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Perturbative corrections to the rotating-wave approximation for two-level molecules and the effects of permanent dipoles on single-photon and multiphoton spectra

Mary Ann Kmetic*[†] and William J. Meath*
Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

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Perturbative corrections are derived for the rotating-wave approximation (RWA) for the single-photon and multiphoton resonance profiles due to the interaction between a two-level molecule, with nonzero permanent dipoles, and a sinusoidal time-dependent electric field. The derivation is carried out through the use of a Floquet secular equation that introduces the effects of the permanent dipole moments into the problem through the argument, $\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}/\omega$, of Bessel functions contained in molecule-laser coupling parameters; here $\mathbf{d}=\boldsymbol{\mu}_{22}-\boldsymbol{\mu}_{11}$, where $\boldsymbol{\mu}_{ii}$ is the permanent dipole of molecular state i, and $\mathcal{E}$, $\hat{\mathbf{e}}$, and ω are the field strength, direction of polarization unit vector, and the circular frequency of the electromagnetic field (EMF). Expansions for the N-photon resonance profiles and the associated resonance frequencies and full widths at half maximum, in powers of the couplings between the transition and permanent dipole moments and the applied EMF, are obtained by expanding the Bessel functions in the perturbative results and are compared with those in the literature (available mostly for $\mathbf{d}=0$ only). The perturbative results, and a series of exactly calculated two-level model absorption spectra, are used to discuss (1) the ability of the explicit perturbative corrections to the RWA to explain the differences between exact and RWA resonance profiles (for example, the positive or negative Block-Siegert shifts and dynamic backgrounds absent in the RWA), (2) the usefulness of the perturbative corrections in general, and (3) the effects of permanent dipoles on single-photon and multiphoton absorption spectra.

I. INTRODUCTION

Recently a rotating-wave approximation (RWA) has been derived[1-3] for the single-photon and multiphoton resonance profiles arising from the interaction between a two-level system ("molecule"), with nonzero diagonal dipole moment matrix elements ("permanent dipole moments"), and an applied continuous-wave laser (sinusoidal electric field). These simple analytical results have been used to help discuss, interpret, and predict some of the effects of permanent dipole moments on resonance profiles and molecule-laser interactions in general.[1-6] The limitations of the RWA results have been discussed with the aid of comparisons with exact calculations of the absorption spectra for model systems.[1-5,7] Part of the purpose of this paper is to augment these discussions with the derivation of the perturbative corrections to the RWA through the use of a Floquet secular equation which includes permanent dipole moment effects; see also Hattori and Kobayashi.[8] In addition to the perturbative results, the original RWA, and some model exact calculations for a series of "giant dipole" molecules, are used to augment other literature discussions[1-9] of the spectral effects related to large differences $\mathbf{d}$ between the permanent dipoles of the states involved in a transition. The usefulness and validity of the perturbative corrections to the RWA are also discussed.

Section II contains a derivation of the perturbative corrections to the RWA result for the N-photon resonance profile for a two-level molecule with permanent dipole moments; the RWA result itself is summarized briefly at the end of the Introduction. The derivation of the perturbative corrections involves the development, and use, of a Floquet secular equation that is analogous, in many ways, to the approach used by Shirley[10] for the atomic $\mathbf{d}=0$ case. However, the development in Sec. II involves a crucial transformation to an interaction representation[1] which introduces the effects of $\mathbf{d}$ into the problem through the arguments of Bessel functions contained in molecule-laser coupling parameters and yields results for arbitrary N directly. The perturbative corrections themselves are obtained from the secular equation by using near-degenerate perturbation theory as developed by Certain and Hirschfelder;[11,12] see also Aravind and Hirschfelder[13] for an application to the $\mathbf{d}=0$ two-level problem. Expansions for the N-photon resonance profiles, and the associated resonance frequencies (ω_{res}^{N}) and full widths at half maximum (W_{FWHM}^{N}), in powers of the couplings between the transition ($\boldsymbol{\mu}$) and permanent dipole moments and the applied electric field, are obtained by expanding the Bessel functions in the perturbative results and are compared with those in the literature.

The usefulness and range of validity of the perturbative corrections to the RWA, including their $(\boldsymbol{\mu},\mathbf{d})$ expansions, are discussed in Secs. II and III. Both analytic expressions and numerical comparison with exact model calculations are used for this purpose. Section IV contains the results for the single-photon and multiphoton absorption spectra for a series of giant dipole two-level model molecules and a discussion of some of the spectral effects related to $\mathbf{d}\neq 0$. Finally, Sec. V contains a brief summary and discussion of the more important results and conclusions of this paper.

The RWA expression for the N-photon resonance profile for a two-level molecule is given by[1-3]

$$\bar{P}_2^N=\frac{|C(N)|^2}{2[(\Delta E-N\omega)^2+|C(N)|^2]}\,, \tag{1.1}$$

where the coupling between the molecule and the applied (plane-polarized) sinusoidal electromagnetic field is

$$C(N)=\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}2N(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}/\omega)^{-1}J_N(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}/\omega)\,. \tag{1.2}$$

$\bar{P}_2^N$ is the steady-state transition probability for finding the molecule in an excited energy state 2, assuming it was in the ground state 1 at $t=0$; $\Delta E=E_2-E_1$, $\boldsymbol{\mu}=\boldsymbol{\mu}_{12}$ is the transition dipole matrix element connecting states 1 and 2; $\mathbf{d}=\boldsymbol{\mu}_{22}-\boldsymbol{\mu}_{11}$ is the difference between the permanent dipoles of states 1 and 2; J_N is a Bessel function of integer order N; and $\mathcal{E}$, $\hat{\mathbf{e}}$, and ω are the field strength, direction of polarization unit vector, and the circular frequency of the electromagnetic field [in the RWA, the resonance profile is independent of the phase δ of the electromagnetic field (EMF)]. The RWA predicts an N-photon resonance frequency of $\omega_{\text{res}}^N=\Delta E/N$ and a full width at half maximum (FWHM) for the N-photon resonance profile given by[1,3]

$$W_{\text{FWHM}}^N\approx\frac{2}{N}[|C(N)|]_{\omega=\omega_{\text{res}}^N}$$
$$=4\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}\left[\frac{\Delta E}{N\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}}\right]J_N(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}N/\Delta E)\,, \tag{1.3}$$

under the assumption that $C(N)$ does not vary appreciably with ω across the main N-photon resonance. As $\mathbf{d}\to 0$, $C(N)=\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}\delta_{N,1}$, and the coupling parameter, the molecular RWA result for $\bar{P}_2^N$, and the W_{FWHM}^N all yield the familiar "atomic" RWA or Rabi results;[10,14,15] in the $\mathbf{d}=0$ limit the RWA supports one-photon ($N=1$) transitions only.

Many of the effects of permanent dipole moments on single-photon and multiphoton resonances, relative to the atomic case, can be qualitatively deduced from Eq. (1.1). Some of these are related to the fact that the molecule-EMF coupling $C(N)$ is an oscillatory function of frequency ω. Thus the usual Rabi-Lorentzian resonance profiles can be modified, as a function of ω, by oscillatory fringes and asymmetries with zeros occurring at the zeros of the Bessel function present in Eq. (1.2). Another effect of $\mathbf{d}\neq 0$ is to reduce the width of the one-photon resonance relative to the atomic case especially for $(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}/\omega)$ sufficiently large and near a zero of the Bessel function J_1. Often the widths of the N-photon resonances decrease with increasing N because of the factor of N^{-1} occurring in Eq. (1.3) and because $J_N(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}N/\Delta E)$ often decreases as N increases. Examples of these effects and others have been discussed in previously cited references; see also Figs. 1–3 to be discussed later.

The RWA result of Eq. (1.1) indicates that two-level molecules with $\mathbf{d}\neq 0$ can support even as well as odd photon transitions; for example, in atoms, a third level is required for two-photon transitions and these transitions should therefore often be weaker for atoms than for heteronuclear diatomic molecules. In this context it is easy to see that the RWA for molecules, as in the case of the usual result for atoms, is not adequate[1,5] as $\mathbf{d}\to 0$ since, for example, a two-level atom will support a three-photon transition, whereas Eq. (1.1) will not (in this limit). Also, for example, the RWA is not capable of predicting the shifts in the resonance frequencies away from $\Delta E/N$ that occur as the strengths of the applied field are increased; this shift is to high frequency for atoms[10,13,16] but can be to either[1-5,7,8] high or low frequency for $\mathbf{d}\neq 0$ two-level molecules. More detailed discussions of the validity, deficiencies, and applications of the RWA for molecules (atoms) can be found elsewhere.[1-5,17-19] Like all RWA approximations, for two-level systems, Eq. (1.1) becomes more reliable as the coupling $[C(N)]$ between the transition dipole and the applied electromagnetic field (EMF) decreases, that is, as $\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}$ decreases and $\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}$ increases for fixed values of ΔE. The perturbative corrections to the RWA, derived and applied in what follows (see also Hattori and Kobayashi[8]) also aid in the understanding of the limitations of the RWA.

Atomic units are used in what follows. The atomic units of energy, circular frequency, length, dipole moment, and electric field strength are E_H, $E_H/\hbar$, a_0, ea_0, and $E_He^{-1}a_0^{-1}$, where E_H is the Hartree of energy, a_0 is the Bohr radius, e is the absolute value of the charge of an electron, and $\hbar$ is the reduced Planck's constant.

II. PERTURBATIVE CORRECTIONS TO THE TWO-LEVEL RWA FOR $\mathbf{d}\neq 0$

A. The Floquet secular equation and steady-state transition probabilities

In the interaction representation defined in our earlier work,[1,3] the time-dependent wave equation for the interaction of a two-level molecule, having permanent dipoles, with a continuous wave laser is given by

$$i\frac{d}{dt}\underline{b}=i\frac{d}{dt}\begin{bmatrix}b_1\\ b_2\end{bmatrix}=\underline{H}_{\text{I}}\underline{b}\,, \tag{2.1}$$

where $H_{\text{I},11}=H_{\text{I},22}=0$ and

$$H_{\text{I},12}=H_{\text{I},21}^{*}=-\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}\cos(\omega t+\delta)\exp\left[-i\left[\Delta E t-\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}\int_0^t\cos(\omega t'+\delta)dt'\right]\right]\,, \tag{2.2}$$

where the molecular and field parameters occurring in Eq. (2.2) have been defined in Sec. I. To derive the Floquet secular equation for the problem it is convenient to transform Eq. (2.1) into a phase factored form[10] by writing

$$b_{(1,2)}=K_{(1,2)}\exp[-i(\pm\tfrac{1}{2}\Delta E+\alpha_{(1,2)})t]\,. \tag{2.3}$$

Choosing $\alpha_1 = -\frac{1}{2}N\omega$ and $\alpha_2 = \frac{1}{2}N\omega$, in order to help identify the N-photon resonances in the Floquet matrix equations to follow, gives

$$i\frac{d}{dt}\underline{K} = i\frac{d}{dt}\begin{bmatrix} K_1 \\ K_2 \end{bmatrix} = \underline{H}\,\underline{K} \ , \tag{2.4}$$

where

$$H_{11} = -H_{22} = -\Delta = -\tfrac{1}{2}(\Delta E - N\omega) \tag{2.5}$$

and

$$H_{12} = H_{21}^{*} = -\tfrac{1}{2}\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}\exp(-iY\sin\delta)\sum_{k=-\infty}^{\infty} J_k(Y)(\exp[i(k+1)\delta]\exp\{-i[N-(k+1)]\omega t\} + \exp[i(k-1)\delta]\exp\{-i[N-(k-1)]\omega t\}) \tag{2.6}$$

with

$$Y = \mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}/\omega \ . \tag{2.7}$$

Since $\underline{H}$ is periodic in time, with period $2\pi/\omega$, the general solution of Eq. (2.4) can be written as[10,20]

$$\underline{G} = \underline{Z}\exp(-i\underline{Q}t) \ , \tag{2.8}$$

where $\underline{Q}$ is a diagonal constant matrix $Q_{ij} = q_i\delta_{ij}$ and $\underline{Z}$ is periodic in time with period $2\pi/\omega$. Then, substituting Eq. (2.8) into Eq. (2.4), and following Shirley's work[10] for the $\mathbf{d}=\mathbf{0}$ case, yields

$$Z_{\sigma\xi} = \sum_{k=-\infty}^{\infty} Z_{\sigma\xi}^{(k)}\exp(ik\omega t) \ , \tag{2.9}$$

$$H_{\sigma\xi} = \sum_{p=-\infty}^{\infty} H_{\sigma\xi}^{(p)}\exp(ip\omega t) \ , \tag{2.10}$$

where

$$q_\beta Z_{\alpha\beta}^{(n)} = \sum_{\gamma=1}^{2}\sum_{k=-\infty}^{\infty} \mathcal{H}_{\alpha\gamma}^{(n-k)} Z_{\gamma\beta}^{(k)} \tag{2.11}$$

and the matrix elements

$$\mathcal{H}_{\alpha\gamma}^{(n-k)} = H_{\alpha\gamma}^{(n-k)} + n\omega\delta_{\gamma\alpha}\delta_{kn} \tag{2.12}$$

define an effective time-independent Hamiltonian (Floquet) matrix for the problem. Equation (2.11) has nontrivial solutions for the eigenvectors $Z_{\gamma\beta}^{(k)}$ only if the determinantal equation

$$\det|H_{\alpha\gamma}^{(n-k)} + (n\omega - q_\beta)\delta_{\gamma\alpha}\delta_{kn}| = 0 \tag{2.13}$$

is satisfied. The rows and columns of the Floquet Hamiltonian matrix are denoted by the indices $n\alpha$ and $k\gamma$, respectively, where α and γ are the atomic indices 1 and 2 and n and k are Fourier indices ranging from $-\infty$ to $+\infty$. The matrix elements $H_{\alpha\gamma}^{(n-k)}$, completing the definition of the Floquet Hamiltonian matrix elements defined by Eq. (2.12), can be identified by comparing Eqs. (2.5) and (2.6) with Eq. (2.10) and are given by

$$H_{11}^{(0)} = -H_{22}^{(0)} = -\Delta \ , \tag{2.14}$$

$$H_{11}^{(m)} = -H_{22}^{(m)} = 0, \quad m = n - k \neq 0 \tag{2.15}$$

$$H_{12}^{(m)} = [H_{21}^{(-m)}]^{*} = -\tfrac{1}{2}C(N+m)\xi(N+m) \ , \tag{2.16}$$

where

$$C(N+m) = 2\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}Y^{-1}(N+m)J_{N+m}(Y) \tag{2.17}$$

and

$$\xi(N+m) = \exp\{-i[Y\sin\delta - (N+m)\delta]\} \ . \tag{2.18}$$

The secular equation corresponding to Eq. (2.13) is easily constructed and is much more dense than that[10,13] corresponding to $\mathbf{d}=\mathbf{0}$.

Following Shirley,[10] whose analysis corresponds to $\mathbf{d}=\mathbf{0}$, the solution of the time-dependent Schrödinger equation Eq. (2.1) can be obtained, subject to the initial conditions that only state 1 is populated at $t=t_0$, in terms of the eigenvalues q_β and the eigenvectors $Z_{\gamma\beta}^{(k)}$ of the Floquet secular equation problem. After considerable manipulation, analogous to that for the $\mathbf{d}=\mathbf{0}$ problem, one can show that the time-dependent population of state 2, $P_2(t) = |K_2(t)|^2$, is given by

$$P_2(t) = \sum_{\gamma,\gamma'=1}^{2}\sum_{n,n'=-\infty}^{\infty}\sum_{s,s'=-\infty}^{\infty}[Z_{2\gamma'}^{(s')}]^{*}Z_{2\gamma}^{(s)}Z_{1\gamma'}^{(n'+s')}[Z_{1\gamma}^{(n+s)}]^{*}\exp[i(n'-n)\omega t_0]\exp\{-i[q_\gamma - q_{\gamma'} - (s-s')\omega](t-t_0)\} \tag{2.19}$$

For the interaction of a continuous-wave laser with a molecule, the initial time t_0, or equivalently the initial phase of the field "seen" by the molecule, is not well defined. Thus the time-dependent transition probability of interest corresponds to Eq. (2.19) averaged over t_0, with the elapsed time $(t-t_0)$ kept constant.[10] The absorption spectrum of the molecule, which corresponds to the initial time and long-time average of Eq. (2.19), is obtained[10] from this result by averaging over the elapsed time $(t-t_0)$. The steady-state population of state 2, for a given frequency ω, is then given by

$$\bar{P}_2^N = \sum_{\gamma=1}^{2} \sum_{s=-\infty}^{\infty} \sum_{p=-\infty}^{\infty} |Z_{2\gamma}^{(s)}|^2 |Z_{1\gamma}^{(p)}|^2 , \tag{2.20}$$

where the absorption spectrum is $\bar{P}_2^N$ as a function of frequency ω. Equation (2.20) is completely analogous to Shirley's result[10] for $\mathbf{d}=0$.

The absorption spectrum can then be obtained by solving the Floquet secular equation problem for the eigenvectors $Z_{\gamma\beta}^{(k)}$ corresponding to the eigenvalues q_β, $\beta=1,2$. This can be done for each N, as a function of ω, for progressively larger Floquet secular equations until convergence, as a function of s and p, is obtained. There are, of course, far more efficient methods for carrying out calculations of this type numerically.[5,21–23] However, the Floquet secular equation results, summarized here for $\mathbf{d}\neq 0$, are very convenient for a perturbation analysis of the N-photon absorption spectrum as illustrated, for example, by Shirley[10] for $\mathbf{d}=0$. They are so used in what follows in order to discuss the correction terms to the RWA result of Eq. (1.1).

B. Perturbation theory expansions of the Floquet results

To apply perturbation theory, the set of linear equations given by Eq. (2.11) is rewritten as

$$\sum_{\gamma=1}^{2} \sum_{k=-\infty}^{\infty} (H_{\alpha\gamma}^{(n-k)} - q_\beta \delta_{\gamma\alpha} \delta_{kn}) Z_{\gamma\beta}^{(k)} = 0 , \tag{2.21}$$

with the matrix element $H_{\alpha\gamma}^{(n-k)}$ expressed as

$$H_{\alpha\gamma}^{(n-k)} = E_{n\alpha,k\gamma}^{(0)} + V_{\alpha\gamma}^{(n-k)} , \tag{2.22}$$

where

$$E_{n\alpha,k\gamma}^{(0)} = [(-1)^\alpha \Delta + n\omega]\delta_{\gamma\alpha}\delta_{kn} = E_{n\alpha}^{(0)} \tag{2.23}$$

and

$$V_{\alpha\gamma}^{(n-k)} = \begin{cases} -\frac{1}{2}C(N+n-k)\xi(N+n-k), & \alpha<\gamma \\ -\frac{1}{2}C(N-n+k)\xi^*(N-n+k), & \alpha>\gamma \\ 0, & \alpha=\gamma . \end{cases} \tag{2.24}$$

The desired N-photon resonances can be identified in the Floquet secular equation, Eq. (2.13), by setting $\Delta E \approx N\omega$, $N=1,2,3,\ldots$, and hence $\Delta = \frac{1}{2}(\Delta E - N\omega) \approx 0$. Two of the diagonal Floquet Hamiltonian matrix elements $H_{11}^{(0-0)} = H_{11}^{(0)} = -\Delta$ and $H_{22}^{(0-0)} = H_{22}^{(0)} = \Delta$ will be almost equal. These two elements, together with their associated off-diagonal matrix elements, define a 2×2 secular equation having nearly degenerate roots q_β and therefore on N-photon resonance the zeroth-order states $|0,1\rangle$ and $|0,2\rangle$ are nearly degenerate.

The perturbation theory derived by Certain and Hirschfelder,[11] see also Hirschfelder,[12] can be applied to these nearly degenerate states. In Shirley's original treatment[10] of the $\mathbf{d}=0$ case, the problem was analyzed by using what amounts to Brillouin-Wigner perturbation theory[24]—this yields results that are implicit functions of the energy and requires iterative steps to obtain the transition probabilities in terms of the zeroth-order energies and the perturbation matrix elements given by Eqs. (2.23) and (2.24), respectively. The perturbation theory used here is of the Rayleigh-Schrödinger type and is designed for treating near-degenerate problems of the kind considered in this work—the results are given directly and explicitly in terms of the zeroth-order energies and perturbation matrix elements. The $\mathbf{d}=0$ problem has been discussed using this perturbation theory by Aravind and Hirschfelder.[13] The treatment of the problem including permanent dipoles ($\mathbf{d}\neq 0$) is analogous but considerably more complicated since the Floquet matrix is much more dense for $\mathbf{d}\neq 0$ than for $\mathbf{d}=0$. Details of the calculation will not be given because of the complexity of the equations and because the methodology is, in principle, the same as that discussed previously for the $\mathbf{d}=0$ calculations; interested readers can find details of the $\mathbf{d}\neq 0$ calculations elsewhere (Kmetic[25]).

After considerable algebraic manipulation, the perturbation expansion of the steady-state population of excited state 2 for the N-photon resonance is given by

$$\bar{P}_2^N = (2\rho^2)^{-1}\{|E_{01,02}^{(1)}|^2(1+8F_{01,1}^{(2)}) + 2E_{01,02}^{(1)}[E_{01,02}^{(3)}]^* + \delta^{(6)} + O(5)\} - 4F_{01,1}^{(2)} + O(3) , \tag{2.25}$$

where

$$\rho^2 = |E_{01}^{(0)}|^2 + 2E_{01}^{(0)}E_{01,01}^{(2)} + |E_{01,01}^{(2)}|^2 + \delta^{(4)} + |E_{01,02}^{(1)}|^2 + 2E_{01,02}^{(1)}[E_{01,02}^{(3)}]^* + \delta^{(6)} + O(5) \tag{2.26}$$

and

$$\delta^{(4)} = 2E_{01}^{(0)}E_{01,01}^{(4)}, \quad \delta^{(6)} = |E_{01,02}^{(3)}|^2 , \tag{2.27}$$

$$E_{01}^{(0)} = -E_{02}^{(0)} = -\Delta = -\tfrac{1}{2}(\Delta E - N\omega) , \tag{2.28}$$

$$E_{01,02}^{(1)} = [E_{02,01}^{(1)}]^* = -\tfrac{1}{2}C(N)\xi(N) , \tag{2.29}$$

$$E_{01,01}^{(2)} = -E_{02,02}^{(2)} = -\tfrac{1}{4}\sum_{s(\neq 0)} \frac{[C(N+s)]^2}{(2\Delta - s\omega)} , \tag{2.30}$$

$$F^{(2)}_{01,1}=F^{(2)}_{02,2}=-\tfrac{1}{8}\sum_{s(\neq 0)}\left[\frac{C(N+s)}{(2\Delta-s\omega)}\right]^2 , \tag{2.31}$$

$$\begin{aligned}E^{(3)}_{01,02}=[E^{(3)}_{02,01}]^*=&\tfrac{1}{8}\sum_{s(\neq 0)}\frac{[C(N+s)]^2C(N)\xi(N)}{(2\Delta-s\omega)^2}\\&+\tfrac{1}{8}\sum_{s(\neq 0)}\sum_{l(\neq 0)}\frac{C(N-s)C(N-s+l)C(N+l)}{(2\Delta-l\omega)(2\Delta+s\omega)}\xi(N-s)\xi^*(N-s+l)\xi(N+l) ,\end{aligned} \tag{2.32}$$

$$\begin{aligned}E^{(4)}_{01,01}=&-\tfrac{1}{16}\sum_{p(\neq 0)}\sum_{r(\neq 0)}\sum_{s(\neq 0)}\frac{C(N-p+r)C(N+r-s)C(N-s)C(N-p)}{(2\Delta+p\omega)(r\omega)(2\Delta+s\omega)}\\&-\tfrac{1}{16}\sum_{p(\neq 0)}\sum_{r(\neq 0)}\left[\frac{2C(N-p+r)C(N+r)C(N-p)C(N)}{(2\Delta+p\omega)(2\Delta-r\omega)(r\omega)}-\frac{[C(N-p)]^2[C(N+r)]^2}{(2\Delta+p\omega)^2(2\Delta-r\omega)}\right]\\&+\tfrac{1}{16}\sum_{r(\neq 0)}\frac{[C(N-r)]^2[C(N)]^2}{(r\omega)(2\Delta+r\omega)^2} .\end{aligned} \tag{2.33}$$

In these results $\sum_{s(\neq 0)}$ implies a sum over s ranging from $-\infty$ to $+\infty$ excluding the $s=0$ term and the superscript (n) on the various quantities, as in $E^{(n)}$, implies terms of (explicit) order n in the perturbation matrix elements of Eq. (2.24), or equivalently the couplings $C(N+m)$ between the molecule and the EMF defined by Eq. (2.17). $O(n)$ indicates terms of order n or higher that are not given explicitly.

In the above, and in what follows, use is made of the fact that $E^{(0)}_{01}=-\frac{1}{2}(\Delta E-N\omega)$ is of second order in the coupling $(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})$ for frequencies around ω^N_{res}, which are of the most significance in the analysis of this section [see, for example, Eqs. (2.40)–(2.42)]. Thus $E^{(0)}_{01}$ is actually of the same order as $|E^{(1)}_{01,02}|^2$, and $\delta^{(4)}$, as well as $\delta^{(6)}$, is of sixth order. The term $\delta^{(4)}$ is required for the derivation of the Bloch-Siegert shifts associated with the N-photon resonance profiles and both $\delta^{(4)}$ and $\delta^{(6)}$ are required for purposes of comparison with the literature. In general, our result for the N-photon resonance profile, Eq. (2.25), is explicitly accurate through only fourth order in the perturbative expansion of the numerator and denominator of the main resonance term, the first term in Eq. (2.25), and only through second order in the (small) background term.

The application of near-degenerate perturbation theory also yields perturbation expressions for the eigenvalues of the Floquet secular equation, $q_{\pm}=\pm p$, where p is given by Eq. (2.26). Using this result it can be shown that the N-photon steady-state transition probability given by Eq. (2.25) can be written as

$$\bar{P}^N_2=\tfrac{1}{2}\{1-4[\partial p/\partial(\Delta E)]^2\} \tag{2.34}$$

in agreement with Shirley's result[10] for $\mathbf{d}=0$.

Perturbation expressions for the full width at half maximum, W^N_{FWHM}, for the N-photon resonance profiles, $\bar{P}^N_2$ versus ω, can be obtained from Eq. (2.25). The derivation is analogous to that given previously[1,3,5] for the RWA and involves the assumption that the perturbation energies of order greater than zero, and $F^{(2)}_{01,1}$ occurring in Eq. (2.25) do not vary appreciably over the width of the main N-photon resonance. One obtains, after some manipulation,[25]

$$W^N_{\text{FWHM}}=\frac{2}{N}|C(N)-8C(N)F^{(2)}_{01,1}-2\xi(N)[E^{(3)}_{01,02}]^*|_{\omega=\omega^N_{\text{res}}}+O(4) . \tag{2.35}$$

C. Discussion of perturbation results and limiting cases

The RWA expression for the steady-state N-photon transition probability, discussed in the Introduction [Eq. (1.1)], is obtained from our perturbation expression for $\bar{P}^N_2$ by neglecting the background term $[-4F^{(2)}_{01,1}+O(3)]$ and by retaining terms through $O(2)$ only in the numerator and denominator of the remaining part of Eq. (2.25). Substituting Eqs. (2.28), (2.29), and (2.18) into the resulting expression,

$$\bar{P}^N_2=\frac{|E^{(1)}_{01,02}|^2}{2[(E^{(0)}_{01})^2+|E^{(1)}_{01,02}|^2]} , \tag{2.36}$$

yields the RWA result of Eq. (1.1) which supports an N-photon resonance profile or absorption spectrum with a maximum of 0.5, occurring at $\omega^N_{\text{res}}=\Delta E/N$, and having a W^N_{FWHM} given by the first term in the perturbation expansion of Eq. (2.35) (under assumptions already discussed). These RWA results predict the overall qualitative features of the absorption spectrum for two-level systems even for relatively high molecule-EMF coupling strengths, see Sec. I for a brief discussion and for references to previous papers with detailed examples and discussions.

Perturbative corrections to the RWA

The RWA fails to predict important features of the absorption spectra as the molecule-EMF coupling increases; for example, the shifts of the main resonances to the high or low frequency side of $\omega=\Delta E/N$ or the background observed in spectra obtained from exact solutions for the two-level problem. The perturbative corrections to the RWA expression for the absorption spectrum, the lead terms of which are contained in the perturbation expression for $\bar{P}^N_2$ given by Eq. (2.25), contain contributions to both of these effects seen in the exact spectra.

Setting Eq. (2.34) equal to 0.5 indicates that the resonance maxima occur when

$$\frac{\partial\rho}{\partial(\Delta E)}=\frac{1}{2\rho}\frac{\partial\rho^2}{\partial(\Delta E)}=0\ . \tag{2.37}$$

An expression for the N-photon resonance frequency can be obtained by substituting ρ^2 given by Eq. (2.26) into this result:

$$\omega=\frac{\Delta E}{N}-\frac{2}{N}E^{(2)}_{01,01}-\frac{2}{N}E^{(4)}_{01,01}+\frac{4}{N}(\Delta E-N\omega)F^{(2)}_{01,1}-\frac{8}{N}E^{(2)}_{01,01}F^{(2)}_{01,1}+\frac{4}{N}E^{(1)}_{01,02}\frac{\partial[E^{(3)}_{01,02}]^*}{\partial(\Delta E)}+O(5)\ , \tag{2.38}$$

where use has been made of $[\partial E^{(2)}_{01,01}/\partial(\Delta E)]=-2F^{(2)}_{01,1}$ and

$$\begin{aligned}\frac{\partial[E^{(3)}_{01,02}]^*}{\partial(\Delta E)}=&-\tfrac{1}{4}\sum_{s(\neq 0)}\frac{[C(N+s)]^2C(N)\xi^*(N)}{[\Delta E-(N+s)\omega]^3}\\&-\tfrac{1}{8}\sum_{s(\neq 0)}\sum_{l(\neq 0)}\frac{C(N-s)C(N-s+l)C(N+l)\xi^*(N-s)}{[\Delta E-(N+l)\omega][\Delta E-(N-s)\omega]}\xi(N-s+l)\xi^*(N+l)\\&\times\{[\Delta E-(N+l)\omega]^{-1}+[\Delta E-(N-s)\omega]^{-1}\}\ .\end{aligned} \tag{2.39}$$

Since most of the terms on the right-hand side of Eq. (2.38) are functions of ω, an iterative technique must be used to obtain an explicit expression for the resonance frequency through a given order in perturbation theory; the lead term will be the RWA result $\Delta E/N$.

While Eq. (2.38) can be solved iteratively in a numerical manner for ω^N_{res}, for each N, it is more instructive qualitatively to carry out the iteration analytically and to obtain an expression for ω^N_{res}, and hence for the shift of the resonance frequency from the RWA limit, in powers of the couplings $\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}$ and $\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}$. The results will be obtained through fourth order in the product of the two couplings, that is, through order $(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^n(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E})^m$ for $n+m\leq 4$.

To begin, the right-hand side of Eq. (2.38) is expanded in powers of the couplings, assuming, initially, that $\Delta E-N\omega$ is of unknown order and that ω is fixed. This step is accomplished by making use of the expansion,[26] in powers of Y, for the Bessel function in the molecule-EMF coupling parameter $C(N+m)$, see Eq. (2.17), which occurs in the spectral results for the various quantities in Eq. (2.38). Then the procedure followed is similar to that employed for the $\mathbf{d}=\mathbf{0}$ case previously[10] where $\omega=\Delta E/N$ is used as a first approximation in the iteration to obtain ω^N_{res}. The result of the first iteration is then used to obtain a second result for ω^N_{res}, and so on. The resulting expressions for the resonance frequencies are

$$\omega^1_{\text{res}}=\Delta E+\frac{(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^2}{4(\Delta E)}-\frac{7(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^2(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E})^2}{48(\Delta E)^3}+\frac{(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^4}{64(\Delta E)^3}+O((\mu d)^5)\ , \tag{2.40}$$

$$\omega^2_{\text{res}}=\frac{\Delta E}{2}+\frac{2(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^2}{3(\Delta E)}-\frac{13(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^2(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E})^2}{24(\Delta E)^3}-\frac{10(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^4}{27(\Delta E)^3}+O((\mu d)^5)\ , \tag{2.41}$$

and for $N\geq 3$

$$\omega^N_{\text{res}}=\frac{\Delta E}{N}+\frac{(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^2}{(\Delta E)}T_1+\frac{(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^2(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E})^2}{(\Delta E)^3}T_2+\frac{(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^4}{(\Delta E)^3}T_3+O((\mu d)^5)\ , \tag{2.42}$$

where

$$T_1=\frac{N}{N^2-1}\ ,\qquad T_2=\frac{3N^3}{4(N^2-1)(N^2-4)}\ ,\qquad T_3=\frac{N^3(7-3N^2)}{4(N^2-1)^3} \tag{2.43}$$

and $O((\mu d)^5)$ indicates terms of fifth or higher order, overall, in the two coupling parameters. These results agree with those in the literature for certain special cases, mostly involving $\mathbf{d}=\mathbf{0}$. For $N=1$, $\mathbf{d}=\mathbf{0}$, Eq. (2.40) agrees with the original work of Bloch and Siegert,[16] Shirley,[10] and others.[27] For $N\geq 3$ and odd, $\mathbf{d}=\mathbf{0}$, Eq. (2.42) yields our inversion of the expressions of Hioe,[28] who presents results for ΔE as a function of ω through $O(\mu^8)$, and with other literature expansions[10,29] to lower order in the coupling $\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}$. When $\mathbf{d}=\mathbf{0}$ there are no even photon transitions for the two-level system. Finally, for $\mathbf{d}\neq\mathbf{0}$, our expressions agree with the only analogous literature results[8] which are available for $N=1$ through $O((\mu d)^4)$ and for $N\geq 2$ through $O(\mu^2)$ only.

For all N, when $\mathbf{d}\neq\mathbf{0}$, it is clear from Eqs. (2.40)–(2.42) that the shift from the weak field or RWA resonance frequency of $\Delta E/N$ can be either to high or low frequency depending on the magnitude of the couplings $\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}$ and $\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}$ relative to each other; for $\mathbf{d}=\mathbf{0}$ the shift is always to high frequency. These results then give analytical and qualitative backup, see also Hattori and Kobayashi,[8] for the effects of permanent dipoles on resonance frequencies that were discussed and observed some time ago[1–5,7] in exact calculations of two-level multiphoton molecular absorption spectra. It is relevant to note that the results of Eqs. (2.40)–(2.42) are valid only for small couplings $\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}$ and $\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}$. For large couplings the higher-order terms (in $\mu^n d^m$) can become larger than the lower-order terms and the power-series expressions for ω_{res}^N diverge (see also Ref. 8 and Sec. III).

Expansions in powers of the two couplings can also be obtained for the W_{FWHM}^N. Since[1,3,5] the major effects of $\mathbf{d}\neq 0$ on the FWHM are contained within the RWA, see also Sec. I, and expansions of this type are not of great usefulness, only a limited set of results is given here explicitly. Using Eq. (2.35), the above results for ω_{res}^N, and techniques similar to those used to obtain Eqs. (2.40)–(2.42), it can be shown that

$$W_{\text{FWHM}}^N=\begin{cases}\left|2\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}-\dfrac{1}{4(\Delta E)^2}(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E})^2+O(\mu^3)\right|, & N=1\\[2ex] \left|\dfrac{1}{\Delta E}(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E})+O((\mu d)^4)\right|, & N=2\\[2ex] \left|\dfrac{3}{8(\Delta E)^2}(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^3-\dfrac{3}{4(\Delta E)^2}(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E})^2+O((\mu d)^5)\right|, & N=3\\[2ex] \left|\dfrac{2}{3(\Delta E)^3}(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E})^3-\dfrac{8}{9(\Delta E)^3}(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^3(\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E})+O((\mu d)^5)\right|, & N=4\,.\end{cases}\tag{2.44}$$

Equations (2.44) are sufficient to demonstrate, analytically, that two of the effects of $\mathbf{d}\neq 0$ are to reduce the widths of the resonances and to induce even, as well as odd, photon transitions relative to atoms ($\mathbf{d}=0$). Both these effects have been discussed previously[1–5,7] through the use of the RWA and exact multiphoton calculations. The expressions for the W_{FWHM}^N given in Eq. (2.44) are in essential agreement with those in the literature[8] for $\mathbf{d}\neq 0$ and for $N=2,3,4$; for $N=3$ and 4 the disagreement involves overall multiplicative factors involving N only. For $N=1$ and 3 our results agree precisely with well-known literature results[10] in the limit $\mathbf{d}=0$.

It is also of interest to compare the perturbative results for the resonance profile given by Eq. (2.25) with analogous results obtained by Shirley[10] which are available only for $\mathbf{d}=0$. Using $px^{-1}J_p(x)\rightarrow\frac{1}{2}\delta_{p,1}(\delta_{p,-1})$ for $p>0$ ($p<0$) as $x\rightarrow 0$, the $\mathbf{d}=0$ limit of the quantities occurring in Eq. (2.25) that are needed for the comparison are given (for all N) by

$$E_{01,02}^{(1)}\rightarrow-\tfrac{1}{2}\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}\delta_{N,1}\exp(iN\delta)\ ,\tag{2.45}$$

$$F_{01,1}^{(2)}\rightarrow-\frac{(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^2}{8}[(\Delta E+\omega)^{-2}+(\Delta E-\omega)^{-2}(1-\delta_{N,1})]\ ,\tag{2.46}$$

$$E_{01,01}^{(2)}\rightarrow-\frac{(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^2}{4}[(\Delta E+\omega)^{-1}+(\Delta E-\omega)^{-1}(1-\delta_{N,1})]\ ,\tag{2.47}$$

and

$$E_{01,02}^{(3)}\rightarrow\tfrac{1}{8}(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^3\left[\frac{\exp(i\delta)}{(\Delta E+\omega)^2}\delta_{N,1}+\frac{\exp(3i\delta)}{(\Delta E-\omega)^2}\delta_{N,3}\right]\ .\tag{2.48}$$

An expression for $\bar{P}_2^1$, $\mathbf{d}=0$, can be obtained by using these results with $N=1$ in Eqs. (2.25) and (2.26). Upon setting $\Delta E+\omega\sim 2\omega$ in the energy denominators arising from Eqs. (2.46)–(2.48), and neglecting $\delta^{(4)}$ and $\delta^{(6)}$ which are of sixth order, the resulting expression agrees with the analogous result due to Shirley[10] through $O(\mu^4)$ in the main resonance term [aside from the presence of $(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^4/(\Delta E+\omega)^2$, which occurs in both the numerator and the denominator of our result]; the background term is identical to that of Shirley.

When $N>3$ is odd, and for $\mathbf{d}=0$, all contributions of $O(5)$ and $O(6)$, except $\delta^{(6)}$ and $\delta^{(4)}$, vanish in both the numerator and the denominator of the resonance part of Eq. (2.25) and to this order of approximation the transition probability for $N>3$, N odd, will consist only of a background term. Higher-order perturbative corrections are necessary to obtain the steady-state transition probability for odd photon transitions when $\mathbf{d}=0$ and $N>3$. Setting $\Delta E\sim 3\omega$ in all energy denominators, and neglecting $\delta^{(4)}$ and the background term, our result for $\bar{P}_2^3$ agrees with that of Shirley;[10] $\delta^{(4)}$, which occurs in the denominator of the resonance term, is not very significant relative to

$$\delta^{(6)}=(\tfrac{1}{64})(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E})^6\delta_{N,3}/(\Delta E-\omega)^4\ ,$$

which is the only contributor to the resonance numerator through $O(\mu^6)$. A similar analysis for $N>1$, even, gives a result for the steady-state transition probability, to the order of the coupling parameter indicated explicitly in Eq. (2.25), that consists only of a dynamic background term. This of course is correct to all orders for a two-level system with $\mathbf{d}=0$ and in the absence of static electric fields.

III. USEFULNESS OF THE EXPRESSIONS FOR THE PERTURBATIVE CORRECTIONS TO THE RWA

Here the perturbative corrections to the RWA are discussed for three two-level models that have been used in the literature[1,3] to discuss the effects of permanent dipoles on single-photon and multiphoton resonance profiles. The three models all correspond to $\boldsymbol{\mu}\|\mathbf{d}\|\hat{\mathbf{e}}$, and the RWA resonance profiles for each have previously been compared with corresponding exact numerical results.[1,3] Each model will be summarized briefly below in the context of discussions of the usefulness of the perturbative corrections in representing the differences between the RWA and the exact results.

The quantities occurring in the perturbation expansion of the steady-state transition probability given by Eq. (2.25), and in the analogous expression for W_{FWHM}^{N}, involve single or double infinite sums over molecule-EMF couplings involving Bessel functions of argument $\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}/\omega$. The various terms in these sums can be either negative or positive depending on the values of the parameters involved in the problem, including the frequency ω. For the two-level models studied here it was found that truncations of the summation indices to $-m \leq l \leq +m$, with $m \approx 90$, were sufficient to guarantee much more than graphical accuracy for the resulting spectra.[30]

Based on the model calculations to be discussed in this section, and on others not discussed explicitly here, the calculated absorption spectra obtained from the perturbative expression of Eq. (2.25) are not well behaved in general. For example, the third-order energy $E_{01,02}^{(3)}$ as a function of ω often becomes large compared to the first- and second-order energies and, as a result, the values of the spectra can become much too large ($\gg 0.5$) and/or negative. For strong molecule-EMF coupled examples (e.g., model 3 below) even the second-order energy misbehaves relative to the lower-order energies and only the RWA itself is meaningful. For these reasons, in what follows, we discuss explicitly only the absorption spectra calculated using the following expression, obtained from Eq. (2.25) by setting $E_{01,02}^{(3)}$ equal to zero,

$$\bar{P}_{2}^{N}=(2\rho^{2})^{-1}|E_{01,02}^{(1)}|^{2}(1+8F_{01,1}^{(2)})-4F_{01,1}^{(2)} , \tag{3.1}$$

where

$$\rho^{2}=|E_{01}^{(0)}|^{2}+2E_{01}^{(0)}E_{01,01}^{(2)}+|E_{01,01}^{(2)}|^{2}+|E_{01,02}^{(1)}|^{2} . \tag{3.2}$$

Similarly, the W_{FWHM}^{N} is also adversely affected by the third-order energy in general and, from Eq. (2.35), is now taken to be

$$W_{\mathrm{FWHM}}^{N}=\frac{2}{N}|C(N)-8C(N)F_{01,1}^{(2)}|_{\omega=\omega_{\mathrm{res}}^{N}} . \tag{3.3}$$

In what follows the absorption spectra will be discussed with the aid of the coupling strength parameters

$$b=|\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}|/\Delta E ,$$

$$\eta=\eta(1)=|\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}|/\Delta E ,$$

$$\beta(N)=[|C(N)|/\Delta E]_{\omega=\omega_{\mathrm{res}}^{N}} ;$$

for more examples, and details, see Refs. 1, 3–5, 10, 15, and 17–19. The usual RWA resonance profile, Eq. (1.1) with $\mathbf{d}=\mathbf{0}$, becomes more reliable if $b \ll 1$; $\beta(N)$ is the N-photon analog of b for problems where $\mathbf{d}\neq\mathbf{0}$. The parameter η is related to the argument of the Bessel functions occurring in the molecule-EMF coupling parameter $C(N)$ for $\omega=\omega_{\mathrm{res}}^{N}\approx\Delta E/N$; it can be used to indicate the reduction of $C(N)$, relative to $\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}$, due to $\mathbf{d}\neq\mathbf{0}$. In evaluating $\beta(N)$, and W_{FWHM}^{N} through Eq. (3.3), $\omega_{\mathrm{res}}^{N}$ is taken to be that which corresponds to the spectra generated from Eq. (3.1).

Model 1. $\mu=1.0$, $d=20.0$, $\Delta E=1.0$, and $\mathcal{E}=0.5$. The $N=1$, 2, and 3 photon resonance profiles, obtained from the second-order perturbation expression for $\bar{P}_{2}^{N}$ given by Eq. (3.1), are compared to the RWA spectra in Fig. 1. The molecule-EMF couplings are small for this example, for $\mathbf{d}\neq\mathbf{0}$, and very good agreement between the RWA and the exact results is obtained for all N and ω; for details see Kmetic and Meath.[1] Setting $\mathbf{d}=\mathbf{0}$ leads to

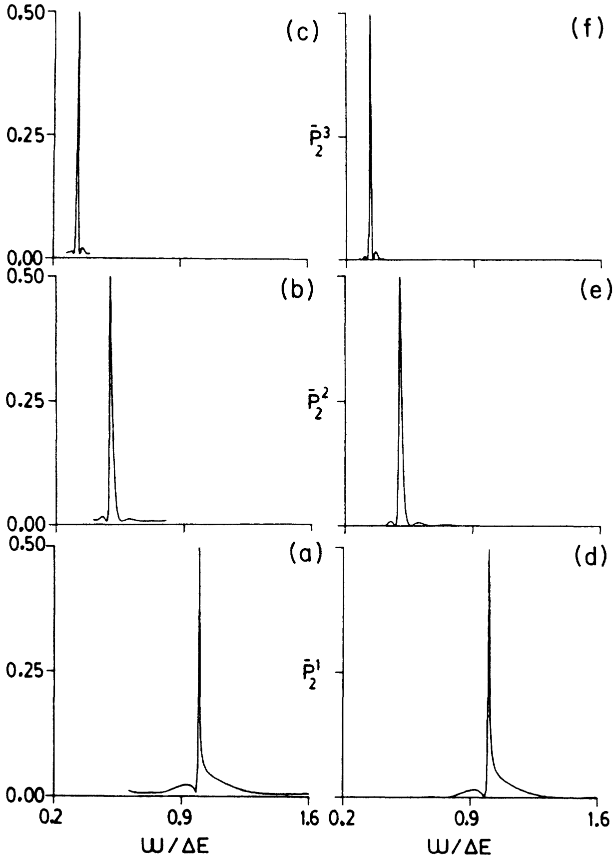

FIG. 1. Comparison of the RWA and the second-order perturbation results for the absorption spectra $\bar{P}_{2}^{N}$ as a function of $\omega/\Delta E$, for the two-level model characterized by $\mu=1.0$, $d=20.0$, $\Delta E=1.0$, and $\mathcal{E}=0.5$. The second-order perturbation resonance profiles for $N=1$, 2, and 3 are illustrated in (a), (b), and (c) and are calculated from Eq. (3.1). Parts (d), (e), and (f) contain the corresponding RWA resonance profiles for $N=1$, 2, and 3 and are calculated from Eqs. (1.1) or (2.36). In this example $b=0.5$ and $\eta=10.0$. The corresponding exact spectrum can be found in Ref. 1.

a relatively strongly coupled system ($b=0.5$) with broad semisaturated resonances.

The parameters characterizing the spectra of Fig. 1 are $b=0.5$, $\eta=10.0$, and $\beta(N)=3.1\times10^{-3}$, 1.5×10^{-2}, and 1.4×10^{-2} for $N=1$, 2, and 3, respectively, in the "second-order" spectra. Since the $\beta(N)$ are small there is good agreement between the RWA, second-order, and exact results[1] for the resonance profiles, and the profiles are narrow with the W_{FWHM}^{N} evaluated from Eq. (3.3), namely 0.0062, 0.015, and 0.0092 for $N=1$, 2, and 3, agreeing well with those obtained from the directly calculated spectra. The resonances in the second-order spectra occur at $\omega/\Delta E=0.995$, 0.498, and 0.332 for $N=1$, 2, and 3 and are shifted slightly to the low-frequency side of the RWA resonances, which occur at $\omega/\Delta E=1/N$, in agreement with the exact calculations[1] of the spectra. In addition, and also in agreement with the exact spectra, a very low background is present in the second-order perturbation resonance profiles that is absent in the RWA.

Model 2. $\mu=-0.5072$, $d=2.0$, $\Delta E=3.706\times10^{-5}$, and $\mathcal{E}=5\times10^{-4}$. The single-photon and multiphoton resonance profiles obtained from Eq. (3.1) are compared to the RWA spectra in Fig. 2. This is an example of a more strongly molecule-EMF coupled system where the agreement between the RWA and the exact spectra is only qualitative, see Kmetic and Meath[1] for details. With $\mathbf{d}=\mathbf{0}$ the EMF-molecule coupling is massive ($b=6.84$) and the absorption spectra[5] are essentially fully saturated for all ω.

The parameters characterizing the second-order spectra of Fig. 2 are $b=6.84$, $\eta=26.98$, and $\beta(N)=6.3\times10^{-2}$, 5.7×10^{-3}, and 3.4×10^{-2} for $N=1$, 2, and 3, respectively. The RWA, Eq. (1.3), and the second-order results of Eq. (3.3), predict W_{FWHM}^{N} for $N=1$, 2, and 3, of 4.26×10^{-6}, 2.01×10^{-6}, 1.09×10^{-6} and 2.40×10^{-6}, 1.85×10^{-7}, and 1.07×10^{-6}, respectively. Those deduced from the second-order spectrum of Fig. 2 are 2.63×10^{-6} and 6.31×10^{-7}, for $N=1$ and 2, respectively, in good agreement with W_{FWHM}^{N} of 2.22×10^{-6} and 6.30×10^{-7} obtained from the exact spectra;[1,5] the width of the three-photon resonance cannot be estimated graphically due to the occurrence of high oscillatory fringes close to the three-photon resonance peak. The predictions of Eq. (3.3) agree well with the exact results for $N=1$ and $N=2$ and seem an improvement over those obtained from the RWA in at least this respect. In general, for strongly coupled molecule-EMF systems the use of either Eq. (3.3), or its RWA analog Eq. (1.3), is questionable[1,3,5] since there can be considerable fluctuation of $\bar{P}_{2}^{N}$ over the width of the "resonance."

A background of approximately 0.15 is present in all the second-order perturbation spectra of Fig. 2; it is absent in the RWA. As well, the resonances are shifted significantly to the low-frequency side of the RWA resonances and are in very good agreement with the exact calculations reported earlier,[1,5] $\omega_{\mathrm{res}}^{N}/\Delta E=0.88$, 0.43, and 0.29 versus the exact results of 0.87, 0.44, and 0.31 for $N=1$, 2, and 3, respectively. In general, the second-order spectra are in much better agreement with the exact results than are those for the RWA, compare Fig. 2 with Fig. 1 of Ref. 1.

Model 3. $\mu=3.0$, $d=6.5$, $\Delta E=0.10$, and $E=5\times10^{-3}$. The parameters characterizing the absorption spectra for this system are $b=1.5$, $\eta=3.25$, and $\beta(N)=0.223$, 0.28, and 0.25×10^{-2} for $N=1$, 2, and 3, respectively. This is an example of a strong molecule-EMF coupled system (with $\mathbf{d}\neq\mathbf{0}$). As pointed out earlier only the RWA and the exact calculations are meaningful for this model and these have been discussed and contrasted in detail previously.[3] For this type of system, where the multiphoton resonances are overlapping and are reasonably saturated,[3,5] even for $\mathbf{d}\neq\mathbf{0}$, the perturbative corrections to the RWA are unreliable; the RWA itself still yields useful qualitative interpretations[3,5] of the spectra.

In summary, the perturbative corrections to the RWA contained in the expression for $\bar{P}_{2}^{N}$ given by Eq. (3.1) can account for the "negative Bloch-Siegert" shifts and the background seen in exactly calculated single-photon and

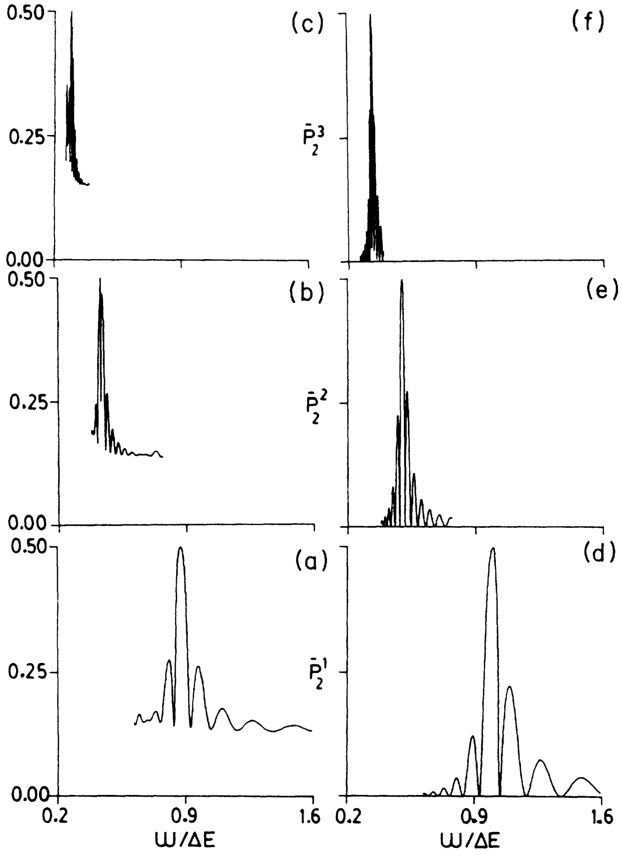

FIG. 2. Comparison of the RWA and the second-order perturbation results for the absorption spectra $\bar{P}_{2}^{N}$ as a function of $\omega/\Delta E$, for the two-level model characterized by $\mu=-0.5072$, $d=2.0$, $\Delta E=3.706\times10^{-5}$, and $\mathcal{E}=5.0\times10^{-4}$. The second-order perturbation resonance profiles for $N=1$, 2, and 3 are illustrated in (a), (b), and (c) while (d), (e), and (f) contain the corresponding RWA resonance profiles. Here $b=6.84$ and $\eta=26.98$. The corresponding exact spectrum can be found in Ref. 1.

multiphoton spectra and that are absent in the RWA. The perturbation-theory results, correct through second order, give almost quantitative agreement with the exact results for weak molecule-EMF coupled systems (e.g., model 1) and account for the differences between the RWA and the exact results reasonably well for moderately coupled cases (e.g., model 2); for strongly coupled systems the perturbation corrections are essentially meaningless for computational purposes. We also point out that the perturbative corrections to the RWA can become unreliable, for certain ω, even for weak and moderate molecule-EMF coupled systems. For example, the perturbative corrections occurring in Eq. (3.1) contain terms of the form $(\Delta E - c\omega)^{-p}$ where c and p are positive integers. These terms become large as $\omega \rightarrow \Delta E/c$ and can cause divergent results for some values of frequency (for the examples of Figs. 1 and 2 this occurs for small ω and the plots are terminated accordingly).

Finally we emphasize that the results for the resonance frequencies and the W_{FWHM}^{N} obtained from the $(\boldsymbol{\mu},\mathbf{d})$ expansions of Eqs. (2.40)–(2.44) are essentially meaningless for the explicit examples considered in this paper; the couplings $\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}$ and $\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}$ and the coupling strength parameters b and η are large and the perturbative expansions in $\boldsymbol{\mu}$ and $\mathbf{d}$ do not converge. However, for example, the implicit perturbation result for $\omega_{\mathrm{res}}^{N}$ given by Eq. (2.38) can be used, without making a $(\boldsymbol{\mu},\mathbf{d})$ expansion, iteratively to obtain meaningful results. With terms of third- and higher-order set equal to zero, Eq. (2.38) yields values for $\omega_{\mathrm{res}}^{N}=0.88$, 0.44, and 0.30 for $N=1$, 2, and 3, respectively, for model 2; these are in excellent agreement with the exact results.

The difficulties with perturbation theory can be avoided by using exact methods for the solution of two- (or many-) level problems and results using such techniques are used to augment previous discussions of $\mathbf{d}\neq 0$ effects in single-photon and multiphoton spectra in what follows.

IV. COMMENTS ON SINGLE-PHOTON AND MULTIPHOTON SPECTRA OF LARGE $\mathbf{d}\neq 0$ MOLECULES

Here we discuss some exact two-level model resonance profiles that illustrate some of the spectral effects related to large differences between the permanent dipoles of the states involved in a transition. The discussion augments recent papers[8,31] on "giant dipole molecules," or more precisely molecules with giant differences $\mathbf{d}$, and serves as a connection between these recent papers and earlier work[1–4,7,9] on this subject.

The two-level model molecules chosen are based on the ground and lowest excited singlet states of the 1-[p-(N,N-dimethylamino)phenyl]-4-(p-nitrophenyl)-1,3-butadiene molecule with the molecular parameters[8,31] chosen to be $\Delta E = 8.56\times 10^{-2}$, $d=11.80$, and $\mu=3.93$, with $\mathbf{d}\|\boldsymbol{\mu}\|\hat{\mathbf{e}}$. In addition to the coupling strength parameters b, $\eta=\eta(1)$, and $\beta(N)$ employed earlier, the parameter $\alpha=\frac{1}{2}|\mathbf{d}|/|\boldsymbol{\mu}|$, introduced in the work of Hattori and Kobayashi,[8] is also used in what follows to help discuss the spectral effects of $\mathbf{d}\neq 0$. Various two-level models, and their single-photon and multiphoton spectra, as a function of $b=|\boldsymbol{\mu}\cdot\hat{\mathbf{e}}\mathcal{E}|/\Delta E$, $\eta=|\mathbf{d}\cdot\hat{\mathbf{e}}\mathcal{E}|/\Delta E$, and α can be generated by varying the field strength $\mathcal{E}$, and d, relative to those characterizing the original model molecule. The exact absorption spectra or resonance profiles, or the phase and long-time average of the population of the excited state 2 as a function of frequency ω, correspond to the interaction of the molecule with a continuous-wave laser with the molecule being in the ground state at the initial time $t=0$. The calculations are carried out by using the Riemann product integral method[5,32,33] to obtain the solution to the time-dependent wave equation over the first period of the Hamiltonian for the problem, as a function of frequency, followed by the use of Floquet and related techniques[4,5,7,21–23,32] to obtain the absorption spectra. In Fig. 3 the exact two-level spectra in columns (a), (b), and (c), respectively, correspond to $\alpha=0$, 1.1, and 1.5. In addition, the labels 1, 2, 3, and 4 correspond to $b=0.2$, 0.6, 1.0, and 1.8, respectively. The values of $\omega_{\mathrm{res}}^{N}/\Delta E$, $N=1,2,\ldots,6$, for each spectrum shown are summarized in Table I.

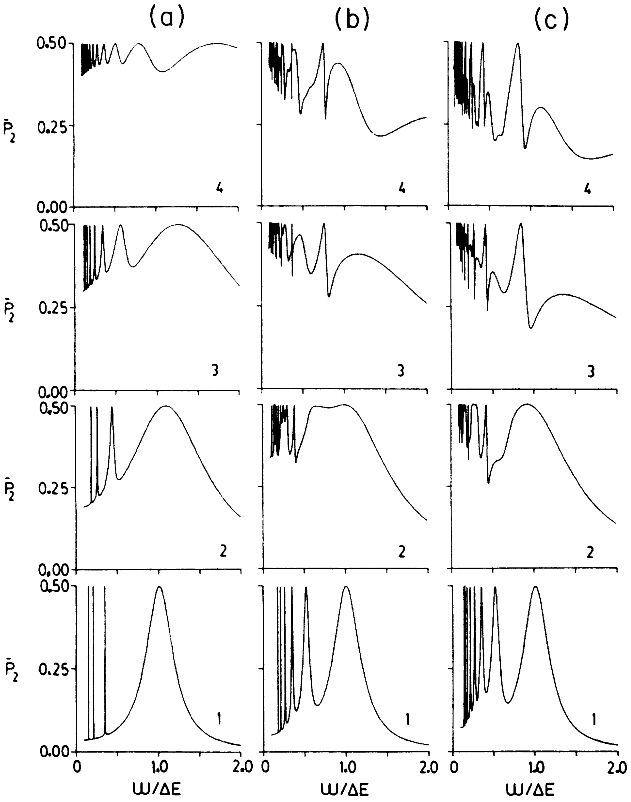

FIG. 3. Comparison of the absorption spectra $\bar{P}_2$ as a function of $\omega/\Delta E$, obtained from exact calculations for the two-level systems specified by $\mu=3.93$, $\Delta E=8.56\times 10^{-2}$, and $d=0$ [(a)-1–(a)-4], $d=8.65$ [(b)-1–(b)-4], and $d=11.80$ [(c)-1–(c)-4]. In (a)-1, (b)-1, and (c)-1, $\mathcal{E}=4.36\times 10^{-3}$ and $b=0.2$ while $\mathcal{E}=1.31\times 10^{-2}$ and $b=0.60$ for (a)-2, (b)-2, and (c)-2, $\mathcal{E}=2.18\times 10^{-2}$ and $b=1.00$ for (a)-3, (b)-3, and (c)-3, and $\mathcal{E}=3.92\times 10^{-2}$ and $b=1.80$ for (a)-4, (b)-4, and (c)-4. Also, $\alpha=0$ and $\eta=0$ for (a)-1–(a)-4, $\alpha=1.1$ and $\eta=0.44$, 1.32, 2.20, and 3.96 for (b)-1–(b)-4, respectively, and $\alpha=1.5$ and $\eta=0.60$, 1.80, 3.00, and 5.40 for (c)-1–(c)-4. The parameters b, η, and α are defined in the main text.

TABLE I. Summary of the values of $\omega_{\text{res}}^{N}/\Delta E$ for the exact spectra given in Fig. 3. These spectra correspond to the two-level systems specified by $\mu=3.93$, $\Delta E=8.56\times10^{-2}$, and $\mathbf{d}=\mathbf{0}$ [Figs. 3(a)-1–3(a)-4], $d=8.65$ [Figs. 3(b)-1–3(b)-4], and $d=11.80$ [Figs. 3(c)-1–3(c)-4]. The parameters b, $\eta=\eta(1)$, and α are defined in the main text.

b	η	$\omega_{\text{res}}^{1}/\Delta E$	$\omega_{\text{res}}^{2}/\Delta E$	$\omega_{\text{res}}^{3}/\Delta E$	$\omega_{\text{res}}^{4}/\Delta E$	$\omega_{\text{res}}^{5}/\Delta E$	$\omega_{\text{res}}^{6}/\Delta E$
				$\alpha=0.0$			
0.20	0.00	1.01		0.35		0.21	
0.60	0.00	1.09		0.44		0.26	
1.00	0.00	1.25		0.56		0.34	
1.80	0.00	1.73		0.79		0.51	
				$\alpha=1.1$			
0.20	0.44	1.01	0.52	0.35	0.26	0.21	0.17
0.60	1.32	0.99	0.65	0.38	0.29	0.25	0.22
1.00	2.20	0.76	0.37	0.28	0.24	0.21	0.20
1.80	3.96	0.75	0.37	0.26	0.24	0.19	0.18
				$\alpha=1.5$			
0.20	0.60	1.01	0.52	0.35	0.26	0.21	0.18
0.60	1.80	0.92	0.43	0.30	0.27	0.26	0.21
1.00	3.00	0.85	0.42	0.28	0.21	0.17	0.15
1.80	5.40	0.85	0.42	0.28	0.21	0.17	0.14

To begin, consider the spectra corresponding to a fixed value of α. When $\alpha=0$, $\eta=0$ for the spectra in Figs. 3(a)-1–3(a)-4. As b increases on going from 3(a)-1 to 3(a)-4 the spectra become more saturated as expected and as is evident from the increasing background; the resonances shift significantly to higher values of $\omega/\Delta E$ (see Table I). Only the odd-photon resonances occur, as usual, since $\mathbf{d}=\mathbf{0}$ and only two levels are involved.

When $\alpha=1.1$, $\eta=0.44$, 1.32, 2.20, and 3.96, and $b=0.2$, 0.6, 1.0, and 1.8 for Figs. 3(b)-1, 3(b)-2, 3(b)-3, and 3(b)-4, respectively. Initially as η increases, some of the resonances approach each other and eventually overlap very strongly. This effect is evident when $\eta=1.32$ and $b=0.6$ [Fig. 3(b)-2]. Here, the one- and two-photon resonances are very close and appear as one large broad resonance with two maxima separated by a very slight minimum. The one-photon resonance has shifted slightly to a lower value of $\omega/\Delta E$ while the two-photon resonance has shifted significantly to a higher value of $\omega/\Delta E$ relative to smaller $\mathbf{d}$ or to $\mathbf{d}=\mathbf{0}$ (see Table I). The three-, four-, five-, and six-photon resonances shift slightly to higher values of $\omega/\Delta E$ as well. When $\eta=2.20$, the large, broad resonance of the $\eta=1.32$ case has been replaced by a one-photon resonance with a large oscillatory fringe on the high $\omega/\Delta E$ side. The one-, two-, and three-photon resonance positions have undergone large negative shifts from those associated with the $\eta=1.32$ calculation (their ω_{res}^{N} have become less than $\Delta E/N$) and an oscillatory fringe associated with the two-photon resonance is also clearly present. An additional increase in η, Fig. 3(b)-4, further complicates the spectra for low frequency. There is an interesting interplay between increasing b and increasing η in proceeding from 3(b)-1 to 3(b)-4 in Fig. 3. Increases in b tend to broaden and saturate, while increases in η tend to narrow and sharpen, the absorption spectra as discussed previously[1–5,19] (see also Sec. I). For $\mathbf{d}\neq\mathbf{0}$ the appearance of even, as well as odd, photon resonances is clear and this can add to the crowding of the resonances, relative to the $\mathbf{d}=\mathbf{0}$ spectra of part (a) of Fig. 3, as a function of ω and η.

Figures 3(c)-1 to 3(c)-4 correspond to the absorption spectra of the original model molecule, 1-[*p*-(*N*,*N*-dimethylamino)phenyl]-4-(*p*-nitrophenyl)-1,3-butadiene, as a function of $\mathcal{E}$, where $\alpha=1.5$. Here $\eta=0.6$, 1.8, 3.0, and 5.4, and $b=0.2$, 0.6, 1.0, and 1.8 for Figs. 3(c)-1, 3(c)-2, 3(c)-3, and 3(c)-4, respectively. In this example, no merging of the lower photon resonances is observed; for each b value, the value of η is larger in this example than in Fig. 3(b). The four-, five-, and six-photon resonances shift to slightly higher values of $\omega/\Delta E$ when $b=0.6$ and $\eta=1.8$ relative to $b=0.2$ and $\eta=0.6$. In general, though, all resonances shift to lower values of $\omega/\Delta E$ as b and η increase, illustrating again the negative Bloch-Siegert shifts due to the presence of $\mathbf{d}$.

Now consider the spectra for fixed values of b. When $b=0.2$, Figs. 3(a)-1, 3(b)-1, and 3(c)-1 correspond to $\eta=0$, 0.44, and 0.60, respectively. The resonances occur at the same positions in each spectra for $N=1$, 3, and 5 (see Table I) and, when $\mathbf{d}\neq\mathbf{0}$, for $N=2$ and 4, as well. The coupling strengths are quite similar for each resonance. For example, when $N=1$, $\beta(1)=0.20$, 0.195, and 0.191 for 3(a)-1, 3(b)-1, and 3(c)-1, respectively, and $\beta(1)\approx b$. The effect of $\mathbf{d}\neq\mathbf{0}$ is minimized for the small values of η occurring in this example.

The spectra characterized by $b=0.6$ correspond to Fig. 3(a)-2 where $\eta=0$, $\beta(1)=b=0.60$, 3(b)-2 where $\eta=1.32$, $\beta(1)=0.48$, and 3(c)-2 where $\eta=1.80$, $\beta(1)=0.36$. As η increases the one-photon resonance shifts to lower values of $\omega/\Delta E$. As discussed previously, the $N>1$ resonances shift to high frequency when $\eta=1.32$. However as η increases further to $\eta=1.8$ the overall effect of increasing $\mathbf{d}$ from zero again becomes clear in that it tends to induce shifts in the resonance frequency to the low-frequency side of the zero field or RWA limit of $\Delta E/N$.

Finally, Figs. 3(a)-3, 3(b)-3, and 3(c)-3 correspond to

$b = 1.0$ and to the parameters $\eta = 0$ and $\beta(1) = b = 1.00$, $\eta = 2.20$ and $\beta(1) = 0.26$, and $\eta = 3.00$ and $\beta(1) = 0.071$, respectively, while Figs. 3(a)-4, 3(b)-4, and 3(c)-4 correspond to $b = 1.8$ and are characterized by $\eta = 0$ and $\beta(1) = b = 1.80$, $\eta = 3.96$ and $\beta(1) = 0.24$, and $\eta = 5.40$ and $\beta(1) = 0.11$. Both these examples illustrate the effect of $\mathbf{d} \neq 0$ on the absorption spectra of molecules. When $\mathbf{d} = 0$, the spectra are highly saturated and the resonances are quite broad; when $\mathbf{d} \neq 0$, the background is greatly reduced, the resonances are narrowed appreciably, and oscillatory fringes occur in the spectra as explained and discussed previously.[1-5,7,19] For fixed b, as η increases, the "real" molecule-EMF coupling parameter $\beta(1)$ differs more appreciably from b.

Hattori and Kobayashi[8] carried out frequency sweep absorption spectra for a system characterized by $\alpha = 0.3$ and $b = 0.2$, 0.6, 1.0, and 1.8. Solving for the corresponding η values yields $\eta = 0.12$, 0.36, 0.60, and 1.08 and hence these calculations show only some of the effects discussed here, and previously,[1-5,7,19] for $\mathbf{d} \neq 0$; for example, oscillatory fringes associated with main resonances were not observed. More importantly the analysis of the effects of $\mathbf{d} \neq 0$ on the absorption spectra given by these authors was carried out using a Floquet secular equation not derived from the interaction representation[1,3] used in Sec. II. The form of the Floquet secular equation used in Ref. 8 is the $\mathbf{d} \neq 0$ analog of Shirley's results[10] and leads to results like those of Eqs. (2.40)–(2.44) which, see Sec. III and Hattori and Kobayashi,[8] cannot be used to analyze spectra like those of Figs. 1–3 reliably. Further, the RWA arising from the $\mathbf{d} \neq 0$ analog of Shirley's secular equation corresponds to the usual atomic result for the absorption spectrum corresponding to the $\mathbf{d} = 0$ limit of Eqs. (1.1) or (2.36); the effects of $\mathbf{d} \neq 0$ in this approach arise from higher-order perturbation expansions of the secular equation. On the other hand, the interaction representation used in Sec. II leads to a discussion of the molecule-EMF interaction in terms of the important molecule-EMF coupling given by $C(N)$, defined by Eqs. (1.2) or (2.17), and to the analytic molecular RWA resonance profile of Eqs. (1.1) or (2.36). These analytic results are crucial in discussing, interpreting, and predicting many of the effects of $\mathbf{d} \neq 0$ in the single-photon and multi-photon absorption spectra of molecules.[1-7,17-19]

V. DISCUSSION

The perturbative corrections to the rotating wave approximation for the N-photon absorption spectrum of a two-level molecule, including the effects of permanent dipole moments, are obtained in Secs. II A and II B. They are obtained from a time-independent N-photon Floquet Hamiltonian matrix description of the problem through the use of a Fourier expansion of the time-dependent Hamiltonian, phase factoring techniques, and Floquet theory. The derivation of the results is a generalization of earlier work[10,13] for the $\mathbf{d} = \boldsymbol{\mu}_{22} - \boldsymbol{\mu}_{11} = 0$ case and involves the use of a crucial transformation to an interaction representation that enables the problem to be discussed in terms of the important molecule-EMF coupling given by $C(N)$, see Eqs. (1.2) or (2.17), rather than the usual coupling $\boldsymbol{\mu}_{12} \cdot \hat{\mathbf{e}} \mathcal{E}$ used by previous workers.

The perturbation treatment of this problem is not easily carried out. Not only are the zeroth-order energies near degenerate but they can also be of the same magnitude as the second-order energy, especially for frequencies associated with the N-photon resonances, which are, of course, of particular importance. As pointed out in Secs. II B and III, this makes the ordering of the terms, in order of smallness, difficult in the perturbation expansion of the N-photon resonance profile $\bar{P}_2^N$. This difficulty is compounded by the fact that the Floquet perturbation energies and wave functions are functions of frequency as well as the couplings $\boldsymbol{\mu}_{12} \cdot \hat{\mathbf{e}} \mathcal{E}$ and $\mathbf{d} \cdot \hat{\mathbf{e}} \mathcal{E}$; $C(N)$ is a function of frequency for $\mathbf{d} \neq 0$. The perturbation-theory results can converge for certain frequencies, and misbehave for others, for a given problem (see Sec. III for examples). For the models investigated here it was found that, aside from the RWA, only the second-order perturbation-theory expression was useful for numerical calculations of N-photon resonance profiles.

The perturbation-theory expressions for the corrections to the RWA are used, in Secs. II C and III, to help investigate and explain effects observed in exact two-level resonance profiles that are missing in the RWA. For problems where the molecule-EMF couplings are relatively weak the result for $\bar{P}_2^N$, through second order, often agrees quite well with exact calculations for two-level molecular resonance profiles and can account for the shifts of the resonance frequencies from the RWA result of $\Delta E/N$ and for the dynamic spectral background absent in the RWA. On the other hand (see Sec. III), for strong couplings, where the various N-photon resonances begin to overlap appreciably, the perturbation results for $\bar{P}_2^N$ are apparently not particularly useful aside from qualitative results obtained from the RWA. It is likely that the use of the perturbation-theory expressions obtained from the $\mathbf{d} \neq 0$ Floquet secular equation will not yield computationally useful results in general. If the fourth-order energies and other higher-order effects are required to obtain reasonable results, the use of perturbation theory for this purpose is doubtful. It is probably easier to perform exact computations which avoid the difficulties associated with perturbation theory and which are relatively inexpensive for few-level systems (see Sec. IV).

It seems, in general, that the usefulness of the explicit perturbation corrections to the RWA lies in the qualitative and conceptual understanding of the differences between the RWA and exact single-photon and multiphoton spectra. An example of this application is the expansion for the shift of the resonance frequencies relative to $\Delta E/N$, in powers of the couplings between both the transition and the permanent dipole moments and the EMF, obtained in Sec. II C; see also Hattori and Kobayashi.[8] This result is obtained by iteration from an implicit result for the N-photon resonance frequency obtained by the perturbation-theory treatment of the problem and gives an analytical demonstration of the possibility, if $\mathbf{d} \neq 0$, of low-frequency shifts in the resonance frequencies relative to $\Delta E/N$. These "negative Bloch-Siegert shifts" are in contradistinction to the usual shifts to high frequency seen in atomic ($d=0$) spectra and are observed in exactly calculated two-level spectra.

Single- and multiphoton absorption spectra for a series of giant dipole (more precisely large $\mathbf{d}\neq 0$) two-level molecules, evaluated using exact computational techniques, are presented in Sec. IV. They are used to illustrate some of the effects of $\mathbf{d}\neq 0$ in the spectra, relative to the $\mathbf{d}=0$ case, and the discussion helps to link some of the relatively recent literature[1-8,31] on the subject together including that on the use of the RWA to interpret such spectra. The advantages of using the interaction representation defined by Eqs. (2.1)–(2.6) to develop the Floquet secular equation used in our perturbation treatment of the problem, relative to a more direct extension of the $d=0$ approach used by Shirley,[10] are discussed briefly in Sec. IV.

The two-level system, in the electric dipole approximation, studied in this paper has long provided a basis for the study of a wide variety of linear and nonlinear interactions between electromagnetic radiation and atoms and molecules; see, for example, some references already cited and Refs. 34–37. This paper is particularly concerned with the effects of permanent dipoles on such interactions. While two-level calculations are relevant and important in understanding and/or predicting the effects of varying the various parameters defining the interaction of radiation with matter, they should be regarded as models unless it is verified in explicit applications that the effects of neighboring energy levels are not significant. The usefulness and the limitations of the two-level system as an approximation for more realistic atoms and molecules have been discussed often previously, see, for example Refs. 5, 17–19, 34, and 38–42.

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[*] Also at Centre for Interdisciplinary Studies in Chemical Physics, University of Western Ontario, London, Ontario, Canada N6A 5B7.

[†] Present address: Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

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