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Two-level rotating-wave approximations for molecules in a static electric field with an application to rotationally averaged spectra

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A rotating-wave approximation (RWA) for the single-photon and multiphoton resonance profiles for a two-level molecule interacting with both sinusoidal and static electric fields is derived. Included is a useful expression for the coupling between the molecule and the applied sinusoidal field which exhibits the effects of both diagonal dipole matrix elements (permanent dipole moments) and the applied static electric field. Comparisons of the RWA results with exact two-level calculations provide qualitative information concerning the validity of the RWA as a function of molecular and field parameters. These examples are also used to illustrate the interpretive nature of the RWA results for the resonance profiles and some of the effects of permanent dipoles and static fields on the profiles. Of particular interest are examples involving Boltzmann rotationally averaged spectra as a function of temperature where it is shown that minima in the spectra occurring for high temperatures can be reduced or removed completely if the temperature or applied static field is reduced.

I. INTRODUCTION

Recently rotating-wave-type approximations (RWA's) have been derived[1] for the single-photon and multiphoton resonance profiles for a two-level system, with nonzero diagonal dipole matrix elements or "permanent dipole moments," interacting with an applied sinusoidal electric field. These simple analytic results have been used to help discuss some of the effects of permanent dipole moments on resonance profiles including (free) rotationally averaged spectra.[1,2] One of the purposes of this paper is to derive analogous RWA results which include the effects of an applied static electric field. The validity of these analytic results is illustrated by comparison with exact calculations, in the semiclassical dipole approximation, for several examples including Boltzmann-weighted rotationally averaged spectra as a function of temperature.

Some preliminary results, including the transformation of the time-dependent Schrödinger equation for the two-level problem into a form suitable for an RWA analysis including nonzero permanent moments and static electric fields, are summarized in Secs. II and III. The RWA results for the N-photon resonance profiles are derived in Sec. III, which also contains a brief discussion of a method for evaluating Boltzmann-weighted rotationally averaged spectra. Included is an expression for the coupling between the molecule and the applied sinusoidal electric field which exhibits the effects of both permanent dipoles and an applied static electric field. Section IV contains examples comparing the RWA results for single-photon and multiphoton spectra with exact two-level calculations for the same molecular and field parameters. These are used, in part, to illustrate the validity of the RWA approximations as a function of the parameters and to discuss the interpretive nature of these results, including the RWA expression for the coupling between the molecule and the time-dependent field. Of particular interest is the effect of permanent dipole moments; for example, they can cause (1) shifts of the resonance frequency to either the low- or high-frequency side of that associated with the energy separation between the states involved in the transition and (2) a minimum in the Boltzmann rotationally averaged spectra for high temperatures which is reduced or removed completely as the temperature or the applied static electric field is reduced. Section IV also contains a brief discussion of the general usefulness of the results of the paper and of the relation between our RWA results and a more complete analysis of the problem.

In what follows atomic units are employed: the 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. WORKING EQUATIONS

Consider a molecule with stationary states 1 and 2 characterized by energies E_j, $E_2 > E_1$, and orthonormalized time-independent wave functions $\Phi_j(\mathbf{r})$, $j=1,2$. The transition ($\boldsymbol{\mu}=\boldsymbol{\mu}_{12}$) and permanent ($\boldsymbol{\mu}_{jj}$) dipoles for these stationary states are defined by $\boldsymbol{\mu}_{ij}=\langle\Phi_i(\mathbf{r})\,|\,\boldsymbol{\mu}\,|\,\Phi_j(\mathbf{r})\rangle$ where here $\boldsymbol{\mu}$ is the dipole moment operator for the molecule. The Hamiltonian operator for the interaction of this two-level system with both static and sinusoidal electric fields is given, in matrix form, by

$$\underline{H}(t)=\begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} - [\hat{\mathbf{e}}_s E_s + \hat{\mathbf{e}} E \cos(\omega t+\delta)]\cdot \begin{bmatrix} \boldsymbol{\mu}_{11} & \boldsymbol{\mu}_{12} \\ \boldsymbol{\mu}_{21} & \boldsymbol{\mu}_{22} \end{bmatrix}, \tag{1}$$

where $\hat{\mathbf{e}}_s$ is the unit vector specifying the direction of the static field of magnitude E_s and E, ω, δ, and $\hat{\mathbf{e}}$ are the amplitude, circular frequency, phase, and direction of polarization, respectively, of the applied sinusoidal field. After removing the traces of the energy and dipole matrices in Eq. (1), which introduces an overall phase factor of absolute value unity into the time-dependent wave function, and diagonalizing the static part of the resulting Hamiltonian one can show[3] that the time-dependent populations of states 1 and 2 are given by $|C_1(t)|^2 = 1-|C_2(t)|^2$, and

$$|C_2(t)|^2=\tfrac{1}{2}+\tfrac{1}{2}[(|C_+|^2-|C_-|^2)\cos(2\theta)+(C_+^*C_-+C_+C_-^*)\sin(2\theta)] , \tag{2}$$

where

$$\cos(2\theta)=(\Delta E-\mathbf{d}\cdot\hat{\mathbf{e}}_sE_s)\gamma^{-1},\quad \sin(2\theta)=2(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}_sE_s)\gamma^{-1} , \tag{3}$$

$$\begin{gathered}\Delta E=E_2-E_1,\quad \mathbf{d}=\boldsymbol{\mu}_{22}-\boldsymbol{\mu}_{11} ,\\ \gamma=[(\Delta E-\mathbf{d}\cdot\hat{\mathbf{e}}_sE_s)^2+4(\boldsymbol{\mu}\cdot\hat{\mathbf{e}}_sE_s)^2]^{1/2}\geq 0 .\end{gathered} \tag{4}$$

The time-dependent coefficients C_+ and C_- are obtained by solving the coupled differential equations

$$i\frac{d}{dt}\begin{bmatrix}C_-\\C_+\end{bmatrix}=\underline{H}(t)\underline{C}=\left\{\begin{bmatrix}E_- & 0\\0 & E_+\end{bmatrix}-\left[\begin{bmatrix}-1 & 0\\0 & 1\end{bmatrix}\frac{\mathbf{D}}{2}+\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}\mathbf{M}\right]\cdot\hat{\mathbf{e}}E\cos(\omega t+\delta)\right\}\underline{C} , \tag{5}$$

where

$$\begin{gathered}E_{(-,+)}=(-,+)\gamma/2 ,\\ \mathbf{D}=\mathbf{d}\cos(2\theta)-2\boldsymbol{\mu}\sin(2\theta) ,\\ \mathbf{M}=\boldsymbol{\mu}\cos(2\theta)+\tfrac{1}{2}\mathbf{d}\sin(2\theta) ,\end{gathered} \tag{6}$$

and $E_{(-,+)}$ are the energy eigenvalues arising from the diagonalization of the static Hamiltonian; details of the connection between the (1,2) and $(-,+)$ representations have been discussed previously.[3] The probabilities of finding the molecule in the $-$ or $+$ states are given by $|C_{(-,+)}|^2$ and these results, together with C_- and C_+, yield the corresponding results for the (1,2) representation; see Eq. (2). Of particular interest is the steady-state spectrum of the molecule. Assuming relaxation effects are negligible this usually corresponds to the long-time and phase average of Eq. (2) and is defined by[4–8]

$$\bar{P}_2=\lim_{\tau\to\infty}\frac{1}{2\pi\tau}\int_0^{\tau}\int_0^{2\pi}|C_2(t)|^2d\delta\, dt . \tag{7}$$

All these results depend on the initial conditions for the system and in what follows we will be particularly interested in the situation where only the ground state 1 is populated at $t=0$; this corresponds to

$$\begin{gathered}C_1(0)=1,\quad C_2(0)=0\\ \text{or}\\ C_-(0)=\cos\theta,\quad C_+(0)=-\sin\theta .\end{gathered} \tag{8}$$

III. RWA RESULTS

It is not possible to solve Eq. (5) in closed form in general. However, simple closed-form results can be obtained by making an "on-resonance" or rotating-wave approximation.[6,9,10]

In order to locate the resonances in the transition probabilities it is useful to transform Eq. (5) into an interaction representation defined by

$$C_{(-,+)}=b_{(-,+)}\exp\left[\pm i\frac{\gamma}{2}t\right]\times\exp\left[\mp\frac{i}{2}\mathbf{D}\cdot\hat{\mathbf{e}}E\int_0^t\cos(\omega t'+\delta)dt'\right] . \tag{9}$$

The coefficients $b_{(-,+)}$ satisfy

$$i\frac{d}{dt}\underline{b}=i\frac{d}{dt}\begin{bmatrix}b_-\\b_+\end{bmatrix}=\underline{H}_I(t)\underline{b} , \tag{10}$$

$$H_{I,--}=H_{I,++}=0 , \tag{11}$$

$$\begin{aligned}H_{I,-+}=H_{I,+-}^*&=-\mathbf{M}\cdot\hat{\mathbf{e}}E\cos(\omega t+\delta)\exp\left[-i\left[\gamma t-\mathbf{D}\cdot\hat{\mathbf{e}}E\int_0^t\cos(\omega t'+\delta)dt'\right]\right]\\ &=-\tfrac{1}{2}\mathbf{M}\cdot\hat{\mathbf{e}}E\exp\left[-i\frac{\mathbf{D}\cdot\hat{\mathbf{e}}E}{\omega}\sin\delta\right]\\ &\quad\times\sum_{k=-\infty}^{\infty}J_k(\mathbf{D}\cdot\hat{\mathbf{e}}E/\omega)\{\exp[i(k-1)\delta]\exp[-i(\gamma+\omega-k\omega)t]+\exp[i(k+1)\delta]\exp[-i(\gamma-\omega-k\omega)t]\} ,\end{aligned} \tag{12}$$

where we have used the expansion[11]

$$\exp(iz\sin x)=\sum_{k=-\infty}^{\infty}J_k(z)\exp(ikx) \tag{13}$$

and $J_k(z)$ is a Bessel function of integer order k. For certain frequencies $H_{I,-+}$ will contain terms that are slowly varying functions of time; the resonances in the transition probabilities occur approximately at these frequencies. The slowly varying terms are identified by $\omega=\gamma/N$, $N=1,2,3,\ldots$ with $k=N+1$ in the first term in Eq. (12)

and $k=N-1$ in the second term. Neglecting all other terms in Eq. (12), which correspond to off-resonance or counterrotating terms, yields a simple RWA approximation for $\underline{H}_I$ in Eq. (10) with Eq. (12) replaced by

$$H_{I,-+}=H^*_{I,+-}=-\tfrac{1}{2}C(N)\zeta\exp[-i(\gamma-N\omega)t]\ , \tag{14}$$

where

$$\zeta=\exp\left[-i\left[\frac{\mathbf{D}\cdot\hat{\mathbf{e}}E}{\omega}\sin\delta-N\delta\right]\right] \tag{15}$$

and for the N-photon resonance the effective coupling between the sinusoidal field and the atom or molecule is given by

$$\begin{aligned}C(N)&=\mathbf{M}\cdot\hat{\mathbf{e}}E[J_{N+1}(\mathbf{D}\cdot\hat{\mathbf{e}}E/\omega)+J_{N-1}(\mathbf{D}\cdot\hat{\mathbf{e}}E/\omega)]\\&=2\mathbf{M}\cdot\hat{\mathbf{e}}EN(\omega/\mathbf{D}\cdot\hat{\mathbf{e}}E)J_N(\mathbf{D}\cdot\hat{\mathbf{e}}E/\omega)\ .\end{aligned} \tag{16}$$

Equations (10) can be solved when $\underline{H}_I(t)$ is given by Eqs. (11) and (14) by using standard techniques to yield

$$\begin{aligned}b_{(-,+)}=&\left[A_{(-,+)}\exp\left[i\frac{\kappa}{2}t\right]+B_{(-,+)}\exp\left[-i\frac{\kappa}{2}t\right]\right]\\&\times\exp\left[(-,+)\frac{i}{2}(\gamma-N\omega)t\right]\ ,\end{aligned} \tag{17}$$

where

$$\kappa=[(\gamma-N\omega)^2+C^2(N)]^{1/2} \tag{18}$$

and the constants A and B satisfy

$$\begin{aligned}&A_-(\gamma-N\omega-\kappa)=-C(N)\zeta^*A_+\ ,\\&B_-(\gamma-N\omega+\kappa)=-C(N)\zeta^*B_+\ ,\\&A_+(\gamma-N\omega+\kappa)=C(N)\zeta A_-\ ,\\&B_+(\gamma-N\omega-\kappa)=C(N)\zeta B_-\ .\end{aligned}$$

These results can be used to evaluate C_+ and C_-, or C_1 and C_2, for any given initial conditions. Specializing to the initial conditions given in Eq. (8) yields $A_-=\frac{1}{2}(\cos\theta-\beta)$, $A_+=-\frac{1}{2}(\sin\theta+\alpha)$, $B_-=\frac{1}{2}(\cos\theta+\beta)$, and $B_+=-\frac{1}{2}(\sin\theta-\alpha)$, where

$$\begin{aligned}\alpha&=-\frac{1}{\kappa}[(\gamma-N\omega)\sin\theta+C(N)\zeta^*\cos\theta]\ ,\\\beta&=-\frac{1}{\kappa}[(\gamma-N\omega)\cos\theta-C(N)\zeta\sin\theta]\ .\end{aligned} \tag{19}$$

Substitution of Eq. (9), and the results of this paragraph into Eq. (2), gives the phase-dependent temporal spectrum of the system (initially in state 1 at $t=0$). Using this in Eq. (7), the steady-state spectrum can be evaluated. We begin with the long-time average occurring in Eq. (7). It is easy to show that

$$\begin{aligned}|C_+|^2&=|b_+|^2\\&=|\alpha|^2\sin^2(\kappa/2)t+\sin^2\theta\cos^2[(\kappa/2)t]\\&\quad+i(\alpha-\alpha^*)\sin\theta\cos[(\kappa/2)t]\sin[(\kappa/2)t]\ ;\end{aligned}$$

the corresponding long-time average is $(|\alpha|^2+\sin^2\theta)/2$. Similarly the long-time average of $|C_-|^2$ is $(|\beta|^2+\cos^2\theta)/2$. Further algebraic manipulations yield

$$\begin{aligned}C^*_+(t)C_-(t)=&\left[\alpha^*\beta\sin^2[(\kappa/2)t]-\tfrac{1}{2}\sin^2\theta\cos^2[(\kappa/2)t]+i(\alpha^*\cos\theta+\beta\sin\theta)\cos\left[\frac{\kappa}{2}t\right]\sin\left[\frac{\kappa}{2}t\right]\right]\\&\times\sum_{k=-\infty}^{\infty}J_k(\mathbf{D}\cdot\hat{\mathbf{e}}E/\omega)\exp(-ik\delta)\exp[i(N-k)\omega t]\exp\left[i\frac{\mathbf{D}\cdot\hat{\mathbf{e}}E}{\omega}\sin\delta\right]\ .\end{aligned} \tag{20}$$

The long-time average of the third term in this result is zero[12] for all k and the first and second terms give nonzero results only[12] for $k=N$. Combining all the results of this paragraph, one obtains

$$\begin{aligned}\lim_{T\to\infty}\frac{1}{T}\int_0^T|C_2(t)|^2dt=&\tfrac{1}{2}+\tfrac{1}{4}[|\alpha|^2-|\beta|^2-\cos(2\theta)]\cos(2\theta)\\&+\tfrac{1}{4}\{[\alpha^*\beta-\tfrac{1}{2}\sin(2\theta)]\zeta^*J_N(\mathbf{D}\cdot\hat{\mathbf{e}}E/\omega)+\text{c.c.}\}\sin(2\theta)\ ,\end{aligned} \tag{21}$$

where from Eq. (19)

$$\begin{aligned}|\alpha|^2-|\beta|^2=&-\frac{1}{\kappa^2}\{[(\gamma-N\omega)^2-C^2(N)]\cos(2\theta)\\&-(\zeta+\zeta^*)C(N)(\gamma-N\omega)\sin(2\theta)\}\ ,\end{aligned} \tag{22}$$

$$\begin{aligned}\alpha^*\beta=&\frac{1}{\kappa^2}\{(\gamma-N\omega)C(N)\zeta\cos(2\theta)\\&-\tfrac{1}{2}[C^2(N)\zeta^2-(\gamma-N\omega)^2]\sin(2\theta)\}\ .\end{aligned} \tag{23}$$

It is clear from Eqs. (22) and (23) that the only phase-dependent factors occurring in Eq. (21) are ζ and ζ^* and using Eq. (13) one finds the phase average of both is $J_N(\mathbf{D}\cdot\hat{\mathbf{e}}E/\omega)$. The phase average of Eq. (21), after some simplification, gives the steady-state spectrum (or steady-state population) of state 2 for the N-photon resonance ($\omega\sim\gamma/N$):

$$\bar{P}_2^N=\frac{1}{2}-\frac{[(\gamma-N\omega)\cos(2\theta)-C(N)J_N(\mathbf{D}\cdot\hat{\mathbf{e}}E/\omega)\sin(2\theta)]^2}{2\kappa^2}\ . \tag{24}$$

If the applied static field $\mathbf{E}_s=\hat{\mathbf{e}}_s E_s$ is nonzero the spectrum consists[13,14] of a static background $\bar{P}_2(\text{stat})$ and a frequency-dependent part $\Delta\bar{P}_2=\bar{P}_2-\bar{P}_2(\text{stat})$. The static background is obtained by setting $E=0$ in Eq. (24) to obtain

$$\bar{P}_2(\text{stat})=\tfrac{1}{2}[1-\cos^2(2\theta)] \tag{25}$$

which vanishes if $\mathbf{E}_s=0$.

The N-photon resonance frequencies, the values of ω such that $\bar{P}_2^N=\frac{1}{2}$, satisfy

$$\begin{aligned}\chi(\omega)=[&(\gamma-N\omega)\cos(2\theta)\\&-C(N)J_N(\mathbf{D}\cdot\hat{\mathbf{e}}E/\omega)\sin(2\theta)]=0,\quad \omega\to\omega_{\text{res}}\end{aligned} \tag{26}$$

while the full width at half maximum (Δ_{FWHM}) associated with the height of the resonance profile above the static background, that is with $\Delta\bar{P}_2$, is given by $\Delta_{\text{FWHM}}=\omega_+-\omega_-$ where ω_+ and ω_- are the roots of $[\chi^2(\omega)-\frac{1}{2}\kappa^2\cos^2(2\theta)]=0$ lying closest to $\omega=\omega_{\text{res}}$ and such that $\omega_-<\omega_{\text{res}}<\omega_+$. For sufficiently narrow resonances, where $C(N)$ and J_N do not vary appreciably over the width of the resonance, one obtains

$$\Delta_{\text{FWHM}}^N\approx\frac{2}{N}\left\{\left|\frac{C(N)}{\cos(2\theta)}\right|[2J_N^2(\mathbf{D}\cdot\hat{\mathbf{e}}E/\omega)\sin^2(2\theta)+\cos^2(2\theta)]^{1/2}\right\}\Bigg|_{\omega=\omega_{\text{res}}} . \tag{27}$$

The zeros in $\Delta\bar{P}_2$ occur for frequencies satisfying $[\chi^2(\omega)-\kappa^2\cos^2(2\theta)]=0$. All the results of this paragraph reduce to those obtained previously[1,6,9,10] for $E_s=0$.

The coupling between the molecule and the applied sinusoidal field in the RWA results of this section is given by $C(N)$; see Eq. (16). In the limit $\mathbf{d}=0$ and $\mathbf{E}_s=0$ the RWA steady-state spectrum Eq. (24) reduces to the usual result[6,9,10]

$$\bar{P}_2^N(\mathbf{E}_s=0,\mathbf{d}=0)=\frac{|\boldsymbol{\mu}\cdot\mathbf{E}|^2\delta_{N,1}}{2[(\Delta E-\omega)^2+|\boldsymbol{\mu}\cdot\mathbf{E}|^2]} , \tag{28}$$

where the coupling is given by $C(N)=\boldsymbol{\mu}\cdot\mathbf{E}=\boldsymbol{\mu}\cdot\hat{\mathbf{e}}E$. In general the effect of permanent dipole moments and/or static electric fields is to modify and modulate the normal coupling $\boldsymbol{\mu}\cdot\mathbf{E}$ by the Bessel functions of argument $\mathbf{D}\cdot\hat{\mathbf{e}}E/\omega$ and the factor $\mathbf{M}$ occurring in Eq. (16); $\mathbf{M}\to\boldsymbol{\mu}$ as $E_s\to 0$. The vectors $\mathbf{M}$ and $\mathbf{D}$ contain the effects of $\mathbf{d}$ and $\mathbf{E}_s$ through the "primitive" coupling parameters $\boldsymbol{\mu}\cdot\mathbf{E}_s$, $\boldsymbol{\mu}\cdot\mathbf{E}$, $\mathbf{d}\cdot\mathbf{E}_s$, and $\mathbf{d}\cdot\mathbf{E}$ occurring in $\mathbf{M}$ and $\mathbf{D}$; see Eqs. (6), (3), and (4).

In what follows, several examples involving the use of the RWA expression for the transition probability $\bar{P}_2$ will be discussed. Part of the idea is to illustrate the validity of this result and to this end comparisons will be made with exact two-level calculations for the same molecular and field parameters. These exact calculations are carried out using Floquet techniques[14–16] which do not use the so-called Floquet secular equation.[6,17]

In the discussion that follows, and in general, the rotational average, $\langle\bar{P}_2^N\rangle_{\text{rot}}$, of the transition probability $\bar{P}_2^N$ over all orientations of the molecule with respect to the applied field directions is of importance. In the absence of static electric fields all orientations are weighted equally whereas in the presence of static fields each orientation is weighted by a Boltzmann factor. The numerical scheme for evaluating the free rotational average of $\bar{P}_2$ has been discussed in detail previously.[2] The modification to incorporate the Boltzmann factor is relatively straightforward[18,19] and is summarized here only for the situation in which we use it in this paper, namely when $\boldsymbol{\mu}\,||\,\mathbf{d}$ (and defines the molecular z axis) and $\mathbf{E}\,||\,\mathbf{E}_s$ (and defines the space-fixed z axis). Clearly for this case E_-, E_+, and the fixed configuration transition probability $\bar{P}_2$ depend only on the angle β between the space- and body-fixed z axes, $0\le\beta\le\pi$, and note $\mathbf{d}\cdot\mathbf{E}=dE\cos\beta$, $\boldsymbol{\mu}\cdot\mathbf{E}=\mu E\cos\beta$, and similarly for $\boldsymbol{\mu}\cdot\mathbf{E}_s$ and $\mathbf{d}\cdot\mathbf{E}_s$. Integrating over the other Euler angles of rotation[2,20] specifying the orientation of the molecule with respect to the space-fixed axes leads to

$$\langle\bar{P}_2^N\rangle_{\text{rot}}=\frac{\int_{-1}^{1}\bar{P}_2^N(\omega,\Delta E,\mu Ex,dEx,\mu E_s x,dE_s x)e^{-\Delta W/kT}dx}{\int_{-1}^{1}e^{-\Delta W/kT}dx} , \tag{29}$$

where

$$\Delta W=E_--E_1=-\gamma/2-E_1,\quad x=\cos\beta . \tag{30}$$

The energy difference ΔW occurring in the Boltzmann factor can be written in a recognizable form by expanding γ given in Eq. (4) to obtain

$$\Delta W=-\boldsymbol{\mu}_{11}\cdot\mathbf{E}_s-(\boldsymbol{\mu}\cdot\mathbf{E}_s)(\boldsymbol{\mu}\cdot\mathbf{E}_s)/\Delta E+\cdots . \tag{31}$$

Thus ΔW is the interaction energy, in the two-level approximation, arising from the interaction of the molecule in state 1 with the applied static field in the absence of the time-dependent oscillating field; the first term on the right-hand side of Eq. (31) represented the interaction of the permanent dipole of the molecule with the applied static field whereas the second term is the field-induced dipole induction energy. The Boltzmann factor used in Eq. (29) is appropriate for the initial conditions for which Eq. (24) is valid, namely the molecule is in state 1 at $t=0$. In calculating the exact rotationally averaged results, $\bar{P}_2^N$ in Eq. (29) is replaced by $\bar{P}_2$ as evaluated using the Floquet techniques referred to previously.

IV. EXAMPLES AND DISCUSSION

Setting $\mathbf{E}_s=0$ in Eq. (24) yields a previous RWA result[1] for the resonance profile of a two-level molecule with nonzero diagonal dipole matrix elements (permanent dipole moments):

$$\bar{P}_2(E_s=0)=\frac{|C(N,E_s=0)|^2}{2[(\Delta E-N\omega)^2+|C(N,E_s=0)|^2]}\ , \tag{32}$$

where

$$C(N,E_s=0)=2\boldsymbol{\mu}\cdot\hat{\mathbf{e}}EN(\mathbf{d}\cdot\hat{\mathbf{e}}E/\omega)^{-1}J_N(\mathbf{d}\cdot\hat{\mathbf{e}}E/\omega)\ . \tag{33}$$

As $\mathbf{d}\rightarrow 0$, $C(N,E_s=0)=\boldsymbol{\mu}\cdot\hat{\mathbf{e}}E\delta_{N,1}$ and Eq. (32) gives the usual RWA result Eq. (28) for a one-photon transition in the absence of permanent dipole moments. Equation (33) is a generalization of the standard result for arbitrary N which corresponds to replacing the usual coupling between molecule and sinusoidal field, $\boldsymbol{\mu}\cdot\mathbf{E}$ by an effective frequency-dependent coupling term Eq. (33). The effects of permanent dipoles arise through a modulation of $\boldsymbol{\mu}\cdot\mathbf{E}$ by a multiplicative factor involving the Bessel function of argument $\mathbf{d}\cdot\hat{\mathbf{e}}E/\omega=(\boldsymbol{\mu}_{22}-\boldsymbol{\mu}_{11})\cdot\hat{\mathbf{e}}E/\omega$.

These results have been used to discuss some of the effects of nonzero diagonal dipole matrix elements on single-photon and multiphoton resonance profiles previously.[1,2] We augment our previous examples with the two-level model characterized by $\Delta E=0.10$, $\mu_{11}=2.35$, $\mu_{22}=8.85$, $\mu=\mu_{12}=3.0$, $E=5\times10^{-2}$ ($E_s=0$) for a fixed molecular configuration specified by $\boldsymbol{\mu}\|\mathbf{d}\|\mathbf{E}$; the molecular parameters are representative of a level configuration in substituted aromatic molecules exhibiting intense one-photon transitions.[21] The resonance profiles, for frequencies associated with the $N=1$, 2, and 3 photon resonances, evaluated from the RWA result Eq. (32) are compared with exact results in Figs. 1(a)–1(c). In qualitative agreement with an analysis[1] of Eq. (32) the RWA results [Figs. 1(a) and 1(b)] show resonances at $\omega=\Delta E/N$, resonance widths that decrease as N increases, and oscillatory fringes[1,2,22] since the frequencies correspond to values of $\mathbf{d}\cdot\hat{\mathbf{e}}E/\omega$ associated with the zeros of the Bessel functions occurring in $C(N,E_s=0)$. Since the parameters $\beta_N=N\mu E/\Delta E=1.5$, 3.0, 4.5, $N=1$, 2, and 3, respectively, are large, the agreement of the RWA results with the exact calculations [Fig. 1(c)] is not particularly good. However, it is much better than one would expect since the effective interaction parameters $\beta_N^{\text{eff}}=NC(N,E_s=0,\omega=\Delta E/N)/\Delta E=0.22$, 0.56, 0.01, for $N=1$, 2, and 3, respectively, are much smaller than β_N. The RWA results do not exhibit the dynamic background or the shifts from the zero-field resonance frequencies $\omega=\Delta E/N$ shown by the exact calculations, but they do suggest the oscillations observed in $\bar{P}_2$(exact) as a function of frequency and the narrowing of the resonance profiles as N increases. Also shown in Fig. 1(c) is the exact spectrum for $\mu_{11}=\mu_{22}=0$ ($d=0$) which corresponds to the coupling parameters β_N, $N=1$ and 3; the two-photon resonance is absent since the levels have definite parity under these conditions. The resonances are very broad and their dynamic background high corresponding to the large values of β_N. The comparison of the $d\neq0$ and $d=0$ calculations clearly shows the effect of the permanent dipoles on the resonance profiles and this is predicted, qualitatively, by the RWA model since $\beta_N^{\text{eff}}\ll\beta_N$. The Bloch-Siegert shifts of the resonance positions when $\mathbf{d}=\mathbf{0}$ are large and to the high-frequency side of the zero-field predictions. In contrast, when $d\neq0$ the shifts are again large but to the low-frequency side of the zero-field results. These "negative shifts" are due to the influence of the nonzero diagonal dipole matrix elements.[1,2,22]

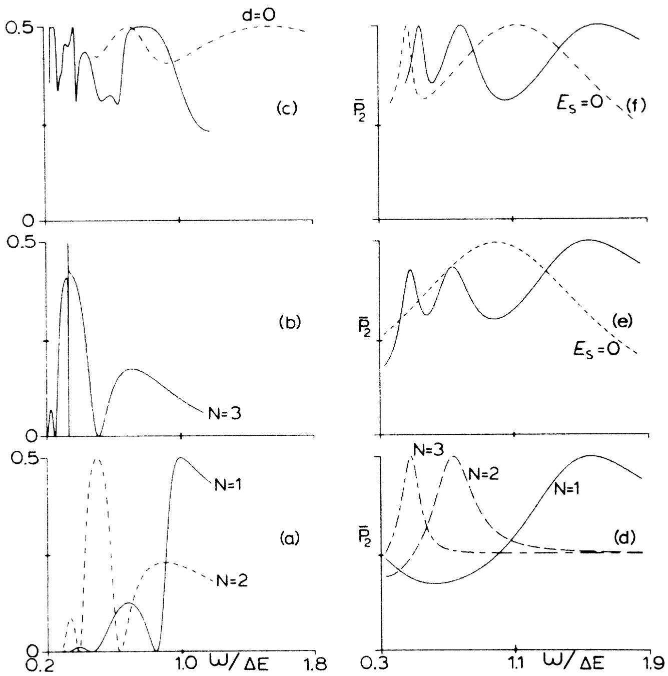

FIG. 1. Comparison of RWA and exact results for the steady-state transition probabilities $\bar{P}_2$, as a function of $\omega/\Delta E$, for two-level models specified by $\Delta E=0.1$, $\mu_{11}=2.35$, $\mu_{22}=8.85$, $\mu=\mu_{12}=3.0$, $d=\mu_{22}-\mu_{11}=6.5$, $E=5\times10^{-2}$, $E_s=0$ with $\boldsymbol{\mu}\|\mathbf{d}\|\mathbf{E}$ (left) and $\Delta E=2.151\times10^{-7}$, $d=0$, $\mu=2.6398$, $E=5.76\times10^{-8}$, $E_s=4.07\times10^{-8}$ with $\boldsymbol{\mu}\|\mathbf{E}\|\mathbf{E}_s$ (right). RWA resonance profiles for $N=1,2,3$ are illustrated in (a) and (b), and in (d), as evaluated from Eqs. (32) and (24), respectively. The sum of the profiles in (d) is given in (e), together with the analogous RWA result for $E_s=0$, see Eq. (28). The exact multiphoton spectra are illustrated in (c) and (f), (c) contains the spectra for $d=0$ for comparative purposes.

When $\mathbf{E}_s\neq0$ the RWA results become considerably more complicated, compare Eqs. (32) and (33) with Eqs. (24) and (16). In the presence of a static electric field one would expect[3,13,14,23] the resonances, in the RWA approximation, to occur at $\omega=\gamma/N$ since γ is the energy-level separation in the diagonalized $(+,-)$ representation of Sec. II. This in fact occurs for small but not for large values of E_s, see below.

As specific examples we first consider two where $d=0$, again for fixed molecule-field configurations specified by $\boldsymbol{\mu}\|\mathbf{E}\|\mathbf{E}_s$. Here $\mathbf{D}=-2\boldsymbol{\mu}\sin(2\theta)$, $\mathbf{M}=\boldsymbol{\mu}\cos(2\theta)$, $\gamma=[(\Delta E)^2+4(\mu E_s)^2]^{1/2}$, and in the coupling $C(N)$, connecting the molecule with the sinusoidal field, $\mathbf{D}$ and $\mathbf{M}$ play roles analogous to $\mathbf{d}$ and $\boldsymbol{\mu}$ in the $\mathbf{d}\neq\mathbf{0}$, $E_s=0$ problem. Also one would expect resonance frequency shifts to the high-frequency side of $\omega=\Delta E$ in the presence of a static field.

In Figs. 1(d) and 1(e) we consider the spectrum of a two-level system characterized by $\Delta E=2.151\times10^{-7}$, $d=0$, $\mu=2.6398$, $E=5.76\times10^{-8}$, and $E_s=4.07\times10^{-8}$; the molecular parameters[24] correspond to the $J=0\rightarrow J=1$ rotational transition in the ground vibrational level of

CsI. Figure 1(d) shows $\overline{P}_2^N$ for $N=1,2,3$ as a function of frequency and the resonance validity of the RWA-type expressions for $\overline{P}_2^N$ is clearly illustrated for this rather strong-coupled example where $\beta_N = N\mu E/\gamma = 0.50$, 1.0, 1.5, and $\beta_N^{\text{eff}} = [NC(N)/\gamma]_{\omega=\omega_{\text{res}}} = 0.34$, 0.41, 0.43, for the $N=1$, 2, and 3 resonances. For example, the RWA absorption profiles can be less than the static background $\overline{P}_2(\text{stat}) = 0.25$ for frequencies sufficiently far off resonance. In Fig. 1(e) the sum of the RWA results for $\overline{P}_2^N$, $N=1$, 2, 3, is compared with the RWA resonance profile with $E_s = 0$. Since $\mathbf{E}_s = 0$ and $\mathbf{d} = \mathbf{0}$, the RWA result of Eq. (24) reduces to the usual RWA expression Eq. (28) which supports only a one-photon transition. The effects of the static electric field are clear from Fig. 1(e); the occurrence of both even and odd photon transitions when $E_s \neq 0$ arises due to the mixing of the original states 1 and 2, of definite opposite parity, by the static field to produce two states of mixed parity in the diagonalized $(+,-)$ representation. As pointed out earlier one would expect the resonance frequencies to be shifted from $\omega = \Delta E/N$ when $E_s = 0$ to higher frequencies $\omega = \gamma/N$ for $E_s \neq 0$. In fact the RWA shift to higher frequencies is considerably greater than this since the coupling between the sinusoidal field and the molecule is reasonably large $(\mu E/\Delta E \sim 0.70)$: $\Delta E/N \approx 2.15\times10^{-7}$, 1.075×10^{-7}, and 0.717×10^{-7}; $\gamma/N \approx 3.04\times10^{-7}$, 1.52×10^{-7}, and 1.013×10^{-7}; $\gamma/\Delta E = 1.41$; while $\omega_{\text{res}}(\text{RWA}) \approx 3.35\times10^{-7}$, $1.58\ \times10^{-7}$, and 1.034×10^{-7}, for $N=1$, 2, and 3, respectively. The off-resonance difficulties associated with RWA solutions are again evident in these results; for example, the $N=2$ and 3 resonance peaks are below 0.5 and for $N=1$ the peak is slightly above 0.5. The adding of the RWA results for the various resonances profiles is not generally a reliable representation of $\overline{P}_2$ unless the applied fields are quite weak (see below). In Fig. 1(f) the exact two-level steady-state spectrum is compared with the spectrum for the same system with $E_s = 0$. The influence of $E_s \neq 0$ is clearly illustrated with the occurrence of the even two-photon transition and the large shifts of the odd photon resonances to higher frequency. The qualitative agreement of the RWA results of Figs. 1(d) and 1(e) with these exact results is reasonable for $E_s \neq 0$ and for $N=1$ when $E_s = 0$. When $E_s \neq 0$ the RWA predictions for the resonance positions agree reasonably well with the exact results and in all cases are more reliable than the expected result γ/N; $\omega_{\text{res}}(\text{exact}) = 3.45\times10^{-7}$, 1.70×10^{-7}, and 1.18×10^{-7}, for $N=1$, 2, and 3, respectively. Apparently the RWA result for $E_s \neq 0$ contains some of the Bloch-Siegert shift of the resonance frequencies to higher frequencies relative to γ/N.

An example of a weak-coupling case where the RWA results agree extremely well with the exact calculations is illustrated in Fig. 2; again $\boldsymbol{\mu} \| \mathbf{E} \| \mathbf{E}_s$, and the molecular parameters are identical to those in the example just discussed while $E = 5.0\times10^{-9}$ and $E_s = 3.24\times10^{-8}$ so that $\beta_N = 0.05$, 0.1, 0.15 and $\beta_N^{\text{eff}} = 0.038$, 0.005, 0.0005 for $N=1$, 2, and 3, respectively, and the static background $\overline{P}_2(\text{stat}) = 0.194$. The RWA and the exact results agree to much better than graphical accuracy and the resonance frequencies coincide with γ/N to four significant figures $(\gamma/\Delta E = 1.28)$. Also shown in this figure are the exact results for $\overline{P}_2$ when $E_s = 0$, the analogous RWA calculation agrees precisely with these except for the omission of the three-photon spike. The influence of the static field is again clear and is essentially precisely predicted using RWA results.

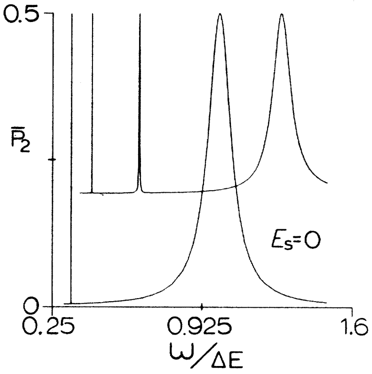

FIG. 2. The steady-state transition probability $\overline{P}_2$, as a function of $\omega/\Delta E$, for a two-level model system characterized by $\Delta E = 2.151\times10^{-7}$, $d=0$, $\mu = 2.6398$, $E = 5\times10^{-9}$, $E_s = 3.24\times10^{-8}$ with $\boldsymbol{\mu} \| \mathbf{E} \| \mathbf{E}_s$. The spectrum with $E_s = 0$ is included for comparative purposes.

As a final example we consider the two-level molecular model characterized by $\Delta E = 0.1899$, $\mu_{11} = 4.760$, $\mu_{22} = 8.415$, and $\mu = \mu_{12} = 2.486$ representative of the (linear) pentadienal molecule with intense $\pi \rightarrow \pi^*$ transitions.[25] Taking $\boldsymbol{\mu} \| \mathbf{d}$ and $\mathbf{E} \| \mathbf{E}_s$ we have evaluated the steady-state spectrum for frequencies associated with the $N=1-3$ photon resonances, for a variety of fixed molecular configurations relative to the field directions with $E = E_s = 10^{-3}$. Comparison of the RWA results with the corresponding exact calculations shows agreement to far better than graphical accuracy for all frequencies. The fixed configuration results for the one-photon resonance profiles for $(\boldsymbol{\mu},\mathbf{d}) \| (\mathbf{E},\mathbf{E}_s)$ and for $(\boldsymbol{\mu},\mathbf{d})$ antiparallel to $(\mathbf{E},\mathbf{E}_s)$ are shown in Fig. 3(a); the interaction parameters for the coupling to the sinusoidal field are $\beta_1 \sim \beta_1^{\text{eff}} = 0.0135$ and -0.0126, and the resonances occur at $\omega/\Delta E = 0.981$ and 1.020, i.e., $\omega/\gamma = 1$ for the given configuration, respectively. The two- and three-photon resonances, not shown explicitly in the figure, are sharp spikes of height 0.5 occurring at $\omega/\gamma = 0.5$ and $\frac{1}{3}$. The (free) rotationally averaged steady-state spectrum related to these fixed-orientation spectra is also included in the figure.

The differences between the fixed configuration and the rotational-averaged spectra in Fig. 3(a) can be qualitatively understood from the definition of $\langle \overline{P}_2 \rangle_{\text{rot}}$, Eq. (29), since the integrand in this result is just $\overline{P}_2$ evaluated at effective values of the primative coupling parameters μE, μE_s, dE, and dE_s given by μEx, etc., where $-1 \leq x \leq 1$. The effective coupling between the molecule and the oscillatory electric field is in fact $C(N)$ which involves the primitive coupling parameters in a complicated manner; see Eqs. (16), (6), (3), and (4). An analysis of $C(1)$, at $\omega = \gamma$, shows that it has a maximum value of $\sim 0.253\times10^{-2}$ when $x=1$, decreases smoothly to zero at $x=0$, and then increases in magnitude to $\sim 0.244\times10^{-2}$

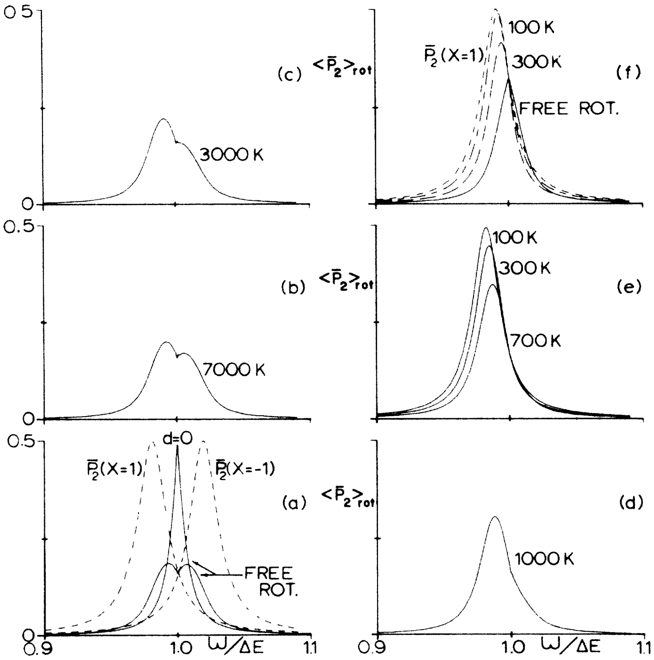

FIG. 3. Steady-state rotationally averaged one-photon resonance profiles $\langle \bar{P}_2 \rangle_{\text{rot}}$, as a function of $\omega/\Delta E$, for a two-level model molecule characterized by $\Delta E = 0.1899$, $\mu_{11} = 4.760$, $\mu_{22} = 8.415$, $d = 3.655$, and $\mu = \mu_{12} = 2.486$. The amplitude of the oscillating electric field is $E = 10^{-3}$ and the static field is $E_s = 10^{-3}$ for (a)–(e) and $E_s = 5 \times 10^{-4}$ for (f): (a) Fixed-configuration spectra with $\boldsymbol{\mu} \| \mathbf{d} \| \mathbf{E} \| \mathbf{E}_s$ ($x = 1$) and $\boldsymbol{\mu} \| \mathbf{d}$ antiparallel to $\mathbf{E} \| \mathbf{E}_s$ ($x = -1$); the free rotationally averaged spectrum with $\mathbf{d} = 3.655$ and, for comparative purposes, with $d = 0$. (b)–(e) The Boltzmann rotationally averaged spectra for $T = 7000$–100 K. (f) Fixed-configuration, free, and Boltzmann rotationally averaged spectra for $E_s = 5 \times 10^{-4}$.

at $x = -1$; further $C(1)$ is almost symmetrical about $x = 0$, being slightly smaller in magnitude for $x < 0$ than for $x > 0$. For a given configuration of the molecule with respect to the applied fields the resonance occurs when $\omega = \gamma$ for that configuration and, depending on the orientation, γ can be greater or less than ΔE, see the expression for γ given in Eq. (4); for example, the maximum and minimum values of γ are $\gamma(x = -1) = 0.1936$ and $\gamma(x = 1) = 0.1863$ while $\Delta E = 0.1899$. In general in the presence of permanent dipole moments the resonance can be either to the high- or low-frequency side of $\omega = \Delta E$ for a given fixed configuration of the molecule in the fields in contrast to the case[14,26] when $\mathbf{d} = 0$.

From the discussion of the last paragraph the steady-state spectrum for each configuration will show a resonance at $\omega = \gamma$ with a height of 0.5 and a width, see Eq. (27), which decreases with $C(1)$ as $|x|$ decreases from unity to zero. The free rotational-averaged spectrum is the sum of all such fixed-configuration spectra used to evaluate $\bar{P}_2$ divided by the number of configurations (x values); it was found that 41 values of x symmetrically placed about $x = 0$ were more than sufficient for this purpose. The parallel ($x = 1$) and antiparallel ($x = -1$) configuration $\bar{P}_2$ are the two end points in the evaluation of the rotationally averaged spectrum via Eq. (29); all other contributions to $\langle \bar{P}_2 \rangle_{\text{rot}}$ show resonances at frequencies between those for these two extremes and have narrower profiles which decrease to zero as $|x| \to 0$. This suggests the rotationally averaged spectrum lies between the two fixed-configuration extremes with two maxima substantially reduced from that (0.50) associated with fixed-configuration spectra and a minimum located at $\omega = \Delta E$ between the maxima [$C(N) = 0$ and $\gamma = \Delta E$ when $x = 0$]. This is in qualitative agreement with Fig. 3(a). The minimum in the averaged spectra is clearly due to the presence of $\mathbf{d} \neq 0$, as is clear from the expression for γ given in Eq. (4); the rotationally averaged spectrum for the molecule with $\mathbf{d} = 0$ is shown in Fig. 3(a) and consists of a single peak centered at $\omega = \Delta E$.

The Boltzmann-averaged single-photon resonance profiles related to Fig. 3(a) are shown in Figs. 3(b)–3(e) for temperatures $T = 7000$, 3000, 1000, and 700–100 K, respectively; the free rotational-averaged spectrum corresponds to "$T = \infty$." The Boltzmann factor occurring in $\langle \bar{P}_2 \rangle_{\text{rot}}$ favors the attractive ($x > 0$, $\gamma < \Delta E$) versus the repulsive ($x < 0$, $\gamma > \Delta E$) configurations of the molecule relative to the directions of the applied electric fields and thus, relative to the free rotational-averaged spectrum, the Boltzmann-averaged results increase for $\omega < \Delta E$ and decrease for $\omega > \Delta E$ as T decreases. The minimum occurring in the free rotational-averaged spectrum in Fig. 3(a) at $\omega = \Delta E$ gradually changes to a point of inflection at $T \sim 1000$ K [Fig. 3(d)] and then disappears for lower temperatures [Fig. 3(e)].

Finally, for the same molecule, with $E = 10^{-3}$ and $E_s = 5 \times 10^{-4}$, we compare the Boltzmann rotationally averaged spectra for $T = 300$ and 100 K with the free rotationally averaged spectrum and the fixed-configuration spectrum with $x = 1$. The lower static field leads to $\gamma(x = -1) = 0.1917$ and $\gamma(x = 1) = 0.1881$ which closely bracket $\Delta E = 0.1899$. Following the arguments used to discuss the spectra for the higher static field ($E_s = 10^{-3}$) this suggests the essential elimination of the minima in the free rotational-averaged spectrum on the graphical scale used in Fig. 3 and this is observed in Fig. 3(f). The enhancement of the spectra for $\omega < \Delta E$ relative to $\omega > \Delta E$ as T decreases is clearly evident in this figure.

In this paper we have developed a simple analytic expression for single-photon and multiphoton resonance profiles for a model two-level system, with permanent dipoles or nonzero diagonal dipole matrix elements, interacting with applied sinusoidal and static electric fields. These RWA results are applied to several illustrative examples chosen, in part, to show qualitatively the validity of the results as a function of the molecular and field parameters and their usefulness in understanding and interpreting spectra, including rotationally averaged spectra. In particular Eq. (16) provides a simple analytic expression which is very useful in helping to understand the effects of permanent dipole moments and the applied static field on the coupling between the molecule and the applied time-dependent sinusoidal field. As in all RWA or Rabi-type approximations our results for the resonance profiles become more reliable as the coupling between the transition dipole and the applied oscillating field becomes small. While the RWA results are designed to be valid on resonance, they often do remarkably well off resonance if this coupling is not too large.

The expression for the resonance profile $\bar{P}_2^N$ given by Eq. (24) is a generalization of the well-known RWA result for a one-photon transition in the absence of permanent dipoles or static fields, Eq. (28). It is relevant to point out our general result is not acceptable when $E_s=0$ for small d if $N=3,5,7,\ldots$, since $\bar{P}_2^N$ given by Eq. (24) goes to zero as $d\rightarrow 0$ under these conditions, a result physically correct only for even values of N. The corrections to our RWA results, including those required to rectify the latter problem, can be obtained by using Fourier expansions for $\underline{H}$ (see Sec. III and Ref. 1) to obtain a Floquet secular equation following earlier work[6,17,27–29] for the case $d=0$. Our result Eq. (24) corresponds to the zeroth- plus first-order terms of a complete Floquet perturbative analysis of the problem; the development of higher-order correction terms is in progress.

In Sec. IV a series of exact two-level model calculations were discussed, in part, to help investigate the validity of our RWA results. These calculations were mostly carried out using a recently developed Riemann product integral method[16] to determine the solution of the time-dependent wave equation over the first period of the time-dependent Hamiltonian; the solution for all other times, and the temporal and steady-state transition probabilities, are then readily obtained.[6,14–17] In past work a power-series technique[14,15] was often used to determine the solution over the first period of the Hamiltonian. A comparison of the power-series and Riemann methods for identical problems indicates that the Riemann technique is more efficient, particularly for problems involving permanent dipole moments and/or static electric fields,[30] and sinusoidal fields that result in large couplings $[\sim NC(N)/\Delta E]$ between the molecule and the field. For these situations, relative to weak-field problems, the power-series techniques require the initial period of the Hamiltonian to be subdivided into a large number of subintervals, with the power series being reexpanded in each subinterval and matched with the solution in the previous subinterval; often about 20–40 terms are used in each expansion. To obtain good convergence using the Riemann integral method the number of time steps used in the representation of the evolution operator on the first time period must be increased as the coupling between the sinusoidal field and the molecule grows. However, this increase is often not excessive and, more importantly, the approach avoids expansions and the matching of solutions at subinterval boundaries. Without attempting to completely optimize test calculations, it appears qualitatively that the Riemann integral method is, on the average, at least a factor of 4 more efficient than the power-series methods for the types of calculations considered in the paper. The Riemann product integral approach has been used previously in a study of multiphoton vibrational excitation in near-degenerate anharmonic systems using nonrotating rare-gas dimers as models,[22] in an application to nonsinusoidal fields involving a Gaussian pulse and the dependence of time-resolved and steady-state frequency sweep spectra on pulse characteristics,[16] and in an investigation of the enhancement of multiphoton processes by a static electric field.[26]

Detailed studies of the effects of permanent dipole moments on resonance profiles, including the effects of static fields, rotational averaging, and the influence of neighboring levels, will be the subject of future publications.

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