rangle$, remembering that the initial and final states are now denoted by $|u\rangle$, only *u*00*u* occurs for the sequence $u \to r \to s \to u$, so that;

$$\beta_{ijk}^{uu} = -\left(\frac{\mu_i^{0u} d_j \mu_k^{0u}}{\left(\tilde{E}_{0u} - 2\hbar\omega\right)\left(\tilde{E}_{0u} - \hbar\omega\right)} + \frac{\mu_j^{0u} d_i \mu_k^{0u}}{\left(\tilde{E}_{0u} + \hbar\omega\right)\left(\tilde{E}_{0u} - \hbar\omega\right)} + \frac{\mu_j^{0u} d_k \mu_i^{0u}}{\left(\tilde{E}_{0u} + \hbar\omega\right)\left(\tilde{E}_{0u} + 2\hbar\omega\right)} \right) = -\beta_{ijk}^{00} \quad . \tag{14}$$

If the 'mirror' identities $\alpha_{ij}^{00} + \alpha_{ij}^{uu} = 0$ and $\beta_{ijk}^{00} + \beta_{ijk}^{uu} = 0$ do not exactly hold, the two-level approximation clearly fails; physically this will indeed be the case for most molecules. Similarly, the summation over all molecular states for the hyperpolarizability, *i.e.* following from Eq. (7), is shown to be zero:

$$\begin{aligned}
\sum_{\zeta} \beta_{ijk}^{\zeta\zeta} &= \sum_{r,s,\zeta} \left(\frac{\mu_i^{\zeta s} \mu_j^{sr} \mu_k^{r\zeta}}{\left(\tilde{E}_{s\zeta} - 2\hbar\omega\right)\left(\tilde{E}_{r\zeta} - \hbar\omega\right)} + \frac{\mu_j^{r\zeta} \mu_i^{\zeta s} \mu_k^{sr}}{\left(\tilde{E}_{\zeta r} + \hbar\omega\right)\left(\tilde{E}_{sr} - \hbar\omega\right)} + \frac{\mu_j^{sr} \mu_k^{r\zeta} \mu_i^{\zeta s}}{\left(\tilde{E}_{rs} + \hbar\omega\right)\left(\tilde{E}_{\zeta s} + 2\hbar\omega\right)} \right) \\
&= \sum_{r,s,\zeta} \left(\mu_i^{\zeta s} \mu_j^{sr} \mu_k^{r\zeta} \left[\frac{1}{\left(\tilde{E}_{\zeta r} + \hbar\omega\right)} \left(\frac{1}{\left(\tilde{E}_{\zeta s} + 2\hbar\omega\right)} + \frac{1}{\left(\tilde{E}_{sr} - \hbar\omega\right)} \right) + \frac{1}{\left(\tilde{E}_{rs} + \hbar\omega\right)\left(\tilde{E}_{\zeta s} + 2\hbar\omega\right)} \right] \right) \\
&= \sum_{r,s,\zeta} \left(\frac{\mu_i^{\zeta s} \mu_j^{sr} \mu_k^{r\zeta}}{\tilde{E}_{\zeta s} + 2\hbar\omega} \left[\frac{1}{\left(\tilde{E}_{sr} - \hbar\omega\right)} - \frac{1}{\left(\tilde{E}_{sr} - \hbar\omega\right)} \right] \right) \\
&= 0 \quad .
\end{aligned} \tag{15}$$

Here, the variables r, s and ζ are cyclically permuted within the second and third term (on the first line) to obtain the desired result. In fact it has been shown in previous work that *the sum over all matter states of any optical susceptibility is exactly zero*.[56] This was specifically verified for optical processes comprising two-, three- and four-photon interactions. The general result emerges in the form of a traceless operator in Hilbert space, which is symbolized by;

$$\sum_{\zeta} \langle \zeta | \hat{A} | \zeta \rangle = 0 \quad . \tag{16}$$

where the operator $\hat{A}$ is identified with the general form of the operator whose expectation value delivers the polarizability $\hat{\alpha}_{ij}$, hyperpolarizability $\hat{\beta}_{ijk}$ or higher-order hyperpolarizability.

5. Conclusion

This paper has brought a variety of new perspectives to bear on the applicability of the two-level approximation in nonlinear optics. In Section 2 we examined fundamental reasons why there should be doubt over the fidelity of using such an approach, despite its widespread application. On consideration of a recently derived theorem on the expectation values of quantum mechanical operators, illustrated by a very simple case, it was concluded that there are many systems in which erroneous results will ensue from the hidden assumption that two energy levels constitute a complete basis set.

In Section 3 the detailed calculations of parameters for elastic Rayleigh scattering and second harmonic generation (or second harmonic scattering which invokes the same material tensor) were used to exemplify the effect of curtailing the perturbative sum over states at either two, or three levels. The latter case can provide a basis for estimating the likely significance of all higher level corrections, since it will usually provide the largest contribution to such a correction. The contour map depiction, which we introduced to visualize these features, should itself prove directly amenable as a tool for those who design new molecular materials for nonlinear optics. Knowledge of the positioning of the first and second electronic excited states, and the chosen wavelength for the laser input, will readily enable the sufficiency of using a two-level approach to be decided. Lastly, in Section 4, we drew attention to the strikingly different nonlinear optical response that can be anticipated when any excited electronic states are significantly populated; again, the consequences of adopting a two-level model lead to results that are seldom likely to be a true representation. In each respect, it appears that the extent of widespread usage of two-level calculations is more a reflection of its simplicity than accuracy.

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