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# Floquet theory response of two- and three-level systems interacting with pulsed electric fields

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Using Floquet theory together with a density matrix formalism, analytic expressions are derived that describe a typical pump-probe experiment on (a) a two-level, one-photon resonant model that mimics a system with two electronic states, and (b) a two-photon resonant three-level model. The time dependence of the amplitude of the pulsed electric fields is approximated by a square envelope. These expressions, which include all orders of the electric field, can be used to describe systems interacting with very intense fields, where perturbation theory fails. This description allows variation of both the order of the pump and probe pulse, as well as the pulse durations. These expressions, once expanded, are equivalent to the usual perturbative series expansion, within the square-envelope approximation. Using a  $\delta$  function approximation for the pulsed fields, a two-level system with an excited state vibrational manifold is also considered in a nonperturbative manner.

## I. INTRODUCTION

Ultrafast, multiple pulsed laser techniques have recently allowed measurements of transient or dynamical phenomena in a variety of systems. Transient spectral hole burning, arising from pump-induced changes in the spectrum, and interrogated with a probe pulse, has been observed,<sup>1,2</sup> as well as coherent vibrational states in the ground and excited electronic states of large molecules.<sup>3-5</sup>

These pump-probe techniques have recently allowed direct observation of reaction dynamics, such as the excited state *trans-cis* isomerization of the retinal chromophore in bacteriorhodopsin.<sup>5</sup> A perturbative theory in which the response, or polarization, is expanded around the time-dependent perturbation arising from the applied electric field, and the third-order polarization,  $P^{(3)}$ , proportional to the intensity of the pump pulse, is used to describe the nonlinear interactions, has successfully explained these dynamics.<sup>6,7</sup> For a pump-probe experiment, this usually assumes a second-order electric field dependence on the pump pulse and a first-order dependence on the probe pulse. This type of perturbative description has also been used to explain the dynamics of spectral hole burning, photon echoes, and pump-probe experiments of two-level and three-level systems.<sup>8-10</sup>

For a very intense pulsed laser, however, there is the possibility that higher-order terms such as  $P^{(5)}$  may also be present in the nonlinear optical response. Recent efforts to understand population transfer via stimulated Raman scattering also require inclusion of higher-order, intensity-dependent polarizabilities.<sup>11-13</sup> For monochromatic, continuous wave lasers, higher-order nonlinear polarizations have been shown to be important for three-level systems describing nonlinear optical polymers.<sup>14</sup>

Both numerical and analytic nonperturbative descrip-

tions of the interaction of a medium with strong fields have been obtained in the past by assuming a steady-state approximation, where the amplitude of the electric field is monochromatic, or time independent. These descriptions have been obtained by using Floquet theory,<sup>14-16</sup> or a dressed states method,<sup>17</sup> as well as population-pulsation methods.<sup>18-23</sup> In this paper, we remove that steady-state approximation; we present an analytic, nonperturbative methodology for calculating the response due to pump and probe pulsed electric fields, with a time-dependent electric field. Removal of the steady-state approximation is essential to understanding the evolution of wave packets on the ground and excited surfaces: when the probe pulse is long compared to the characteristic period of the initial wave function, for example, time-dependent behavior of the wave packets will no longer be observed. The introduction of symbolic manipulation software makes it possible to go further than previous calculations using a nonperturbative, time-dependent procedure.

A square-envelope approximation for the time dependence of the electric field is used. This formulation allows a nonperturbative calculation of the electric-field-dependent density matrix, which includes all orders of the electric field. Previous nonperturbative work on pulsed fields has focused on situations where lifetime and dephasing rates can be neglected.<sup>24</sup> Here, the nonperturbative description allows variation of both the pump and probe order and duration, as well as the lifetime and dephasing rates. Upon expansion, the third-order term is equivalent to the usual perturbation expression for a square envelope amplitude. While we only consider interactions within the rotating wave approximation, the technique can also be extended to describe antirotating wave interactions. Since the present nonperturbative method contains higher-order terms in the electric field, the accuracy of perturbation theory at each order can be evaluated.

In Sec. II we will consider two and three electronic level systems, which do not contain vibrational manifolds,

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undergoing typical pump-probe interactions. We compare our nonperturbative result to the usual perturbative expression proportional to  $P^{(3)}$ . In some experimentally realizable cases, especially near resonance, third-order perturbation theory does not adequately describe the response. The presence of a two-photon resonant third level, as well as higher-order dependencies on the electric field, begins to play an important role in the nonperturbative description of the response.

In Sec. III a two-level system with an excited state vibrational manifold is considered. Within the model of  $\delta$  function pump and probe pulses, this type of system can also be treated in a nonperturbative manner, and compared to the usual perturbative expression. In this case, we find that within the limit of  $\delta$  function pulses perturbation theory remains valid for very large electric field intensities.

## II. TWO AND THREE ELECTRONIC STATE SYSTEMS

In order to calculate the transient response of a system, a density matrix formalism is employed. Traditional treatments for finding the density matrix solution for a system interacting with a time-dependent electric field amplitude have relied on perturbation techniques which involve time-ordered integrals and use an iteration scheme. Outlined below is a route for solving for the density matrix nonperturbatively, within the approximation of square envelope pump and probe pulses. This technique is used to derive an analytic solution for a two-level system, and in certain special cases, for a three-level system. We will then compare our nonperturbative, nonlinear intensity-dependent results to perturbation theory and discuss where perturbation theory might fail.

The Liouville equation that governs the response is given by

$$i \frac{\partial \rho}{\partial t} = [H(t), \rho(t)] + i[R, \rho(t)] = L(t) \rho(t) \quad (1)$$

with

$$H(t) = H_0 + V(t). \quad (2)$$

$H_0$  is the time-independent Hamiltonian for the electronic states, and the time-dependent interaction potential is simply

$$V(t) = -\mu E(t), \quad (3)$$

where  $\mu$  is the coordinate-independent transition dipole moment between electronic states, and the time-dependent electric field  $E(t)$  for a pump and probe pulse experiment is

$$E(t) = E_{pu}(t) \cos(\omega_{pu}t) + E_{pr}(t) \cos(\omega_{pr}t). \quad (4)$$

The relaxation terms  $i[R, \rho(t)]$  in Eq. (1) can be defined for electronic processes as lifetime, feeding, and dephasing terms:

$$[\hat{R}, \rho(t)]_{\alpha\alpha} = -\Gamma_{\alpha\alpha} \rho_{\alpha\alpha} + \sum_{\beta} \gamma_{\beta\alpha} \rho_{\alpha\beta} \quad (T_1 \text{ process}), \quad (5)$$

$$[\hat{R}, \rho(t)]_{\alpha\beta} = -\Gamma_{\alpha\beta} \rho_{\alpha\beta}, \quad \alpha \neq \beta \quad (T_2 \text{ process}), \quad (6)$$

where  $\Gamma_{\alpha\alpha} = \sum_{\beta} \gamma_{\beta\alpha}$ . Pure radiative decay is assumed throughout.

We assume a square wave envelope for both the pump and probe pulse, so that the time dependence of the electric field amplitude is

$$E(t) = \begin{cases} 0, & t < 0 \\ E \cos \omega t, & \tau > t \geq 0 \\ 0, & t > \tau, \end{cases} \quad (7)$$

where  $\tau$  is the duration of the pulse. The sinusoidal time dependence of the electric field,  $\cos \omega t$ , can be transformed into a diagonal frequency dependence using Floquet theory.<sup>15,16</sup> As a consequence, the effective Liouville operator, within the approximation of Eq. (7), is time independent during the pulse, as well as in the absence of the pulse.

Within this approximation, the formal solution of Eq. (1), for a pulse turned on at  $t=0$ , becomes

$$\rho(t) = \begin{cases} \rho(0), & t < 0 \\ e^{-iL_{\text{eff}}t} \rho(0), & \tau > t \geq 0, \\ e^{-iL_0(t-\tau)} \rho(\tau), & t > \tau \end{cases} \quad (8)$$

where  $L_0$  is the Liouville operator in the absence of the electric field, and  $\rho(\tau)$  is the density matrix evaluated at time  $\tau$ .  $L_{\text{eff}}$  is the effective Liouville operator which includes the field governed by Eq. (7). Since both  $L_{\text{eff}}$  and  $L_0$  are time independent, Eq. (8) does not involve time-ordered integration of the Liouville operator.

To describe a typical pump-probe experiment, Eq. (8) is evaluated twice, once for the pump pulse, and once for the probe pulse. Assuming that the pump pulse precedes the probe pulse, the first evaluation of Eq. (8), with an arbitrary initial condition dependent on the population of the electronic levels, describes a system evolving some time after the pump pulse is turned off. The density matrix  $\rho(t-\tau)$  (dependent on both the coherences and populations stemming from the interaction with the pump pulse) becomes the new initial condition. The second evaluation of Eq. (8) now yields the response of the pump and probe, with variable delay times and pulse durations.

This technique is not limited to situations where the pump follows the probe with no significant temporal overlap. With correct ordering, both pump polarization coupling and perturbed free induction decay terms<sup>8</sup> can also be described in this manner. However, we will limit further discussion to situations where the pump pulse precedes the probe pulse, i.e., the level population component of the response.

Since  $L_{\text{eff}}$  is not a diagonal operator, the individual density matrix elements cannot be written down directly from Eq. (8). Instead, the method of Laplace transforms is used to solve Eq. (1), within the approximation of Eq. (7). This method has been used previously to solve the Liouville equation.<sup>24</sup> The transform of Eq. (1) becomes

$$isr - i\rho(0) = L_{\text{eff}} r, \quad (9)$$

where  $\rho(0)$  is the initial condition and  $r$  is the Laplace transform of  $\rho$ :

$$r(s) = \int_0^\infty dt e^{-st} \rho(t). \quad (10)$$

Rearranging, the transform becomes

$$r = -(L_{\text{eff}} - is)^{-1} \rho(0). \quad (11)$$

Taking the inverse Laplace transform of Eq. (11) leads to the density matrix  $\rho(t)$ .

The limiting factor in the analytic analysis of a many-level system is finding the roots of higher-order polynomials to facilitate the inversion of the transform. An analytic solution for a two-level system is easily obtained, and in certain cases, analytic solutions for a three- (or more) level system is also possible. Formalism developed in this section is applied to two- (one-photon resonant) and three- (one- and two-photon resonant) level systems below. While two-level systems have been considered extensively using both numerical and perturbative approaches,<sup>25,26</sup> three-level systems with a two-photon resonant third level have been not been treated.

## A. Two-level systems

The procedure outlined in the preceding section can be illustrated by using a two-level system. The time-independent Hamiltonian is

$$H_0 = |a\rangle h_a \langle a| + |b\rangle h_b \langle b| \quad (12)$$

with the transition dipole operator

$$\mu = |a\rangle \mu_{ab} \langle b|. \quad (13)$$

In this section we assume only pure electronic states which are not associated with a vibrational manifold. Therefore  $H_a|a\rangle = \omega_a|a\rangle$  where  $\omega_a$  is simply the energy of the electronic state  $|a\rangle$ .

Using the square-envelope approximation for the electric field, Eq. (7), and invoking Floquet theory, which transforms the time- and frequency-dependent part of the

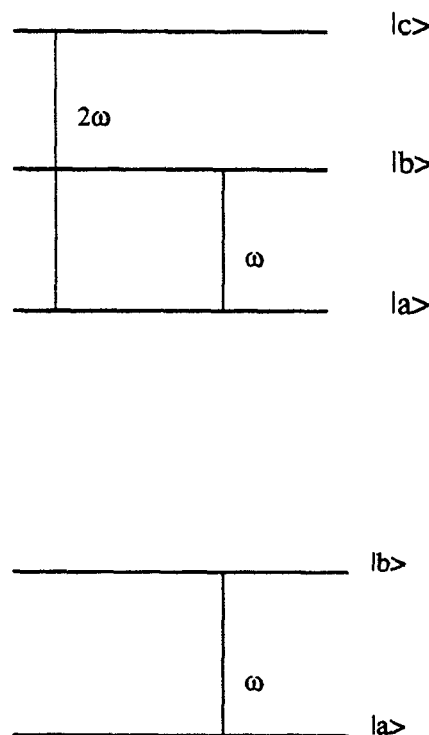


FIG. 1. Two- and three-level systems described in Sec. II. The transition dipoles are  $\mu_{ab}$ ,  $\mu_{bc} \neq 0$ ,  $\mu_{ca} = 0$ .

electric field  $\cos \omega t$ , into a diagonal frequency dependence,<sup>15,16</sup> Eq. (1) can now be spanned by the Floquet-Liouville basis set  $|\alpha\beta; \{m\}\rangle \equiv |\alpha\rangle \langle\beta| \otimes |\{m\}\rangle$ , where  $\{m\}$  is the set of Fourier indices and  $|\alpha\rangle, |\beta\rangle$  are the eigenfunctions of the unperturbed Hamiltonian.

Within the rotating wave approximation (RWA) the two-level system shown in Fig. 1 is spanned by the Floquet-Liouville basis set  $|aa; 0\rangle$ ,  $|bb; 0\rangle$ ,  $|ab; -1\rangle$ ,  $|ba; +1\rangle$ . Although only the one-photon resonance condition is considered, i.e.,  $\omega_{ba} - \omega \approx 0$ , multiphoton resonances can also be dealt with in a similar manner.<sup>15,27</sup> Equation (1) can now be written as

$$i \begin{bmatrix} \frac{\partial \rho_{aa}}{\partial t} \\ \frac{\partial \rho_{bb}}{\partial t} \\ \frac{\partial \rho_{ab}}{\partial t} \\ \frac{\partial \rho_{ba}}{\partial t} \end{bmatrix} = \begin{bmatrix} -i\Gamma_{aa} & -i\gamma_{ba} & -u & u \\ 0 & -i\Gamma_{bb} & u & u \\ -u & u & -\Delta_{ba} - i\Gamma_{ba} & 0 \\ u & -u & 0 & \Delta_{ba} - i\Gamma_{ba} \end{bmatrix} \begin{bmatrix} \rho_{aa} \\ \rho_{bb} \\ \rho_{ab} \\ \rho_{ba} \end{bmatrix}, \quad (14)$$

where

$$\Delta_{ba} = h_b - h_a - \omega, \quad u = \frac{\mu_{ab} E}{2\hbar}. \quad (15)$$

Taking the Laplace transform of Eq. (14) leads to the set of coupled equations

$$\begin{bmatrix} r_{aa} \\ r_{bb} \\ r_{ab} \\ r_{ba} \end{bmatrix} = \begin{bmatrix} -is - i\Gamma_{aa} & -i\gamma_{ba} & -u & u \\ 0 & -i\Gamma_{bb} - is & u & -u \\ -u & u & -\Delta_{ba} - i\Gamma_{ba} - is & 0 \\ u & -u & 0 & \Delta_{ba} - i\Gamma_{ba} - is \end{bmatrix}^{-1} \begin{bmatrix} -i\rho_{aa}(0) \\ -i\rho_{bb}(0) \\ -i\rho_{ab}(0) \\ -i\rho_{ba}(0) \end{bmatrix}. \quad (16)$$

Solving Eq. (16) is equivalent to solving the optical Bloch equations for a two-level system. The required matrix inversion in Eq. (16) is easily accomplished with the use of symbolic manipulation software. Solving for  $\mathbf{r}$  yields

$$\begin{aligned} r_{bb} = & \frac{[2\Gamma_{ba} + 2s]u^2\rho_{aa}(0)}{D} \\ & + \frac{[s^3 + 2s^2\Gamma_{ba} + (\Delta_{ba}^2 + \Gamma_{ba}^2 + 2u^2)s + 2u^2\Gamma_{ba}]\rho_{bb}(0)}{D} \\ & + \frac{[-is^2 - (\Delta_{ba} + i\Gamma_{ba})s]u\rho_{ab}(0)}{D} \\ & + \frac{[is^2 + (-\Delta_{ba} + i\Gamma_{ba})s]u\rho_{ba}(0)}{D}, \end{aligned} \quad (17)$$

$$\begin{aligned} r_{ab} = & \frac{[i\Gamma_{ba} - \Delta_{ba} + is]u\rho_{aa}(0)}{D} + \frac{[-i\Gamma_{ba} + \Delta_{ba} - is]u\rho_{bb}(0)}{D} \\ & + \frac{[(s^2 + \Gamma_{ba})s + i\Delta_{ba}s + 2u^2]\rho_{ab}(0)}{D} + \frac{[2u^2]\rho_{ba}(0)}{D}, \end{aligned} \quad (18)$$

where

$$D = s[s^3 + 2\Gamma_{ba}s^2 + (\Delta_{ba}^2 + \Gamma_{ba}^2 + 4u^2)s + 4u^2\Gamma_{ba}] \quad (19)$$

and we have used  $\Gamma_{aa} = \Gamma_{bb} = \gamma_{ba} = 0$  for clarity.

The backtransform of Eqs. (17) and (18) can also be evaluated exactly, since the roots of the cubic polynomial in Eq. (19) can be found analytically. With the help of symbolic manipulation, the time-dependent density matrix which describes the system with the electric field can then be written down.

For a pump-probe experiment, the initial condition is usually assumed to be  $\rho_{aa}(0) = 1$ ,  $\rho_{bb}(0) = \rho_{ba}(0) = \rho_{ab}(0) = 0$ , with all population initially in the ground state  $|a\rangle$ . During the pump pulse, the dipole-electric-field matrix variable in Eq. (14) becomes  $u = \mu_{ba}E_{pu}/2\hbar$ , where  $E_{pu}$  is the amplitude of the pump pulse. The response directly after the pump pulse is governed by the density matrix evaluated at  $\tau_{pu}$ , the arbitrary pulse length of the pump. The response after the field is turned off is the solution to the Liouville equation governed by  $L_0$ , with  $u = 0$ , using  $\rho(\tau_{pu})$  as the initial condition. For example, the backtransform of Eq. (18),  $\rho_{ab}(t)$ , is evaluated at  $\tau_{pu}$ , and the new initial condition corresponding to the coherence after some time  $t > \tau_{pu}$  is [using Eq. (8)]  $\rho_{ab}(\tau_{pu})e^{(-\Delta_{ba} - i\Gamma_{ba})(t - \tau_{pu})}$ .

The new initial condition is now used in Eq. (16). All elements of the initial density matrix, including the coherences, are now nonzero and  $u = \mu_{ba}E_{pr}/2\hbar$ , where  $E_{pr}$  is the amplitude of the probe pulse. For example, the initial value  $\rho_{aa}(0)$  is replaced by  $\rho_{aa}(\tau_{pu})e^{-i\Gamma_{aa}(t - \tau_{pu})}$ . Again backtransforming Eq. (16) yields the density matrix solution for both the pump and probe interaction, with an arbitrary delay time between pulses.

When the pump pulse precedes the probe pulse with no significant temporal overlap, the most important elements of the density matrix which describes the pump interaction are the population elements  $\rho_{aa}(\tau_{pu})e^{-i\Gamma_{aa}(t - \tau)}$  and  $\rho_{bb}(\tau_{pu})e^{-i\Gamma_{bb}(t - \tau)}$ . A perturbative description of the pump usually considers only the second-order electric field contribution to the population. In this formulation, all orders of the electric field are present in the population elements, as well as in the minor contributions from the coherent terms. Using these initial conditions for the probe pulse, the final density matrix element of interest is the coherence  $\rho_{ab}$ , usually calculated to first order in the probe field in a perturbative description. Here, the coherences due to the probe, as well as the population terms due to the pump, are obtained to all orders of the electric field.

### B. Three-level systems

For special cases, nonperturbative analytic solutions for a system with three levels can also be found using the procedure outlined in the preceding section. We assume the three-level system shown in Fig. 1. The corresponding time-independent Hamiltonian is

$$H_0 = |a\rangle h_a \langle a| + |b\rangle h_b \langle b| + |c\rangle h_c \langle c| \quad (20)$$

with the transition dipoles

$$|a\rangle\mu_{ab}\langle b|, \quad |b\rangle\mu_{bc}\langle c|. \quad (21)$$

The first and third level are of the same symmetry, and therefore  $\mu_{ca} = 0$ .

The third level is two-photon resonant with the ground state,  $\omega_{ca} - 2\omega \approx 0$ , and one-photon resonant with the second state  $\omega_{bc} - \omega \approx 0$ . In this case, the density matrix solution for this three-level case should be identical to the two-level system unless higher-order terms in the electric field, which depend on the presence of the two-photon resonance, become significant.

The three-level system is spanned by the basis  $|aa;0\rangle$ ,  $|bb;0\rangle$ ,  $|cc;0\rangle$ ,  $|ab;-1\rangle$ ,  $|ba;+1\rangle$ ,  $|ac;-2\rangle$ ,  $|ca;+2\rangle$ ,  $|bc;-1\rangle$ ,  $|cb;+1\rangle$  by invoking the RWA, and considering only one- and two-photon resonant terms. The effective Liouville operator of Eq. (9) becomes

$$\begin{bmatrix}
 -i\Gamma_{aa} & -i\gamma_{ba} & -i\gamma_{ca} & -u_{ab} & u_{ab} & 0 & 0 & 0 & 0 \\
 0 & -i\Gamma_{bb} & -i\gamma_{cb} & u_{ab} & -u_{ab} & 0 & 0 & -u_{bc} & u_{bc} \\
 0 & 0 & -i\Gamma_{cc} & 0 & 0 & 0 & 0 & u_{bc} & -u_{bc} \\
 -u_{ab} & u_{ab} & 0 & -\Delta_{ba}-i\Gamma_{ba} & 0 & -u_{bc} & 0 & 0 & 0 \\
 u_{ab} & -u_{ab} & 0 & 0 & \Delta_{ba}-i\Gamma_{ba} & 0 & u_{bc} & 0 & 0 \\
 0 & 0 & 0 & -u_{bc} & 0 & -\Delta_{ca}-i\Gamma_{ca} & 0 & u_{ba} & 0 \\
 0 & 0 & 0 & 0 & u_{bc} & 0 & \Delta_{ca}-i\Gamma_{ca} & 0 & -u_{ba} \\
 0 & -u_{bc} & u_{bc} & 0 & 0 & u_{ba} & 0 & -\Delta_{cb}-i\Gamma_{cb} & 0 \\
 0 & u_{bc} & -u_{bc} & 0 & 0 & 0 & -u_{ba} & 0 & \Delta_{cb}-i\Gamma_{cb}
 \end{bmatrix}, \quad (22)$$

using the relationships given in Eq. (15) as well as

$$\Delta_{cb} = h_c - h_b - \omega, \quad \Delta_{ca} = h_c - h_a - 2\omega, \quad u_{bc} = \frac{\mu_{bc}E}{2\hbar}. \quad (23)$$

Using Eq. (22) in Eq. (1), and inverting the corresponding matrix, leads to a high-order polynomial in the Laplace variable  $s$ , which cannot be backtransformed analytically. However, approximations can be made that lead to an analytic solution for the density matrix.

We chose a situation where the rate constants associated with the lifetime of states can be assumed negligible during the pulse, i.e.,  $\gamma_{ba} = \gamma_{cb} = \gamma_{ca} = 0$ . Since we will consider only short pulses, presumably shorter than the lifetimes of the excited states, this is a valid assumption. We will also assume the dipole moments of the two transitions are equal,  $\mu_{ba} = \mu_{bc}$ . Since temporal overlap between the

pump and the probe pulse is not considered here, this assumption implies  $u_{ba} = u_{bc} = u$ .

When both the resonance condition and the dephasing rate are nonzero, the density matrix is still analytically unsolvable. Here we consider the case where the field is on resonance,  $\Delta_{ba} = \Delta_{cb} = \Delta_{ca} = 0$ , i.e., the molecular energies are *equally* spaced. When the laser is on resonance with the electronic transition, perturbation theory is likely to fail, and an exact solution is necessary. An analytic solution is also possible for the case  $\Gamma_{ba} = \Gamma_{cb} = \Gamma_{ca} = 0$ .

Using these approximations, the solutions for the density matrix are algebraically simple, but lengthy. When the probe pulse interacts with a system prepared by the pump pulse, the most important terms will be associated with the population terms of the density matrix. Below are the Laplace transforms, Eq. (11) for these terms:

$$r_{aa} = \left[ \frac{s^5 + (2\Gamma_{ba} + \Gamma_{ca})s^4 + (\Gamma_{ba}^2 + 2\Gamma_{ba}\Gamma_{ca} + 8u^2)s^3}{D} + \frac{(\Gamma_{ba}^2\Gamma_{ca} + 6\Gamma_{ca}u^2 + 8\Gamma_{ba}u^2)s^2 + (6u^4 + 6u^2\Gamma_{ba}\Gamma_{ca})s + 4u^4\Gamma_{ca}}{D} \right] \rho_{aa}(0), \quad (24)$$

$$r_{cc} = \frac{2(3s + 2\Gamma_{ca})u^4}{D} \rho_{aa}(0), \quad (25)$$

$$r_{ab} = iu \frac{s^3 + (\Gamma_{ca} + \Gamma_{ba})s^2 + (5u^2 + \Gamma_{ba}\Gamma_{ca})s + 4u^2\Gamma_{ca}}{D} \rho_{aa}(0) - iu \frac{s^3 + (\Gamma_{ca} + \Gamma_{ba})s^2 + (2u^2 + \Gamma_{ba}\Gamma_{ca})s + 2u^2\Gamma_{ca}}{D} \rho_{bb}(0) - iu \frac{3u^2s - 2u^2\Gamma_{ca}}{D} \rho_{cc}(0), \quad (26)$$

$$r_{bc} = \frac{i u^3 (3s + 2\Gamma_{ca})}{D} + iu \frac{s^3 + (\Gamma_{ca} + \Gamma_{ba})s^2 + (\Gamma_{ba}\Gamma_{ca} - u^2)s}{D} \rho_{bb}(0) - iu \frac{s^3 + (\Gamma_{ca} + \Gamma_{ba})s^2 + (\Gamma_{ba}\Gamma_{ca} + 8u^2)s + 6u^2\Gamma_{ca}}{D} \rho_{cc}(0), \quad (27)$$

where

$$D = (2u^2 + \Gamma_{ba}s + s^2)[s^3 + (\Gamma_{ca} + \Gamma_{ba})s^2 + (8u^2 + \Gamma_{ca}\Gamma_{ba})s + 6u^2\Gamma_{ca}] \quad (28)$$

for the case  $\Gamma_{cb} = \Gamma_{ba}$ . The density matrix elements are related by  $\rho_{bb} = 1 - \rho_{aa} - \rho_{cc}$  and  $\rho_{ba} = \rho_{ab}^*$ ,  $\rho_{cb} = \rho_{bc}^*$ .

### C. Comparison to perturbation theory

Below we will compare the results of the nonperturbative evaluation of the density matrix of the two- and three-level systems to the usual perturbation theory expressions.

For a two-level system, where the probe pulse follows the pump pulse with no overlap, perturbation theory to second order in the pump field and first order in the probe, yields<sup>7</sup> (with  $\hbar=1$ )

$$\rho_{ba}^{(1)} = i \int_{-\infty}^t dt' e^{-\Gamma_{ba}(t-t')} e^{i\Delta_{ba}(t-t')} \mu_{ba} E_{pu}(t') \rho_{aa}(0), \quad (29)$$

$$\rho_{aa}^{(2)} = i \int_{-\infty}^t dt' e^{-\gamma_{ba}(t-t')} \mu_{ba} E_{pu}(t') (\rho_{ba}^{(1)} - \rho_{ba}^{(1)*}), \quad (30)$$

and

$$\rho_{ba}^{(3)} = 2i \int_{-\infty}^t dt' e^{-\Gamma_{ba}(t-t')} e^{i\Delta_{ba}(t-t')} \mu_{ba} E_{pr}(t') \rho_{aa}^{(2)}(t'). \quad (31)$$

The density matrix is usually obtained indirectly in a pump-probe experiment via the polarizability due to the probe pulse. The polarizability is simply related to the density matrix by the relation

$$P_{pr}(t) = \text{Tr}[\mu \rho(t)]. \quad (32)$$

For the two-level system considered here, this reduces to

$$P_{pr}(t) = \mu_{ba} \rho_{ba}(t). \quad (33)$$

However, for the three-level system, there is an extra term due to the presence of the third level:

$$P_{pr}(t) = \mu_{ab} \rho_{ab}(t) + \mu_{bc} \rho_{bc}(t). \quad (34)$$

The second term is related to the inverse transform of Eq. (27),  $\rho_{bc}$ . This term has a linear dependence on the electric field when there is population present in the second level, which only occurs after the pump pulse. Expanding the backtransform of Eq. (27) to first order yields

$$\rho_{bc}^{(1)} = i \frac{(\rho_{bb} - \rho_{cc})(1 - e^{-\Gamma_{ba}t})}{\Gamma_{ba}}. \quad (35)$$

The coherence  $\rho_{bc}$  contains higher-order intensity-dependent terms as well. For the three-level systems considered here,  $\rho_{bc}$  is an order of magnitude smaller than that of  $\rho_{ab}$ .

If the inverse transform of Eqs. (17) and (18), corresponding to the population and coherence for a two-level system, and Eqs. (24)–(27) corresponding to a three-level system with a two-photon resonant term, are expanded around the pump and probe electric field, respectively, the

first nonlinear term, which is second order in the pump field and first order in the probe field, should be identical to that obtained from Eq. (31), using the time dependence of the electric field in Eq. (7). In order to compare the two-level system and the three-level system addressed here, the relation  $\Delta_{ba}=0$  is used in Eqs. (17) and (18), together with the limit  $\gamma_{ba} \rightarrow 0$ . In this limit, both the two- and three-level systems reduce to

$$\begin{aligned} \rho_{ba}^{(3)} = & -i \left[ \frac{\Gamma_{ba}\tau_1 + e^{-\Gamma_{ba}\tau_1} - 1}{\Gamma_{ba}^2} \right] \\ & \times \left[ \frac{1 - e^{-\Gamma_{ba}\tau_2}}{\Gamma_{ba}} \right] 2\mu_{ab}^3 E_{pu}^2 E_{pr} e^{-\gamma_{ba}(t'-\tau_1)} \\ & \times e^{-(i\Delta_{ba} - \Gamma_{ba})(t-\tau_2)}, \end{aligned} \quad (36)$$

where  $\tau_1$  is the pump duration,  $\tau_2$  is the probe duration,  $t'$  is the delay time between pump and probe, and  $t$  is the time after pump and probe.

For an experimental situation corresponding to an intense pump pulse where all orders of the electric field should be considered, but with a weak probe pulse that can be described perturbatively, the two-level response reduces to

$$\begin{aligned} \rho_{ba} = & R(\tau_1) \left[ \frac{e^{(-\Gamma_{ba} + i\Delta_{ba})\tau_2}}{2(\Delta_{ba} + i\Gamma)} \right] \mu_{ab} E_{pr} e^{-\gamma_{ba}(t'-\tau_1)} \\ & \times e^{-(i\Delta_{ba} - \Gamma_{ba})(t-\tau_2)}, \end{aligned} \quad (37)$$

where  $R(\tau_1)$  is the nonperturbative population difference  $R = \rho_{aa}(\tau_1) - \rho_{bb}(\tau_1)$  stemming from the pump pulse, and determined by Eq. (17). In the steady-state limit, for populations at the end of the pump pulse, Eq. (37) reduces to previous work,<sup>23</sup> and shows the effects of saturation.

The nonperturbative density matrix and the corresponding perturbation expression should be compared using typical pump and probe pulse variables. To do so, the linear contributions  $\rho^{(1)}$  are subtracted from the total density matrix, leaving all nonlinear contributions intact. This allows us to compare perturbation theory, Eq. (36), with the nonperturbative solution.

Figure 2 plots the nonlinear coherent density matrix element  $\rho_{ba} - \rho_{ba}^{(1)}$  as a function of the dephasing constant  $\Gamma_{ba}$ , with  $\Gamma_{cb} = \Gamma_{ba}$ . The pump and probe pulses are 50 and 5 fs respectively, with a 5 fs delay time between pulses. During the pump and probe the decay times are assumed to be zero,  $\gamma_{aa} = \gamma_{bb} = \gamma_{cc} = 0$ , but, after the pump pulse, decay at a rate corresponding to  $T_1 = 1$  ps. Both figures assume  $E_{pu} = E_{pr}$ , with the field amplitude in Fig. 2(a) corresponding to an intensity of 100 MW/cm<sup>2</sup>, and with Fig. 2(b) corresponding to 1 GW/cm<sup>2</sup>. The transition dipole  $\mu_{ba} = \mu_{cb}$  is 6.0 D. The solid line is the result from perturbation theory, with the dotted and dashed lines the nonperturbative two- and three-level results. Since the exact density matrix has been obtained in the limit of on-resonance interaction, the coherent density matrix consists only of pure imaginary terms.

The dephasing rate for the two-photon resonance is  $\Gamma_{ca} = 10^{13} \text{ s}^{-1}$  for both figures. For the 100 MW/cm<sup>2</sup> case,

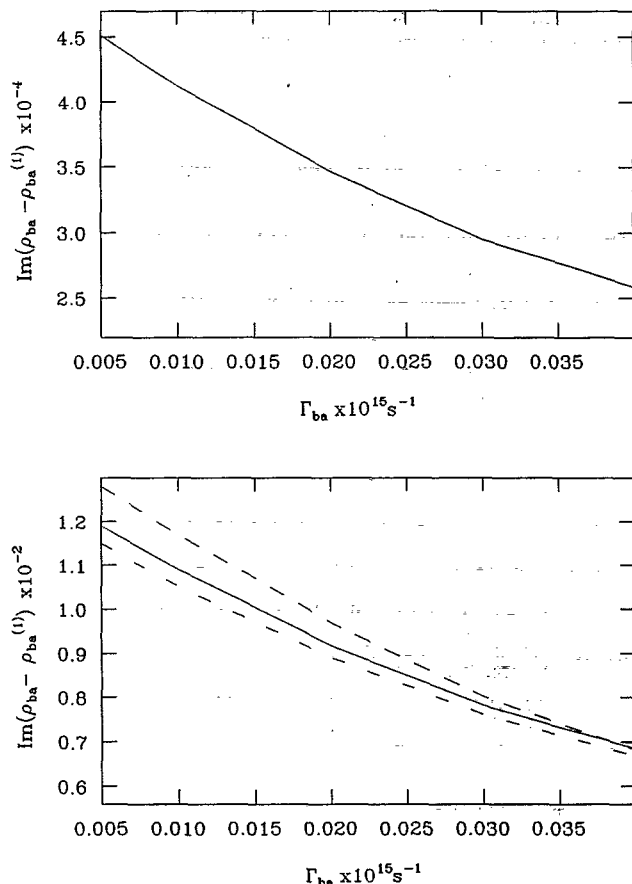


FIG. 2. The imaginary part of the coherent density matrix element which describes a 50 fs pump, 5 fs probe interaction with 5 fs delay, minus the probe interaction only. The solid line corresponds to the perturbation result. The dash-dotted (lower) and dashed (upper) lines are the non-perturbative three-level and two-level result, respectively. (a) Electric field amplitude corresponds to 100 MW/cm<sup>2</sup>; (b) electric field amplitude corresponds to 1 GW/cm<sup>2</sup>.

Fig. 2(a), the difference between the perturbation and non-perturbative results is indiscernible. However, at 1 GW/cm<sup>2</sup>, higher-order nonlinear terms have appeared. For the two-level system, a lower value is obtained, as compared to perturbation theory. The presence of the third level is apparent in the higher values in this case.

The sharpest difference between the nonperturbative and perturbative density matrix results when the dephasing time is long, i.e.,  $\Gamma_{ba}$  is small. This has the effect of allowing higher-order nonlinear terms to approach each other in magnitude. In other words, not only does the first nonlinear term  $\rho_{ab}^{(3)}$  appear, terms such as  $\rho_{ab}^{(5)}$  also contribute to the response. As the dephasing time becomes shorter, the nonperturbative results for both the two- and three-level system approach perturbation theory.

The difference between nonperturbative and perturbative values for the density matrix should not depend on the delay time between the pump and probe pulses. If the population density matrix elements display higher-order dependencies on the pump electric field, the population then decays at a uniform rate once the pump is turned off. This is apparent in Fig. 3, where  $\Gamma_{ca} = \Gamma_{ba} = 10^{13} \text{ s}^{-1}$ , and the

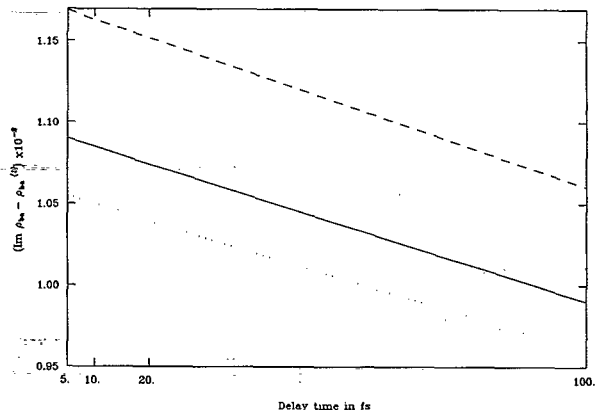


FIG. 3. The imaginary part of the coherent density matrix element which describes a 50 fs pump, 5 fs probe interaction with variable delay. The solid line corresponds to the perturbation result. The dotted and dashed lines are the exact three-level and two-level result, respectively. The electric field amplitude corresponds to 1 GW/cm<sup>2</sup>.

amplitude of the electric field corresponds to 1 GW/cm<sup>2</sup>.

We have shown that in certain cases, third-order perturbation theory no longer accurately predicts the dynamics of the system. Furthermore, the presence of a third level has become important: the three-level system is no longer equivalent to the two-level system.

### III. TWO-LEVEL SYSTEM WITH AN EXCITED STATE VIBRATIONAL MANIFOLD INTERACTING WITH $\delta$ FUNCTION PULSES

For very short pump and probe pulses, shorter than the period of typical vibrational modes, it is possible to observe the coherent vibrational states of many systems. We use the procedure for electronic states, as outlined above, to calculate nonperturbatively the response for the two-level system in Fig. 4, which consists of a single ground-state level, and an excited electronic level with a manifold of vibrational states. This type of system has been analyzed previously in a perturbative manner.<sup>6</sup> Here, the system interacts with a  $\delta$  function pulse, which mimics the short pulses used, and at the same time facilitates a non-perturbative calculation.

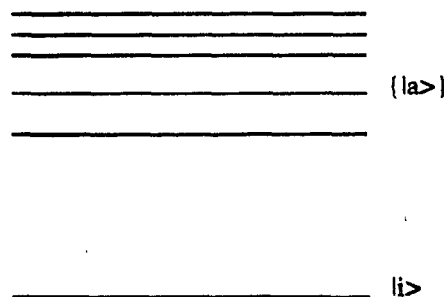


FIG. 4. Two-level system with excited state vibrational manifold.



For this system, the time-independent Hamiltonian in Eq. (12) becomes (Fig. 4)

$$H_0 = |i\rangle\omega_i\langle i| + \sum_a |a\rangle\omega_a\langle a| \quad (38)$$

with

$$\mu = \sum_a |a\rangle\mu_{ai}\langle i| + \text{c.c.} \quad (39)$$

The transition dipole moment now consists of both an electronic part and a Franck-Condon type overlap between the ground and excited state,  $\mu = \mu_e S_{ai}$  where  $S_{ai} = \langle a|i\rangle$ .

Transitions within the excited state manifold are neglected. The system is spanned by the basis  $|ii;0\rangle$   $|aa;0\rangle$   $|bb;0\rangle$   $|ai;-1\rangle$   $|ia;+1\rangle$   $|bi;-1\rangle$   $|ib;+1\rangle$   $|ab;0\rangle$   $|ba;0\rangle$ , within the RWA. Only one-photon resonant states are considered. The state  $|ba;0\rangle$  reflects the individual vibronic populations. The effective Liouville operator of Eq. (9) becomes

$$\begin{bmatrix} -i\Gamma_{ii} & -i\gamma_{ai} & i\gamma_{bi} & -u_{ai} & u_{ai} & -u_{bi} & u_{bi} & 0 & 0 \\ 0 & -i\Gamma_{aa} & 0 & u_{ai} & -u_{ai} & 0 & 0 & 0 & 0 \\ 0 & 0 & -i\Gamma_{bb} & 0 & 0 & u_{bi} & -u_{bi} & 0 & 0 \\ -u_{ai} & u_{ai} & 0 & \Delta_{ai} - i\Gamma_{ai} & 0 & 0 & 0 & 0 & u_{bi} \\ u_{ai} & -u_{ai} & 0 & 0 & \Delta_{ai} - i\Gamma_{ai} & 0 & 0 & -u_{bi} & 0 \\ -u_{bi} & 0 & u_{bi} & 0 & 0 & -\Delta_{bi} - i\Gamma_{bi} & 0 & u_{ai} & 0 \\ u_{bi} & 0 & -u_{bi} & 0 & 0 & 0 & \Delta_{bi} - i\Gamma_{bi} & 0 & -u_{ai} \\ 0 & 0 & 0 & 0 & -u_{bi} & u_{ai} & 0 & -\omega_{ba} - i\gamma'_{ba} & 0 \\ 0 & 0 & 0 & u_{bi} & 0 & 0 & -u_{ai} & 0 & \omega_{ba} - i\gamma'_{ba} \end{bmatrix} \quad (40)$$

with  $\gamma'_{ba}$  corresponding to pure vibrational dephasing.

A  $\delta$  function pulse implies the limit  $t \rightarrow 0$ ,  $E \rightarrow \infty$ , and therefore the area of the pulse,  $Et$ , becomes a constant. In this limit, all dephasing and lifetime processes become unimportant during the pulse, and as a result, are easily calculated:

$$\rho_{ii}(t) = [\frac{1}{2} \cos(2c\mu_e) + \frac{1}{2}] \rho_{ii}(0), \quad (41)$$

$$\rho_{aa}(t) = -\frac{1}{2} \frac{\mu_{ai}[\cos(2c\mu_e) - 1]}{\mu_e} \rho_{ii}(0), \quad (42)$$

$$\rho_{ab}(t) = -\frac{1}{2} \frac{\mu_{ai}\mu_{bi}[\cos(2c\mu_e) - 1]}{\mu_e^2} \rho_{ii}(0), \quad (43)$$

$$\begin{aligned} \rho_{ai}(t) = i \frac{1}{2} \left[ \frac{(2\mu_{ai}^3\mu_{bi}^2 + \mu_{ai}\mu_{bi}^4 + \mu_{ai}^5)\sin(2c\mu_e)}{\mu_e^5} \rho_{ii}(0) + \frac{(-\mu_{ai}^3\mu_{bi}^2 - \mu_{ai}^5)\sin(2c\mu_e) + (-2\mu_{ai}^3\mu_{bi}^2 - \mu_{ai}\mu_{bi}^4)\sin(c\mu_e)}{\mu_e^5} \rho_{aa}(0) \right. \\ \left. + \frac{(-\mu_{ai}^2\mu_{bi}^3 - \mu_{ai}\mu_{bi}^4)\sin(2c\mu_e) + (2\mu_{ai}^2\mu_{bi}^3 + 2\mu_{bi}\mu_{ai}^4)\sin(2c\mu_e)}{\mu_e^5} \rho_{ab}(0) \right. \\ \left. + \frac{(-\mu_{ai}^4\mu_{bi} - \mu_{ai}^2\mu_{bi}^3)\sin(2c\mu_e) + (-2\mu_{ai}^2\mu_{bi}^3 + 2\mu_{bi}^5)\sin(c\mu_e)}{\mu_e^5} \rho_{ba}(0) \right], \quad (44) \end{aligned}$$

where  $c = Et$  the constant area of the pulse, and we have taken advantage of the relation  $\sum_a \mu_e^2 S_{ai}^2 = 1\mu_e^2$ .

Experiments involving a pump and probe pulse usually measure the absorption cross section, or differential transmittance. The absorption cross section is related to the polarization by

$$\sigma(\omega) = (4\pi\omega/c) \text{Im}[P(\omega)/E_{pr}(\omega)]. \quad (45)$$

The polarization is obtained using Eq. (33) and by sum-

ming over all transitions in the coherent density matrix elements as well as the transition dipole moments:

$$P(t) = \sum_{ab} \mu_{ai} \rho_{ai}(t). \quad (46)$$

Figure 5 shows the nonperturbative differential transmittance of a two-level system interacting with  $\delta$  function pump and probe pulses, together with the perturbative result, for varying delay times between the pump and probe pulse.<sup>6</sup> The area of the pulse is constant, with  $\mu_e Et = 6$

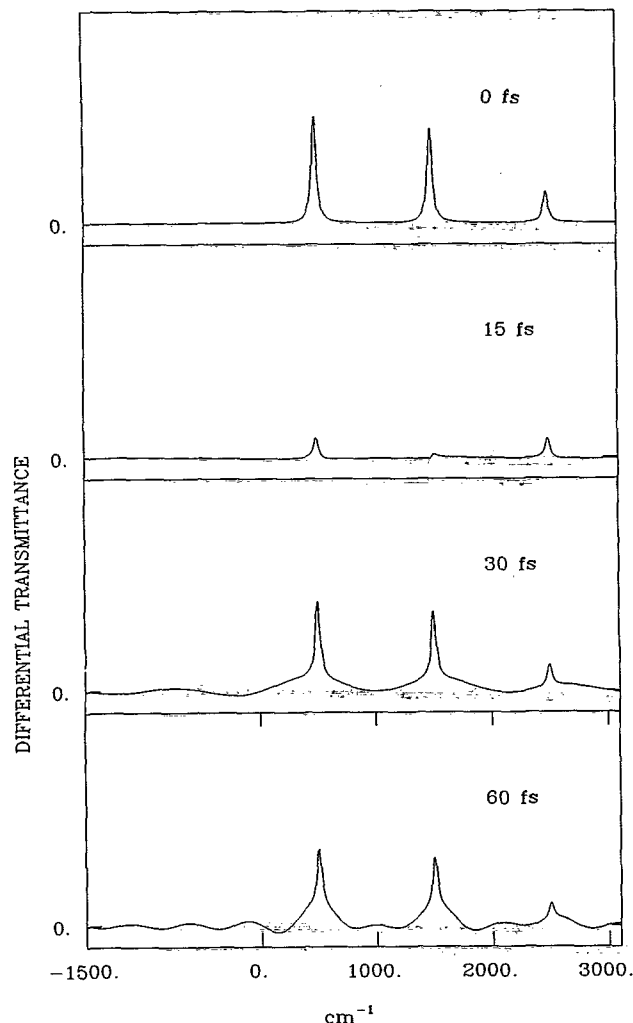


FIG. 5. Exact differential transmittance of a two-level system with ground and vibrational frequencies of  $1000\text{ cm}^{-1}$ . The excited state has a dimensionless displacement of 1.0. The  $\delta$  function pulses have a constant area with field corresponding  $\mu_e E t = 6 \times 3.06 \times 10^{-4}$ .

$\times 3.06 \times 10^{-4}$ , which could be obtained by using an electric field amplitude corresponding to  $1\text{ GW/cm}^2$  with  $t = 1\text{ fs}$ , and  $\mu_e = 6.0\text{ D}$ . The excited state is modeled as an harmonic oscillator with frequency  $1000\text{ cm}^{-1}$  (corresponding to a period of  $\sim 33\text{ fs}$ ) and is displaced from the ground state by a dimensionless displacement factor of 1.0. Since the pure vibrational dephasing rate  $\gamma'_{ba}$  is usually slower than the delay times considered here, the rate is approximated by the relation  $\gamma'_{ba} = \gamma_{ba}$ , where  $\gamma_{ba} = 0.3 \times 10^{12}\text{ s}^{-1}$  and  $\Gamma_{ba} = 4.7 \times 10^{12}\text{ s}^{-1}$ . Delay times of 30 and 60 fs, corresponding to multiples of the oscillator period, show identical Franck-Condon overlap with the ground state, with some broadening due to dephasing, as compared to the zero delay transmittance. At 15 fs, the excited state wave packet is at the far turning point of the excited state, and therefore the Franck-Condon overlap with the ground state is diminished.

As Fig. 5 shows, there is no discernable difference between the nonperturbative and perturbative result. This persists even at unrealistically high values for the area of

the pulse. Since the  $\delta$  function pulse is shorter than all other processes, there is no time for higher-order interactions to develop, and perturbation theory becomes valid.

#### IV. DISCUSSION

We have shown in Sec. II that the response of a pulsed, square-envelope electric field interacting with a many-level system can be calculated without recourse to perturbation theory. This yields a density matrix, and consequently the polarization or the transmittance, which contains all powers of the electric field. Both a two- and three-level system have been used to illustrate this technique. In these special cases, an analytic expression for the density matrix is possible.

The usual perturbative result for a two-laser, pump-probe experiment, where the pump pulse is evaluated to second order in the electric field, and the probe pulse to first order, can be recovered from the exact result by expanding around the electric fields. As shown in Sec. II, for both the two- and three-level cases, situations arise where perturbation theory is no longer valid. In the cases considered here, with no temporal overlap between the pump and probe pulse, the pump pulse prepares a population on the excited states, which is then probed coherently by the probe pulse. Perturbation theory should be valid for the pump probe if there is no significant population change, that is<sup>25,26</sup>

$$\frac{\mu E}{\hbar} \tau \ll \pi, \quad (47)$$

where  $\tau$  is the pulse length. If a significant amount of population is transferred to the excited states, perturbation theory is no longer accurate.

Figures 6 and 7 show the population of two and three levels as a function of the coherence  $\Gamma_{ba}$ , obtained nonperturbatively from Eqs. (19), and (26) and (27). Parameters are the same as in Fig. 2. The population is calculated after the delay time (5 fs) between the pump and the probe pulse.

Figure 6 uses an electric field that corresponds to an intensity of  $100\text{ MW/cm}^2$ . Here the population of the ground state remains near unity, with no significant population in the excited states, and with no noticeable difference between the two- and three-level systems. This situation corresponds to the case in Fig. 2(a), where perturbation theory is equivalent to the exact result. Figure 7 shows the populations for an electric field that corresponds to an intensity of  $1\text{ GW/cm}^2$ . In this case, the population of the excited states has become appreciable, and the difference in population between the two- and three-level systems is apparent.

The level populations are also a function of the dephasing rate. When the dephasing time is long,  $\Gamma$  becomes small and approaches the value of the Rabi frequency,  $\mu E/\hbar$ . This is where perturbation theory is likely to fail. Figures 6 and 7 show that as  $\Gamma$  becomes large, the two- and three-level populations become equal.

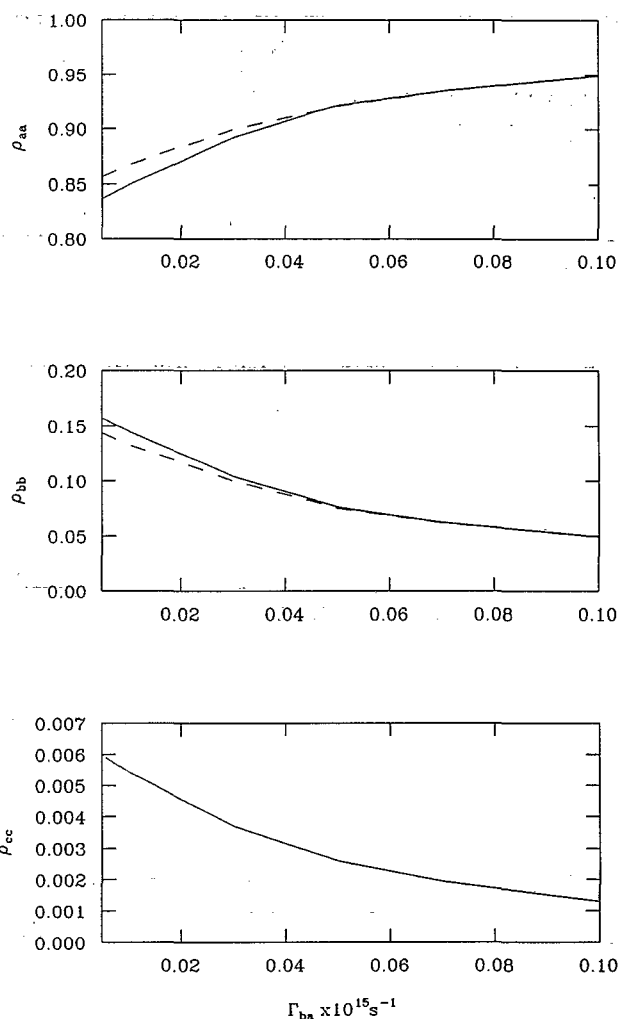
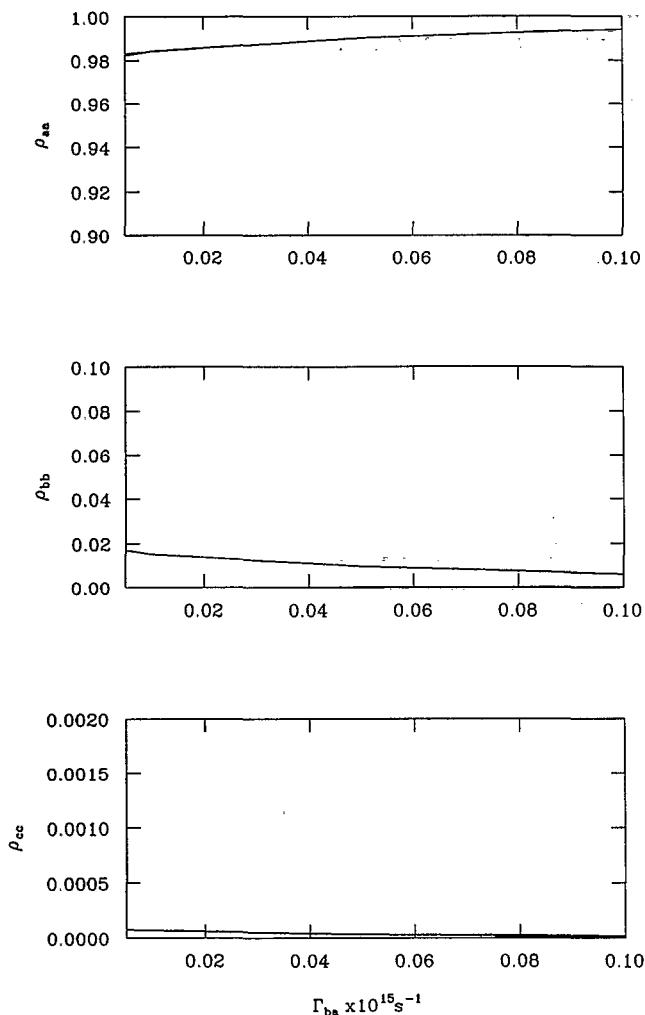


FIG. 6. Populations of levels  $a$ ,  $b$ , and  $c$ . The solid and dashed lines correspond to two- and three-level cases, respectively. Parameters are the same as in Fig. 2. Here the electric field corresponds to 100 MW/cm<sup>2</sup>.

FIG. 7. Populations of levels  $a$ ,  $b$ , and  $c$ . The solid and dashed lines correspond to two- and three-level cases, respectively. Parameters are the same as in Fig. 2. Here the electric field corresponds to 1 GW/cm<sup>2</sup>.

In this paper we have modeled the time-dependent pulse shape as a square envelope, which allows a nonperturbative density matrix calculation. By using the procedure outlined in Sec. II, a pulse shape can be approximated by a quadrature technique: at step times during the pulse, the density matrix is evaluated, and the new initial condition is used for the next step. In this way, the interaction with any pulse shape can be calculated to all orders of the electric field.

For a two-level system with an excited state vibrational manifold, a nonperturbative solution can be obtained in the limit of  $\delta$  function pulses, Sec. III. In this limit perturbation theory remains valid, and a nonperturbative solution is not necessary. However, the results of Sec. II suggest that longer pulses interacting with vibrational manifolds may necessitate a nonperturbative approach as well.

For simple illustrative models, such as those presented here, a perturbative calculation which involves higher-order terms  $P^{(5)}$ ,  $P^{(7)}$ , etc. is also possible. However, the present method shows that more complex models can be

treated easily with the use of numerical and symbolic methods.

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