SOLUTION OF THE SCHRÖDINGER EQUATION FOR SYSTEMS DRIVEN BY AN EXPONENTIAL OR A SEMIEXPONENTIAL PULSE ☆

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The time-dependent probability amplitudes of a general multilevel system can be obtained analytically as power series in the pulse area for quasimonochromatic pulses with special envelope shapes in the rotating-wave approximation. Closed-form solutions can also be found for some cases of interest. These solutions are useful in evaluating the correctness of the adiabatic approximation and in illustrating the dependence of the intramolecular relaxation time on the conditions of excitation.

In view of the importance of nonlinear phenomena in contemporary physics, exact solutions of the time-dependent Schrödinger equation are of considerably greater interest than the perturbative solutions that have played a major role in the past. In this article we describe a new method of obtaining the solution to the time-dependent Schrödinger equation in the rotating-wave approximation in terms of a power series in the area of a quasimonochromatic pulse, the envelope amplitude of which either increases exponentially in time or initially increases exponentially and then approaches a constant value. This method is notably different from other techniques of exact solution of the rotating-wave Schrödinger equation such as the method of dressed states, in which the envelope amplitude is assumed either to be constant after an initial sudden turning on of the field [1] or to vary adiabatically slowly [2].

We have obtained new closed-form analytic solutions in terms of known elementary or special functions for several systems of interest in quantum optics. Further, the exponential pulse solution (EPS) (for a pulse that rises indefinitely) and the semiexponential pulse solution (SEPS) (for a pulse that rises to a constant limiting amplitude) are valid for, and in fact interpolate between, both strong and weak fields. As a result, a rigorous evaluation of the correctness of the sudden approximation [1,3] or the adiabatic-following approximation [2] may be obtained. Such a comparison is of considerable interest for problems in molecular multiple-photon excitation (MPE) [1] and laser pulse-propagation phenomena in molecular gases [2]. Our exact solutions of the time-dependent Schrödinger equation are also useful in calculating the intramolecular relaxation time as a function of the conditions of excitation for a system consisting of one lower level and many nearly degenerate upper levels.

Consider a multilevel system, the time dependence of which is determined by the hamiltonian

$$H(t) = H_0 - E(t)\mu, \tag{1}$$

where H_0 is the unperturbed hamiltonian (which we assume to be diagonal), μ is the matrix of the dipole operator, and $E(t)$ is an applied electromagnetic field. In this paper we confine our attention to systems that may be described by a state vector ψ, the time evolution of which is governed by the Schrödinger equation

$$\mathrm{d}\psi/\mathrm{d}t = -(\mathrm{i}/\hbar)(H_0 - E(t)\mu)\psi. \tag{2}$$

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$$E(t) = E_0(t)\cos(\omega t) \tag{3}$$

where $E_0(t)$ is slowly varying on the time scale ω^{-1}, and when the frequency ω of the driving electromagnetic field is not far from the resonant transition frequencies of the system, the rotating-wave approximation [1] yields the equation of motion

$$\mathrm{d}\tilde{\psi}/\mathrm{d}t = \mathrm{i}(\delta + \epsilon(t)\mu)\tilde{\psi}, \tag{4}$$

where a typical element of the vector $\tilde{\psi}$ is $(\tilde{\psi})_m = \exp[\mathrm{i}\hbar n(m)\omega t](\psi)_m$ (where $n(m)$ is the integer such that the energy E_m of the state $|m\rangle$ is nearest to $n(m)\hbar\omega$). A typical element of the (diagonal) matrix of detunings is $\delta_{m,m} = [n(m)\hbar\omega - E_m]/\hbar$; we have let $\epsilon(t) = E_0(t)/2\hbar$. In the remainder of this paper we consider a pulse with the envelope

$$\epsilon(\tau) = \frac{\lambda\tau}{1 + (\lambda/\epsilon_\infty)\tau}, \tag{5}$$

where λ is the initial (logarithmic) rate of rise ($= \epsilon^{-1}\mathrm{d}\epsilon/\mathrm{d}t$) of the pulse envelope, and ϵ_∞ is the limiting amplitude as $\tau \to \infty$. A solution of the Schrödinger equation (4) for this $\epsilon(t)$ with a finite ϵ_∞ is a SEPS. The special case ϵ_∞ gives an indefinitely rising exponential pulse (EPS). The time dependence of a semiexponential pulse is shown in fig. 1. The new "time" variable τ in (5) is defined as

$$\tau = \int_{-\infty}^{t} \epsilon(t')\,\mathrm{d}t', \tag{6}$$

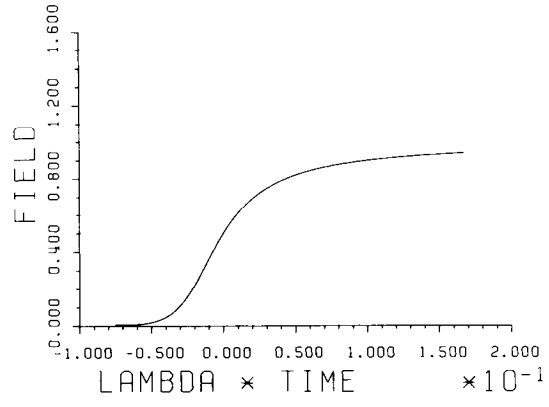

Fig. 1. Time dependence of the semiexponential pulse (5) as a function of the dimensionless variable λt. The ordinate is $\epsilon(t)/\epsilon_\infty$ for the case $\lambda = \epsilon_\infty$.

where the pulse area [4] for a two-level system is $\mu_{01}\tau$. For an exponential pulse $\lambda t = \ln(\lambda\tau/\epsilon_0)$, while for a semiexponential pulse $\lambda t = \ln(\lambda\tau/\epsilon_\infty) + (\lambda\tau/\epsilon_\infty) - 1$. The equation of motion (4) takes on the simple form

$$\mathrm{d}\tilde{\psi}/\mathrm{d}\tau = \mathrm{i}[(1/\lambda\tau + 1/\epsilon_\infty)\delta + \mu]\tilde{\psi}. \tag{7}$$

Eq. (7) is amenable to a series solution in powers of τ:

$$\tilde{\psi}(\tau) = \sum_{r=0}^{\infty} \tilde{\psi}_r \tau^r, \tag{8}$$

where the vectors $\tilde{\psi}_r$ obey the recurrence relation

$$\tilde{\psi}_{r+1} = \mathrm{i}[(r+1)\mathbf{1} - (\mathrm{i}/\lambda)\delta]^{-1}(\mu + \delta/\epsilon_\infty)\tilde{\psi}_r, \tag{9}$$

and where we have assumed that $\delta\tilde{\psi}(\tau = 0) = 0$. The latter condition is automatically fulfilled if the system is initially (at $t = -\infty$) in the ground state. The series (8) converges for all τ, since for sufficiently large r, $\tilde{\psi}_{r+1} \approx \mathrm{i}(r+1)^{-1}(\mu + \delta/\epsilon_\infty)\tilde{\psi}_r$. In many cases the convergence is also sufficiently rapid for (8) to be of practical utility. The fundamental reason for the condition $\delta\tilde{\psi}(\tau = 0) = 0$ is that the transformation (6) compresses the infinite interval $[-\infty, t]$ into the finite interval $[0, \tau(t)]$; any initial state for which $\delta\tilde{\psi}(\tau = 0) \neq 0$ would experience infinitely many oscillations in this interval, and hence would not be describable as an analytic function of τ. By a suitable unitary transformation of the $\tilde{\psi}_m$ it is possible to make any one of the diagonal elements of the transformed δ vanish, so that any one of the states in which H_0 is diagonal may be taken as the initial state.

The coefficient vectors $\tilde{\psi}_r$ in (8) can be found analytically for several systems of interest. For the purpose of numerical calculations eq. (9) is equally easy (or difficult) to handle for a finite or infinite value of ϵ_∞. From an analytical point of view these two cases are quite different, since the structure of the matrix $\mu + \delta/\epsilon_\infty$ leads to considerably more complications than are encountered with the matrix μ alone. We have found a SEPS (ϵ_∞ finite) in closed form for the two-level system; this result will be given below. A closed-form EPS ($\epsilon_\infty = \infty$) is known for nondegenerate two- and three-level systems; for $(1, N)$ systems consisting of a nondegenerate ground state and an upper state with N nearly degenerate sublevels (fig. 2); and for a system with a nondegenerate ground state linked radiatively to a continuously degenerate

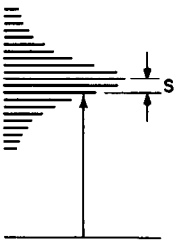

Fig. 2. $(1, N)$ system for which an EPS has been obtained.

upper state by a lorentzian distribution of transition strength.

The SEPS for the ground-state component of a two-level system initially (at $t = -\infty$) in the ground state is

$$(\tilde{\psi}(\tau))_0 = \exp(i\zeta_- \tau) M(i\rho\zeta_-/2\alpha, -i\rho; 2i\alpha\tau), \qquad (10)$$

where M is the confluent hypergeometric function; μ_{01} is the dipole matrix element; $\Delta = \omega - (E_1 - E_0)/\hbar$ is the detuning of the laser frequency from resonance; $\alpha = [(\Delta/2\epsilon_\infty)^2 + (\mu_{01}/2\hbar)^2]^{1/2}$ is one-half of the eventual population Rabi frequency times $(\epsilon_\infty)^{-1}$; $\rho = \Delta/\lambda$ is the ratio of the detuning to the pulse-turn-on rate; and $\zeta_\pm = |\Delta/2\epsilon_\infty| \pm \alpha$ are the eventual frequencies of the amplitudes of the upper (or lower) dressed states $|\pm\rangle$.

In order to assess the validity in this case of the adiabatic approximation, in which one assumes that the system remains in the lower dressed state $|-\rangle$ which is correlated with the initial (ground) state at $\tau = -\infty$ [2], we calculate the limiting probability for the system to be found in $|-\rangle$ at $\tau = \infty$. The absolute value of this limiting amplitude, which must be nearly unity for the adiabatic approximation to be valid, is

$$|c_-|^2 = [1 - \exp(-\pi\rho\zeta_+/\alpha)]/[1 - \exp(-2\pi\rho)]. \qquad (11)$$

Now

$$\zeta_+/\alpha = 1 + [1 + (\mu_{01}\epsilon_\infty/\Delta)^2]^{-1/2} \equiv 1 + b, \qquad (12)$$

where $b \approx 0$ for fields that are sufficiently strong that the resonant (population) Rabi frequency $\mu_{01}\epsilon_\infty$ is large compared to the detuning Δ. For fields that are strong in this sense a necessary and sufficient condition for validity of the adiabatic approximation is therefore

$$\exp(-\pi\rho) \ll 1 \quad \text{(strong fields)}. \qquad (13a)$$

The condition $\rho = \Delta/\lambda \gg 1$ has previously been identified as the condition for validity of the adiabatic approximation for weak fields, as the result of an analytic calculation based on first-order perturbation theory [4]. For an eventual field strength ϵ_∞ such that $\mu_{01}\epsilon_\infty$ is small compared to Δ, one finds from (11) that $\zeta_+/\alpha \approx 2 - (\mu_{01}\epsilon_\infty/\Delta)^2/2$; from (12), it then follows that the criterion for adiabaticity is

$$1 - |c_-|^2 = |c_+|^2 \approx a[\exp(2\pi\rho) - 1]^{-1} \ll 1$$

(weak fields) (13b)

where $a = \exp[(\mu_{01}\epsilon_\infty/\Delta)^2/2] - 1 \approx (\mu_{01}\epsilon_\infty/\Delta)^2/2$. It follows from (13b) that the probability of the dressed state $|+\rangle$ that is *not* reached adiabatically from the initial (ground) state will not exceed a if $\rho \geqslant (\ln 2)/2\pi = 0.11$. If $\rho \ll 1$, (13b) can still be satisfied, provided that

$$a(2\pi\rho)^{-1} \ll 1 \quad \text{(weak field, rapidly switched on)}. \qquad (13c)$$

According to eqs. (13) the adiabatic approximation will be satisfied in the two-level SEPS if the pulse is switched on slowly on the time scale Δ^{-1} (i.e. if $\rho \gg 1$), regardless of the eventual field strength. The adiabatic approximation is also valid for a sufficiently weak rapidly-switched-on pulse, according to (13c).

For a second example, we give the EPS for a system consisting of one lower level and several upper levels that may be discrete or continuous, and that are indexed by the variable Δ, meant to represent a detuning. The upper levels have density $g(\Delta)$ and the dipole matrix elements are $\mu(\Delta)$. We find from (9) that the lower-state probability amplitude $(\tilde{\psi})_0(\tau)$ contains only even terms in τ and that $(\tilde{\psi}_{2(n+1)})_0$ can be computed from $(\tilde{\psi}_{2n})_0$:

$$(\tilde{\psi}_{2(n+1)})_0 = -\frac{1}{2(n+1)}\left(\int \frac{\mu^2(\Delta)g(\Delta)\mathrm{d}\Delta}{2n+1-(i/\lambda)(\Delta+s)}\right)(\tilde{\psi}_{2n})_0, \qquad (14)$$

where $\delta_{\Delta\Delta} = \Delta + s$ is the detuning of the upper state; s is the detuning of the center of the upper-level distribution from resonance.

This subsumes several cases of interest. For a non-degenerate two-level system, we have $\mu^2(\Delta)g(\Delta) = \mu_{01}^2\delta(\Delta)$ (where $\delta(\Delta)$ is a Dirac delta function) so that (14) reduces to

$$(\tilde{\psi}_{2(n+1)})_0 = -\frac{1}{2(n+1)}\frac{\mu_{01}^2}{2n+1-\mathrm{i}/s\lambda}(\tilde{\psi}_{2n})_0.$$

In the case $s = 0$ (on resonance) this reduces further to

$$(\tilde{\psi}_{2(n+1)})_0 = -\frac{\mu_{01}^2}{2(n+1)(2n+1)}(\tilde{\psi}_{2n})_0,$$

which in turn implies that

$$(\tilde{\psi})_0 = \cos(\mu_{01})\tau, \tag{15}$$

a resonant Rabi solution of the two-level system for a time-varying pulse [5].

The $(1, N)$ system consisting of one lower and N upper levels, with transitions allowed only between the lower and upper levels (but not among the upper levels) is the prototype for discussions of a single level $|0\rangle$ interacting with a quasicontinuum or a real continuum of other levels $|1, a\rangle$. As such, it is of interest not only in MPE [1] but also in other areas, such as radiationless transitions in polyatomic molecules [6]. For a $(1, N)$ system (14) reduces to

$$(\tilde{\psi}_{2(n+1)})_0 = -\frac{1}{2(n+1)}\left(\sum_a \frac{\mu_{01}^2(a)}{2n+1-(\mathrm{i}/\lambda)(d(a)+s)}\right)(\tilde{\psi}_{2n})_0, \tag{16}$$

where $\delta_{aa} = d(a) + s$.

Finally, we illustrate the utility of the EPS even in the case of a continuous distribution of levels such that $\mu^2 g$ is a lorentzian:

$$\mu^2(\Delta)g(\Delta) = \frac{\sigma\mu_{01}^2}{\pi}\frac{1}{\Delta^2+\sigma^2}. \tag{17}$$

Then (14) is integrable and

$$(\tilde{\psi}_{2(n+1)})_0 = -\frac{1}{2(n+1)}\mu_{01}^2\frac{1}{2n+1-(\mathrm{i}/\lambda)(s+\mathrm{i}\sigma)}(\tilde{\psi}_{2n})_0. \tag{18}$$

Thus the ground-state amplitude is exactly that of a two-level system with a *complex* detuning consisting of the real detuning plus i times the width of the lorentzian. In the special case $s = 0$ (on resonance) and $\sigma = 2\lambda$ (18) implies that

$$(\tilde{\psi}(\tau))_0 = (\mu_{01}\tau)^{-1}\sin\mu_{01}\tau \tag{19}$$

Remarkably, the series (8) can also be resummed exactly using the full EPS (18), with the result that the ground-state amplitude of a system with a level density and transition-moment distribution obeying (17) is proportional to a Bessel function of complex order:

$$(\tilde{\psi}(\bar{\tau}))_0 = \left(\frac{2}{\bar{\tau}}\right)^{(\alpha-1)/2}\left(\frac{\alpha-1}{2}\right)! J_{(\alpha-1)/2}(\bar{\tau}), \tag{20}$$

where $\alpha = -\mathrm{i}(s + \mathrm{i}\sigma)/\lambda$ and $\bar{\tau} = \mu_{01}E_0 e^{\lambda t}/(2\hbar\lambda)$. This result is shown graphically in fig. 3 for three different values of σ/λ, giving undamped, slowly damped and rapidly damped Rabi oscillations.

The exact solution (20) provides an interesting opportunity to study intramolecular relaxation (IMR) [6–9]. The IMR time is usually defined as the decay time of the nonstationary state produced by optical excitation of a $(1, N)$ system (fig. 2) ([9], fig. 1) or the limiting case of a continuum of upper levels. The IMR time t_I is also the decay time of the expectation value of an off-diagonal observable such as the dipole moment μ [6,8]. The latter interpretation of t_I is intuitively appealing because a nonzero expectation value of an off-diagonal observable is associated with coherence [10], while a zero expectation value is often taken to imply incoherence. In the case of a $(1, N)$ system the dipole expectation value $\langle\mu\rangle$ is approximatly equal to the decay time of $(\tilde{\psi}(\bar{\tau}))_0$ (20).

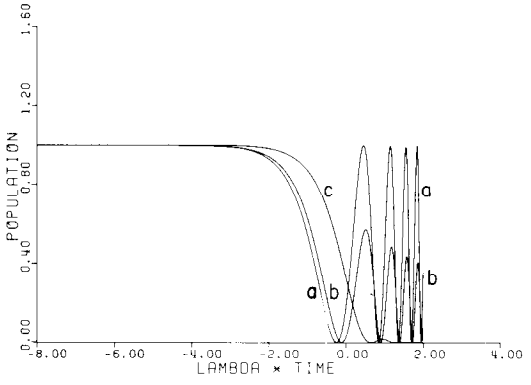

Fig. 3. Time dependence of the lorentzian-continuum EPS (20). In all cases $s/\lambda = 0.025$ and $\mu_{01}E_0/(2\hbar\lambda) = 4.0$. (a) $\sigma/\lambda = 0$ (two-level system); (b) $\sigma/\lambda = 0.25$; (c) $\sigma/\lambda = 3.0$.

For resonant excitation ($s = 0$) and for integer values of $(\alpha - 1)/2 \equiv \nu$, (20) implies that

$$(\tilde{\psi}(\bar{\tau}))_0 = \prod_{s=1}^{\infty} (1 - (\bar{\tau}/j_{\nu,s})^2] \qquad (21)$$

where $j_{\nu,s}$ is the sth zero of $J_\nu(x)$. All dependence on the width of the distribution (σ) is now contained in the dependence of $j_{\nu,s}$ on $\nu = (\sigma - \lambda)/2\lambda$. Consider IMR in the limit of an upper "band" that is broad compared to the reciprocal of the switching-on time (i.e., $\sigma \gg \lambda$). The asymptotic form for $j_{\nu,s}$ [11] in these limits gives the result $j_{\nu,s} \approx (2/3)(-a_s)^{3/2}$; which is completely independent of ν and hence of σ; a_s is the sth negative zero of the Airy function Ai(x). Thus in the limit $\sigma/\lambda \gg 1$, there can be *no* strong dependence of the IMR rate on the width σ of the upper "band", a conclusion that differs appreciably from the rather common intuition that the IMR time for an upper "band" obeying (17) ought to be of the order of σ^{-1}. The physical reason why the IMR rate in this case is nearly independent of σ is that when $\sigma \gg \lambda$ only a subset of states spanning a frequency interval of order λ is effectively pumped by the exponential pulse. A simple calculation shows that in fact $t_I = \lambda^{-1} \ln(\bar{\tau}_1/\bar{\tau}_0)$, where $(\tilde{\psi}(\bar{\tau}_0))_0 = 0.1$ and $(\tilde{\psi}(\bar{\tau}_1))_0 = 0.9$ are taken as a reasonable definition of the beginning and end of the process of IMR. Thus the IMR time t_I in this case depends primarily on the conditions of excitation (i.e. on λ) and only weakly on the width of the upper band of levels (σ), in agreement with the general arguments advanced in [8].

In conclusion, we have demonstrated a new method for solving the time-dependent Schrödinger equation in the RWA that is numerically convenient and that leads to new closed-form solutions in several physically important cases. We have used some of the closed-form solutions to discuss aspects of the adiabatic approximation and intramolecular relaxation that are of current interest in quantum optics.

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