

Rotating-wave approximation for the interaction of a pulsed laser with a two-level system possessing permanent dipole moments

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A rotating-wave approximation (RWA) is developed to describe the evolution of a two-level system, which has permanent dipole moments, interacting with a pulsed laser. Comparisons with exact calculations for one- and two-photon excitations involving the two lowest vibrational states of the ground electronic state of HeH^+ are given to illustrate the validity of the RWA formula.

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I. INTRODUCTION

The two-level rotating-wave approximation (RWA) [1] has been used extensively in the study of laser-atom interactions [2]. The idea behind the RWA is that the fast oscillating terms in the Hamiltonian, i.e., those that vary as $\exp[i\gamma t]$ with $\gamma \neq 0$, tend to average out to zero, and therefore can be neglected. This allows simple analytical formulas to be obtained for the prediction and analysis of the laser-atom interaction. Analytical RWA solutions for a two-level atomic system interacting with a continuous wave (CW) laser or a pulsed laser are known [1–4]. More recently a two-level RWA was developed for a two-level (dipolar) molecule interacting with a CW laser [5–7]. The purpose of this paper is to derive, with illustrative applications, a RWA applicable to the interaction of a two-level (dipolar) molecule with a pulsed laser. In the context of this paper, a dipolar molecule refers to a system where the diagonal dipole moment matrix elements, for the states of the species under consideration, are non-zero ($\mu_{ii} \neq 0$).

The RWA analytical formulas for the observables for a CW laser interacting with a two-level molecule are identical to the analogous atomic formulas if the atom-CW laser coupling is replaced by the molecule-CW laser coupling [5]. Aside from issues concerning the structure of the molecule relative to the structureless atom [6,8], the atomic and non-dipolar molecule-laser couplings are the same, since the diagonal dipole moment matrix elements μ_{ii} are zero in both cases. However, for dipolar molecules, the molecular states do not have definite parity, $\mu_{ii} \neq 0$. Then if d , the difference between the “permanent dipoles” of the two states involved in the transition, is not zero, significant differences can occur between the ($d=0$) atom- and ($d \neq 0$) molecule-CW laser couplings [5–7]. An important characteristic parameter in this context is $z=(d\varepsilon/\omega)$ where ε is the electric field strength and ω is the circular frequency of the laser. For one-photon transitions between two states of a dipolar mol-

ecule, the effects of permanent dipoles become important only if z is relatively large [5–7]. This can arise through a large difference in permanent dipole moments d (“giant dipole molecules” [9,10]), a large electric-field strength ε [7], a small circular frequency ω (e.g., microwave transitions [11,12]), or a combination of all three effects. On the other hand, a situation where these dipolar effects can never be neglected is when there are processes, otherwise forbidden, which are allowed in the presence of “permanent dipole moments.” An example is the two-photon transition between two states of a dipolar molecule; in the two-level model, such a transition is forbidden in an atom [5,6,8,10].

While the RWA for a CW laser-molecule interaction is useful in many contexts, it cannot give reliable results for the dynamics associated with the interaction of a pulsed laser with a two-level molecule. For example, it cannot be used to predict how to control population transfer from one state to another state by adjusting the characteristic parameters of a pulsed laser. In Sec. II, the theoretical development of the RWA for the interaction of a pulsed laser with a molecule is given. The pulsed laser-atom results of Rosen and Zener [3] are obtained in the limit $d=0$, and the CW laser-molecule expression of Kmetc and Meath [5] is recovered in the limit of “infinite” pulse duration. Illustrative examples, comparing the RWA solution for the temporal behavior of the molecular states with exact calculations, involving one- and two-photon excitations induced by Gaussian pulses, are discussed in Sec. III. The ground and first excited vibrational states of the ground electronic state [13,14] of the very anharmonic molecule HeH^+ are used as a two-level system for this purpose. A brief summary of our results, including comments relative to many-level molecules, is given in Sec. IV. Unless indicated otherwise, atomic units are used throughout this paper.

II. THEORETICAL DEVELOPMENT

The time-dependent Schrödinger equation for a two-level system interacting with a pulsed laser in the semiclassical dipole approximation is

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$$\begin{aligned}
i \frac{d}{dt} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} &= \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \\
&= \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} - \underline{\varepsilon}(t) \cdot \begin{pmatrix} \underline{\mu}_{11} & \underline{\mu}_{12} \\ \underline{\mu}_{21} & \underline{\mu}_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix},
\end{aligned} \tag{1}$$

where E_i is the energy of the i th stationary state of the original system, $\underline{\mu}_{ij}$ are the dipole moment matrix elements defined with respect to the stationary states, and $\underline{\varepsilon}(t)$ is the time-dependent electric field associated with a pulsed laser. In order to help identify the resonances in Eq. (1), and to incorporate the effects of the diagonal dipole matrix elements into the RWA, it is convenient [5] to transform from the \underline{a} representation to the interaction representation \underline{b} defined by

$$a_j = b_j \exp \left\{ -i \left[E_j(t-t_0) - \underline{\mu}_{jj} \cdot \int_{t_0}^t \underline{\varepsilon}(t') dt' \right] \right\}, \tag{2}$$

where t_0 is the time the pulse-system interaction begins. Substituting Eq. (2) into Eq. (1) yields

$$i \frac{d}{dt} \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} 0 & \hat{H}_{12} \\ \hat{H}_{21} & 0 \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \end{pmatrix}, \tag{3}$$

where

$$\begin{aligned}
\hat{H}_{12} = \hat{H}_{21}^* &= -\underline{\mu}_{12} \cdot \underline{\varepsilon}(t) \\
&\times \exp \left[-i \Delta E(t-t_0) + i \underline{d} \cdot \int_{t_0}^t \underline{\varepsilon}(t') dt' \right],
\end{aligned} \tag{4}$$

$$\Delta E = E_2 - E_1 > 0, \tag{5}$$

$$\underline{d} = \underline{\mu}_{22} - \underline{\mu}_{11} \tag{6}$$

and assuming $\underline{\mu}_{12}$ is real. We consider here a ‘‘one-color’’ pulsed laser where the time-dependent electric field is given by

$$\underline{\varepsilon}(t) = \hat{\varepsilon} \varepsilon_0 f(t) \cos(\omega_0 t + \delta), \tag{7}$$

where $\hat{\varepsilon}$, ε_0 , $f(t)$, ω_0 , and δ are the polarization vector, field strength, pulse envelope, carrier circular frequency, and phase of the laser; we assume $f(t) = 0$ for $t \leq t_0$.

For our analysis, we follow the methods used previously in the derivation of RWAs for the interaction of a CW laser, i.e., $f(t) = 1$, with a dipolar molecule ($d \neq 0$) [5] coupled with those used for the interaction of a pulsed laser with an atom ($d = 0$) [3]. The crucial part of Eq. (4) is the quantity

$$I = \exp[i \underline{d} \cdot \hat{\varepsilon} \varepsilon_0 Q], \tag{8}$$

where

$$Q = \int_{t_0}^t f(t') \cos(\omega_0 t' + \delta) dt'. \tag{9}$$

Integrating Eq. (9) by parts, one obtains

$$Q = \frac{1}{\omega_0} f(t) \sin(\omega_0 t + \delta) - \frac{1}{\omega_0} \int_{t_0}^t \frac{df(t')}{dt'} \sin(\omega_0 t' + \delta) dt'. \tag{10}$$

Generally, the time derivative of the pulse envelope (df/dt) is inversely proportional to τ , where τ is the duration of the pulse. Therefore, for a pulse whose duration is much longer than $(1/\omega_0)$, the second term in Eq. (10) can be neglected relative to the first term. With this assumption, one obtains

$$I = \exp[izf(t) \sin(\omega_0 t + \delta)], \tag{11}$$

where $z \equiv d \cdot \hat{\varepsilon} \varepsilon_0 / \omega_0$ is a parameter of importance in previous work [5–10] involving CW laser-polar molecule interactions. Using the identity [15]

$$\exp(ix \sin \vartheta) = \sum_{k=-\infty}^{\infty} J_k(x) \exp(ik\vartheta), \tag{12}$$

Eq. (11) can be written as

$$I = \sum_{l=-\infty}^{\infty} J_l(zf(t)) \exp[il(\omega_0 t + \delta)], \tag{13}$$

where $J_l(x)$ is a Bessel function of integer order l and argument x .

Using Eq. (13), via Eq. (8), in Eq. (4) and expanding the cosine function in Eq. (7) in complex exponential form, yields

$$\begin{aligned}
\hat{H}_{12} &= -\frac{1}{2} (\underline{\mu}_{12} \cdot \hat{\varepsilon} \varepsilon_0) f(t) \exp[i \Delta E t_0] \\
&\times \sum_{l=-\infty}^{\infty} J_l(zf(t)) \{ \exp[i(l+1)\delta] \\
&\times \exp[-i(\Delta E - (l+1)\omega_0)t] + \exp[i(l-1)\delta] \\
&\times \exp[-i(\Delta E - (l-1)\omega_0)t] \}.
\end{aligned} \tag{14}$$

Imposing the N -photon resonant condition $\Delta E = N\omega_0$, $N = 1, 2, 3, \dots$, changing the summation indices to $k = l+1$ and $k = l-1$ in terms one and two, respectively, on the right-hand side of Eq. (14), and making the usual rotating-wave approximation by neglecting the off-resonant or counter-rotating terms in Eq. (14), gives

$$\begin{aligned}
\hat{H}_{12} &= -\frac{1}{2} (\underline{\mu}_{12} \cdot \hat{\varepsilon} \varepsilon_0) f(t) [J_{N-1}(zf(t)) + J_{N+1}(zf(t))] \\
&\times \exp[i(\Delta E t_0 + N\delta)] \exp[-i(\Delta E - N\omega_0)t].
\end{aligned} \tag{15}$$

The solution of Eq. (3) with \hat{H}_{12} given by Eq. (15) is generally not attainable analytically unless the pulsed laser is exactly on the RWA resonance, so that $N\omega_0 = \Delta E$ [3,4]. By defining a new independent variable $\Omega(t)$ as

$$\begin{aligned}\Omega(t) &= \int_{t_0}^t [J_{N-1}(zf(t')) + J_{N+1}(zf(t'))]f(t')dt' \\ &= \frac{2N}{z} \int_{t_0}^t J_N(zf(t'))dt',\end{aligned}\quad (16)$$

the transformed equation (3) can be readily solved as a function of Ω [3]. Assuming the system is initially in state 1, the probabilities, $P_j(t)$, of finding the system in states 1 and 2 at time t are given by

$$P_1(t) = |a_1(t)|^2 = |b_1(t)|^2 = \cos^2[\frac{1}{2}\underline{\mu}_{12} \cdot \hat{e}\varepsilon_2\Omega(t)],\quad (17)$$

$$P_2(t) = |a_2(t)|^2 = |b_2(t)|^2 = \sin^2[\frac{1}{2}\underline{\mu}_{12} \cdot \hat{e}\varepsilon_2\Omega(t)],\quad (18)$$

Aside from the assumption involving the RWA itself, the derivation of the state populations to this point involves only one assumption, namely, the neglect of the second term in Eq. (10), which requires $(\omega_0\tau)^{-1}$ to be small. Generally, the evaluation of $\Omega(t)$ will require a numerical integration of Eq. (16). In some situations, one can proceed analytically by using the expansion [15]

$$J_l(zf(t)) = f^l(t) \sum_{n=0}^{\infty} \frac{[z(1-f^2(t))/2]^n}{n!} J_{l+n}(z). \quad (19)$$

Various approximations for $\Omega(t)$ can be obtained by substituting Eq. (19) into Eq. (16), and truncating the infinite series in Eq. (19) appropriately. The relevant integrals can be evaluated, as a function of t , for many choices of pulse envelope $f(t)$. Keeping terms through order z^{N+1} gives

$$\begin{aligned}\Omega(t) &= \int_{t_0}^t \{ [J_{N-1}(z) + (N+1)J_{N+1}(z)]f^N(t') \\ &\quad - NJ_{N+1}(z)f^{N+2}(t') \} dt',\end{aligned}\quad (20)$$

where the correction terms to this result begin with order z^{N+3} . These results yield literature expressions as special cases. Choosing $f(t) = 0$ for $t \leq 0$ and $f(t) = 1$ for $t > 0$, gives $\Omega(t) = 2NJ_N(z)t/z = [J_{N-1}(z) + J_{N+1}(z)]t$ which, upon substitution into Eqs. (17) and (18), yields the CW laser-molecule RWA state populations derived previously [5–7]. Setting $d=0$, corresponding to $z=0$, gives $\Omega(t) = \delta_{N,1} \int_{t_0}^t f(t')dt'$, and substitution into Eqs. (17) and (18) reproduces the original RWA for the state populations for pulsed laser-atom interactions [3], which support only a one-photon transition.

Following previous discussions [3–7] of the RWA approximation, one can identify a pulsed laser-molecule coupling in Eq. (15) for the N -photon transition,

$$\begin{aligned}C^p(N) &= (\underline{\mu}_{12} \cdot \hat{e}\varepsilon_0) [H_{N-1}(zf(t)) + J_{N+1}(zf(t))]f(t) \\ &= (\underline{\mu}_{12} \cdot \hat{e}\varepsilon_0) \frac{2N}{z} J_N(zf(t))f(t).\end{aligned}\quad (21)$$

Since, for a pulsed laser, $C^p(N)$ is a function of time through the pulse envelope $f(t)$, it is more convenient for the discussion of the validity of the RWA to use $C^p(N)$ in the limit $f(t) = 1$, namely,

$$C(N) = (\underline{\mu}_{12} \cdot \hat{e}\varepsilon_0) \frac{2N}{z} J_N(z),\quad (22)$$

which is the CW laser-molecule coupling introduced in the literature previously [5]. Since $0 \leq f(t) \leq 1$, the CW coupling will usually be greater than $C^p(N)$. Defining the dimensionless laser-molecule coupling strength parameter as

$$b(N) = \frac{|C(N)|}{(\Delta E/N)},\quad (23)$$

the criterion for the validity of the pulsed RWA will be that $b(N) \ll 1$ [subject to $(\omega_0\tau)^{-1}$ being ‘‘small’’]. This is the criterion for the validity of the CW laser RWA used in the literature [2,5,6,10,16], and past numerical experience suggests that if $b(N) \ll 0.1$ the RWA works well for a two-level model. That the CW criterion is appropriate is not unreasonable, since the CW laser-molecule interaction underlies the pulsed laser-molecule interaction, with the maximum amplitude of the electric field for the pulsed laser being that of the CW laser. The temporal evolution of the molecular states under the influence of a pulsed laser qualitatively corresponds to the cutting off of the analogous CW laser results for times on the order of $\pm\tau$ [7]. In discussing the time-dependent populations of the states for a pulsed laser, the period p_N , for the underlying populations of the analogous CW laser case, is often useful [5–7,17]:

$$p_N = \frac{2\pi}{|C(N)|}.\quad (24)$$

III. NUMERICAL EXAMPLES

In this section, we give a few numerical examples using the pulsed-laser-molecule RWA expression for the state populations derived in Sec. II. Comparison with exact results for the populations will give insights into the reliability and applicability of the RWA. The two-level model used in the examples corresponds to the two lowest vibrational states of the ground electronic state of HeH^+ [13,14]. The relevant system properties are $\mu_{01} = \mu_{10} = \mu = -0.354 \text{ D}$ (-0.139 a.u.), $d = (\mu_{11} - \mu_{00}) = 0.259 \text{ D}$ (0.102 a.u.), and $\Delta E = E_1 - E_0 = 2901.44 \text{ cm}^{-1}$ (0.0132 a.u.) with $\underline{\mu} \parallel \underline{d}$. The pulsed laser is assumed to have a Gaussian envelope,

$$f(t) = \exp\left[-\frac{t^2}{\tau^2}\right],\quad (25)$$

where τ is the characteristic pulse duration. The system is in the ground state, state 0, initially. Both one- and two-photon transitions from state 0 to state 1 will be considered in what follows.

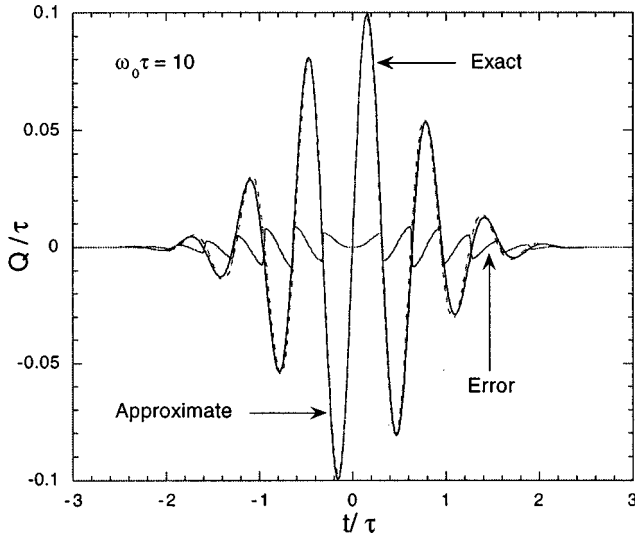


FIG. 1. Plots of the left-hand side of Eq. (10), in the form of Q/τ , the first term on the right-hand side of Eq. (10), and their difference, as a function of t/τ , for a Gaussian pulse with $\omega_0 = 0.0132$ a.u. and $(\omega_0\tau) = 10$.

The exact solution to Eq. (1) for the state populations is obtained by using the Crank-Nicholson method [18–20]. For a small time step Δt , where the pulse can be considered constant, one has

$$\underline{a}(t + \Delta t) = \exp[-i\mathbf{H}\Delta t]\underline{a}(t) \approx \left[\frac{1 - i\mathbf{H}(\Delta t/2)}{1 + i\mathbf{H}(\Delta t/2)} \right] \underline{a}(t). \quad (26)$$

Equation (26) is applied repeatedly to obtain the populations for all times of interest given the appropriate initial conditions. For the examples discussed below, a time step of 0.01 fs is employed which gives results well within graphical accuracy, as verified by comparison with the results from a time step of 0.001 fs.

In the RWA calculations presented here, the state populations are obtained using Eqs. (17) and (18), with $\Omega(t)$ evaluated numerically, via Eq. (16), by employing a simple trapezoidal scheme with time steps of 0.01 and 0.00 fs. In all cases, the effective time domain is taken as $-4\tau \leq t \leq 4\tau$. Finally, while the RWA results for the populations of the molecular states are independent of the phase δ of the laser, the exact results are generally not [21], so our model calculations all correspond to the choice $\delta = 0$.

As discussed in Sec. II, the derivation of the RWA expression for the populations of the molecular states requires the neglect of the second term on the right-hand side of Eq. (10). The condition for this to be valid is $\tau \gg \omega_0^{-1}$ or $(\omega_0\tau)^{-1} \ll 1$. To verify that keeping the first term on the right-hand side of Eq. (10) is sufficient for practical purposes, we have evaluated the left-hand side numerically and compared it with the approximation for $\omega_0 = \Delta E = 0.0132$ a.u. and $(\omega_0\tau)^{-1} = 0.1$ and 0.01, respectively. The results are shown in Figs. 1 and 2, where they are plotted in the form Q/τ versus t/τ . As can be seen, the approximation is a very good one even for the smaller value of $(\omega_0\tau)$

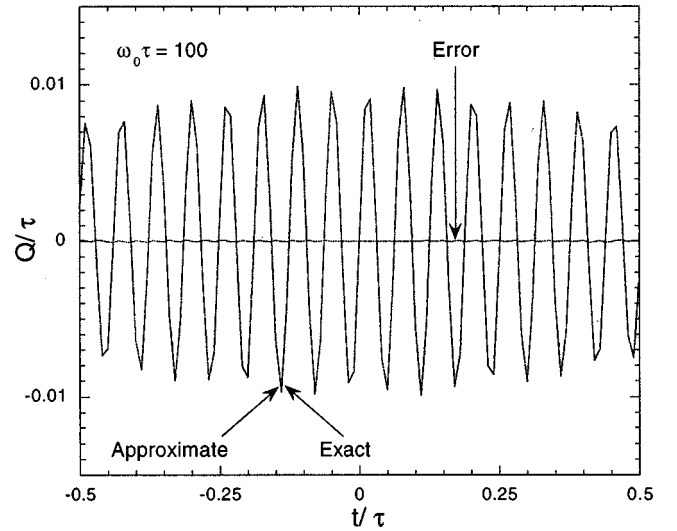


FIG. 2. Same as Fig. 1, with $(\omega_0\tau) = 100$.

$= 10$. These calculations are for the one-photon $0 \rightarrow 1$ resonance frequency, and $(\omega_0\tau) = 10$ and 100 correspond to pulse durations of 18.325 and 183.25 fs, respectively. For a given ΔE and $(\omega_0\tau)$, the validity of the approximation will be the same for a one- versus N -photon transition if the pulse duration of the latter is increased by a factor N relative to the one-photon τ .

In Figs. 3 and 4, the RWA result for the population of state 0, $P_0(t)$ given by Eq. (17), is compared with the exact result for the one-photon $0 \rightarrow 1$ transition with $\omega_0 = \Delta E$, the laser intensity $I = 5 \times 10^{12}$ W/cm² [the conversion factor from intensity to electric field is I (in W/cm²) = $3.5095 \times 10^{16} \epsilon^2$ (in a.u.)], and for $\tau = 18.325$ and 183.25 fs, respectively. The population of state 1 is just $P_1(t) = 1 - P_0(t)$. The RWA and the exact results agree well for both pulse durations with the

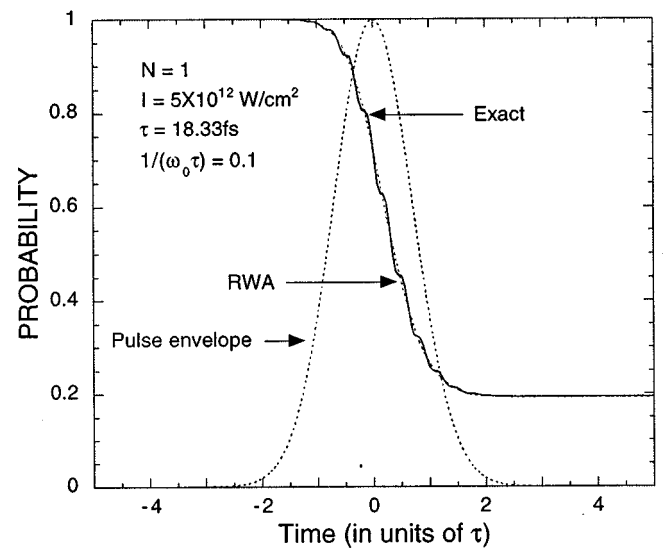
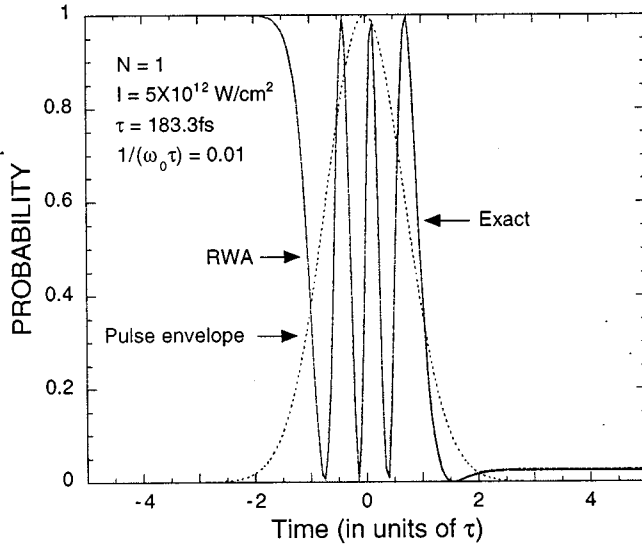


FIG. 3. Plots of the population of the ground state as a function of t/τ with $\tau = 18.33$ fs for $N = 1$ (one-photon transition). The solid curve is an exact calculation, and the dashed curve is the RWA result. Also shown is the pulse envelope.


 FIG. 4. Same as Fig. 3, with $\tau=183.3$ fs.

agreement improving as τ increases, as expected. In both cases, the RWA is valid, since the laser intensity is such that the dimensionless laser-molecule coupling is relatively weak, $b(1)=|C(1)|/\Delta E\sim 0.12$. The period of $P_0(t)$ for a CW laser, i.e., $f(t)=1$, is $p_{N=1}=2\pi/|C(N=1)|\sim 91.7$ fs, and one can see the periodic nature of $P_0(t)$ unfolding in Figs. 3 and 4 as the pulse duration lengthens, appropriately modified due to the “cutoff” imposed by the pulse envelope for large $|t|$.

For the laser intensities associated with Figs. 3 and 4, the effects of $d\neq 0$, i.e., of permanent dipoles, are minimal for one-photon transitions. The results for $d=0$ are graphically indistinguishable from those given in Figs. 3 and 4 for $d=0.102$ a.u. For this value of d , $z=d\cdot\hat{e}\varepsilon_0/\omega_0$ is about 0.092, and so $C(1)\approx\mu_{01}\cdot\hat{e}\varepsilon_0$ which is the well-known atomic ($d=0$) result derived by Rabi [1] many years ago. In order to see a more pronounced effect of permanent dipoles for one-photon transitions, a z value such that $J_1(z)/z$ is not close to the $z=0$ result of 0.5 [5–7] is required. For example, let us consider the case $z=1.5$ where $J_1(z)/z\sim 0.372$. To achieve this z for the one-photon $0\rightarrow 1$ transition in HeH^+ requires a laser intensity $>10^{15}$ W/cm². This z can also be obtained by artificially inflating d from 0.102 to 1.663 a.u. while keeping the laser intensity fixed at $I=5\times 10^{12}$ W/cm². The results of $P_0(t)$ versus t/τ , for $d=1.663$ a.u. and $d=0$, are shown in Fig. 5, with $\tau=183.25$ fs. In both cases, the pulsed RWA and the exact calculation agree well. The effects of permanent dipoles are clearly seen through the decrease in the laser-molecule coupling for $d\neq 0$ versus $d=0$; more Rabi-type oscillations occur for $d=0$ relative to $d\neq 0$. The dimensionless coupling strength parameter and the Rabi period for $d=1.663$ a.u. are $b(1)\sim 0.093$ and $p_1=123$ fs, while for $d=0$ they are $b(1)\sim 0.13$ and $p_1=91.7$ fs. Permanent dipole differences, i.e., d , of 1.663 a.u. or larger can occur in the IR for molecules considerably more anisotropic than HeH^+ . Such d values can be more common in the UV, and are of importance in the optical properties of “giant dipole” molecules. [9,10,17]

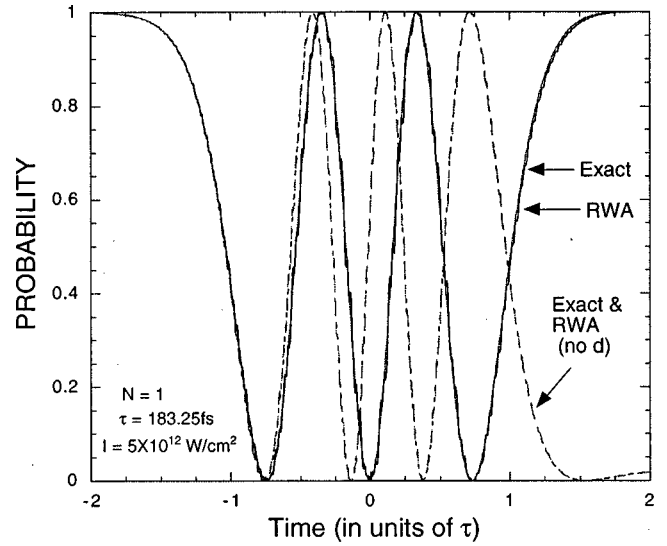


FIG. 5. Plots of the ground-state population for the case $z=1.5$ (see the text for explanation). Results for $d=0$ and $d\neq 0$ are shown for comparison. The exact and RWA results track each other very well for either case. The results for no d ($d=0$) have three maxima, compared to two for the results with d .

We now consider the two-photon $0\rightarrow 1$ transition in HeH^+ . The effects of permanent dipoles are very important for two-photon transitions, since this transition is forbidden in the two-level model for $d=0$ [5,6,8,17]. Furthermore, for many-level dipolar systems, the “direct” permanent dipole mechanism for two-photon transitions can be more effective than those involving virtual states [17]. For $\omega_0=\Delta E/2$ and $I=10^{11}$ W/cm², the agreement between the RWA result for the population of the ground state is compared with the exact result, as a function of (t/τ) , in Figs. (6)–(8) for pulse durations $\tau=8, 20,$ and 40 ps, respectively. The reason for

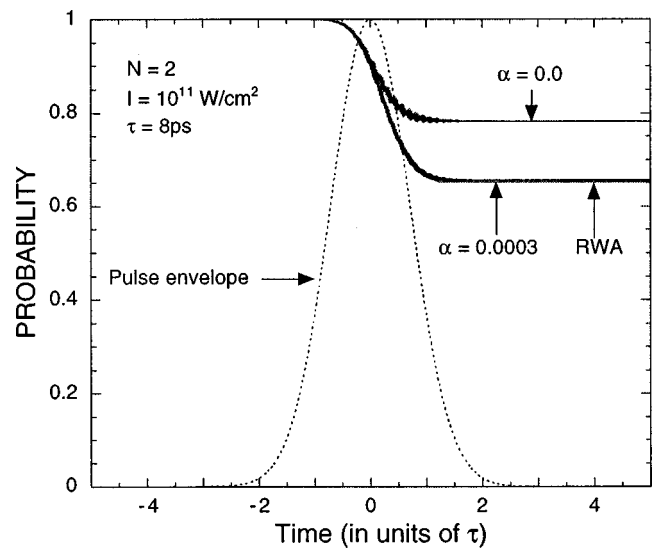


FIG. 6. Plots of the ground-state population as a function of t/τ for $N=2$ (two-photon transition). Exact calculations for $\alpha=0$ and 3.0×10^{-4} (see the text for explanation) and the RWA result are shown. Also shown is the pulse envelope which has $\tau=8$ ps.

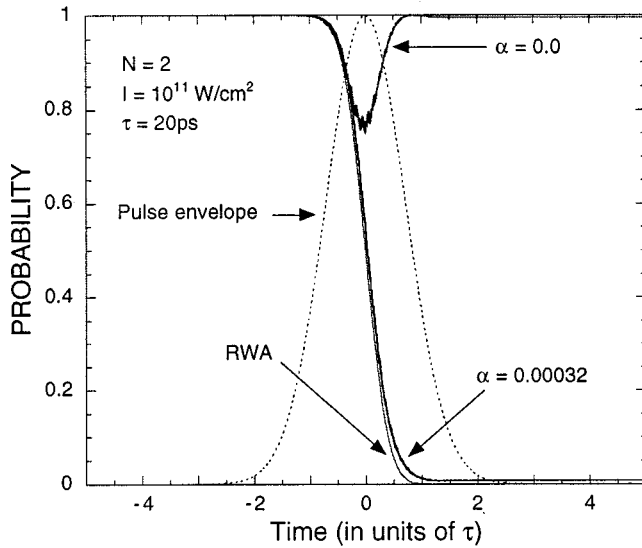


FIG. 7. Same as Fig. 6, with $\tau=20$ ps. The exact calculations are for $\alpha=0$ and 3.2×10^{-4} , respectively.

using pulses of longer duration, relative to the one-photon case, is that the two-photon coupling is weaker and therefore a longer pulse duration is required to probe the Rabi period. Even though the two-photon coupling parameter $b^{(2)} \sim 0.0005$ is much smaller than 0.1, the agreement between the RWA results and the exact calculations (curves labeled $\alpha=0$) is very poor, except for small times where the pulse-molecule interaction is very weak. This discrepancy arises because the RWA two-photon resonance frequency is not in good agreement with the exact resonance frequency for the laser-molecule interaction except for extremely weak laser-molecule couplings, i.e., at small times. For two-photon transitions, in contradistinction to one-photon transitions, the Bloch-Siegert shift $\Delta\omega^{(2)}$ of the exact resonance frequency away from the RWA value of $\Delta E/2$ is generally greater than, or of the same magnitude as, the half width at half maximum

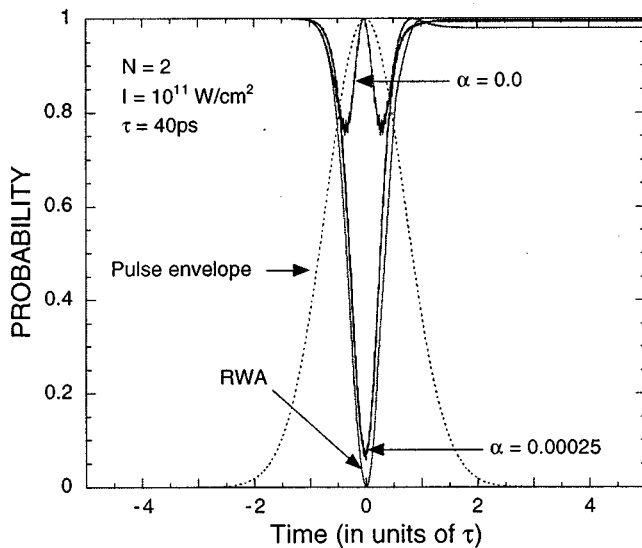


FIG. 8. Same as Fig. 6, with $\tau=40$ ps. The exact calculations are for $\alpha=0$ and 2.5×10^{-4} , respectively.

(HWHM)⁽²⁾ of the resonance [8,10]. Thus the two-photon resonance will often be missed or significantly reduced in the exact calculation when $\omega_0 = \Delta E/2$, and hence there is significant discrepancy in Figs. 6–8 between the RWA and exact results.

For a pulse-laser–molecule interaction, $\Delta\omega^{(2)}$ and HWHM⁽²⁾ are functions of time, and expressions for these quantities are not available. Again one can use the CW expression for these quantities, which are available [10], as a guide. For a field strength corresponding to the peak field strength of the pulse associated with Figs. 6–8, the values of $\Delta\omega^{(2)}$ and HWHM⁽²⁾ are 2.8×10^{-6} and 1.5×10^{-6} a.u., respectively. The corresponding values for the one-photon transition are $\Delta\omega^{(1)} = 1.0 \times 10^{-6}$ a.u. and HWHM^{(1)} = 1.1×10^{-4} a.u. The CW estimates show that the frequency shift $\Delta\omega^{(2)}$ is larger than the HWHM⁽²⁾ of the two-photon transition. To obtain better agreement with the RWA results, one needs to use a “shifted” resonance frequency in the exact calculation. Since there is no expression for the frequency shift in the pulsed-laser situations, an effective resonance frequency can be found only by using a brute force method. We define a parameter α by the relation $\omega_0 = (1 + \alpha)\Delta E/2$. The exact solution for the population of state 0, $P_0(t)$, is calculated as a function of α . The α that has a steady state population, i.e., $P_0(t \rightarrow \infty, \alpha)$, that comes closest to the RWA result is taken to correspond to the resonance shift. The results obtained using this method are included in Figs. 6–8 for comparison. For $\tau=8, 20,$ and 40 ps, the α values (or equivalently the effective frequency shift $\Delta\omega^{(2)} = \alpha\Delta E/2$) are 3.0×10^{-4} (2.0×10^{-6} a.u.), 3.2×10^{-4} (2.1×10^{-6} a.u.), and 2.5×10^{-4} (1.7×10^{-6} a.u.), respectively. As expected, the shift is less than the Bloch-Siegert shift for the peak pulse field strength.}

With the use of the parameter α , we were able to match the final ground-state population quite well. The RWA (exact) steady state ($t \rightarrow \infty$) ground-state population for the cases shown in Figs. 6–8 are 0.652 (0.656), 2.1×10^{-6} (7.70×10^{-3}), and 0.994 (0.997), respectively. Inspection of Figs. 6–8 illustrates how the appropriately modified CW temporal behavior of the populations of the molecular states unfolds as the pulse duration increases from 8 to 40 ps for a constant laser intensity of 10^{11} W/cm². Figure 7 shows a case of complete population transfer from the ground state to the excited state after the laser-molecule interaction has ceased, while Fig. 8 shows the return of the population to the ground state for a longer pulse. We note, however, that the agreement in the overall temporal behavior of the ground-state population between the RWA and exact results is not as good for the longer pulse duration of 40 ps (see Fig. 8) as compared to the shorter pulse durations. This is understandable in light of the fact that the Bloch-Siegert shift is a function of time, whereas we are using a constant frequency shift in our exact calculations throughout the pulse duration.

IV. SUMMARY

RWA formulas for the interaction of a pulsed laser with a two-level system possessing permanent dipole moments have been derived. The derivation requires the pulse duration

to be larger than the inverse of the carrier frequency in addition to the usual RWA conditions; these requirements are achievable in many cases. For example, for IR excitation, a pulse duration in the picosecond range is generally sufficient. Numerical examples, comparing results obtained using the RWA expression with exact calculations for one- and two-photon excitations of a model two-level system based on the two lowest vibrational states of the ground electronic state of HeH^+ , are used for illustrative purposes. The one-photon results agree very well. For two-photon excitation, there is a complication because the Bloch-Siegert shift of the resonance frequency is larger than the HWHM of the resonance. Hence a comparison with the exact results is more difficult. An effective frequency shift was found, in a brute force way, to allow a comparison. Since the frequency shift is a function of time, utilizing an effective frequency shift becomes less effective as the pulse duration increases. This trend can be seen in Figs. 6–8. The problem with the frequency shift does not make the two-photon RWA formula less effective, since in practice the true resonance frequency must be found by scanning the laser carrier frequency whenever the shift is larger than the HWHM. The Bloch-Siegert shift is not a problem for one-photon transitions, since the HWHM is generally much larger than the frequency shift. As far as predicting the final-state population, both the one- and two-photon RWA formulas work quite well. The RWA expression can be used to determine the pulse duration and intensity needed to

achieve the desired population transfer from the initially populated state.

This paper is concerned with the RWA for two-level systems where simple analytical results can be derived for the physical observables of the system as it interacts with a laser. Generalizations of the RWA to the interaction of a many-level system with a CW laser have often been discussed in the literature, both with and without the inclusion of the effects of diagonal dipole matrix elements, see for example [14,22,23]. In such applications, even when full analytical formulas are not possible, the generalized RWA (GRWA) is still very useful since the static Hamiltonian is known analytically. For example, solutions based upon numerical integration of the time-dependent Schrödinger equation can be done with much larger time steps within the GRWA, relative to exact solutions, thereby increasing the computational efficiency. While the two-level model in this paper is useful in its own right, it also provides a basis for constructing a GRWA for a many-level system interacting with a pulsed laser.

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