Nonperturbative theory of the resonant interaction of atoms with laser fields*

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(Received 15 January 1976)

A nonperturbative analysis is given for an n-level atom or molecule dressed by a Stark field and in single-photon or multiphoton (near) resonant interaction with coherent optical field modes, which may be intense. All the field amplitudes and phases may have nonadiabatic time variation. New formulas for probability amplitudes of states *with finite lifetimes* are given for atom-field levels swept or optical Stark shifted through resonance or into close approach. One of these includes the Landau-Zener formula as a special case. Power broadening is contained in these formulas. They are useful for both weak- and strong-field interaction. Further, it is shown that many familiar single-photon coherent transient phenomena have their analogs in the intense-field and the multiphoton domains. Two new effects, pulse-shape dependence in final transition probability and population inversion due to the nonadiabatic passage of an asymmetric pulse, are demonstrated with numerical results for the process $\mathrm{Na}(3s)+2\hbar\omega\rightarrow\mathrm{Na}(5s)$. Finally, double resonance (single-photon and/or multiphoton) is analyzed, with discussion of adiabatic following and a derivation of a formula for level crossing. Generalization of an earlier procedure for solving the adiabatic eigenvalue problem of the whole atom-field system is given.

I. INTRODUCTION

Kroll and Watson[1] (KW) and Lau[2] (hereafter referred to as I) have analyzed atom-atom scattering in intense laser fields. Although some analytic and numerical results specific for an isolated atom irradiated by a Gaussian laser pulse were published in I, the general theoretical development and conditions in KW and I were addressed solely to atomic *scattering* in optical field modes of *constant* amplitude and phases.

We consider here (in Sec. II) the general theory of an isolated atom (or molecule) interacting with one or more coherent optical field modes whose amplitudes and phases may be time dependent. In addition, a dc Stark field, pulsed or not, may be present. A new transition probability formula involving *time-dependent coupling* and level crossing with *dampings* is derived (Sec. III A). This would also be useful in atom-atom scattering theory, and it includes the Landau-Zener formula as a special case. Since finite lifetimes are important in the observable transient responses of an atom (although less so in atom-atom scattering), a new formula, more general than the one given in I, is derived here (Sec. III B) for states with *nonzero* dampings and with energy levels in close approach. They are useful for analyzing experiments where atomic energy levels are swept or optical Stark shifted through a single-photon or multiphoton resonance or into close approach. These formulas are valid in the nonadiabatic regime, which includes the adiabatic limit.

In Sec. IV, the theory is applied to show two new effects: pulse-shape dependence in final transition probability and the possibility of imperfect population inversion after nonadiabatic passage of an *asymmetric* pulse, with numerical results for the process $\mathrm{Na}(3s)+2\hbar\omega\rightarrow\mathrm{Na}(5s)$. As an illustrative extension of the theory to the handling of more complex situation, double resonance, useful for atom-atom scattering as well, is treated in Sec. V. A summary is given in Sec. VI.

Coherent transient phenomena are usually analyzed using the phenomenological Bloch equations.[3] Recently, there has been considerable interest in extending its description to two-photon processes.[4] We also discuss here (in Sec. III) a Bloch equation for *perturbed* atomic states. As opposed to earlier works, it treats single-photon or multiphoton (near) resonance on an equal basis from the start and is applicable to fields of much higher intensity.

As in KW and I, our general analysis does not make any perturbative assumption. The real atom is approximated by its n bound states, where $n \geq 2$. This is generally more useful, as well as essential, for high intensity. On the other hand, the n levels must be low lying or the field must be not too intense, so that multiphoton ionization is of secondary importance. However, it often happens that resonant bound states play a decisive role in multiphoton ionization results[5]; then the analysis given here may contribute as part of the whole analysis. The atom-field interaction in our treatment can occur as higher multipoles as well as electric dipoles. The rotating-wave approximation (RWA) is not made. For two levels in *multiphoton* near resonance or when other nonresonant levels contribute significantly to the shifts and effective coupling, as in the case of an intense field, the so-called antiresonant terms generally cannot be neglected *a priori*.

Among the analyses[6] on interaction with intense fields, Swain and others[7] have used the method of continued fractions to study the importance (for intense fields) of the antiresonant terms. A consequence of not making the RWA is that the calculated energy shift includes the Bloch-Siegert shift as well as the usual optical Stark shift. We are concerned here mainly with resonant coherent effects on the atomic system. However, coupled with the Maxwell's equations, the present treatment is useful in the analysis of effects on the field in a (near-) resonant gaseous medium, although this is not considered in this paper.

II. GENERAL THEORY

We consider here a stationary atom interacting with m optical field modes

$$\vec{E}(\vec{r},t)=\sum_{\lambda=1}^{m}\epsilon_\lambda(t)\hat{\epsilon}_\lambda\sin[\omega_\lambda t+\theta_\lambda(t)]\ ,$$

whose amplitudes $\epsilon_\lambda(t)$ and phases $\theta_\lambda(t)$ may have near-adiabatic time dependence. The time dependence in the phase $\theta_\lambda(t)$ is due to frequency chirping. A Stark field $\vec{E}_0(t)$, which may be pulsed, may also be present. Where some formal similarity exists with I, we shall be brief.

We can treat the atom dressed by the Stark field by defining the *adiabatic* atomic Hamiltonian $h(t)$ to be the sum of the usual Hamiltonian of the bare atom and the interaction Hamiltonian $h_0(t)$,[8] where the parametric time dependence is through $E_0(t)$. The solution of the *adiabatic* eigenvalue problem $h(t)\varphi_\alpha(t)=w_\alpha(t)\varphi_\alpha(t)$ at each parameter t is identical to the corresponding well-known eigensolution with constant static field.[8] A quantity $\epsilon_\lambda(t)$, $\omega_\lambda+d\theta_\lambda/dt$, or $E_0(t)$ is said to have *near-adiabatic* time dependence if Γ, the time rate of fractional change of the quantity, satisfies the following conditions:

$$\Gamma\ll\omega_\lambda\ ,\quad \Gamma\ll\Delta w\ , \tag{2.1}$$

where Δw is the smallest frequency difference of those bare atomic levels likely to be excited by the interactions. Physically this means that the variation of these quantities in time ω^{-1} and $(\Delta\omega)^{-1}$ is very small. However, their time variation in the coarse-grained time [in units larger than ω^{-1} and $(\Delta w)^{-1}$] can be large—described as *nonadiabatic*. The criteria (2.1) enable us to neglect transitions between bare atomic states owing to the time variation of the physical quantities $\epsilon_\lambda(t)$, $\theta_\lambda(t)$, and/or $E_0(t)$ alone (i.e., without absorption or emission of any photons).

The total Hamiltonian H of the atom-field system[9] is $H=h(t)+h_\gamma+h'$, where h_γ and h' are the well-known free-field and charge-field interaction Hamiltonians.[10] The interesting parallel between the adiabatic atomic Hamiltonian and the adiabatic molecular Hamiltonian in KW and I should be noted. Our analysis starts with the Schrödinger equation

$$i\hbar\frac{d\Psi}{dt}=[h(t)+h'(t)]\Psi\ , \tag{2.2}$$

where

$$h'(t)\equiv e^{ih_\gamma t/\hbar}h'e^{-ih_\gamma t/\hbar}\ .$$

We treat the field classically by replacing all of the field operators in $h'(t)$ by their classical values.[11] Substituting the following expansion into Eq. (2.2),

$$\Psi=\sum_{\beta=1}^{n}\sum_{\{\nu_\lambda\}}b_{\{\nu_\lambda\}}(\beta)\,\varphi_\beta\exp\Big(-i\sum_\lambda\nu_\lambda(\omega_\lambda t+\theta_\lambda-\tfrac{1}{2}\pi)\Big),$$

we obtain

$$\begin{aligned}i\frac{d}{dt}b_{\{\nu_\lambda\}}(\alpha)&=W_{\{\nu_\lambda\}}(\alpha)b_{\{\nu_\lambda\}}(\alpha)\\&\quad+\sum_{\gamma=1}^{m}\sum_\beta G_\gamma(\alpha,\beta)[b_{\{\nu_\gamma-1\}}(\beta)+b_{\{\nu_\gamma+1\}}(\beta)]\ ,\end{aligned} \tag{2.3}$$

where $\{\nu_\lambda\}$ denotes a set of m integers and $b_{\{\nu_\lambda\}}(\alpha)$ is the probability amplitude[11] that the atom-field is in atomic state φ_α, with $\nu_\lambda>0$ (<0) photons absorbed (emitted) from the λth mode. In the subscript set $\{\nu_\gamma\pm1\}$ of the last term above, all component indices are the same as those in the set $\{\nu_\lambda\}$ of the first and second terms except the γth, for which one has $\nu_\gamma\pm1$ instead. The unperturbed atom-field levels are defined by

$$W_{\{\nu_\lambda\}}(\alpha)\equiv\frac{w_\alpha}{\hbar}-\sum_\lambda\nu_\lambda\Big(\omega_\lambda+\frac{d}{dt}\,\theta_\lambda(t)\Big),$$

and for electric dipole[12] interaction Hamiltonian $h'(t)\equiv\vec{h}''\cdot\vec{E}(0,t)$,

$$G_\lambda(\alpha,\beta)\equiv(\varphi_\alpha,\vec{h}''\cdot\hat{\epsilon}_\lambda\varphi_\beta)\epsilon_\lambda(t)/2\hbar\ ,$$

is the interaction. Figure 1 illustrates the unperturbed energy-level scheme for the case of two modes. For both the unperturbed levels and the shifted levels calculated below, two (near-) resonant levels of the atom [see Fig. 1(a)] correspond to two (near-) degenerate levels of the atom-field system [see Fig. 1(b)]. Nevertheless, in the rest of the paper, (near-) degenerate levels of the *atom-field* system will still be called (near) resonant. No ambiguity results. If φ_α are chosen real, $G(\alpha,\beta)$ above is real.

In obtaining Eq. (2.3), we have made use of the near-adiabatic conditions (2.1) to approximate

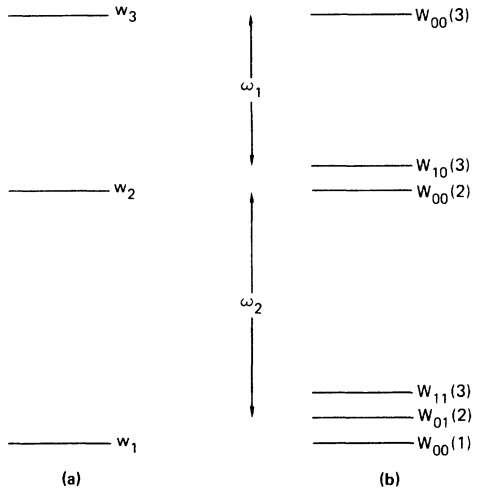

FIG. 1. Illustration for unperturbed energy-level scheme (a) for the atom only and (b) for a noninteracting atom-field system of two modes. Other levels are not drawn.

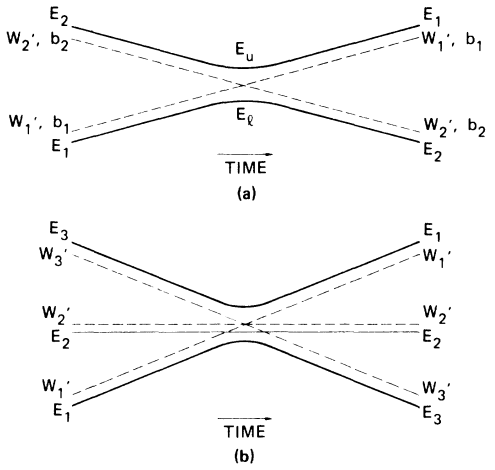

FIG. 2. Relationship between the adiabatic eigenvalue E and the shifted levels W' of the perturbed states (a) for two-level crossing and (b) for three-level crossing. In both diagrams, the gap between any E with the corresponding W' at the sides is exaggerated relative to the center.

$(\varphi_\alpha, d\varphi_\beta/dt) \approx 0$ ($=0$ if $\alpha=\beta$) if a *pulsed* Stark field is present. Also, we have separately equated the slowly time-varying "coefficients" of $e^{-\sum i\nu_\lambda\omega_\lambda t}$ for different $\sum\nu_\lambda\omega_\lambda$ to zero.[13] We note that for the bare atom $G(\alpha,\alpha)=0$ by parity of φ_α, while for the atom dressed by a Stark field, $G(\alpha,\alpha)\neq 0$ in general and may be included.

In the near-adiabatic regime, the stationary states of the atom-field system may be approximated by the *adiabatic states* defined by

$$b_{\{\nu_\lambda\}}(\alpha) = a_{\{\nu_\lambda\}}(\alpha)\exp\left(-i\int^t E(t')\,dt'\right), \qquad (2.4a)$$

and in the adiabatic limit (at fixed parameter t)

$$\frac{d}{dt}\,a_{\{\nu_\lambda\}}(\alpha) = 0\ .$$

Using these expressions in Eq. (2.3) gives

$$Ea_{\{\nu_\lambda\}}(\alpha) = W_{\{\nu_\lambda\}}(\alpha)a_{\{\nu_\lambda\}}(\alpha) + \sum_{\gamma,\beta} G_\gamma(\alpha,\beta)\left[a_{\{\nu_\gamma-1\}}(\beta)+a_{\{\nu_\gamma+1\}}(\beta)\right]\ . \qquad (2.4b)$$

The solution of this adiabatic eigenequation has been given before.[14] We make here some useful remarks to indicate the power of the method. First, the cutoff value $\nu=M$ is usually small (<5). For example, for a dipole matrix element between two states ~3 a.u. and a field intensity of 10^{12} W/cm^2, $M=2$ gives the energy-level shifts due to single-photon virtual process accurate to at least four significant figures. Second, the convergence of the iteration is rapid, from two iterations for 10^9 W/cm^2 to five iterations for 10^{12} W/cm^2, yielding an accuracy of at least five significant figures for the shifts. The calculated effective coupling is much more accurate than the shifts.

For convenience of analysis, we define the *perturbed states* as follows: For example, when two atom-field levels "1" and "2" (e.g., in the notation of I, $\rho\sigma$ and $\mu\tau$ for one mode, or $\rho_1\rho_2\sigma$ and $\mu_1\mu_2\tau$ for two modes) are near resonant, the final two-component equations in Eq. (2.4b) used to obtain the adiabatic eigensolutions $(E_u, \hat{\Psi}_u \equiv \underline{a}^u)$ and $(E_l, \hat{\Psi}_l \equiv \underline{a}^l)$ are[2]

$$E\begin{bmatrix}a_1\\a_2\end{bmatrix} = \begin{bmatrix}W_1' & G\\ G & W_2'\end{bmatrix}\begin{bmatrix}a_1\\a_2\end{bmatrix} \equiv \hat{H}\begin{bmatrix}a_1\\a_2\end{bmatrix}. \qquad (2.5)$$

The *perturbed states* $\hat{\Phi}_1$ and $\hat{\Phi}_2$ are defined as the basis states of Eq. (2.5). They are orthonormal linear combination of $\hat{\Psi}_u$ and $\hat{\Psi}_l$. W_i' is therefore the *shifted energy* associated with $\hat{\Phi}_i$, while G is the *effective coupling* between the two perturbed states. Whether we use $(E_u, \underline{a}^u)$ or $(E_l, \underline{a}^l)$ to calculate them, both W_i' and G are uniquely given if all other atomic levels are far off-resonant. However, at strong fields a small numerical difference in $W_2'-W_1'$ and G owing to a close-lying but off-resonant third level can result.[15] If significant, such difference can be eliminated by including the third or more atom-field levels as near resonant, as will be illustrated in Sec. V. In the limit of vanishing fields, $W_\rho'(\sigma)$, for example, approaches the unperturbed $W_\rho(\sigma)$ and $\hat{\Phi}_{\rho\sigma}$ approaches the unperturbed atom-field state. See Fig. 1(b) and Fig. 2(a) for illustration of relationship of W, W', and

E for the particular configuration of two-level crossings. We label E by the convention $E_i \to W_i$ as $G_\lambda(\alpha, \beta) \to 0$. Far from resonance, $E_i = W_i'$.

When a given *atom-field* adiabatic state is off-resonant by the amount Δ from any other populated state such that $\Delta \gg \Gamma$, the change in magnitude of the probability amplitude in such a state may be neglected. (See Sec. III A for more discussion.) When it is (near) resonant (i.e., $\Delta \gtrsim \Gamma$ or $\Delta < \Gamma$) with another populated state, significant transitions occur, and we must calculate their probability amplitudes. Thus we expand a general state $\Psi(t)$ in the two perturbed states, $\Psi(t) = b_1(t)\hat{\Phi}_1 + b_2(t)\hat{\Phi}_2$, and obtain with the above Hamiltonian $\hat{H}$

$$i\frac{db_1}{dt} = W_1' b_1 + G b_2, \quad i\frac{db_2}{dt} = W_2' b_2 + G b_1 , \tag{2.6}$$

where $(\hat{\Phi}_i, d\hat{\Phi}_i/dt) = 0$ and $(\hat{\Phi}_1, d\hat{\Phi}_2/dt) \approx 0$ have been used. The initial-value conditions most often used are

$$b_2 = 0, \quad b_1 = 1, \quad \text{at } t = t_0 . \tag{2.7}$$

III. ANALYTIC FORMULAS FOR PROBABILITY AMPLITUDES

Single-photon coherent transitions in an atom interacting with a weak radiation field are often discussed in terms of the Bloch equation. Recently it was generalized to two-photon processes.[4] From Eq. (2.6), we can obtain[16] a Bloch equation $d\vec{\rho}/dt = \vec{\Omega} \times \vec{\rho}$, where $\vec{\Omega} \equiv (2G, 0, W_2' - W_1')$ is the torque vector or effective field and $\vec{\rho} \equiv (b_2 b_1^* + b_1 b_2^*, ib_2 b_1^* - ib_1 b_2^*, |b_2|^2 - |b_1|^2)$ is the Bloch vector. The phenomenological decay times T_1 and T_2' can also be inserted.[3] This Bloch equation for the *perturbed* states describes both single-photon and multiphoton (of any order) processes in intense fields and is obtained without use of the RWA. Because of its formal similarity with the usual phenomenological Bloch equation, many of the known analytic results[17,3] can be used directly with the above definition of $\vec{\Omega}$. By implication, the rich coherent transient phenomena[18] have their counterparts in the strong-field and/or the multiphoton domains.

The optical Bloch equation is often a convenient and useful tool for analysis. However, we find it convenient for the analysis below to use the original Eq. (2.6) with two phenomenological damping terms,

$$\begin{aligned} i\frac{db_1}{dt} &= (W_1' - i\Gamma_1) b_1 + G b_2 , \\ i\frac{db_2}{dt} &= (W_2' - i\Gamma_2) b_2 + G b_1 . \end{aligned} \tag{3.1}$$

When $\Gamma_1 = \Gamma_2$, the above equations describe decay behavior in the same manner as does the phenomenological Bloch equation with $T_1 = T_2'$. Otherwise, they describe different decay behaviors. If the "language" of the Bloch vector $\vec{\rho}$ is desired, it can be obtained from the solutions given below. For this and other reasons, we shall write out both b_1 and b_2 and their phases.

A. Nonadiabatic transitions in two-level crossings

In the familiar phenomena adiabatic following[19] and adiabatic inversion,[20] both the interaction and the energy off-resonance (the components of the "torque vector" in the language of Bloch equations) are restricted to negligible change in the coarse-grained time scale. This can be approximated by taking proper choices in some experiments.[20] But more usual situations are such that the interaction and/or the energy off-resonance do change in time by a finite amount.[21] Therefore analysis taking into account transitions due to nonadiabaticity is both useful in giving an estimate of such transitions and is necessary in many circumstances. It can be shown[22,23] that transitions stemming from nonadiabaticity are most probable when $\Delta' \equiv W_2' - W_1'$ is smallest—for example, when the two resonant levels cross in adiabatic inversion. The formulas given below for nonadiabatic situations with $\Gamma_1 \neq 0$, $\Gamma_2 \neq 0$, $d\Delta'/dt \neq 0$, and/or $dG/dt \neq 0$ are new. They are also useful for weak fields with Δ' and G given by standard perturbation theories.

Consider first the case where Γ_1 and Γ_2 are constant, and where

$$\Delta' = -\alpha\tau , \tag{3.2}$$

$$G = \beta + \gamma\tau , \tag{3.3}$$

where α, β, and γ are constant and $\tau = t - t_i$, t_i being the time at which the single-photon or multiphoton resonance occurs [see Fig. 2(a)]. Condition (3.2) may correspond to the physical situation in which the levels are swept through resonance either by chirping the field frequency or by dc or optical Stark shifting the atomic levels. Condition (3.3) may correspond to amplitude variation of the optical field. Eliminating b_1 from Eq. (3.1) and introducing the relation (with $\tau_0 \equiv t_0 - t_i$)

$$b_2(\tau) = U(\tau) \exp\frac{1}{2}\Big(-(\Gamma_2 + \Gamma_1)(\tau - \tau_0) + \int_{\tau_0}^{\tau} d\tau' \left[-i(W_2' + W_1') + g \right] \Big),$$

$$g \equiv \frac{dG}{dt} \Big/ G \tag{3.4}$$

into the resulting differential equation for $b_2(\tau)$,

we obtain

$$\frac{d^2U}{d\tau^2}+\{G^2-\tfrac{1}{2}i\alpha-\tfrac{1}{2}g^2 + [\tfrac{1}{2}\alpha\tau+\tfrac{1}{2}i(g+\Gamma_2-\Gamma_1)]^2\}U=0\ . \quad (3.5)$$

We need to find the solution of $U(\tau;\alpha)$ for positive α only, since with G being real, $U(\tau;-\alpha)=U^*(\tau;\alpha)$, as can be shown from Eq. (3.5) above. On the other hand, γ in Eq. (3.3) may be positive or negative. We shall consider only cases for which the following condition is satisfied:

$$(\gamma\Delta\tau/\beta)^2\ll 1\ , \quad (3.6)$$

where $\Delta\tau$ is the time interval over which the solution of transition probability reaches its asymptotic values. An estimate of this is given by $(\alpha^{1/2}\Delta\tau)^2\gg 1$. Then condition (3.6) implies

$$(1/\alpha)(\gamma/\beta)^2\ll 1\ . \quad (3.7)$$

Condition (3.6) means that over the entire time interval of transition, $G(\tau)$ varies by a small fraction. Thus we shall keep $\gamma\tau/\beta$ terms but will drop its higher-power terms. Making a change of variable,

$$z\equiv\left[\tau+\frac{4\gamma\beta}{\alpha^2}+i\frac{1}{\alpha}\left(\frac{\gamma}{\beta}+\Gamma_2-\Gamma_1\right)\right]\alpha^{1/2}e^{-i\pi/4}\ , \quad (3.8)$$

and defining

$$n\equiv q+ip,\quad p\equiv\alpha^{-1}[\,\beta^2-4(\gamma\beta/\alpha)^2-\tfrac{1}{2}(\gamma/\beta)^2\,], \quad (3.9)$$
$$q\equiv\frac{2\gamma\beta(\gamma/\beta+\Gamma_2-\Gamma_1)}{\alpha^2}\ ,$$

we obtain from Eqs. (3.5) and (3.6) the Weber equation

$$\frac{d^2U}{dz^2}+(n+\tfrac{1}{2}-\tfrac{1}{4}z^2)U=0\ , \quad (3.10)$$

with known solutions called parabolic cylinder functions, $D_n(\pm z)$ and $D_{-n-1}(\pm iz)$.[24] With the definitions of $\varphi(\tau)$, $-\pi<\varphi(\tau)\leq\pi$,

$$z\equiv R(\tau)e^{i\varphi+i3\pi/4},\quad \tau<0\ ,$$
$$z\equiv R(\tau)e^{i\varphi-i\pi/4},\quad \tau>0\ ,$$
$$R(\tau)\equiv\left[\left(\tau+\frac{4\gamma\beta}{\alpha^2}\right)^2+\frac{(\gamma/\beta+\Gamma_2-\Gamma_1)^2}{\alpha^2}\right]^{1/2}\alpha^{1/2}\ ,$$

the solution satisfying the initial values Eq. (2.7) is given as follows:

If in the asymptotic region of negative τ

$$R^2(\tau_0)\gg 1 \quad (3.11)$$

and $\tau_0+4\gamma\beta/\alpha^2<0$, which implies

$$|\varphi(\tau_0)|<\tfrac{1}{2}\pi\ , \quad (3.12)$$

then

$$b_2(\tau)=[G(\tau_0)G(\tau)/\alpha]^{1/2}e^{-\pi p/4}R^q(\tau_0) \times D_{-n-1}(-iz)e^{\Lambda(\tau)-f_0}\ ,$$
$$b_1(\tau)=[G(\tau_0)/G(\tau)]^{1/2}e^{-\pi p/4}R^q(\tau_0) \times[(z-2\gamma\beta\alpha^{-3/2}e^{-i\pi/4}D_{-n-1}(-iz) + i(1+n)D_{-n-2}(-iz)]\exp[\Lambda(\tau)-f_0+\tfrac{1}{4}i\pi]\ , \quad (3.13)$$

where

$$f_0\equiv p\varphi(\tau_0)+\tfrac{1}{4}R^2(\tau_0)\sin 2\varphi(\tau_0)\ ,$$
$$\Lambda(\tau)\equiv-\tfrac{1}{2}(\Gamma_2+\Gamma_1)(\tau-\tau_0)-\frac{i}{2}\int_{\tau_0}^{\tau}(W_2'+W_1')\,d\tau'+i\theta_0\ ,$$

and where θ_0 is a constant phase. The above solution describes both the transient behavior of interest as well as the positive-time asymptotic behavior. The latter is given as follows: At τ such that

$$R(\tau)\gg 1 \quad (3.14)$$

and $\tau+4\gamma\beta/\alpha^2>0$, which implies

$$|\varphi|<\tfrac{1}{2}\pi, \quad (3.15)$$

are satisfied, the above solution becomes

$$b_2(\tau)=[G(\tau_0)G(\tau)/\alpha]^{1/2}[(2\pi)^{1/2}/\Gamma(1+n)][R(\tau)R(\tau_0)]^q \times\exp[-\tfrac{1}{2}\pi p+\Lambda(\tau)-f_0-f+i\theta]\ ,$$
$$b_1(\tau)=[G(\tau_0)/G(\tau)]^{1/2}[R(\tau_0)/R(\tau)]^q\,e^{\Lambda(\tau)-f_0} \times\{\exp[-\pi p+f-i\theta+\tfrac{3}{4}i\pi+i\pi q] - \pi^{1/2}\gamma\beta(2/\alpha)^{3/2}\Gamma^{-1}(1+n)R^{2q} \times\exp[-\pi p/2-f+i\theta]\}, \quad (3.16)$$

where $\Gamma(1+n)$ is the Γ function and

$$f\equiv p\varphi+\tfrac{1}{4}R^2\sin 2\varphi\ ,$$
$$\theta\equiv p\ln R+q(\varphi+\tfrac{1}{4}\pi)+\tfrac{1}{4}R^2\cos 2\varphi\ .$$

For the reason given following Eq. (3.5), the solution for the case $\alpha<0$ is obtained from Eqs. (3.13) and (3.16) by taking the complex conjugate of the entire expression, except for $\Lambda(\tau)$, and by substituting $|\alpha|$ for α there. In the limit $\gamma=0$ (i.e., constant coupling[25] G),

$$q=0,\quad G(\tau)=G(\tau_0)=\beta=(\alpha p)^{1/2}\ , \quad (3.17)$$

then Eq. (3.13) and Eq. (3.16) give exact results derivable without Eqs. (3.6) and (3.7). In particular, the asymptotic probabilities are

$$|b_2(\tau)|^2 = (1-e^{-2\pi p})\exp[-(\Gamma_2+\Gamma_1)(\tau-\tau_0)-2f_0-2f]\ , \quad (3.18)$$
$$|b_1(\tau)|^2=\exp[-2\pi p-(\Gamma_2+\Gamma_1)(\tau-\tau_0)-2f_0+2f]\ .$$

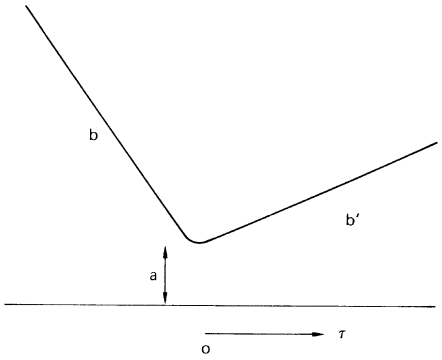

FIG. 3. Two levels in close approach.

Aside from decays, $|b_1(\tau)|^2$ in all of the above formulas is the probability that the system will *not* follow the curve $E_1E_IE_2$ in Fig. 2(a), and it is therefore a convenient estimate of nonadiabaticity. In application, at the initial time τ_0 the condition

$$\varphi(\tau_0)\approx 0 \tag{3.19}$$

is often satisfied; thus $f_0=0$ in Eqs. (3.13), (3.16), and (3.18). Similarly, if we are interested in large τ such that

$$\varphi(\tau)\approx 0, \quad \tau>0\ , \tag{3.20}$$

then $f=0$. The well-known Landau-Zener formula,[26] characterized by the single parameter p, is a special case of Eq. (3.18) when Eqs. (19) and (20) and $\Gamma_1=\Gamma_2=0$ are satisfied.

B. Two-level close approach

Consider two levels shifted into close approach (as shown in Fig. 3), either by tuning the laser frequency or by Stark shifting the levels, while the laser field amplitudes are approximately constant.[25] We have given a formula in I which is a special case of the one derived here. We let

$$W_2'-W_1'=\begin{cases} a-b\tau, & \tau\le 0\ , \\ a+b'\tau, & \tau>0\ , \end{cases}$$

where a is the minimum level separation and b and b' are the well-defined slopes. Such a representation has the disadvantage of a discontinuity in the slope of $W_2'-W_1'$, but rigorous results can be obtained without further assumptions and they are valid even when a is zero. The effective coupling is considered constant. Then eliminating b_1 from Eq. (3.1) and substituting expression (3.4) with $g=0$ into the resulting equation for b_2, we obtain

$$\frac{d^2U}{d\tau^2}+\left[G^2-\frac{ib}{2}+\frac{b^2}{4}\left(\tau-\frac{a}{b}+\frac{i\Gamma_2}{b}-\frac{i\Gamma_1}{b}\right)^2\right]U=0, \quad \tau\le 0\ ,$$

$$\frac{d^2U}{d\tau^2}+\left[G^2+\frac{ib'}{2}+\frac{b'^2}{4}\left(\tau+\frac{a}{b'}-\frac{i\Gamma_2}{b'}+\frac{i\Gamma_1}{b'}\right)^2\right]U=0, \quad \tau>0\ , \tag{3.21}$$

These equations show that it is necessary only to find $U(\tau;a,b,b')$ for a, b, and $b'>0$, since with G real $U(\tau;-a,-b,-b')=U^*(\tau;a,b,b')$. With the definitions

$$z_-\equiv\left(\tau-\frac{a}{b}+\frac{i\Gamma_2}{b}-\frac{i\Gamma_1}{b}\right)b^{1/2}e^{-i\pi/4}, \quad \tau\le 0\ , \tag{3.22}$$

$$z_+\equiv\left(\tau+\frac{a}{b'}-\frac{i\Gamma_2}{b'}+\frac{i\Gamma_1}{b'}\right)b'^{1/2}e^{-i\pi/4}, \quad \tau>0\ ,$$

the above equations are put into the Weber form,[24]

$$\frac{d^2U}{dz_-^2}+\left[n+\tfrac{1}{2}-\frac{z_-^2}{4}\right]U=0, \quad \tau\le 0\ ,$$

$$\frac{d^2U}{dz_+^2}+\left[n'+\tfrac{1}{2}-\frac{z_+^2}{4}\right]U=0, \quad \tau>0\ , \tag{3.23}$$

where

$$n\equiv ip, \quad n'\equiv ip'-1, \quad p\equiv G^2/b, \quad p'\equiv G^2/b'\ . \tag{3.24}$$

Provided that

$$R_0^2\equiv b(|\tau_0|+a/b)^2+(\Gamma_2-\Gamma_1)^2/b\gg 1\ ,$$
$$|\varphi(\tau)|<\tfrac{1}{2}\pi\ , \tag{3.25}$$
$$z_-\equiv R(\tau)e^{-i\varphi+i3\pi/4}, \quad -\pi<\varphi(\tau)\le\pi\ ,$$

are satisfied near $\tau=\tau_0$, the solution for $\tau\le 0$ satisfying the initial conditions (2.7) is

$$U(z_-)=ND_{-n-1}(-iz_-)\ ,$$

where

$$N\equiv p^{1/2}\exp[-\tfrac{1}{4}\pi p+f_0+i\theta_0]\ ,$$
$$f_0\equiv\varphi(\tau_0)p+\tfrac{1}{4}R_0\sin 2\varphi(\tau_0)\ , \tag{3.26}$$

and where θ_0 is a constant phase. For $\tau>0$, the solution is

$$U(z_+)=LD_{-n'-1}(-iz_+)+MD_{n'}(-z_+)\ ,$$

where the constant coefficients L and M, determined by demanding continuity of b_2 and of its slope at $\tau=0$, are

$$L/N=[n'e^{i3\pi/4}D_1D_6-(b/b')^{1/2}(n+1)e^{i\pi/4}D_2D_5]D^{-1}\ ,$$
$$M/N=[e^{i\pi/2}\hat{a}b'^{-1/2}D_1D_3-(n'+1)e^{i\pi/4}D_1D_4$$
$$+(b/b')^{1/2}(n+1)e^{i\pi/4}D_2D_3]D^{-1}\ ,$$

where

$$\hat{a} \equiv a - i\Gamma_2 + i\Gamma_1 ,$$

$$D \equiv e^{i\pi/2}\hat{a}b'^{-1/2}D_3D_5 + n'e^{i3\pi/4}D_3D_6 - (n'+1)e^{i\pi/4}D_4D_5 ,$$

$$D_1 \equiv D_{-n-1}(\hat{a}e^{i\pi/4}/b^{1/2}), \quad D_2 \equiv D_{-n-2}(\hat{a}e^{i\pi/4}/b^{1/2}) ,$$

$$D_3 \equiv D_{-n'-1}(\hat{a}e^{-i3\pi/4}/b'^{1/2}),$$

$$D_4 \equiv D_{-n'-2}(\hat{a}e^{-i3\pi/4}/b'^{1/2}) ,$$

$$D_5 \equiv D_{n'}(\hat{a}e^{i3\pi/4}/b'^{1/2}), \quad D_6 \equiv D_{n'-1}(\hat{a}e^{i3\pi/4}/b'^{1/2}) . \tag{3.27}$$

Thus for $\tau \leq 0$

$$b_2(\tau) = p^{1/2}e^{-\pi p/4}D_{-n-1}(-iz_-)e^{\Lambda(\tau)+f_0} ,$$

$$b_1(\tau) = e^{-\pi p/4}[z_-D_{-n-1}(-iz_-) + i(n+1)D_{-n-2}(-iz_-)] \times \exp[\Lambda(\tau) + f_0 + \tfrac{1}{4}i\pi] ,$$

and for $\tau > 0$

$$b_2(\tau) = p^{1/2}e^{-\pi p/4}[(L/N)D_{-n'-1}(-iz_+) + (M/N)D_{n'}(-z_+)]e^{\Lambda(\tau)+f_0} ,$$

$$b_1(\tau) = \left(\frac{b'}{b}\right)^{1/2} e^{-\pi p/4}\left(\frac{M}{N}z_+D_{n'}(-z_+) + \frac{M}{N}n'D_{n'-1}(-z_+) - i\frac{L}{N}(n'+1)D_{-n'-2}(-iz_+)\right) \times \exp[\Lambda(\tau) + f_0 - \tfrac{3}{4}i\pi] , \tag{3.28}$$

where

$$\Lambda(\tau) \equiv -\tfrac{1}{2}(\Gamma_2 + \Gamma_1)(\tau - \tau_0) - \frac{i}{2}\int_{\tau_0}^{\tau}(W_2' + W_1')\,d\tau' + i\theta_0 .$$

When the asymptotic conditions for $\tau > 0$,

$$R(\tau) \equiv [(\tau + a/b')^2 + (\Gamma_2 - \Gamma_1)^2/b'^2]^{1/2}b'^{1/2} \gg 1 ,$$

and $|\varphi'| < \frac{1}{2}\pi$,

$$z_+ \equiv R(\tau)e^{-i\varphi'-i\pi/4}, \quad -\pi < \varphi'(\tau) \leq \pi , \tag{3.29}$$

are satisfied, then the following asymptotic results are obtained:

$$b_2(\tau) = p^{1/2}e^{-\pi p/4}\left[\frac{L}{N}e^{-3\pi p'/4} + \frac{M}{N}\frac{(2\pi)^{1/2}}{\Gamma(1-ip')}e^{-\pi p'/4}\right] \times \exp[\Lambda(\tau) + f_0 - f - i\theta] ,$$

$$b_1(\tau) = \left(\frac{b'}{b}\right)^{1/2} e^{-\pi p/4}\left[\frac{M}{N}e^{-3\pi p'/4} + i\frac{L}{N}\frac{(2\pi)^{1/2}}{\Gamma(ip')}e^{-\pi p'/4}\right] \times \exp[\Lambda(\tau) + f_0 + f + i\theta + \tfrac{1}{4}i\pi] , \tag{3.30}$$

where

$$f \equiv p'\varphi' + \tfrac{1}{4}R^2\sin 2\varphi', \quad \theta \equiv p'\ln R + \tfrac{1}{4}R^2\cos 2\varphi' .$$

For the special case $r/b^{1/2} \gg 1$ and $r/b'^{1/2} \gg 1$, where $r \equiv [a^2 + (\Gamma_2 - \Gamma_1)^2]^{1/2}$, the coefficients in the above expressions simplify. The leading terms is contained in M/N and not in L/N:

$$\frac{M}{N} = -\frac{i2(\pi b)^{1/2}}{\hat{a}\Gamma(ip')}\exp[-\tfrac{3}{4}\pi p' + \tfrac{1}{4}\pi p + g + ih] ,$$

where

$$g \equiv -\tfrac{1}{2}a(1/b - 1/b')(\Gamma_2 - \Gamma_1) + (p - p')\rho ,$$

$$\hat{a} \equiv re^{i\rho} ,$$

$$h \equiv \frac{1}{4}\left(\frac{1}{b'} - \frac{1}{b}\right)[a^2 - (\Gamma_2 - \Gamma_1)^2] + p'\ln\frac{r}{b'^{1/2}} - p\ln\frac{r}{b^{1/2}} . \tag{3.31}$$

Substitution of this into Eq. (3.28) and especially Eq. (3.30) and neglecting terms proportional to L/N leads to simple expressions for b_1, b_2, and their magnitudes, such as that of $|b_2|$ with $\Gamma_1 = \Gamma_2 = 0$ given in I.

To conclude, we note that all of the formulas in this section are exact, so that the power-broadening effect is included.[27]

IV. PULSE SHAPING AND POPULATION INVERSION

Consider a practically monochromatic laser pulse passing through an atom in the ground state and shifting a near-resonant excited state into single-photon or multiphonon resonance at some critical intensity I', first on the rising slope of the pulse, and then on the descending slope (see Figs. 4 and 5). If the lifetime of the excited state is short compared with the temporal width of the pulse, then each crossing point should be considered separately. On the other hand, if the

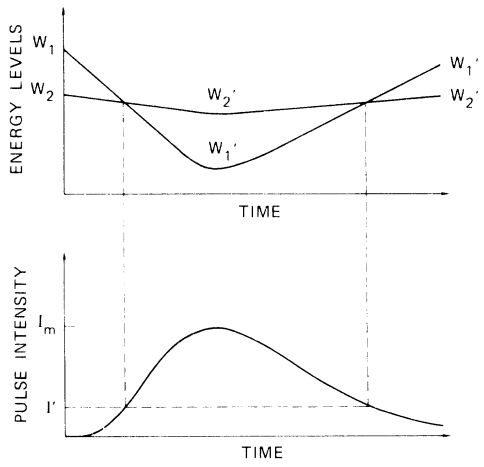

FIG. 4. Unperturbed near-resonant atom-field levels W_1 and W_2 optical Stark shifted through resonances at the critical intensity I' of an asymmetric pulse.

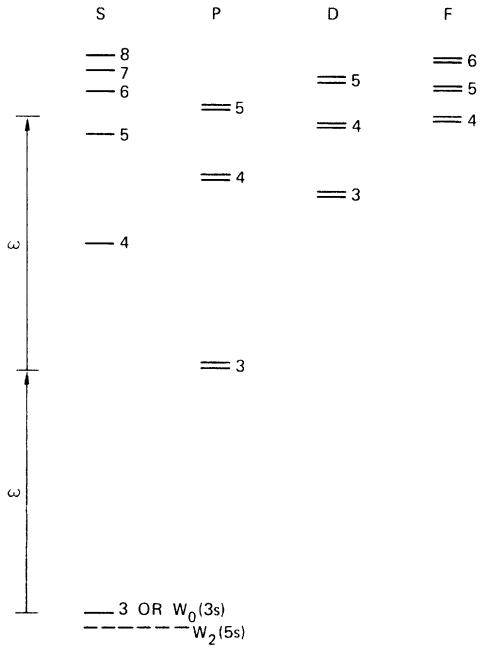

FIG. 5. Energy-level diagram of sodium showing all states included in the numerical calculation of the process $Na(3s)+2\hbar\omega \rightarrow Na(5s)$. The two-photon energy off-resonance is exaggerated. The radiative lifetime of the $5s$ level is 84.5 nsec.

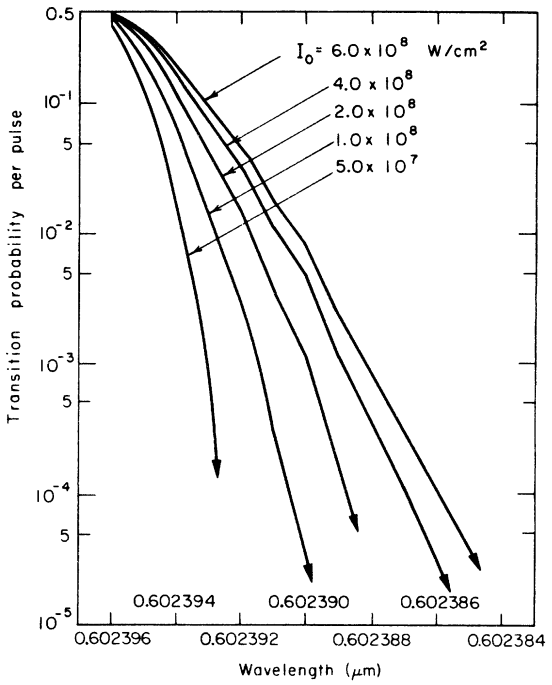

FIG. 6. Transition probability per pulse in the process $Na(3s)+2\hbar\omega \rightarrow Na(5s)$ at several wavelengths for a few Gaussian pulses of the same temporal width $\tau=1$ nsec but with different peak intensities.

lifetime of the excited state is long compared with the temporal width of the pulse, then the two resonance points have to be considered together. In cases treated in this section, the two resonance points are separated, so that asymptotic validity conditions (3.11) and (3.14) are satisfied for each resonance point. Depending on α, these conditions are usually easy to satisfy. We also assume that interference effect between the two resonance points can be removed by some averaging (e.g., over many similar pulses). Then the final transition probability in the excited state per pulse, after the pulse has passed, is

$$f_a \equiv T_1(1-T_2)+(1-T_1)T_2, \quad \text{for } T_1 \neq T_2 , \tag{4.1a}$$

or

$$f_s \equiv 2T(1-T), \quad \text{for } T_1 = T_2 \equiv T , \tag{4.1b}$$

where T_i is the transition probability associated with the ith resonance point. Since the transition probability formulas (3.18) for T_i depends on α_i, which in turn depends on the pulse slope at the resonance point,

$$\alpha_i = \left(\frac{d\epsilon}{dt}\,\frac{d\Delta'}{d\epsilon}\right)_{I'} \tag{4.2a}$$

or

$$\alpha_i = \left(\frac{dI}{dt}\,\frac{d\Delta'}{dI}\right)_{I'} , \tag{4.2b}$$

depending which one is better defined.[28] It is immediately clear that for temporally symmetric pulse ($T_1 = T_2$), the maximum value of f_s for any such pulse is $\frac{1}{2}$, and population inversion of the excited state with respect to the ground state is not possible. However, for asymmetric pulses ($T_1 \neq T_2$), this may be possible. To maximize f_a, it is desirable to have $T_2 \gg T_1$ or $T_2 \ll T_1$, that is, a fast-rising and slow-descending pulse, or vice versa, although the former case occurs more often.

In paper I, we have published numerical values[29] for critical intensity I' and the pulse-independent factor δ for the process $Na(3s)+2\hbar\omega \rightarrow Na(5s)$ (see Fig. 5). From these values, T_i for any pulse shape and parameters can be calculated. To use the values of δ and I' published in paper I, the following conversion relation is useful:

$$\frac{dI}{dt}\,(\text{a.u.}) = 3.758\,06\times10^{-33}\,\frac{dI}{dt}\,(\text{W/cm}^2) , \tag{4.3}$$

since $p=\delta/(dI/dt)_{I'}$ (in a.u.) can then be substituted directly into the appropriate formula. We have also shown that f_s depends on pulse parameters of the pulse as well as the photon wavelength. In par-

TABLE I. Transition probability per pulse f_a for $Na(3s)+2\hbar\omega \rightarrow Na(5s)$ due to an asymmetric pulse of intensity $I(t)=(I_m/2^4e^{-4})(t/\sigma)^4e^{-2t/\sigma}$. The peak intensity I_m is in W/cm^2. The temporal width σ is in nsec.

σ \ I_m	6×10^7	1×10^8	6×10^8	1×10^9	6×10^9
0.1	0.279	0.258	0.219	0.211	0.195
0.2	0.446	0.425	0.378	0.369	0.347
0.4	0.582	0.585	0.574	0.570	0.556
0.6	0.586	0.620	0.666	0.671	0.678
0.8	0.539	0.597	0.700	0.715	0.745
1.0	0.477	0.552	0.701	0.725	0.779
2.0	0.227	0.318	0.567	0.619	0.754
4.0	0.050	0.100	0.324	0.387	0.581
6.0	0.011	0.031	0.184	0.241	0.443
8.0	0.003	0.01	0.105	0.150	0.338

ticular, it was shown that f_s is sensitive to the temporal width τ of a Gaussian pulse $I(t)=I_0e^{-t^2/\tau^2}$, with $I_0=6\times10^8$ W/cm^2. We now illustrate in Fig. 6 the smaller sensitivity of f_s to I_0 with the same τ (= 1 nsec) over a range of wavelengths.

To demonstrate (i) pulse-shape dependece of f and (ii) population inversion with an asymmetric pulse, we consider again the above two-photon process in sodium with pulse (as shown in Fig. 4) $I_a(t)=I_a(t/\sigma)^4e^{-2t/\sigma}\theta(t)$, where $\theta(t)$ is the unit step function. The result in I shows that for photon wavelength $\lambda=6023.96$ Å, $f_s=\frac{1}{2}$ for the above Gaussian pulse, with $I_0=6\times10^8$ W/cm^2 and $\tau=1$ nsec. Now for the above asymmetric pulse with the same pulse energy and peak intensity [hence $I_a=2^{-4}e^4(6\times10^8)$ W/cm^2 and $\sigma=4^3\pi^{1/2}/3e^4$ nsec], $f_a=0.69$; hence shape dependence in the transition probability is demonstrated. Table I gives the values of f_a for different values of peak intensity $I_m\equiv 2^4e^{-4}I_a$ and σ of the above asymmetric pulse. It demonstrates the nonadiabatic population inversion ($f_a>\frac{1}{2}$) with respect to the ground state, and shows that in general f_a is more sensitive to σ than I_m.

For both symmetric and asymmetric pulses, population inversion in the excited states with respect to some intermediate states is of course possible. Furthermore, the above mechanism can be used as an efficient pumping mechanism to maintain laser action between two intermediate levels; for example, the transitions in sodium $4p$ to $4s$ at $\lambda\simeq2.21$ μm and $4p$ to $3d$ at $\lambda\simeq9.10$ μm by the above process. Certainly it should not be assumed that a large transition probability to an excited state can always be found with realistic pulses. Its feasibility depends on the atomic system and the field parameters. For the process $Li(2s)+8\hbar\omega \rightarrow Li(3s)$, whose I' and δ values are published in I, the temporal width of the Gaussian pulse has to be unrealistically large in order to achieve $f_s=\frac{1}{2}$.

The discussion above examines the field parameters for a given atomic system. Another way of looking at these effects is to say that the transition probability is significantly sensitive to the coupling between the states as well as the energy off-resonance between the atomic levels. Both of these dependences can be used for discriminant excitations in different isotopes of an atom or molecule by choosing the appropriate field parameters.

V. DOUBLE RESONANCE

Double resonance is a familiar spectroscopic technique.[30] We shall adopt the name here to denote the configuration in which any three atomic levels are in single-photon or multiphoton resonances owing to interaction with single or many field modes [see Fig. 1(b)]. It is useful as a means of populating a third level inaccessible to single-photon transitions, or an off-resonant third level by choosing the right combination of field frequencies. The analysis is useful in both atom-field interactions, and in atom-atom scattering in laser fields.

A. Adiabatic eigensolution

Suppose in an atom interacting with two field modes three levels $W_{\rho_1\rho_2}(\sigma)$, $W_{\mu_1\mu_2}(\tau)$, and $W_{\delta_1\delta_2}(\eta)$ are (near) resonant, as in Fig. 1(b). We express $a_{\nu_2}(\nu_1\alpha)$, defined in Eq. (2.4), as

$$a_{\nu_2}(\nu_1\alpha)=d_{\nu_2}(\nu_1\alpha)a_{\rho_2}(\rho_1\sigma)+s_{\nu_2}(\nu_1\alpha)a_{\mu_2}(\mu_1\tau)+t_{\nu_2}(\nu_1\alpha)a_{\delta_2}(\delta_1\eta)\ . \tag{5.1}$$

This implies immediately

$$d_{\rho_2}(\rho_1\sigma)=s_{\mu_2}(\mu_1\tau)=t_{\delta_2}(\delta_1\eta)=1\ ,$$
$$d_{\mu_2}(\mu_1\tau)=d_{\delta_2}(\delta_1\eta)=s_{\rho_2}(\rho_1\sigma)=s_{\delta_2}(\delta_1\eta)$$
$$=t_{\rho_2}(\rho_1\sigma)=t_{\mu_2}(\mu_1\tau)=0\ .$$

Since $a_{\rho_2}(\rho_1\sigma)$, $a_{\mu_2}(\mu_1\tau)$, and $a_{\delta_2}(\delta_1\eta)$ are independent of each other, we may substitute $d_{\nu_2}(\nu_1\alpha)\times a_{\rho_2}(\rho_1\sigma)$ in place of $a_{\nu_2}(\nu_1\alpha)$ in Eq. (3.13) in I, which is equivalent to Eq. (2.4b) here.[31] We obtain

$$\underline{D}_{\nu_2}\underline{d}_{\nu_2}=\underline{G}_{\nu_2}(\underline{d}_{\nu_2-1}+\underline{d}_{\nu_2+1})\ . \tag{5.2}$$

Similar equations are obtained for s and t.

Defining $\underline{T}_{\nu_2}$ for $\nu_2>\rho_2$ by $\underline{d}_{\nu_2}\equiv\underline{T}_{\nu_2}\underline{d}_{\nu_2-1}$ and $\underline{T}'_{\nu_2}$ for $\nu_2<\rho_2$ by $\underline{d}_{\nu_2}\equiv\underline{T}'_{\nu_2}\underline{d}_{\nu_2+1}$, and starting from $\underline{T}_{M+1}=0$ and $\underline{T}'_{M+1}=0$, we can generate all $\underline{T}_{\nu_2}$ and $\underline{T}'_{\nu_2}$ by the by-now-familiar recurrence relations for Eq. (5.2), except at $\nu_2=\mu_2$ and $\nu_2=\delta_2$. At $\nu_2=\mu_2$, the $(\mu_1\tau)$th row of the $\underline{T}_{\nu_2}$ (or $\underline{T}'_{\nu_2}$) matrix is set identically equal to zero to satisfy $d_{\mu_2}(\mu_1\tau)=0$, while the other rows are obtained directly by in-

verting the μ_2th set of Eq. (5.2) without the $(\mu_1\tau)$th-component equation. A similar procedure is performed at $\nu_2 = \delta_2$. Then with $d_{\rho_2}(\rho_1\sigma) = 1$, the ρ_2th set of Eq. (5.2) without the $(\rho_1\sigma)$th-component equation is solved to obtain the unknowns $d_{\rho_2}(\nu_1\alpha \neq \rho_1\sigma)$. The s and t are obtained in similar ways. Note that for $\nu_2 > \rho_2$, μ_2, and δ_2 ($< \rho_2$, μ_2, and δ_2), the same $\underline{T}_{\nu_2}$ ($\underline{T}'_{\nu_2}$) is valid for $\underline{s}_{\nu_2}$ and $\underline{t}_{\nu_2}$ as well as $\underline{d}_{\nu_2}$. When $\mu_2 = \delta_2 \equiv \mu$, both the $(\mu_1\tau)$th and the $(\delta_1\eta)$th rows of the same $\underline{T}_\mu$ (or $\underline{T}'_\mu$) are set equal to zero in order to satisfy $d_\mu(\mu_1\tau) = 0 = d_\mu(\delta_1\eta)$.

Finally, substituting Eq. (5.1) into the three singular-component equations in Eq. (2.4b), with $\nu_1\nu_2\alpha = \rho_1\rho_2\sigma$, $\mu_1\mu_2\tau$ and $\delta_1\delta_2\eta$, we obtain

$$\begin{bmatrix} E - W'_{\rho_1\rho_2}(\sigma) & -G_{12} & -G_{13} \\ -G_{21} & E - W'_{\mu_1\mu_2}(\tau) & -G_{23} \\ -G_{31} & -G_{32} & E - W'_{\delta_1\delta_2}(\eta) \end{bmatrix} \times \begin{bmatrix} a_{\rho_1\rho_2}(\sigma) \\ a_{\mu_1\mu_2}(\tau) \\ a_{\delta_1\delta_2}(\eta) \end{bmatrix} = 0 \ , \quad (5.3)$$

where W' and G are, respectively, the shifted levels and the effective couplings,

$$W'_{\rho_1\rho_2}(\sigma) \equiv W_{\rho_1\rho_2}(\sigma) + \sum_\beta G_1(\sigma,\beta)[d_{\rho_2}(\rho_1 - 1\beta) + d_{\rho_2}(\rho_1 + 1\beta)] + \sum_\beta G_2(\sigma,\beta)[d_{\rho_2-1}(\rho_1\beta) + d_{\rho_2+1}(\rho_1\beta)] \ ,$$

$$G_{12} \equiv \sum_\beta G_1(\sigma,\beta)[s_{\rho_2}(\rho_1 - 1\beta) + s_{\rho_2}(\rho_1 + 1\beta)] + \sum_\beta G_2(\sigma,\beta)[s_{\rho_2-1}(\rho_1\beta) + s_{\rho_2+1}(\rho_1\beta)] \ .$$

The expressions for $W'_{\mu_1\mu_2}(\tau)$ and $W'_{\delta_1\delta_2}(\eta)$ can be obtained from $W'_{\rho_1\rho_2}(\sigma)$ by replacing $\rho_1\rho_2\sigma d$ with $\mu_1\mu_2\tau s$ and $\delta_1\delta_2\eta t$, respectively. The expression for G_{13} is obtainable from G_{12} by replacing s by t, while that of G_{23} is found by replacing $\rho_1\rho_2\sigma s$ with $\mu_1\mu_2\tau t$. Hermiticity implies $G_{ij} = G_{ji}$. The s's and d's contain linear and nonlinear powers of both field amplitudes, so that contributions from both modes are contained in each sum.

The resulting cubic characteristic equation of Eq. (5.3) is of the form

$$E^3 + pE^2 + qE + r = 0 \ ,$$

which has well-known solutions.[32] Since here p, q, and r are real, and since we expect in general three distinct real roots, the so-called trigonometric solution expressed in terms of a single variable (the angle) is very convenient in an iteration procedure using any one of the expressions for the roots.

B. Adiabatic following and nonadiabatic transitions

We now consider the special case of double resonance where the three shifted levels cross each other at nearly the same time, as shown in Fig. 2(b). It is clear that when the field amplitudes and sweep frequencies $\dot{\theta}_\lambda$ change very slowly in the coarse-grained time, the atom-field system will adiabatically follow the adiabatic curve E_1E_3, so that in spite of the near-resonant level W'_2 the system can still have final probability of unity in the W'_3 state. The atomic level "3" can be an excited state with the atomic state "2" as a lower intermediate state. The resonances can be multiphoton and adiabatic inversion can result.

When the nonadiabatic situation is involved, we have to solve

$$\begin{aligned} i\frac{db_1}{dt} &= W'_1 b_1 + G_{12}b_2 + G_{13}b_3 \ , \\ i\frac{db_2}{dt} &= G_{12}b_1 + W'_2 b_2 + G_{23}b_3 \ , \\ i\frac{db_3}{dt} &= G_{13}b_1 + G_{23}b_2 + W'_3 b_3 \ , \end{aligned} \quad (5.4)$$

obtained in a manner similar to Eq. (2.6). The quantities W'_i and G_{ij} are defined in Eq. (5.3). The formal solution for Eq. (5.4), satisfying boundary conditions in the remote past ($t = t_0$),

$$b_1 = 1, \quad b_2 = 0, \quad b_3 = 0 \ , \quad (5.5)$$

is

$$b_1 = e^{-iK_1(t)} - ie^{-iK_1(t)}\int_{t_0}^{t} dt' \, (G_{12}b_2 + G_{13}b_3)e^{iK_1(t')} \ , \quad (5.6a)$$

$$b_2 = -ie^{-iK_2(t)}\int_{t_0}^{t} dt' \, (G_{12}b_1 + G_{23}b_3)e^{iK_2(t')} \ , \quad (5.6b)$$

$$b_3 = -ie^{-iK_3(t)}\int_{t_0}^{t} dt' \, (G_{13}b_1 + G_{23}b_2)e^{iK_3(t')} \ , \quad (5.6c)$$

where

$$K_i(t) \equiv \int_{t_0}^{t} dt' \, W'_i \ .$$

We now consider the special case where the G's are small and constant (in the resonance region), so that b_1, b_2, and b_3 on the right-hand sides of Eqs. (5.6b) and (5.6c) are given as first approximations by previous solutions, Eq. (3.13) with Eq. (3.17), for levels 1 and 2 and for levels 1 and 3,

separately. Let b_2' and b_3' denote such solutions. Then the solutions for b_2 and b_3 are

$$b_2(t) = b_2'(t) - ie^{-iK_2(t)} \int_{t_0}^{t} dt'\, e^{iK_2(t')} G_{23} b_3'(t') \,,$$
$$b_3(t) = b_3'(t) - ie^{-iK_3(t)} \int_{t_0}^{t} dt'\, e^{iK_3(t')} G_{23} b_2'(t') \,. \tag{5.7}$$

The second term on the right-hand side of each equation represents the contribution to the respective level due to the presence of the third level. To obtain asymptotic probability formulas, we define the level crossing by

$$W_i' - W_j' \equiv -\alpha_{ij}\tau \equiv -\alpha_{ij}(t - t_k)$$

and obtain $b_2(t)$ and $b_3(t)$ in the asymptotic region $|\alpha_{21}|^{1/2}\tau$ and $|\alpha_{31}|^{1/2}\tau \gg 1$ by the method of steepest descent. With the definitions $P_{ij} \equiv |iG_{ij}^2/\alpha_{ij}|$, $q_{ij} \equiv |\alpha_{ij}|$, $R_{ij} \equiv |\alpha_{ij}^{1/2}\tau|$, and with θ_i being a constant phase, we obtain

$$b_2(\tau) = \left[\frac{(2\pi p_{21})^{1/2}}{\Gamma(1 \pm ip_{21})} \exp\left(-\frac{\pi}{2} p_{21} \pm ip_{21} \ln R_{21}(\tau) R_{21}(\tau_0) \right) \mp i \left(\frac{\pi}{q_{31}} \right)^{1/2} G_{23} \exp\left(-\frac{\pi}{2} p_{31} \pm \frac{ip_{31}}{2} \mp \frac{ip_{31}}{2} \ln \frac{q_{31} p_{31}}{q_{21} R_{31}^2(\tau)} \right) \right]$$
$$\times \exp[-iK_2(\tau) \pm i\theta_2] \,, \tag{5.8a}$$

and hence

$$|b_2(\tau)|^2 = 1 - e^{-2\pi p_{21}} + \pi (G_{23}^2/q_{31}) e^{-\pi p_{31}} + (\text{interference term}) \,, \tag{5.8b}$$

where the upper (lower) signs are for the case α_{12} and $\alpha_{13} > 0$ (< 0). The corresponding expression for $b_3(\tau)$ is obtainable from the expression for $b_2(\tau)$ above with the subscript labels 2 (3) changed to 3 (2). The above formulas apply only when $|b_2(\tau)|^2 + |b_3(\tau)|^2 \ll 1$, i.e., small p_{21}, p_{31}, and G_{23}^2/q_{31}. For small p_{21} and p_{31}, the interference term is negligible compared with the other two terms. Similar formulas can also be derived by the above method using the results of Sec. III for the case $\alpha_{21} > 0$, $\alpha_{31} < 0$, and for nonzero Γ_1 and Γ_2.

VI. CONCLUSION

We have extended a previous computational procedure[2] which, once set up, can be used to calculate accurate energy-level shifts and/or effective coupling for any atom or molecule interacting with laser fields. This procedure is particularly useful for intense fields or whenever the level shift is not negligible compared with the smallest off-resonance energy between unperturbed levels. The exact analytic formulas for probability amplitudes derived here are useful for describing interaction with weak fields as well as with strong fields. The theory can be conveniently applied to many nonlinear as well as linear processes. Furthermore, we have shown that equations identical in form to the usual optical Bloch equation can be used to describe single-photon and multiphoton coherent transient phenomena in intense laser fields, and hence by implication we have shown the existence of such phenomena corresponding to those of single-photon process in weak field. The demonstrated effects of pulse-parameter and pulse-shape dependences in the final transition probability and of nonadiabatic population inversion have potential applications in laser isotope separation and in maintaining laser actions via efficient optical pumping.

ACKNOWLEDGMENTS

It is a pleasure to thank C. K. Rhodes and W. K. Bischel for informative and stimulating discussions, and W. K. Y. Siu for the unpaid work of typing a major portion of the manuscript. Part of the work was carried out while the author was associated with Professor K. M. Watson and the theoretical group of Lawrence Berkeley Laboratory, University of California. Their support is appreciated.

*Work supported by U. S. Energy Research and Development Administration under Contract No. AT(04-3)-115, P/A 99.

[1] N. M. Kroll and K. M. Watson, Phys. Rev. A 13, 1018 (1976).
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[5] See, for example, Refs. 2 and 4 in I.
[6] See, for example, Refs. 2 and, 6–9 in I. See also C. Cohen-Tannoudji, in *Cargese Lectures in Physics*, edited by M. Levy (Gordon & Breach, New York, 1969).
[7] S. Swain, J. Phys. A 6, 1919 (1973). References to earlier works using the continued-fraction method are given there.
[8] See, for example, E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge U.P., New

York, 1967), Chap. 17. We assume *discrete* adiabatic atomic states.

[9]In subsequent discussions, by "atom" we mean either the bare atom or the atom including the static field, and by "field" we refer to the oscillating field only.

[10]W. Heitler, *Quantum Theory of Radiation*, 3rd ed. (Clarendon, Oxford, 1954), Chap. 2; E. A. Power and S. Zienau, Philos. Trans. R. Soc. A 251, 427 (1959).

[11]For our purpose, there is no need to distinguish classical and quantum coherent fields. As in I, with $b_{\{\nu_\lambda\}}(\alpha)$ defined clearly as the probability amplitude, the same Eq. (2.3) can be derived for quantum field with $N_\lambda(t)$ and $\omega_\lambda(t)$. Here, for a classical field, $b_{\{\nu_\lambda\}}(\alpha)$ has the meaning of probability amplitude if the time average on the total probability in an atomic state is taken over the period $2\pi/\omega$.

[12]For electric quadrupole and/or magnetic dipole terms, all expressions remain the same, except that now the $G(\alpha,\beta)$ are different functions.

[13]The question of equating slowly time-dependent coefficients of fast-oscillating functions has been discussed by W. E. Lamb, Jr., in *Quantum Optics and Electronics*, edited by C. DeWitt, A. Blandin, and C. Cohen-Tannoudji (Gordon and Breach, New York, 1965), and Phys. Rev. 134, A1429 (1964).

[14]See Sec. III of Ref. 2. The notation is the same except that here t, ω_λ, and G_λ are, respectively, y, F_λ, and $G_\lambda^\dagger$ there. The change of variable from t to y which resulted in the scaling of W, F_λ, and G_λ there by the factor a_0/v is merely for convenience of numerical computation. This is also true for the measurement of energy from w_p.

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[28]For example, at a node of $\epsilon(t)$ of a 0π pulse, $\epsilon(t)$ is well defined while $I(t)\propto|\epsilon(t)|^2$ is not.

[29]The values of I' and δ given in Ref. 2 were calculated with dipole matrix elements given by formulas in Chap. 3 of Ref. 8. The radial overlap integrals were calculated from the oscillator strengths tabulated in W. L. Wiese, M. W. Smith and B. M. Glennon, *Atomic Transition Probabilities* (Natl. Bur. Stand., U. S. GPO, Washington, D.C., 1966), Vol. I; W. L. Wiese, M. W. Smith, and B. M. Miles, *ibid.* Vol. II (1969), supplemented by E. M. Anderson and V. A. Zilitis, Opt. Spektrosk. 16, 177 (1964) [Opt. Spectrosc. 16, 99 (1964)]; 16, 382 (1964) [16, 211 (1964)].

[30]See, for example, a review article by R. G. Brewer, Science 178, 247 (1972).

[31]Use the upper "+" sign there and replace F_2 with $\omega_2 + d\theta_2/dt$.

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