Failure of the two-level and sum over states methods in nonlinear optics, demonstrated by ab initio methods

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ABSTRACT

When calculating nonlinear susceptibilities, a widely used two-level approximation in a sum-over states formulation is the exclusion of all but the ground state and one single excited state. With the goal of efficient optical frequency conversion, the basis of the two-level model is an assumption that just one excited energy level dominates, when determining the response of a nonlinear optical material. Naturally, any system that can be justifiably modelled as comprising just two energy levels affords numerous advantages, most notably calculational simplicity. 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. In a series of recent works, analytical results regarding the unsuitability of the two-level approximation have been proven. *Ab initio* computations of the hyperpolarizability for a class of merocyanine dyes have further demonstrated a drastic inaccuracy from not including higher energy levels in the calculations. In this paper, we report the results of our recent work testing the general validity of two-level calculations in nonlinear optics, constructed with a precise quantum electrodynamical framework as a basis for the theory. These new results show that, for the first-order dynamic polarizability, successive terms contribute progressively less to the final value of the tensorial components, guaranteeing convergence. In contrast, the values of second harmonic optical susceptibility components, similarly calculated, reveal that contributions from successive energy levels, often assumed to be diminishing, in fact fail to deliver the assumed convergence.

Keywords: nonlinear optics; two-level systems; molecular optics; *ab initio* calculations; electronic excited states; resonance; calculational methods; quantum electrodynamics; polarizability; hyperpolarizability; nonlinear susceptibility

1. INTRODUCTION

The use of a two-level approximation (TLA) to simply characterize the nonlinear optical properties of organic materials is well known[1]. Usually only electronic ground states are significantly populated; higher levels are engaged only in the capacity of virtual states, and it is often assumed that just one electronic excited state dominates in determining the molecular response. Calculating nonlinear optical susceptibilities on this basis, excluding all but the ground and given excited state in a sum-over-states formulation, is a technique widely deployed in the calculation and analysis of nonlinear optical properties. The analytical tool of choice for the theory describing such molecular-scale systems and their interactions with the electromagnetic (EM) field is molecular quantum electrodynamics (QED)[2-4]. Both linear and nonlinear optical processes are readily described by QED (some of the most familiar examples of the former are elastic and inelastic scattering); however, the primary focus of photophysics research in recent years has been the comprehension of novel nonlinear processes, some of these yet to be explored by experimentation[5]. The application of QED to optically nonlinear organic materials has traditionally been inhibited by the difficulty in calculating the essential properties of higher-energy electronic states, and this is one justification for wide application of a two-level approximation[6-11]. Particularly within the last decade, the necessity for such an approach has been diminishing, as the accuracy of *ab initio* calculations has reached previously unattainable levels.

Previously, we have reported, in a series of works[12-14], the results of testing the general validity of two-level calculations in nonlinear optics. First, we presented an analytical theorem on quantum operators that suggested the inapplicability of the TLA even in simple systems, such as a simple harmonic oscillator. Secondly, through the extension of the TLA to a three-level model. we demonstrated that neglecting additional excited states can lead to substantially incorrect results for the hyperpolarizability elements. Thirdly, using high levels of theory and basis sets we reported the results of *ab initio* calculations for both ground and electronically excited states of the optimised structures, for selected merocyanine dyes. These results were used for the calculation of hyperpolarizabilities by a rigorous sum-over-states formulation, whereby systematic comparison with the two-level approach provided graphical means to identify the limitations of the model[12-14].

The theoretical basis for a two-level system has appeal in the context of quantum computing and information theory; the similarity between two-level atoms and qubit operation has been well addressed[15]. Any system that can be justifiably modelled as having just two energy levels affords the advantages of calculational simplicity, generating formulae with few enough parameters to realistically be experimentally tested. However, within the last decade the accuracy of *ab initio* calculations has reached unprecedented levels, presenting an opportunity to precisely appraise the validity of the two-level model using real molecular structures[16-19].

The implementation of any model where the available energy from the electromagnetic field spans the gap between realizable molecular states requires extreme caution as, with the typical intensities of pulsed laser light, there is a high probability of multiple photons, within the limits of quantum uncertainty, interacting simultaneously with each optically distinct center. Despite the fact that those nonlinear materials best suited for frequency conversion have complicated energy level structures, the two-level approximation has been widely applied[20-35] – largely due to the fact that the media involved are generally subjected to substantially off-resonant input radiation. As such, it is usually only the electronic ground state of the material that possesses a significant photon population; higher levels are engaged only in the capacity of virtual states.

The TLA offers simple representations of molecular response that relate well to established concepts of chemical structure, and it is the origin of the oft-proven connection between a 'push-pull' character to the electronic properties of juxtaposed chromophores[36-42] and an enhanced susceptibility to second harmonic generation. Thus, it is of utmost importance to determine when, and to what degree, a system can be approximated in this context as consisting of just two energy levels. In this paper, computational calculations are used to obtain *ab initio* numerical results for the polarizability tensor α and second harmonic generation (SHG) hyperpolarizability tensor β of two structurally similar molecules, representative of a well known class of laser dyes: these are **1)** 1-methyl-4-[(oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine (also known as Brooker's dye) and **2)** 1-methyl-4-[(dicyanomethylidene)hexadienylidene]-1,4-dihydropyridine. The two structures are depicted in Fig. 1.
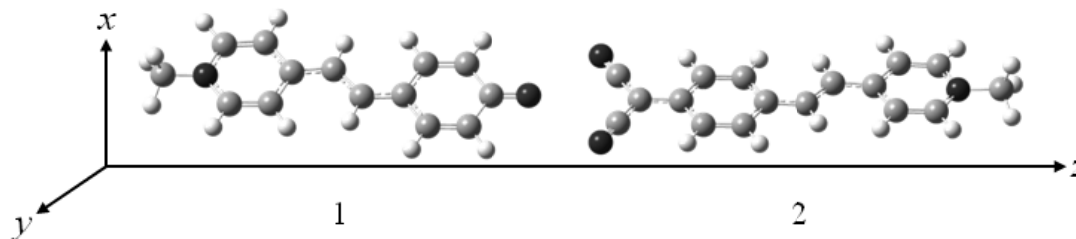

Fig. 1. Structure of the two merocyanine dyes analyzed in this paper.

The polarizability and hyperpolarizability tensor components are calculated under an N-level model, $N \in \{2, 3, .., 21\}$, and the ratios of tensor values for successive N-level approximations and the two-level approximation are displayed. It will be shown that the widely anticipated convergence of the numerical values of the tensor components – necessary to ensure meaningful TLA results – is exhibited only in the case of the α tensor.

2. BACKGROUND PRINCIPLES

The interaction between radiation and matter is most precisely explained by QED. For the systems described in this paper (Fig. 1), under the conditions of normally applied laser intensities, the strength of molecular coupling to the radiation field is much less than the intramolecular Coulomb binding energies (the latter equivalent to around 10^{17} W cm^{-2}); accordingly time-dependent perturbation theory can be deployed for the combined system comprising both the molecules and the radiation field. The quantum amplitude M_{FI} that couples the initial and final states of the system is thus generated from the following infinite series:

$$M_{FI} = \sum_{n=1}^{\infty} M_{FI}^{(n)} \equiv \langle F | \sum_{n=1}^{\infty} \left(H_{\text{int}} \frac{1}{\left(\tilde{E}_I - H_0 \right)} \right)^{n-1} H_{\text{int}} | I \rangle \tag{1}$$

where $|I\rangle$ and $|F\rangle$ represent the initial and final system states, and where the interaction Hamiltonian H_{int} acts upon both matter and radiation components. Moreover, $H_0 = H_{\text{rad}} + H_{\text{mol}}$ is the unperturbed system Hamiltonian and E_I is the energy of the initial state. Implementing the completeness relation $\sum_J |J\rangle\langle J| = 1$ gives:

$$M_{FI} = \langle F | H_{\text{int}} | I \rangle + \sum_R \frac{\langle F | H_{\text{int}} | R \rangle \langle R | H_{\text{int}} | I \rangle}{\left(E_I - \tilde{E}_R \right)} + \sum_{R,S} \frac{\langle F | H_{\text{int}} | S \rangle \langle S | H_{\text{int}} | R \rangle \langle R | H_{\text{int}} | I \rangle}{\left(E_I - \tilde{E}_R \right)\left(E_I - \tilde{E}_S \right)}$$
$$+ \sum_{R,S,T} \frac{\langle F | H_{\text{int}} | T \rangle \langle T | H_{\text{int}} | S \rangle \langle S | H_{\text{int}} | R \rangle \langle R | H_{\text{int}} | I \rangle}{\left(E_I - \tilde{E}_R \right)\left(E_I - \tilde{E}_S \right)\left(E_I - \tilde{E}_T \right)} + ... \quad, \tag{2}$$

where the intermediate virtual states are denoted by $|R\rangle$, $|S\rangle$, $|T\rangle$... upon which H_0 operates, E_n is the energy of a state indicated by its subscript, and the tilde denotes inclusion of a damping factor. The interaction Hamiltonian H_{int} is linear in the electromagnetic fields, which have corresponding mode expansions that are linear in the photon annihilation and creation operators. Therefore, the nth term in Eq. (2) delivers the leading contribution to the quantum amplitude for any process involving n photons.

It is instructive to proceed using the electric dipole approximation in the multipolar formalism, the transition/static dipole moments denoted by $\boldsymbol{\mu}^{sr}$. The transition dipole moments are assumed to be real – as is always possible with a suitable choice of basis set for the molecular wavefunctions, and hence $\boldsymbol{\mu}^{0u} \equiv \boldsymbol{\mu}^{u0}$, where $|u\rangle$ is an excited energy level. Obtained from the second and third terms of Eq. (2), the metrics calculated for the systems analyzed in this paper are the polarizability tensor, $\alpha(-\omega, \omega)$, and the hyperpolarizability tensor responsible for second harmonic generation, $\beta(-2\omega; \omega, \omega)$, respectively[2,4]. The components of the polarizability are given by:

$$\alpha_{ij}^{00} (-\omega, \omega) = \sum_r \left\{ \frac{\mu_i^{0r} \mu_j^{r0}}{\tilde{E}_{ro} + \hbar\omega} + \frac{\mu_j^{0r} \mu_i^{r0}}{\tilde{E}_{ro} - \hbar\omega} \right\}, \tag{3}$$

where $\hbar$ is Planck's constant and ω is the circular frequency of the emitted and absorbed photon. Furthermore, $\tilde{E}_{r0} \equiv \tilde{E}_r - \tilde{E}_0$, in which r represent virtual molecular states, in principle summed over every solution of the unperturbed molecular Schrödinger equation. A sum over bound electronic states is still infinite in number for all real systems; for pragmatic considerations, summation is therefore limited to include N states, with $N = 2$ representing the two-level approximation. Determining the hyperpolarizability components, β_{ijk}^{00}, from the third term of Eq. (2) delivers the following expression; the three terms relate to the time-order permutations of the three photon events (the annihilations of two input frequency photons, and the creation of one harmonic photon):

$$\beta_{ijk}^{00}(-2\omega;\omega,\omega) = \sum_{r,s} \left(\frac{\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}}{\left(\tilde{E}_{s0} - 2\hbar\omega\right)\left(\tilde{E}_{r0} - \hbar\omega\right)} + \frac{\mu_j^{0s}\mu_i^{sr}\mu_k^{r0}}{\left(\tilde{E}_{s0} + \hbar\omega\right)\left(\tilde{E}_{r0} - \hbar\omega\right)} + \frac{\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}}{\left(\tilde{E}_{s0} + \hbar\omega\right)\left(\tilde{E}_{r0} + 2\hbar\omega\right)} \right) \quad , \qquad (4)$$

where the index i is assigned to emission and j,k to absorption; r and s represent virtual molecular states, each one again limited to a set of N.

To illustrate the applicability of the two-level approximation in non-linear optics it is expedient to plot:

$$\breve{\alpha}_{ij}(N) = 100 \cdot \frac{\overline{\left|\alpha_{ij}(N)\right|}}{\left|\alpha_{ij}(2)\right|}, \qquad (5)$$

where an overbar represents averaging of $\alpha_{ij}(N)$ over the appropriate frequency interval, and the argument N, of the tensors indicates the number of excited states used in the calculations. Similarly, for the hyperpolarizability tensor, we have:

$$\breve{\beta}_{ijk}(N) = 100 \cdot \frac{\overline{\left|\beta_{ijk}(N)\right|}}{\beta_{ijk}(2)}. \qquad (6)$$

These measures are indicative of the percentage departure, in the values of the tensor components of the α and β tensors, from the two-level result; a value close to 100% in either case therefore indicates justification for use of the two-level approximation.

3. RESULTS OF N-LEVEL *AB INITIO* CALCULATIONS

To determine the values of the measures displayed in Eq. (5) and (6), two compounds from the merocyanine class of laser dyes have been used as a basis for *ab initio* calculations. These are the enol and dicyanide derivatives shown in Fig. 1. Calculating the values of polarizability and hyperpolarizability components as a function of input frequency, with the inclusion of resonance damping, provides data for the construction of the plots featured in Fig. 2. The additional terms computed for the plot take into account the first twenty excited states of the merocyanine dyes, allowing for a comparison of the TLA with a more thorough analysis.

All calculations were performed using the Gaussian 03[43] computational package. The ground state structures of the merocyanine compounds were geometry-optimised using the crystal structures as a starting point, deploying the three-parameter exchange functional of Becke[44] (B3) and the correlation functional of Lee, Yang, and Parr (LYP), B3LYP,[45]

with the triple-zeta split valence basis set, 6-311++G(d,p). The molecular structures were confirmed as conforming to potential energy minima through frequency calculations, and in each case these structures were used throughout the excited state calculations. The electronic excited states were investigated using configuration interaction singles (CIS)[46] method with the 6-311++g(d,p) basis set. For each merocyanine the first 20 excitations were calculated, these being used in the subsequent tensor element calculations and analysis.
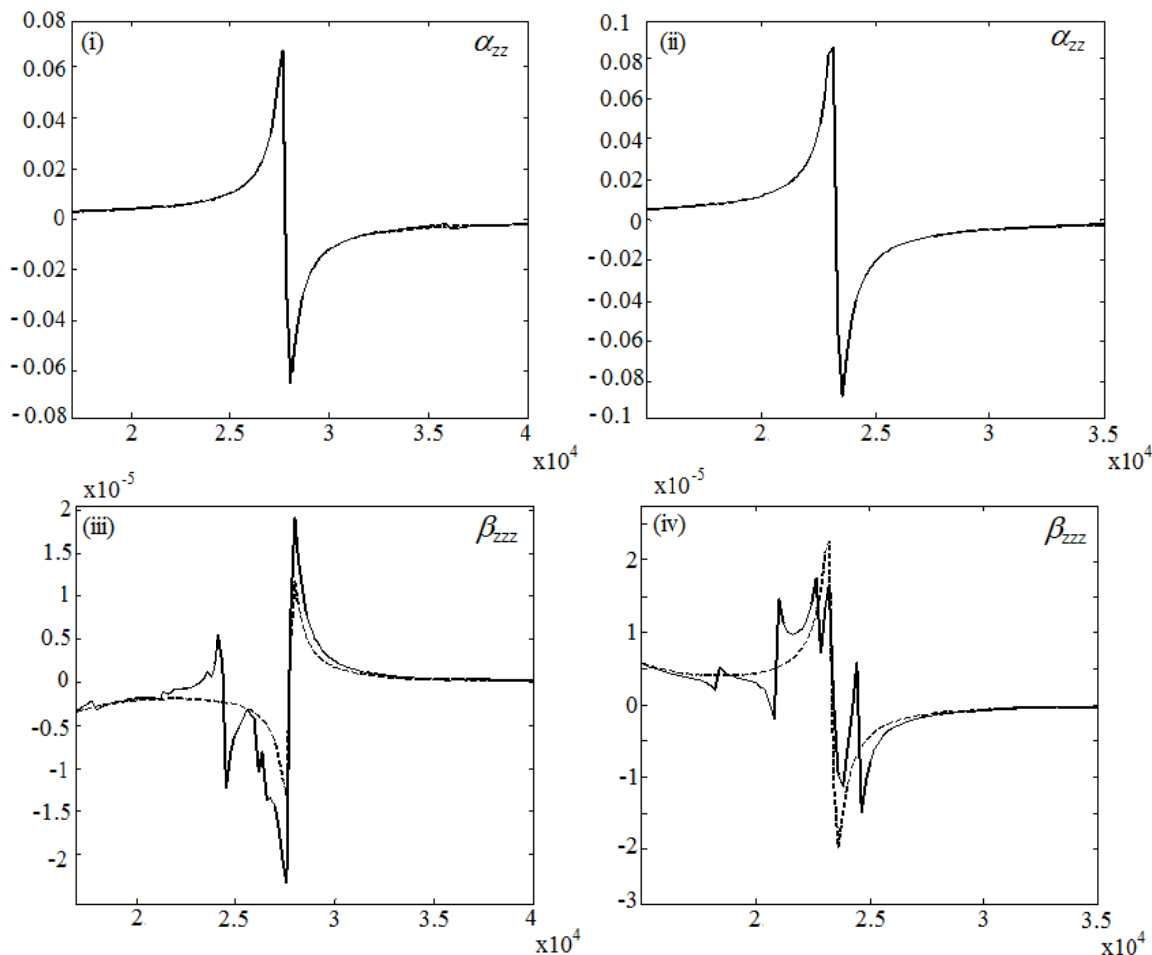

Fig 2. The most intense features in the spectra of compounds **1** – (i) and (iii), and **2** – (ii) and (iv) – arising from the *zz* and *zzz* components of the polarizability and hyperpolarizability, respectively. The horizontal scale is in wavenumbers (cm^{-1}).

A computer simulation program has been developed to enable calculation of the α and β tensor components from *ab initio* results for a range of frequency values in the visible and near-uv range. Results have been determined both using the complete sum-over-states formulation with 20 excited energy levels, and also with the two-level approximation. The corresponding ratios have also been determined and plotted. The *zz*- and *zzz*- components of the polarizability and hyperpolarizability tensors, respectively, have been chosen to exemplify the response of the two tensors, as the other components have significantly smaller values.

The dispersion curves of both compounds are exhibited in Fig. (2), where dotted lines indicate the value of the calculations under the assumption of the two-level approximation, and the solid lines indicate the value of the tensor components when 20 excited energy levels are taken into consideration. Significantly, the dispersion curves for the polarizability components, (i) and (ii), when using the TLA and when using 20 excited states, are almost indistinguishable at this scale; at around 3.5×10^4 cm^{-1} some small structural deviations from the TLA are apparent. However, except for values far from resonance, the observations of the hyperpolarizability components are greatly different, providing a preliminary indication that the two-level approximation might fail for optical processes of this order.
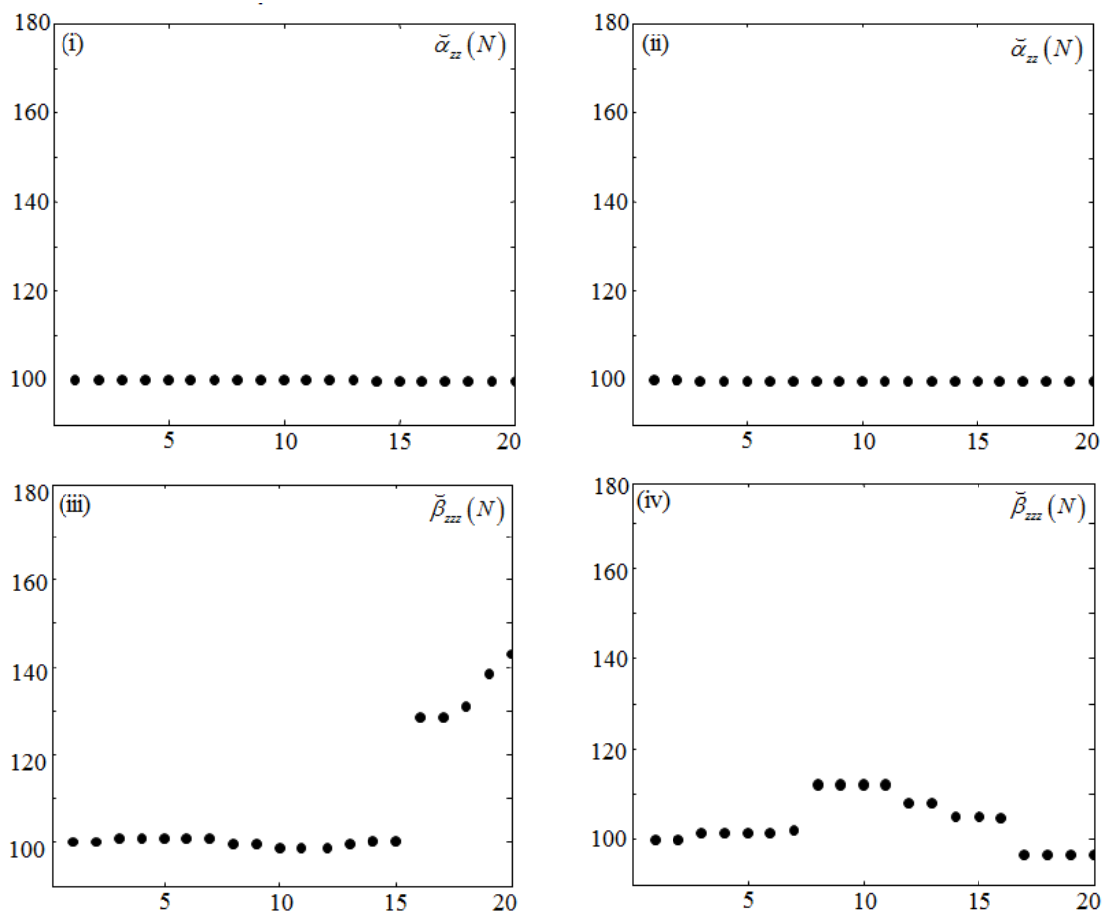

Fig 3. Quantifying the usability of the two-level approximation: compound **1** – (i) and (iii) , compound **2** – (ii) and (iv). The horizontal scale is the number of excited states engaged in the calculations and the vertical scale represents values of the polarizability and hyperpolarizability measures displayed in Eq. (5) and (6).

In Fig. (3) the quantities defined in Eq. (5) and (6) are displayed for both compounds. A data point that lies on the line $\breve{\alpha}_{zz}(N) = 100$ or $\breve{\beta}_{zzz}(N) = 100$ indicates an N-level approximation, which delivers values of the α and β tensor components showing no significant deviation from the TLA. Plots (i) and (ii) support the hypothesis that the TLA is a fully satisfactory description when considering optical processes that depend on the polarizability of the active molecules. Plots (iii) and (iv), however, do not indicate any justification of an equivalent hypothesis for the SHG

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hyperpolarizability. The plot for compound **1** (iii) reveals significant and increasing divergence from the two-level result as the value of *N* rises above 15. Plot (iv) for compound **2** displays an approximately 16% departure from the TLA when considering 8-11 excited energy levels, further contributions reducing the value of the β tensor component. Thus, it is not obvious whether the TLA gives a realistic description of compound **2** as $N \rightarrow \infty$; in fact neither of the hyperpolarizability plots offer any guarantee of convergence.

An inspection of the values of dipole moments for transitions between the ground and the first 20 excited states confirms that for both compounds studied in this work the most intense transition is to the first excited state (5.2 D and 6.1 D for the first and second compounds, respectively). This transition is predominantly polarised along the *z* axis. Other transitions are associated with dipole moments that are significantly lower in magnitude. Generally, the overlap between the multi-electron state function describing the ground state (consisting mainly of occupied one electron orbitals) and configuration state functions describing the excited states (with increasing contributions from vacant orbitals) is progressively reduced for higher lying excited states. As a result, the intensities of successive transitions and associated terms in (3) tend to decrease. The situation is substantially different in the case of the hyperpolarizability, where terms in the sum (4) additionally include μ^{rs}, transition dipole moments between the pairs of excited states. Such transition dipole moments can have significant values between excited states, even with high *N*. Indeed, in compound **2** for example, the *z* component of transition dipole moment between the first excited state and state 8 is -4.9 D, while its value between the states 15 and 20 is 6.2 D. Such relatively large values of μ^{rs} have a noticeable impact on the associated terms in (4), making the components of β strongly dependent on the number *N* of excited states involved in the model.

4. CONCLUSION

It is tempting to assume, when a sum-over-states formulation is deployed in the calculation of optical response tensors such as polarizabilities and hyperpolarizabilities, that the larger the number of excited states included in the calculation, the more accurate will be the result. Since precise analytical formulae are not available for the energy levels and transition moments for any but the simplest atoms, there is no simple test that can ensure convergence in any sum over states, when applied to real molecular systems. As a matter of pragmatism, if the results of such a calculation exhibit little change when an additional level is added in to the state summation, it might therefore be taken that convergence has been achieved, and that the inclusion of any further levels would be unnecessary. The attraction of such a view is compounded by the rapidly increasing degree of calculational complexity, and hence computational time, introduced by every additional level. Our results nonetheless show that such assumptions are generally unsupportable, and the reason is not hard to identify. The sum over states in the hyperpolarizability expression (4), for example, has summations over two virtual states, and so the number of contributions rises quadratically with the number of levels used in the calculation – whereas in the polarizability case, the number of contributions rises linearly with the number of states, as follows from the single state summation. This feature, whose impact is very clearly exhibited in our calculations on specific dyes, is likely to be of still greater import for the molecular tensors associated with higher orders of optical nonlinearity.

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