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Control of collisionless and collisional processes by nonresonant laser fields*

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The presence of coherent radiation fields can modify various atomic, ionic, and molecular processes. We examine cases where the changes can be effected without actual absorption or emission of photons. The radiation fields cause optical Stark shifts of the energies and dress the nonadiabatic couplings between states. Rates of processes such as dissociation, predissociation, atomic and molecular collisions can be radiatively controlled. Formation of new avoided crossings due to radiative interaction gives rise to new phenomena. We give both exact numerical results from which the influences of the radiation field on arbitrary configurations can be calculated, and simple but accurate analytic results, from which these effects can be conveniently assessed. It is shown that the inelastic transition probability is decreased at a true crossing and is increased at an avoided crossing as a result of the presence of the nonresonant radiation field. Furthermore, for two parallel levels with constant nonadiabatic coupling, it is shown that the amplitudes of the nonadiabatic transition are invariant, but its flopping frequency is reduced by the field. Depending on final measurements with the field on or off, general behaviors of the inelastic transition probability as a function of the field parameters and the charge-system parameters are predicted and the possibility of inversion (from a field-free value of less than 1/2 to a value greater than 1/2) is demonstrated. Experimental investigation with iodine molecules is suggested. Comparison of our nonperturbative results with those of stationary perturbation theory shows that the latter is inadequate in an important parameter region where the field modification of processes is greater than 1%.

I. INTRODUCTION

In the abscence of laser fields, nonadiabatic transitions during molecular dissociation, predissociation or in slow collision of atoms, ions, or molecules are known to occur predominantly in regions where the relevant energy surfaces are lying close together.[1] These include the important cases of avoided crossing (pseudocrossing), true crossing, and parallel-level configurations.

With the application of a laser field whose frequency ω is nonresonant with these near-degenerate energy surfaces (including the optically induced shifts), no actual absorption and emission of photons can take place. We show in the present work that an *intense* laser field can nevertheless significantly modify these processes through energy structural change and through dressing the field-free nonadiabatic coupling. This work is motivated by the anticipated use of intense laser radiation to control chemical reactions (e.g., to enhance the production of electronically excited species), to modify energy-flow pathways, and to provide a means of controlling isotopically selective intra- and intermolecular processes.

Molecular energy surfaces are significantly distorted in the presence of a sufficiently intense optical field.[2] The field-dressed energy surfaces are functions of the field polarization[3] as well as the intensity and the frequency. Thus, for a diatomic radiative-dressed quasimolecule,[4] the electronic energy surfaces are *not* spherically symmetric. Both the energy shifts and its polarization dependence can have dramatic effects on purely *elastic* processes.[5]

Energy level shifts and the polarization dependence of the effective coupling are also important for optically resonant processes. The actual location of the resonance on the energy surfaces and its relative energy structure (and hence the line profile and center) can change as a function of the laser intensity, frequency and polarization.[2,3,6] For atom-atom scattering in intense laser field, the polarization dependence in the couplings at the two crossings (the "same" crossing traversed twice during one collision) can be exploited to enhance population in the excited state by single or multiphoton processes.[7]

In general both optically resonant[2,3,6,8,9] and optically nonresonant inelastic processes can occur in a given charge-field system [see Fig. 1(a)]. The present analysis examines the extent to which a coherent field can alter the latter processes and thereby complements the earlier studies[2,3,6] in which inelastic transitions resulting in real absorption and emission of photons were emphasized. We also note that for a process of interest, the charge-field parameters can be such that only

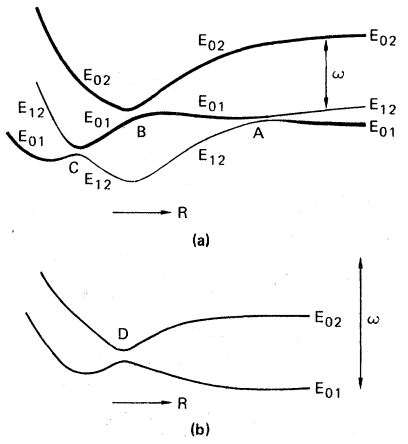

FIG. 1. (a) Illustration of charge-field adiabatic energy surfaces E_{01}, E_{02}, and E_{12} as functions of the internuclear separation(s) $\underline{R}$. Photon absorption and/or emission are involved at *charge-field avoided crossings A* and *C*. No real photon absorption or emission is involved in the *field-dressed avoided crossing B*. The change in transition probabilities at *B* due to the presence of the laser field with frequency ω is an example studied in this work. The thicker lines in the figure are intended to make the two "principal" surfaces outstanding. (b) Illustration of situation where no resonant absorption or emission of photon can occur between energy surfaces E_{01} and E_{02} at any $\underline{R}$, but the intense laser field changes the transition probabilities at *D*.

transitions at optically nonresonant energy regions have to be considered [see Fig. 1(b)].

In Sec. II, we give the general theory applicable to analysis of nonadiabatic transitions between an n-level charge system[4] interacting with m field modes. Formulas expressing transition probabilities for representative field-dressed true crossing, avoid crossing and the parallel-level configuration are given. In Sec. III, many general relationships are demonstrated and numerical results for the optical Stark shifts and field-dressed nonadiabatic coupling are given for a two-level charge system interacting with one field mode. These numerical and analytic results can be used to construct the field modification of any arbitrary configuration. In addition, we show that the configurations noted above in the presence of a constant-amplitude field have the same *form* as their field-free configurations. Furthermore, we demonstrate that the entire effect of the field can be reduced to a single multiplicative factor, for which accurate numerical values as well as approximate analytic expressions are given.

In Sec. IV, we compare the transition probabilities in the presence of the field as against those in its absence for both collisionless and collisional processes. Many behaviors of the transition probabilities under the influence of the field are predicted. It is emphasized that different final results are obtained depending on the field and charge parameters at which final measurements are taken. In Sec. V, we show the inadequacy of the stationary perturbation theory for those interaction strengths that give rise to significant nonresonant effects.

In Sec. VI, we consider a charge system with more than two levels which is of more general applicability especially for intense radiations. Some results for the two-level charge system become qualitatively valid while others have to be modified. Through radiative interaction with other levels, two true-crossing levels can give rise to a new avoided crossing even at low-field intensity. Possible experiment with iodine molecules is suggested as an example.

II. GENERAL THEORY

The Hamiltonian for the entire charge-field system is

$$H = h + h_\gamma + h' , \tag{2.1}$$

where h_γ and h' are the free-field and the charge-field interaction Hamiltonians, respectively. The adiabatic Hamiltonian h for the charge system[4] is a function of a set of dynamical variables $\underline{r}$ denoting the fast motion of the charge system, while also depending on a set of parameter(s) $\underline{R}$ denoting the slow motions. Depending on the (quasi)molecular processes of interest, h may be the well-known adiabatic electronic Hamiltonian (including the nuclear repulsion terms) or the electronic-vibrational Hamiltonian.[10] The energy surfaces w_α and interaction matrix elements between wave functions φ_α are obtained from the solution of the eigenvalue problem,[11]

$$h\varphi_\alpha = w_\alpha \varphi_\alpha , \tag{2.2}$$

or from experimental measurements.

The solution of the eigenvalue problem of the n (≥ 2) level charge system interaction with m (≥ 1) oscillating modes,

$$H\hat{\Psi} = \hbar E \hat{\Psi} , \tag{2.3}$$

has been given earlier.[2,3,6] The wave function $\hat{\Psi}$ is expanded in terms of the φ_α and the photon number state $\Omega(N-\nu)$ with N being the initial mean photon number in the single coherent field mode (the case explicitly considered here),

$$\hat{\Psi} \equiv \sum_{\nu=-M}^{M} \sum_{\beta=1}^{n} a_\nu(\beta)\varphi_\beta e^{i\nu\pi/2}\Omega(N-\nu) , \tag{2.4}$$

where the cutoff integer $M \ll N$ and $a_\nu(\beta)$ is the probability amplitude in the $\varphi_\beta\Omega(N-\nu)$ state when

the charge-field system is in the eigenstate $\hat{\Psi}$. With $h' \equiv h''(a - a^+)$,[12] the substitution of Eq. (2.4) into Eq. (2.3) gives

$$Ea_\nu(\alpha) = W_\nu(\alpha)a_\nu(\alpha) + \sum_{\beta=1}^{n} G(\alpha,\beta)\,[a_{\nu-1}(\beta) + a_{\nu+1}(\beta)],$$

$$-M \le \nu \le M, \quad (2.5)$$

which are solved by numerical iteration. The solution gives both the eigenvalue E and the expansion coefficients $a_\nu(\beta)$ of the eigenstate $\hat{\Psi}$. The unperturbed charge-field levels $W_\nu(\alpha)$ and the interaction $G(\alpha,\beta)$ are given by

$$W_\nu(\alpha) = (w_\alpha - \nu\hbar\omega)/\hbar$$

and (2.6)

$$G(\alpha,\beta) = -iN^{1/2}(\varphi_\alpha, h''\varphi_\beta)/\hbar\,.$$

The $G(\alpha,\beta)$ depend on the field intensity and polarization. In our convention, energies are measured from $N\hbar\omega$ and in angular frequency. We label the charge-field adiabatic eigensolution $(E_{\rho\sigma}, \hat{\Psi}_{\rho\sigma})$ such that as the interaction $G(\alpha,\beta) \to 0$,

$$\begin{aligned} &E_{\rho\sigma} \to W_\rho(\sigma)\,, \\ &\hat{\Psi}_{\rho\sigma} \to \varphi_\sigma e^{i\rho\pi/2}\Omega(N-\rho)\,. \end{aligned} \quad (2.7)$$

Classical or quantum treatment of the remaining slow motion denoted by $\underline{R}$ should be based on the charge-field energy surfaces E, whose dependence on the field intensity, frequency, and polarization (besides $\underline{R}$) can be significant for intense fields.

To be useful, the above separation of the system into a fast subsystem and a slow subsystem places an upper bound on the motion of the latter. For example, if the relative nuclear motions are treated as slow compared to the electronic motion, then the relative nuclear velocity $v < 10^8$ cm/sec. This is often denoted as *slow* or *near-adiabatic*. On the other hand, for the sake of simplicity (but not essential, as noted above) we shall treat the slow motion classically. This requires, generally speaking, large quanta or De Broglie wavelengths for the relative motions small compared to the interaction scale length.[13] Such description is adequate for a large class of (quasi)molecular processes of interest, including atomic and molecular collisions in thermal gases.

By substituting into the Schrödinger equation,

$$i\hbar\frac{d}{dt}\Psi(t) = H\Psi(t)\,, \quad (2.8)$$

the following expansion of $\Psi(t)$ in terms of the charge-field adiabatic eigenstates $\hat{\Psi}_{\rho\sigma}$,

$$\Psi(t) = \sum_{\rho'\sigma'} B_{\rho'\sigma'}(t)\hat{\Psi}_{\rho'\sigma'}, \quad (2.9)$$

we obtain

$$i\frac{d}{dt}B_{\rho\sigma} = E_{\rho\sigma}B_{\rho\sigma} + \sum_{\rho'\sigma'} C_{\rho\sigma,\rho'\sigma'}B_{\rho'\sigma'}, \quad (2.10)$$

where

$$C_{\rho\sigma,\rho'\sigma'} \equiv -i\left(\hat{\Psi}_{\rho\sigma}, \frac{d}{dt}\hat{\Psi}_{\rho'\sigma'}\right) \quad (2.11)$$

is the nonadiabatic coupling between the charge-field adiabatic states. The nonadiabaticity arises from the parametric dependence of $\hat{\Psi}_{\rho'\sigma'}$ on $\underline{R}(t)$, with $\underline{R}(t)$ determined classically on the appropriate field-dressed energy surfaces E.

Using Eq. (2.4), we obtain

$$C_{\rho\sigma,\rho'\sigma'} = -i\left[\sum_{\nu\beta} a_\nu^{\rho\sigma}(\beta)\frac{d}{dt}a_\nu^{\rho'\sigma'}(\beta) + \sum_{\substack{\nu\beta\beta' \\ \beta\neq\beta'}} a_\nu^{\rho\sigma}(\beta)a_\nu^{\rho'\sigma'}(\beta')\left(\varphi_\beta, \frac{d}{dt}\varphi_{\beta'}\right)\right], \quad (2.12)$$

which is pure imaginary if we choose φ_β's to be real and the field polarization to be linear. By hermiticity, $C_{\rho'\sigma',\rho\sigma} = C^*_{\rho\sigma,\rho'\sigma'}$. The second sum in Eq. (2.12) arises from field-free nonadiabatic transitions which are now dressed by the field. The first sum is nonadiabatic coupling through interaction with the field, with the origin of the nonadiabaticity being the slow motions of the charge system and/or the nonadiabatic variation of the field parameters.[6] Because of the latter, this sum may not be zero even when the slow motion of the charge system is negligible. On the other hand, this first sum may be identically zero because the radiation field does not *radiatively* couple the two charge-field adiabatic eigenstate $\hat{\Psi}_{\rho\sigma}$ and $\hat{\Psi}_{\rho'\sigma'}$. An explicit example of this is given in Sec. III. In the limit of zero interaction $G(\alpha,\beta) = 0$, $C_{\rho\sigma,\rho'\sigma'}$ has the expected field-free value $-i(\varphi_\sigma, (d/dt)\varphi_{\sigma'})\delta_{\rho\rho'}$.

In general, Eq. (2.10) with the appropriate initial values can be integrated numerically. On the other hand, we expect that nonadiabatic transitions occur predominantly where separations between energy surfaces are small.

Earlier works have considered simultaneous nonadiabatic transition between two[2,3] or more[6] states with photons emitted or absorbed, e.g., between $\hat{\Psi}_{\rho\sigma}$ and $\hat{\Psi}_{\rho'\sigma'}$ where $\rho \neq \rho'$ and $\sigma \neq \sigma'$. Here, we consider the class of situations for which $\rho = \rho'$ but $\sigma \neq \sigma'$, that is, transitions between states of the charge system *without* real absorption or emission of photons. We shall study in detail nonadiabatic transitions between only two charge-field states denoted by $\hat{\Psi}_l$ and $\hat{\Psi}_u$ by examining several important solutions of the coupled equations

$$i\frac{dB_l}{dt} = E_l B_l + C_{lu} B_u \,,$$
$$i\frac{dB_u}{dt} = E_u B_u + C_{ul} B_l \,, \tag{2.13}$$

with initial-value conditions

$$B_l = 1, \quad B_u = 0, \quad \text{at } t = t_0 \,. \tag{2.14}$$

A. True crossing of field-dressed levels

One frequently encountered configuration in field-free molecular energy surfaces is the true crossing of two energy surfaces. For example, a Σ state may cross a Π state with the nonadiabatic coupling provided by the rotational motion of the internuclear axis.[1] In the presence of the field, a field-free true crossing may remain as a true crossing under certain situations (see Sec. III).

A true crossing can sometimes be described by the Landau-Zener model[14]:

$$E_u - E_l = -\alpha_t \tau \,, \tag{2.15}$$

$$C_{lu} = \text{const} \,, \tag{2.16}$$

where α_t is a constant and $\tau \equiv t - t_i$ with t_i being the time at which the two levels E_u and E_l cross each other. The solutions of Eqs. (2.13) with Eqs. (2.15) and (2.16) are known.[15] The particular solution satisfying the initial-value condition Eq. (2.14) gives the simple asymptotic formula,

$$|B_l(\tau)|^2 = e^{-2\pi p_t} \,, \tag{2.17}$$

$$|B_u(\tau)|^2 = 1 - e^{-2\pi p_t} \,, \tag{2.18}$$

where

$$p_t \equiv |C_{lu}|^2 / |\alpha_t| \,,$$

if Eqs. (2.15) and (2.16) remain good approximation in the time interval τ_0 to τ such that $|\alpha_t| \tau_0^2 \gg 1$ and $|\alpha_t| \tau^2 \gg 1$. This time interval defines a corresponding "region of transition" on the energy surfaces. See Fig. 2(a).

B. Avoided crossing between field-dressed levels

For convenience of analysis of avoided crossing between two field-dressed levels, we shall express Eqs. (2.13) in terms of *radiative-dressed diabatic states* $\hat{\Phi}_1$ and $\hat{\Phi}_2$ as basis states. Defining $\Psi(t) = B_l(t)\hat{\Psi}_l + B_u(t)\hat{\Psi}_u = D_1(t)\hat{\Phi}_1 + D_2(t)\hat{\Phi}_2$ and hence defining the unitary transformation $\underline{U}$ by $\underline{B} = \underline{U}\underline{D}$, we obtain from Eq. (2.13) the following equations describing the coupling between the probability amplitudes D_1, D_2 in the two radiative-dressed diabatic states,

$$i\frac{d}{dt}\underline{D} = \underline{\hat{H}}\underline{D} + \underline{C}''\underline{D} \,, \tag{2.19}$$

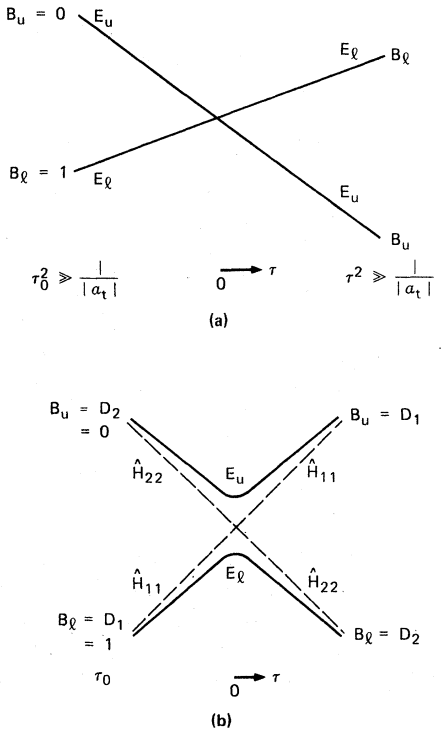

FIG. 2. (a) A *field-dressed true crossing*, and (b) a *field-dressed avoided crossing* between energy surfaces E_u and E_l. The B's are probability amplitudes in E_u or E_l. τ is the time and α_t is the relative temporal slope between E_u and E_l. $\hat{H}_{ij}$ are the *field-dressed diabatic energy surfaces* with the corresponding probability amplitudes D_i.

where

$$\underline{\hat{H}} \equiv \underline{U}^+ \begin{bmatrix} E_l & 0 \\ 0 & E_u \end{bmatrix} \underline{U} \,, \tag{2.20}$$

$$\underline{C}'' \equiv \begin{pmatrix} 0 & -i(\hat{\Phi}_1, d\hat{\Phi}_2/dt) \\ -i(\hat{\Phi}_2, d\hat{\Phi}_1/dt) & 0 \end{pmatrix} . \tag{2.21}$$

In arriving at Eq. (2.19), we have made use of

$$\underline{U}^+\underline{C}\underline{U} = i\underline{U}^+\frac{d\underline{U}}{dt} + \underline{C}'' \,.$$

Furthermore, from the definition Eq. (2.20) we can obtain relations between the $\hat{H}_{ij}$'s in terms of the known quantities E_l and E_u:

$$\hat{H}_{22} + \hat{H}_{11} = E_l + E_u \,, \tag{2.22}$$

$$(\hat{H}_{22} - \hat{H}_{11})^2 + 4\hat{H}_{12}^2 = (E_u - E_l)^2 \,. \tag{2.23}$$

The radiative-dressed diabatic states are defined explicitly when $\underline{U}$ as a function of t is chosen. Since the charge-field adiabatic eigensolutions

$(E_{\rho\sigma}, \hat{\Psi}_{\rho\sigma})$ and $(E_{\rho'\sigma'}, \hat{\Psi}_{\rho'\sigma'})$ are uniquely given whether $\rho = \rho'$ (no real photon emission or absorption) or $\rho \neq \rho'$ (actual photon absorption or emission), the "perturbed states" defined in Ref. 6 may be regarded as a specific set of radiative-dressed diabatic states which are already given explicitly in the process of solving the charge-field adiabatic eigenvalue problem.

The Landau-Zener model[14] for the radiative-dressed diabatic states assumes that $\underline{U}$ is chosen[16] such that

$$\left(\hat{\Phi}_1, \frac{d}{dt}\hat{\Phi}_2\right) = 0\,, \tag{2.24}$$

$$\hat{H}_{22} - \hat{H}_{11} = -\alpha_a \tau, \quad \tau \equiv t - t_i\,, \tag{2.25}$$

and

$$\hat{H}_{12} = \text{const}\,. \tag{2.26}$$

Then from Eq. (2.23) we have

$$2\hat{H}_{12} = (E_u - E_l)_{\min}\,, \tag{2.27}$$

and

$$\hat{H}_{22} - \hat{H}_{11} = \pm[(E_u - E_l)^2 - 4\hat{H}_{12}^2]^{1/2}\,. \tag{2.28}$$

It can further be shown from explicit expressions for U_{ij} that as $(\hat{H}_{22} - \hat{H}_{11})^2 \gg 4\hat{H}_{12}^2$,

$$\hat{\Psi}_l \to \hat{\Phi}_1 \text{ and } \hat{\Psi}_u \to \hat{\Phi}_2, \quad \text{for } \hat{H}_{22} - \hat{H}_{11} > 0\,, \tag{2.29}$$

and

$$\hat{\Psi}_l \to \hat{\Phi}_2 \text{ and } \hat{\Psi}_u \to \hat{\Phi}_1, \quad \text{for } \hat{H}_{22} - \hat{H}_{11} < 0\,, \tag{2.30}$$

[see Fig. 2(b)]. Therefore, the asymptotic formula for the solution[15] to Eq. (2.19), satisfying the initial-value conditions (2.14) and subject to the approximations (2.24)–(2.26) over the entire time interval (τ_0, τ) such that $\tau_0^2 \gg |\alpha_a|^{-1}$ and $\tau^2 \gg |\alpha_a|^{-1}$, is

$$|B_l(\tau)|^2 = |D_2(\tau)|^2 = 1 - e^{-2\pi p_a}\,, \tag{2.31}$$

$$|B_u(\tau)|^2 = |D_1(\tau)|^2 = e^{-2\pi p_a}\,, \tag{2.32}$$

where

$$p_a \equiv \hat{H}_{12}^2/|\alpha_a|\,.$$

C. Parallel levels with constant nonadiabatic coupling

For special and limited regions of the energy surfaces, the energies and the nonadiabatic coupling may be approximated by

$$E_u - E_l \equiv \Delta = \text{const}, \tag{2.33}$$

and

$$C_{lu} = \text{const}. \tag{2.34}$$

The solution to Eqs. (2.13) and (2.14) for this configuration is straightforward:

$$B_l(\tau) = \frac{A}{2C_{lu}}\left(-\Delta \sin\tfrac{1}{2}\Omega\tau + i\Omega\cos\tfrac{1}{2}\Omega\tau\right)e^{-i\Lambda\tau/2}\,,$$

$$B_u(\tau) = A(\sin\tfrac{1}{2}\Omega\tau)e^{-i\Lambda\tau/2}\,, \tag{2.35}$$

where

$$\Omega \equiv [\Delta^2 + 4|C_{lu}|^2]^{1/2}, \quad A \equiv -i2C_{lu}/\Omega\,,$$

$$\Lambda \equiv E_u + E_l, \quad \text{and } \tau \equiv t - t_0\,.$$

Returning to the general state $\Psi(t)$ given by Eq. (2.9), we note that the probability of measuring the charge-field system in a given state $\varphi_\beta e^{i(\pi/2)\nu}\Omega(N-\nu)$ is

$$|[\varphi_\beta e^{i(\pi/2)\nu}\Omega(N-\nu), \Psi(t)]|^2 = \left|\sum_{\rho'\sigma'} B_{\rho'\sigma'}(t) a_\nu^{\rho'\sigma'}(\beta)\right|^2\,. \tag{2.36}$$

Thus the probability $P(\beta)$ of finding the charge system in the state φ_β with all its sidebands is given by

$$P(\beta) = \sum_\nu \left|\sum_{\rho'\sigma'} B_{\rho'\sigma'}(t) a_\nu^{\rho'\sigma'}(\beta)\right|^2\,. \tag{2.37}$$

It depends not only on time t through $B_{\rho'\sigma'}(t)$ but also on the field parameters at t through the $a_\nu^{\rho'\sigma'}(\beta)$'s. For example if the system is probed after the laser field is slowly "turned off" $[G(\alpha,\beta) \to 0]$, $a_\nu^{\rho'\sigma'}(\beta) = \delta_{\rho'\nu}\delta_{\sigma'\beta}$, and we have simply

$$P(\beta) = \sum_\nu |B_{\nu\beta}(t)|^2\,. \tag{2.38}$$

III. TWO-LEVEL CHARGE SYSTEM WITH SINGLE FIELD MODE

In Secs. III–V, we shall restrict ourselves to a two-level charge system interacting with one field mode. Equation (2.5) becomes

$$[E - W_\nu(\alpha)]a_\nu(\alpha) = G(\alpha,\beta)[a_{\nu-1}(\beta) + a_{\nu+1}(\beta)]\,,$$

$$\alpha \neq \beta, \quad \alpha,\beta = 1, 2, \quad -M \leq \nu \leq M\,, \tag{3.1}$$

where $G(\alpha,\alpha)$ contributing to the photoprocesses in the slow motion has been neglected.[3] The eigenvalue problem is completely characterized by only two ratios,

$$G(1,2)/\omega = G(2,1)/\omega \text{ and } W/\omega\,, \tag{3.2}$$

where $W \equiv w_2 - w_1$ is assumed to be ≥ 0 without loss of generality. Since nonadiabatic transitions are expected to be important where w_1 and w_2 lie close together and since we are interested in changing these transitions by optically nonresonant effects, the range of parameters of interest is described by $W/\omega < 1$.

It can be seen from Eq. (3.1) that $a_{\nu_e}(1)$ for *even* ν_e are coupled with $a_{\nu_0}(2)$ with *odd* ν_0 only. Be-

cause of our convention Eq. (2.7), these are the only nonzero coefficients in $\hat{\Psi}_{\rho\sigma}$ where $(-1)^{\rho+\sigma} = -1$ and we shall call such charge-field adiabatic eigensolutions "odd-parity." On the other hand, $a_{\nu_0}(1)$'s are coupled with only $a_{\nu_e}(2)$'s and they together form the nonzero components of any "even-parity" charge-field adiabatic eigensolution $\hat{\Psi}_{\rho\sigma}$ where $(-1)^{\rho+\sigma} = +1$. For the same reason, the following method of solving Eq. (3.1) to obtain $(E_{01}, \hat{\Psi}_{01})$ or $(E_{02}, \hat{\Psi}_{02})$ belongs to the nondegenerate case, even when w_2 and w_1 are (near) degenerate. The procedure is equivalent to that used by Kroll and Watson.[17] To obtain all the numerical results in Secs. IV and V, we require the eigensolution $(E_{01}, \hat{\Psi}_{01})$ only, a fact that will be shown in subsections A–D below.

To obtain $(E_{01}, \hat{\Psi}_{01})$, we let

$$a_\nu(\alpha) \equiv d_\nu(\alpha) a_0(1), \quad \alpha = 1, 2, \tag{3.3}$$

which implies

$$d_0(1) = 1. \tag{3.4}$$

For $\nu > 0$, we let

$$d_\nu(\alpha) \equiv T_\nu(\alpha, \beta) d_{\nu-1}(\beta), \quad \alpha \neq \beta, \tag{3.5}$$

where ν and α are of *opposite* parities (even or odd integers), since we are solving for an odd-parity solution. It can be shown from Eq. (3.1) that T_ν satisfies the following *scalar* recurrence relation

$$T_\nu(\alpha, \beta) = \frac{G(\alpha, \beta)}{E - W_\nu(\alpha) - G(\alpha, \beta) T_{\nu+1}(\beta, \alpha)}, \tag{3.6}$$

and

$$T_\nu(\alpha, \beta) \to \frac{G(\alpha, \beta)}{\nu\omega} \approx 0, \tag{3.7}$$

for a sufficiently large positive integer $\nu \equiv M + 2$ such that $\nu \gg (E - w_\alpha)/\omega$ and $\nu \gg G(1, 2)/\omega$. In $\nu < 0$, the $T'_\nu(\alpha, \beta)$ defined by

$$d_\nu(\alpha) \equiv T'_\nu(\alpha, \beta) d_{\nu+1}(\beta), \tag{3.8}$$

satisfies a similar scalar recurrence relation and limit for a large negative $\nu = -M - 2$. The eigenvalue E_{01} is obtained by iterating the expression based on Eq. (3.1) for $\nu = 0$, $\alpha = 1$,

$$E_{01} = W_0(1) + G(1, 2)[T'_{-1}(2, 1) + T_1(2, 1)], \tag{3.9}$$

where $d_0(1) = 1$ has been used. Thus, starting with $T_{M+2} = 0$ ($T'_{-M-2} = 0$) for an *even* integer M ($-M$), we obtain all T_ν (T'_ν) for $\nu > 0$ (< 0), and hence the right-hand side of Eq. (3.9). This iteration procedure gives both E_{01} and after normalization, the eigenvector $\hat{\Psi}_{01} = \underline{a}$ through Eqs. (3.3), (3.5), and (3.8).

All the nonperturbative numerical results given below have been obtained by the above method with $M = 6$. These results are accurate to at least 5 significant figures. For example, using $M = 100$ would not improve the accuracy of the results shown. Table I gives the values of the shift

$$\frac{\delta}{\omega} \equiv \frac{E_{01} - W_0(1)}{\omega}.$$

For $0.55 \gtrsim G(1, 2)/\omega \gtrsim 0.3$, the results show that δ increases roughly linearly with $G(1, 2)$. The initial trial value for iteration was generated by $\delta = 0$ for $G(1, 2)/\omega \lesssim 0.05$ and by linear extrapolation for larger values of $G(1, 2)/\omega$. (Alternatively, the result in Eq. (3.34) can be used.) Convergence became difficult for $G(1, 2)/\omega \gtrsim 0.55$ and $W/\omega > 0.2$. We ascribe this to the necessity of treating the $W_0(1)$ and $W_1(2)$ levels as near degenerate for such strong interaction. This is reasonable because

TABLE I. Exact values of ac Stark shifts of energy level w_1, $\delta/\omega \equiv [E_{01} - W_0(1)]/\omega$, for a two-level charge system interacting with single laser-field mode of frequency ω. $G(1, 2)/\omega$ is the interaction and $W/\omega \equiv (w_2 - w_1)/\omega$ is the field-free energy difference between the two levels w_1 and w_2. The energy shifts of energy level w_2 is $-\delta/\omega$. The notation $A\,(n)$ means $A \times 10^n$.

$G(1,2)/\omega$ \ W/ω	10^{-4}	0.01	0.1	0.2	0.3	0.4	0.5
0.01	1.9998 (–8)	2.0000 (–6)	2.0200 (–5)	4.1662 (–5)	6.5924 (–5)	9.5218 (–5)	1.3329 (–4)
0.05	4.9875 (–7)	4.9880 (–5)	5.0373 (–4)	1.0385 (–3)	1.6421 (–3)	2.3686 (–3)	3.3077 (–3)
0.1	1.9801 (–6)	1.9803 (–4)	1.9991 (–3)	4.1165 (–3)	6.4941 (–3)	9.3300 (–3)	1.2939 (–2)
0.15	4.3998 (–6)	4.4001 (–4)	4.4394 (–3)	9.1244 (–3)	1.4343 (–2)	2.0482 (–2)	2.8116 (–2)
0.2	7.6856 (–6)	7.6863 (–4)	7.7489 (–3)	1.5888 (–2)	2.4862 (–2)	3.5239 (–2)	4.7800 (–2)
0.25	1.1740 (–5)	1.1741 (–3)	1.1826 (–2)	2.4179 (–2)	3.7644 (–2)	5.2922 (–2)	7.0904 (–2)
0.3	1.6443 (–5)	1.6444 (–3)	1.6548 (–2)	3.3732 (–2)	5.2235 (–2)	7.2831 (–2)	9.6427 (–2)
0.35	2.1657 (–5)	2.1658 (–3)	2.1773 (–2)	4.4249 (–2)	6.8159 (–2)	9.4291 (–2)	1.2349 (–1)
0.4	2.7230 (–5)	2.7231 (–3)	2.7350 (–2)	5.5420 (–2)	8.4943 (–2)	1.1667 (–1)	1.5135 (–1)
0.45	3.3001 (–5)	3.3002 (–3)	3.3116 (–2)	6.6927 (–2)	1.0212 (–1)	1.3938 (–1)	1.7935 (–1)
0.5	3.8805 (–5)	3.8806 (–3)	3.8911 (–2)	7.8454 (–2)	1.1925 (–1)	1.6188 (–1)	2.0689 (–1)
0.55	4.4482 (–5)	4.4483 (–3)	4.4573 (–2)	8.9693 (–2)	...	...	...

as W/ω approaches 1, $W_0(1)$ and $W_1(2)$ are degenerate for any $G(1,2)/\omega$. But for strong interaction where the radiative interaction becomes comparable to the photon frequency ($2G(1,2)\approx\omega$), for better convergent property, the new eigenvalue of apparently nondegenerate level should be obtained by the degenerate case in the charge-field adiabatic eigensolution.[2,3,6]

A. General relations

General relations exist among the eigensolutions of the charge-field system that considerably simplify the calculations. From Eq. (3.1), it can be shown that[17,3]

$$E_{\rho+\mu,\sigma}=E_{\rho,\sigma}-\mu\omega \tag{3.10}$$

and

$$a_\nu^{\rho+\mu,\sigma}(\alpha)=a_{\nu-\mu}^{\rho,\sigma}(\alpha)\,. \tag{3.11}$$

If μ is even (odd), these relations give new eigensolutions of the same parity (different parities) of the same σ as $(E_{\rho\sigma},\hat{\Psi}_{\rho\sigma})$. Another set of relations[17] is

$$E_{\rho_0\sigma}=w_2+w_1-\rho_0\omega-E_{0\tau} \tag{3.12}$$

and

$$a_\nu^{\rho_0\sigma}(\alpha)=(-1)^{\nu+1}a_{\rho_0-\nu}^{0\tau}(\beta)\,, \tag{3.13}$$

where ρ_0 is odd integer and $\sigma\neq\tau$. For $\sigma=1$, these relations connect even-parity solution $(E_{\rho_01},\hat{\Psi}_{\rho_01})$ with even-parity solution $(E_{02},\hat{\Psi}_{02})$. For $\sigma=2$, they connect odd-parity solution $(E_{\rho_02},\hat{\Psi}_{\rho_02})$ with odd-parity solution $(E_{01},\hat{\Psi}_{01})$. As a consequence of Eqs. (3.10)–(3.13), we have

$$E_{\rho_e2}=w_2+w_1-\rho_e\omega-E_{01}\,,\qquad \rho_e=\text{even integer}\,, \tag{3.14}$$

and

$$a_\nu^{\rho_e2}(\alpha)=(-1)^\nu a_{\rho_e-\nu}^{01}(\beta)\,,\quad \alpha\neq\beta\,. \tag{3.15}$$

Thus, once $(E_{01},\hat{\Psi}_{01})$ is known, *all* other eigensolutions can be obtained conveniently by Eqs. (3.10)–(3.15).

We now show that *for a two-level charge system, a true crossing remains as a true crossing for any oscillating field strength*, contrary to the case for static fields. Indeed, at $W=w_2-w_1=0$,

$$E_{01}=E_{02}=w_2=w_1\,, \tag{3.16}$$

for any interaction strength $G(1,2)$. This can be seen by substituting explicit expressions of T_ν and T'_ν into Eq. (3.9). Then the ansatz, $E_{01}=w_1$, indeed satisfies Eq. (3.9). Finally, use of Eq. (3.14) with $\rho_e=0$ gives $E_{02}=w_2$. This result is also expected from consideration of the symmetrical nature of the interaction between the two degenerate states. Furthermore, one has the following relation for the case $W=0$,

$$a_\nu^{02}(\alpha)=a_\nu^{01}(\beta),\quad \alpha\neq\beta\,, \tag{3.17}$$

for any $G(1,2)$. This can be shown by writing out the explicit expressions for $T_\nu^{01}(\beta,\alpha)$ and $T_\nu^{02}(\alpha,\beta)$ and making use of Eq. (3.16). It is then obvious that the equality, $T_\nu^{01}(\beta,\alpha)=T_\nu^{02}(\alpha,\beta)$ immediately implies the result of Eq. (3.17). Note that Eq. (3.15), which is true for any W, is valid for $W=0$:

$$a_\nu^{02}(\alpha)=(-1)^\nu a_{-\nu}^{01}(\beta),\quad \alpha\neq\beta\,. \tag{3.18}$$

This result and Eq. (3.17) imply the relation $a_\nu^{01}(\beta)=(-1)^\nu a_{-\nu}^{01}(\beta)$ between components of $\hat{\Psi}_{01}$.

For $G(1,2)/\omega\lesssim 0.1$ and $W/\omega\lesssim 0.1$, it can be shown that

$$a_\nu^{02}(\alpha)\approx a_\nu^{01}(\beta)\,,$$

and furthermore,

$$a_\nu^{\rho\sigma}(\alpha)\approx(-1)^\nu a_{-\nu}^{\rho\sigma}(\alpha)\,, \tag{3.19}$$

within an uncertainty of a few percent.

B. Simplification of field-dressed nonadiabatic coupling

Use of the relationships in the preceding subsection simplifies the expression for the nonadiabatic coupling $C_{\rho\sigma,\,\rho'\sigma'}$ given in Eq. (2.12). For the case of a two-level charge system ($\beta=1,2$ only),

$$C_{01,02}=-i\Big[\sum_{\nu\beta}a_\nu^{01}(\beta)\frac{d}{dt}a_\nu^{02}(\beta)+\sum_{\substack{\nu\beta\beta'\\ \beta\neq\beta'}}a_\nu^{01}(\beta)a_\nu^{02}(\beta')\Big(\varphi_\beta,\frac{d}{dt}\varphi_{\beta'}\Big)\Big]\,. \tag{3.20}$$

The first sum vanishes because one of the two factors in each term is identically zero. A similar argument and use of $(\varphi_1,(d/dt)\varphi_2)=-(\varphi_2,(d/dt)\varphi_1)$, Eq. (3.15) with $\rho_e=0$, and Eq. (3.3) enable us to write the second sum in the following form:

$$r\equiv\frac{C_{01,02}}{-i(\varphi_1,(d/dt)\varphi_2)}=|a_0^{01}(1)|^2\Big(1+2\sum_{\nu_e>0}^{M}d_{\nu_e}^{01}(1)d_{-\nu_e}^{01}(1)+2\sum_{\nu_0>0}^{M}d_{\nu_0}^{01}(2)d_{-\nu_0}^{01}(2)\Big)\,. \tag{3.21}$$

The factor r, therefore, denotes the ratio of the field-dressed nonadiabatic coupling to the field-free value. As the interaction $G(1,2)/\omega\to 0$, $a_0^{01}(1)\to 1$, and $d_{\nu\neq 0}^{01}(\beta)\to 0$. Thus, r has the correct limit of unity.

It can be shown that *the radiation field always reduces the nonadiabatic coupling*, i.e., $r<1$. Al-

though the numerical results obtained for a wide range of parameters $G(1,2)/\omega$ and W/ω in Table II substantiate this assertion, this fact can also be established analytically for a more limited range. For $W/\omega = 0$ and for any $G(1,2)/\omega$, use of Eqs. (3.17) and (3.18) in Eq. (3.21) yields the rigorous expression,

$$r = \frac{\left(1 + 2\sum_{\nu_e>0}^{M} |d_{\nu_e}^{01}(1)|^2 - 2\sum_{\nu_0>0}^{M} |d_{\nu_0}^{01}(2)|^2\right)}{\left(1 + 2\sum_{\nu_e>0}^{M} |d_{\nu_e}^{01}(1)|^2 + 2\sum_{\nu_0>0}^{M} |d_{\nu_0}^{01}(2)|^2\right)}, \tag{3.22}$$

where we have inserted the expression for the normalization constant $|a_0^{01}(1)|$. It can be seen that $r \leq 1$ always. Furthermore, as the interaction $G(1,2)/\omega$ becomes larger, there is more probability P_s in the sidebands (see Sec. V below) with the leading term being $2|d_1^{01}(2)|^2$, and hence r becomes smaller. For $G(1,2)/\omega \lesssim 0.1$ and $W/\omega \lesssim 0.1$, use of Eq. (3.19) shows that the result in Eq. (3.22) is approximately valid.

C. Invariance of the form of some configurations

Results for r in Table II for given $G(1,2)/\omega$, but different W/ω clearly show that over a range of $W/\omega \lesssim 0.3$,

$$r = \text{const}, \tag{3.23}$$

to a good approximation.[18] This is shown in Eq. (3.35b) below. Thus if the original near degenerate levels w_1 and w_2 and field frequency falls within this range, we should expect that the field-dressed nonadiabatic coupling C_{1u} will follow the variation of the field-free nonadiabatic coupling $-i(\varphi_1, (d/dt)\varphi_2)$. Since the important region of transition in the Landau-Zener model for true crossing corresponds to small W/ω, C_{1u} is constant over this region if the field-free quantity $-i(\varphi_1, (d/dt)\varphi_2)$ is also.

Values of the shift δ/ω in Table I show that there is a range of W/ω ($\lesssim 0.3$ for values of $G(1,2)/\omega \leq 0.5$ in Table I) over which for a given $G(1,2)/\omega$,

$$\delta/W = \text{const}, \tag{3.24}$$

to a very good approximation.[18] This can be seen from Eq. (3.34b) below. Using this result and Eq. (3.16) we can show that for the Landau-Zener model of true crossing.

$$-\alpha_t = \frac{d(E_{02} - E_{01})}{d\tau} = -\alpha_t^0 D, \tag{3.25}$$

where

$$D \equiv \frac{E_{02} - E_{01}}{w_2 - w_1} = 1 - \frac{2\delta}{W}, \tag{3.26}$$

and $-\alpha_t^0 \equiv dW/dt$ is the relative slope of the field-free true crossing. This and the result of the previous paragraph lead us to the conclusion that in the presence of a constant-amplitude laser field, if the region of transition is within the range of W/ω such that Eqs. (3.23) and (3.24) are valid, then *the field-dressed configuration of a field-free Landau-Zener true crossing is also a Landau-Zener true crossing.*

For the avoided crossing, similar conclusions can be drawn as well. Use of Eq. (3.24) shows that $(E_{02} - E_{01})^2$ is minimum where W^2 is minimum. Furthermore, from Eqs. (2.27), (2.28), and (3.24) we obtain

$$\hat{H}_{12} = \tfrac{1}{2} W_m D, \tag{3.27}$$

TABLE II. Exact values of r, the ratio of the field-dressed nonadiabatic coupling $-i(\hat{\Psi}_1, (d/dt)\hat{\Psi}_u)$ to the field-free nonadiabatic coupling $-i(\varphi_1, (d/dt)\varphi_2)$, for a two-level charge system interacting with a single field mode of frequency ω. $G(1,2)/\omega$ and W/ω are defined as in Table I.

$G(1,2)/\omega$ \ W/ω	10^{-4}	0.01	0.1	0.2	0.3	0.4	0.5
0.01	0.999 60	0.999 60	0.999 59	0.999 57	0.999 52	0.999 43	0.999 29
0.05	0.990 02	0.990 02	0.989 83	0.989 19	0.987 99	0.985 96	0.982 49
0.1	0.960 40	0.960 39	0.959 64	0.957 24	0.952 76	0.945 29	0.932 99
0.15	0.912 00	0.911 99	0.910 45	0.905 54	0.896 53	0.881 91	0.858 91
0.2	0.846 28	0.846 26	0.843 84	0.836 22	0.822 50	0.800 94	0.768 76
0.25	0.765 20	0.765 17	0.761 96	0.751 95	0.734 31	0.707 56	0.669 64
0.3	0.671 13	0.671 09	0.667 32	0.655 69	0.635 63	0.606 22	0.566 44
0.35	0.566 85	0.566 81	0.562 80	0.550 55	0.529 84	0.500 40	0.462 14
0.4	0.455 40	0.455 36	0.451 45	0.439 62	0.419 97	0.392 73	0.358 47
0.45	0.339 99	0.339 95	0.336 45	0.325 91	0.308 66	0.285 23	0.256 47
0.5	0.223 89	0.223 86	0.220 97	0.212 32	0.198 30	0.179 55	0.156 94
0.55	0.110 36	0.110 34	0.108 15	0.101 63	...	...	...

and

$$\hat{H}_{22}-\hat{H}_{11}=\pm(W^2-W_m^2)^{1/2}D\,, \tag{3.28}$$

and hence,

$$-\alpha_a=-\alpha_a^0 D\,, \tag{3.29}$$

where W_m is the minimum value of W in the avoided crossing and α_a^0 is the relative slope of field-free diabatic levels

$$-\alpha_a^0\equiv\frac{d}{d\tau}(W^2-W_m^2)^{1/2}. \tag{3.30}$$

Thus, α_a is constant if α_a^0 is. Therefore, if Eq. (3.24) is valid over the region of transition, then *the field-dressed configuration of a field-free Landau-Zener avoided crossing is also a Landau-Zener avoided crossing.*

For the configuration of parallel levels with nonadiabatic coupling that is *not* necessarily constant, it is obvious that the energy levels will remain parallel for a constant interaction $G(1,2)$ and according to Eq. (3.21), the nonadiabatic coupling is scaled by a constant ratio. Thus, this configuration will also remain invariant in form. Of course, a configuration will not in general remain invariant in form for an interaction $G(1,2)$ with variation due to field intensity and/or transition moments.[6]

D. Reduction of the formulas

The single parameter p_t in the Landau-Zener formula for field-dressed true crossing appearing in Eqs. (2.17) and (2.18) can now be written in the following form by use of Eqs. (3.21) and (3.25).

$$p_t=p_t^0 q_t\,, \tag{3.31a}$$

where

$$q_t\equiv r^2/D\,, \tag{3.31b}$$

is a *multiplicative* factor due to the presence of the field and the quantity

$$p_t^0\equiv|(\varphi_1,(d/dt)\varphi_2)|^2/|\alpha_t^0|$$

is the field-free parameter that would occur in the field-free Landau-Zener formula. Note that q_t approaches unity as $G(1,2)$ vanishes, as expected physically.

Similarly, the parameter p_a in the Landau-Zener formula for field-dressed avoided crossings appearing in Eqs. (2.31) and (2.32) can be written as a product of the corresponding field-free parameter $p_a^0\equiv W_m^2/4|\alpha_a^0|$ and the factor

$$q_a=D\,, \tag{3.32a}$$

by use of Eqs. (3.27) and (3.29). That is

$$p_a=p_a^0 q_a\,, \tag{3.32b}$$

in which q_a has the expected limit of unity as $G(1,2)\to 0$.

Since $W\geq 2\delta\geq 0$, $q_a=D$ is always ≤ 1. Thus, the field-dressed parameter p_a for avoided crossing is always less than the field-free parameter p_a^0. According to the Landau-Zener formula Eqs. (2.31) and (2.32), *for avoided crossings the presence of the laser radiation always increases the inelastic transition probability* $|B_u|^2$ *and decreases the elastic transition probability* $|B_l|^2$. This can be understood as follows. For $W<\omega$, the two levels shift closer together such that the shift is larger for larger level separation W [see Eq. (3.24)]. Therefore, the relative slope is reduced by a factor of D as shown in Eq. (3.29). However, the minimum of the level separation W_m is also reduced by a factor of D in the presence of the field as in Eq. (3.27). The latter mechanism dominates over the change in relative slope because it is the ratio of the square of the level separation to the relative slope that enters into the Landau-Zener parameter p_a. Thus, it may be stated for simplicity that because the laser field shifts the energy levels of the avoided crossing closer together, the probability of an inelastic event is increased.

We have shown above in Eq. (3.22) that $r\leq 1$. It is shown immediately below that $D=r$ as a good approximation[18] at least over the ranges of parameters $G(1,2)/\omega\leq 0.5$ and $W/\omega\leq 0.3$. Therefore, $q_t\leq 1$ and the field dressed parameter p_t is always smaller than the field-free parameter p_t^0 for true crossing. According to the Landau-Zener formula Eqs. (2.17)-(2.18) *for true crossing, the inelastic transition probability* $|B_u|^2$ *is decreased in the presence of the laser field while the probability for the elastic process* $|B_l|^2$ *is increased.* This can be understood because the field reduces the nonadiabatic coupling. Although the field also reduces the relative slope ($\alpha=\alpha_0 D$), the parameter p_t in the Landau-Zener formula for true crossing contains the ratio of the square of the nonadiabatic coupling to the relative slope, so that effect of the former dominates.

A comparison of the values of D in Table III with the corresponding values of r in Table II reveals the interesting fact that over the range of $G(1,2)/\omega$ (≤ 0.5) considered,

$$D=r\,, \tag{3.33}$$

with a relative difference less than 0.04 for $W/\omega\leq 0.3$ and with a relative difference less than 0.06 for $W/\omega\leq 0.5$. The agreement between D and r is actually better than the approximations (3.23) and (3.24). We can derive Eq. (3.33) and at the same time obtain approximate formulas for δ, D and r. By keeping terms (a) of order $G^2(1,2)/\omega^2$ or (b)

TABLE III. Values of $D \equiv 1 - 2\delta/W$, the multiplicative factor measuring the change of energy level separation or relative slope of energy levels under the interaction with laser field. Note the (near) equality of D with the corresponding value of r in Table II. This (near) equality leads us to represent the entire effect of field on several configurations by this single multiplicative factor.

$G(1,2)/\omega$ \ W/ω	10^{-4}	0.01	0.1	0.2	0.3	0.4	0.5
0.01	0.999 60	0.999 60	0.999 60	0.999 58	0.999 56	0.999 52	0.999 47
0.05	0.990 02	0.990 02	0.989 92	0.989 62	0.989 05	0.988 16	0.986 77
0.1	0.960 40	0.960 39	0.960 02	0.958 84	0.956 71	0.953 35	0.948 24
0.2	0.846 29	0.846 27	0.845 02	0.841 12	0.834 25	0.823 81	0.808 80
0.3	0.671 14	0.671 12	0.669 04	0.662 68	0.651 77	0.635 85	0.614 29
0.4	0.455 40	0.455 38	0.453 00	0.445 80	0.433 71	0.416 65	0.394 60
0.5	0.223 90	0.223 88	0.221 78	0.215 46	0.205 00	0.190 60	0.172 44
0.55	0.110 36	0.110 34	0.108 54	0.103 07	...	...	...

of order $(W - E_{01})/\omega$ in T_1 and T'_{-1}, we obtain from Eq. (3.9) the formulas for optical Stark shifts:

$$\delta_{(a)} = \frac{2W[G(1,2)/\omega]^2}{\{1-\frac{1}{2}[G(1,2)/\omega]^2\}^2 + 2[G(1,2)/\omega]^2 - (W/\omega)^2}, \tag{3.34a}$$

$$\delta_{(b)} = \frac{2W[G(1,2)/\omega]^2}{\{1-\frac{1}{2}[G(1,2)/\omega]^2\}^2 + 2[G(1,2)/\omega]^2}, \tag{3.34b}$$

and from Eq. (3.21) the formula for the ratio of nonadiabatic couplings,

$$r_{(a)} = \frac{\{1-\frac{1}{2}[G(1,2)/\omega]^2\}^2 - 2[G(1,2)/\omega]^2 - (W/\omega)^2}{\{1-\frac{1}{2}[G(1,2)/\omega]^2\}^2 + 2[G(1,2)/\omega]^2 - (W/\omega)^2}, \tag{3.35a}$$

$$r_{(b)} = \frac{\{1-\frac{1}{2}[G(1,2)/\omega]^2\}^2 - 2[G(1,2)/\omega]^2}{\{1-\frac{1}{2}[G(1,2)/\omega]^2\}^2 + 2[G(1,2)/\omega]^2}. \tag{3.35b}$$

In Fig. (3), we compare values of these formulas with the exact numerical results and found them to be good approximations for $W/\omega \lesssim 0.3$. Eqs. (3.34a) and (3.35a) are better approximations for $G(1,2)/\omega \lesssim 0.4$ while Eqs. (3.34b) and (3.35b) are better for $G(1,2)/\omega \gtrsim 0.4$. Using the definition for D in Eq. (3.26) we obtain with either set of formulas the important result, Eq. (3.33). For $[G(1,2)/\omega] \lesssim 0.35$ and $(W/\omega) \leq 0.3$, results of D based on Eq. (3.34a) agree with the exact D value to the same extent as the agreement between the exact r and D values, namely with relative differences less than 3%. For $0.5 \gtrsim G(1,2)/\omega > 0.35$ and $W/\omega \leq 0.4$, calculated D values using Eq. (3.34b) agrees with the exact D values within 7%.

The significance of Eq. (3.33) is that D, defined in terms of energies, is more easily and accurately known than r, defined in terms of wavefunctions. Another important consequence is that a *single factor q accurately characterizes the entire effect of the field on both the true and avoided*

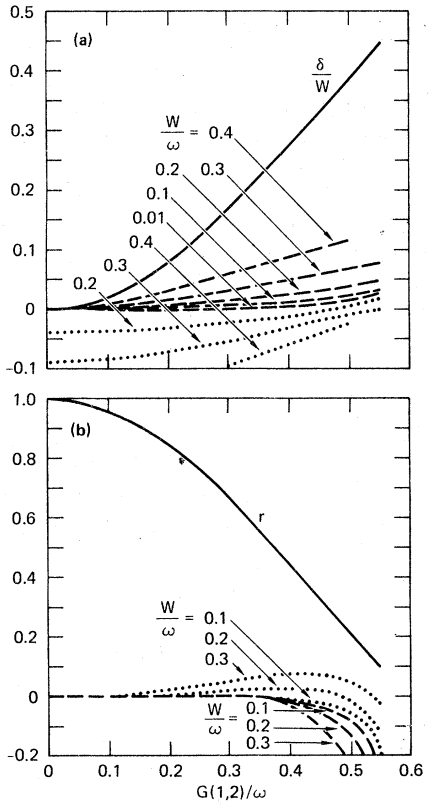

FIG. 3. (a) Comparison of the analytic results Eq. (3.34) for the ratio of the optical Stark shift δ to the unperturbed energy separation W between two levels, with exact numerical results; and (b) comparison of the analytic result Eq. (3.35) for the ratio of field-dressed nonadiabatic coupling to its field-free value, with exact numerical results. In both figures, the solid line shows the behavior of the respective quantities, where their approximately linear dependence on the interaction $G(1,2)/\omega$ for values $\gtrsim 0.3$ should be noted. To bring out the differences, the dashed lines and the dotted lines labeled by W/ω are plots of the expression [(analytic value/numerical value) − 1], for analytic values given by Eqs. (3.34a), (3.35a), and by Eqs. (3.34b) and (3.35b); respectively.

crossings in the Landau-Zener model. Therefore we have

$$q \equiv q_a = D = r = q_t . \tag{3.36}$$

We now have available an approximate expression in the form of Eq. (3.35) which enables rapid and reasonably accurate estimates of the q factor to be made.

The solution, Eq. (2.35), for the configuration of parallel levels with constant nonadiabatic coupling can also be simplified. Similar to Eqs. (3.24), it can be shown that

$$\Delta = WD , \tag{3.37}$$

where D is previously defined in Eq. (3.26). Use of this and Eqs. (3.21) and (3.33) shows that the field-dressed "flopping" frequency is reduced by the multiplicative factor $D(\leq 1)$,

$$\Omega = D\Omega_0 , \tag{3.38}$$

where Ω_0 is simply the field-free "flopping" frequency,

$$\Omega_0 \equiv \left[W^2 + 4 \left| -i\left(\varphi_1, \frac{d}{dt}\varphi_2\right) \right|^2 \right]^{1/2} ,$$

and that the amplitude A of inelastic transition is invariant in the presence of the field,

$$A = A_0 \equiv -i2\left[-i\left(\varphi_1, \frac{d}{dt}\varphi_2\right)\right] \Big/ \Omega_0 . \tag{3.39}$$

By Eq. (3.14), $\Lambda = E_u + E_l = w_2 + w_1$. Thus if $W/\omega \leq 0.3$, and $G(1,2)/\omega \leq 0.5$, the amplitudes (coefficients of $\sin\frac{1}{2}\Omega t$ and $\cos\frac{1}{2}\Omega t$) in Eq. (2.35) remain approximately invariant in the presence of the nonresonant field, but the flopping frequency is reduced by a factor D.

Finally, we point out that the many simple relations in subsec. $B-D$ remain to be valid for larger $G(1,2)/\omega$ than those shown. However, the corresponding region of W/ω will be smaller than $W/\omega \leq 0.3$.

E. Symmetries of the two states

In the above discussions, we have assumed that the radiative interaction $G(1,2)$ between the two states φ_1 and φ_2 is nonzero. Furthermore, according to Eq. (3.21), the field-dressed nonadiabatic coupling $C_{01,02}$ for a two-level charge system remains to be zero if its field-free counterpart $C^0_{01,02} \equiv -i(\varphi_1, (d/dt)\varphi_2)$ vanishes. Therefore, if either $G(1,2)$ or $C^0_{01,02}$ vanishes in a particular energy surface region, the presence of the laser field does not modify the field-free transition probabilities. We consider below the symmetry properties of the two states such that $G(1,2)$ and $C^0_{01,02}$ are nonzero.

For specific discussion, we consider diatomic molecules. For simplicity we shall assume that spin-orbit interaction is negligible. The above theory is applicable to magnetic dipole and electric quadrupole transitions as well as electric dipole.[3,6] The selection rules for electron-radiative interactions in diatomics are well known[19]:

Electric dipole	Magnetic dipole	Electric quadrupole	
$g \nleftrightarrow u$	$g \nleftrightarrow g,\ u \nleftrightarrow u$	$g \nleftrightarrow g,\ u \nleftrightarrow u$	
$g \not\leftrightarrow g,\ u \not\leftrightarrow u$	$g \not\leftrightarrow u$	$g \not\leftrightarrow u$	(3.40a)
$\Delta\Lambda = 0, \pm 1$	$\Delta\Lambda = 0, \pm 1$	$\Delta\Lambda = 0, \pm 1, \pm 2$	(3.40b)

where g and u stand for *gerade* and *ungerade* symmetry for equal nuclear charges; and Λ is the component of the electronic angular momentum along the internuclear axis. Similarly, the field-free nonadiabatic coupling is nonzero if

$$g \nleftrightarrow g, u \nleftrightarrow u , \tag{3.41a}$$

$$\Delta\Lambda = 0, \pm 1 . \tag{3.41b}$$

For diatomics of unequal nuclear charges, a true crossing is possible only for $\Delta\Lambda \neq 0$ while an avoided crossing requires $\Delta\Lambda = 0$. Corresponding but different statements can be made for one-electron diatomics. For other configurations, both $\Delta\Lambda = 0$ and $\Delta\Lambda \neq 0$ are possible. These considerations together with Eqs. (3.40b) and (3.41b) lead to the conclusion that for unequal nuclear charges, $G(1,2)$ (electric dipole or higher multipoles) and $C^0_{01,02}$ are nonzero for a true crossing if $\Delta\Lambda = \pm 1$; for an avoided crossing if $\Delta\Lambda = 0$; and for other configurations if $\Delta\Lambda = 0, \pm 1$.

For diatomics of equal nuclear charges, a true crossing between two electronic energies is possible if $\Delta\Lambda \neq 0$ or $g \nleftrightarrow u$ is true. If the relations $\Delta\Lambda = \pm 1$ and $g \nleftrightarrow g$ or $u \nleftrightarrow u$ hold, then $C^0_{01,02}$ is nonzero and the radiative interaction $G(1,2)$ is due to magnetic dipole or electric quadrupole. In all other cases, $C^0_{01,02} = 0$ or $G(1,2) = 0$. The symmetries of the two states giving rise to an avoided crossing must satisfy both $\Delta\Lambda = 0$ and $g \nleftrightarrow g$ (or $u \nleftrightarrow u$). In such cases, $C^0_{01,02}$ is nonzero and the radiative interaction is magnetic dipole or electric quadrupole. For other configurations, $C^0_{01,02}$ and $G(1,2)$ are nonzero if both $\Delta\Lambda = 0, \pm 1$, and $g \nleftrightarrow g$

or $u \rightarrow u$ hold true. Thus we see that in all cases for a *two-level* diatomic of equal nuclear charges, the radiative interaction is through magnetic dipole or electric quadrupole if $C^0_{01,02}$ has to be nonzero.

IV. RESULTS FOR FIELD MODIFICATION OF COLLISIONLESS AND COLLISIONAL PROCESSES

Collisionless and collisional processes may involve only a single transit of the crossing region per elementary event, as often the case in dissociation, predissociation and in molecular collisions. In atomic collision, however, at least two crossings are involved. Application of an intense laser can change these processes as shown by numerical results in this section and gives rise to new processes due to formation of new crossings (see Sec. VI). Based on analysis of the previous sections, we will compare the various probabilities of processes taking place in presence of radiation field with the probability for the same process in its absence. The difference is a function of both the interaction parameter $G(1,2)/\omega$ and the field-free Landau-Zener parameter p_0, which may be evaluated as either p_t^0 for true crossings or p_a^0 for avoided crossings.

A. Processes with single crossing

Based on the Landau-Zener formulas Eqs. (2.17)–(2.18) and Eqs. (2.31)–(2.32), we define

$$S_i = e^{-2\pi p_0 q_i}, \quad i \equiv t \text{ or } a \tag{4.1}$$

and

$$S_0 = e^{-2\pi p_0}. \tag{4.2}$$

For true crossings ($i=t$), $S_t \equiv |B_l|^2$ is the probability of the elastic process, and $T_t \equiv 1 - S_t$ is the inelastic transition probability. For avoided crossings ($i=a$), $S_a = |B_u|^2$ is the inelastic transition probability, and $T_a \equiv 1 - S_a$ is the probability of the elastic process. S_0 and $T_0 \equiv 1 - S_0$ are the corresponding field-free probabilities. Note that

$$T_i - T_0 = -(S_i - S_0). \tag{4.3}$$

Although we use either q_t or q_a in the actual evaluation,

$$S_t \approx S_a, \tag{4.4}$$

because $q_t \approx q_a \equiv q$ to a good approximation. Thus, the results for one kind of crossing are applicable to the other with the above interpretation.

The dependence of S_i on the field intensity is in general exponential, not linear. Furthermore, for a given interaction strength $G(1,2)/\omega$, the effect of the field can be strongly amplified by the multiplicative factor $2\pi p_0$ appearing in the exponent. Thus for given $G(1,2)/\omega$ (that is, for a given laser intensity, polarization, and frequency), the other experimental conditions can be chosen such that p_0 is of the right magnitude in order to see the desired effects of the field. When $2\pi p_0$ (hence $2\pi p_0 q_i$) is small, only the following quantities are linear in $(G(1,2)/\omega)^2$ when $(G(1,2)/\omega)^2 \ll 1$:

$$\begin{aligned} S_i &= 1 - 2\pi p_0 + 8\pi p_0 [G(1,2)/\omega]^2 = 1 - T_i, \\ S_i - S_0 &= 8\pi p_0 G^2(1,2)/\omega^2 = -(T_i - T_0), \end{aligned} \tag{4.5}$$

where Eqs. (4.1), (4.2), (3.32) or (3.31), (3.37), (3.26), and (3.34) have been used. Thus the net effects of the field, $(S_i - S_0)$ or $(T_i - T_0)$, would be proportional to the laser intensity, the square of the cosine of the angle between the polarization and the transition moment, and (for given intensity) inversely proportional to the square of the laser frequency, only if $2\pi p_0$ and $[G(1,2)/\omega]^2$ are both small compared to unity.

Table IV gives the numerical results of the field-free probability S_0 and the field-dressed probability $S_i (= S_t \approx S_a)$. Although these results were computed from values of r and D for a given value of $W/\omega = 0.1$, their values for any other $W/\omega \leq 0.3$ could have been used [cf. Eqs. (3.23) and (3.24)]. The ranges of parameters $G(1,2)/\omega$ and p_0 are chosen to give an indication of some regions where the presence of the field increases S_0 by more than 1%. For a given p_0, S_i increases as the interaction $G(1,2)/\omega$ increases. In all cases, $S_i \geq S_0$. Furthermore, the region where $S_i > 0.5$ while $S_0 < 0.5$ means that *the inelastic transitions at avoided crossing is inverted due to the application of the intense field.* It is seen that for given $G(1,2)/\omega$, the multiplicative exponent $2\pi p_0$ certainly amplifies the effects of the field many fold. The range of p_0 illustrated is that typically encountered in molecular systems: e.g., for a minimum energy separation of avoided crossing ≈ 0.1 eV, a force dW/dR at the crossing $= 0.1$ eV/a_0, and a thermal relative velocity of 10^5 cm/sec, $p_0 \approx 2$.

If the charge system is measured after the field turns off slowly, Eq. (2.38) indicates that $P(2)$, the probability of finding the charge system in state φ_2, equals S_a for avoided crossings and equals $1 - S_t$ for true crossings. For this case, Table IV indicates that the influence of the field on crossings is less than 1% if *both* $p_0 \leq 0.1$ *and* $G(1,2)/\omega \leq 0.05$ are valid. To obtain the intensity I corresponding to the dimensionless quantity $G(1,2)/\omega$, the following relation is useful,

$$G(1,2)/\omega = 5.8577 \times 10^{-8} \lambda \mu I^{1/2},$$

where the wavelength λ is in μm, I is in W/cm^2, and μ in atomic unit is the appropriate dipole or

TABLE IV. The Landau-Zener probability S_i ($\equiv e^{-2\pi p_i}$) in the presence of the field for various interaction $G(1,2)/\omega$ and field-free parameter p_0. S_i is the elastic probability for field-dressed true crossing or the inelastic transition probability for field-dressed avoided crossing. $S_0 = e^{-2\pi p_0}$ is the corresponding field-free probability. S_i always $\geq S_0$. Values marked with an asterisk are those $S_i > 0.5$ for which the corresponding $S_0 < 0.5$. Notation A (n) means $A \times 10^n$.

		$G(1,2)/\omega$					
p_0	S_0	0.05	0.1	0.3	0.45	0.50	0.55
0.1	0.939	0.940	0.942	0.959	0.979	0.986	0.993
0.10	0.533	0.537	0.547	0.658	0.810	0.871	0.935
0.12	0.470	0.474	0.485	0.605*	0.777*	0.847*	0.922*
0.15	0.390	0.393	0.405	0.534*	0.729*	0.813*	0.903*
0.26	0.195	0.199	0.209	0.337	0.578*	0.698*	0.839*
0.50	0.43 (−1)	0.45 (−1)	0.49 (−1)	0.124	0.349	0.501*	0.713*
1.0	0.19 (−2)	0.20 (−2)	0.24 (−2)	0.15 (−1)	0.122	0.251	0.508*
3.0	0.65 (−8)	0.79 (−8)	0.14 (−7)	0.36 (−5)	0.18 (−2)	0.16 (−1)	0.131
5.0	0.23 (−13)	0.31 (−13)	0.82 (−13)	0.82 (−9)	0.27 (−4)	0.99 (−3)	0.33 (−1)
7.5	0.34 (−20)	0.56 (−20)	0.23 (−19)	0.24 (−13)	0.14 (−6)	0.31 (−4)	0.62 (−2)
10	0.52 (−27)	0.98 (−27)	0.67 (−26)	0.69 (−18)	0.71 (−9)	0.98 (−6)	0.11 (−2)

quadrupole transition moment defined by $G(1,2) = \frac{1}{2}\epsilon\mu/\hbar$ with ϵ being the physical electric or magnetic field amplitude.[3,6]

If the charge-field system is measured in the presence of the field, the probability of finding it in a state φ_β of the charge system is given by $P(\beta)$ of Eq. (2.37). Assuming that only the two charge field adiabatic states $\hat{\Psi}_{01}$ and $\hat{\Psi}_{02}$ are populated after the crossing(s), we obtain

$$P(2) = |B_{02}|^2 p_2 + |B_{01}|^2 p_1 = 1 - P(1),$$

where $p_2 \equiv \sum_{\nu_e} |a^{02}_{\nu_e}(2)|^2$ is the probability of finding the charge system being in the state φ_2 if the charge-field system is in the state $\hat{\Psi}_{02}$, and $p_1 \equiv \sum_{\nu_0} |a^{01}_{\nu_0}(2)|^2$ is that in the state $\hat{\Psi}_{01}$. By Eq. (3.15), $p_2 = \sum_{\nu_e} |a^{01}_{\nu_e}(1)|^2$ and $p_1 = \sum_{\nu_0} |a^{02}_{\nu_0}(1)|^2$ and thus $p_1 + p_2 = 1$. After one true crossing, $|B_{01}|^2 = 1 - |B_{02}|^2 = S_t$; and after one avoided crossing, $|B_{02}|^2 = 1 - |B_{01}|^2 = S_a$. For example, if $P(2)$ is measured at the same $G(1,2)/\omega$ value as when the crossing is traversed but at $W/\omega = 0.5$, we can calculate $P_i(2)$ and $P_i(1)$ ($i = t$ or a) with the following values of p_2 and the S_i values corresponding to the same $G(1,2)/\omega$ given in Table IV.

$G(1,2)/\omega$	0.05	0.3	0.5
p_2 (at $W/\omega = 0.5$)	0.9891	0.7457	0.5363 .

While $P_t(2)$ for true crossings equals $1 - P_a(2)$, the following table of $P_a(2)$ for avoided crossings illustrates its dependence on $G(1,2)/\omega$ and p_0:

$G(1,2)/\omega$ \ p_0	0.01	0.1	1.0	5.0
0.05	0.930	0.536	0.013	0.011
0.5	0.535	0.527	0.482	0.464 .

We note that $P_a(2)$ decreases as p_0 increases but it can increase or decrease if $G(1,2)/\omega$ is increased. More important is the fact that for given $G(1,2)/\omega$, $P_a(2)$ is smaller than S_a (and S_0) for small p_0 and can be many times larger than S_a (and hence S_0) for large p_0. Thus for $p_0 = 5$, the field-free inelastic transition probability for avoided crossing S_0 is small (i.e., 2.3×10^{-14}) and so is its field-dressed value $S_a = 3.1 \times 10^{-14}$ for $G(1,2)/\omega = 0.05$. But if the probability $P_a(2)$ is measured in the presence of the field, it is significant (i.e., 0.011) due to the contribution p_1 from the sidebands $\varphi_2 \Omega(N - \nu)$ in $\hat{\Psi}_{01}$ by *state mixing*.

Thus, our general conclusion is that for a given field frequency and polarization, the intensity at which influences of the field are important is a function of the field-free parameter p_0 and of the field parameters at the time when a process takes place or is measured, as well as those field parameters when the inelastic transitions occur.

B. Processes with two crossings

We consider here field modification of processes involving two crossings. For example, in atom-atom scattering, the same true or avoided crossing is traversed twice. In the same sense as explained in Eq. (4.4), we shall not distinguish true crossing from avoided crossing. Indeed the difference would not have shown up in the graphical results of this subsection.

Aside from an interference factor between the two crossings (which would be averaged out in the integration over impact parameter to obtain the total cross section), the final inelastic transition probability after traversing two crossings approximated by the Landau-Zener model is

$$f = e^{-2\pi p}(1 - e^{-2\pi p'}) + e^{-2\pi p'}(1 - e^{-2\pi p}) , \quad (4.6)$$

in the presence of the laser field, and is

$$f_0 = 2e^{-2\pi p_0}(1 - e^{-2\pi p_0}) , \quad (4.7)$$

without the field. Here p and p' are in general different because even though the laser intensity is the same when the two crossings are traversed, the angle between the field polarization and the transition moments of the charge system can be considerably different at the two crossings along the orbit. Hence, the coupling parameter $G(1, 2)/\omega$ is different at the two crossings. Thus in the presence of the field, the inelastic excitation probability f can be $> \frac{1}{2}$, while if $p = p'$, f must $\leq \frac{1}{2}$. Similarly $f_0 \leq \frac{1}{2}$.

When $2\pi p_0$ (and hence $2\pi p$ and $2\pi p'$) is small compared to unity, it can be shown that

$$f \cong 2\pi p(1 + p'/p) , \quad (4.8)$$

and $f_0 \cong 4\pi p_0$. Thus in this region of small $2\pi p_0$,

$$f < f_0 , \quad (4.9)$$

since it is always true that $p_0 \geq p$ or p'. Eq. (4.8) shows that *when* $2\pi p_0 \ll 1$, *an increase in the interaction* $G(1,2)/\omega$ *always decreases* f. On the other hand, when $2\pi p$ and $2\pi p'$ (hence $2\pi p_0$) are large compared to unity,

$$f \cong e^{-2\pi p} + e^{-2\pi p'} , \quad (4.10)$$

and $f_0 \cong 2e^{-2\pi p_0}$, thus indicating

$$f > f_0 . \quad (4.11)$$

Equation (4.10) indicates that *when* $2\pi p$ *and* $2\pi p' \gg 1$, *an increase in the interaction* $G(1,2)/\omega$ *increases* f. The maximum f_0 occurs at

$$p_m^0 = (\ln 2)/2\pi = 0.1103. \quad (4.12)$$

When $p \neq p'$, the value of p_0 at which the maximum of f occurs can be found by graphical solution. However, when $p = p'$, then the maximum of f occurs at

$$p_m = p_m^0 / q_i , \quad (4.13)$$

where Eqs. (3.31a), (3.32b), and (4.12) have been used. As q_i becomes smaller at larger interaction $G(1, 2)/\omega$, the value of p_m becomes larger and is inversely proportional to $(1 - 2\delta/W)$.

Figures 4(a) and 4(b) plot f as a function of p_0 for several values of $G(1, 2)/\omega$ for the cases $p = p'$ and $p \neq p'$, respectively. Fig. 5(a) and Fig. 5(b) show the variation of f as a function of $G(1, 2)/\omega$ for several p_0. As the interaction $G(1, 2)/\omega$ increases, the decrease of inelastic transition probability f for small values of $2\pi p_0$, the increase of f for large $2\pi p_0$, and the shift of location of the maximum of f toward higher p_0 are as expected from the above analysis. Figures 4(b) and 5(b) also illustrate regions in which $f > \frac{1}{2}$ for the case $G'(1, 2)/G(1, 2) = 0.1$. For comparison, the field-free inelastic transition probability f_0 is plotted with a dashed line in Figs. 4(a) and 4(b). It is seen that the presence of the laser field greatly favors transitions for those encounters with larger p_0 and to a smaller extent, suppresses those with the smaller value of p_0. Thus, the choice of appropriate parameters p_0 and $G(1, 2)/\omega$ is important for the desired behavior in experiments using intense laser to control processes.

V. INADEQUACY OF STATIONARY PERTURBATION THEORY

In this section, we compare quantities evaluated by standard stationary perturbation theory[20] with the exact values obtained by the above nonperturbative theory. The perturbative results for a charge system of two levels used by us are the energy shift

$$\tilde{\delta} \equiv \tilde{E}_{01} - W_0(1) = 2WG^2(1, 2)/(\omega^2 - W^2) , \quad (5.1)$$

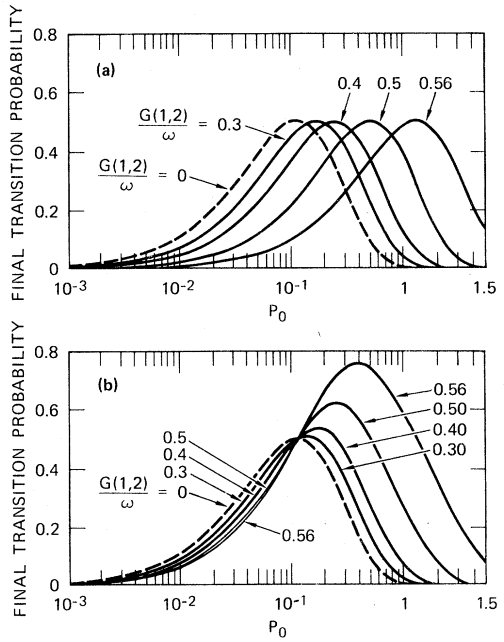

FIG. 4. For processes involving two Landau-Zener crossings with interactions $G(1, 2)/\omega$ and $G'(1, 2)/\omega$ respectively, the final inelastic transition probability f is given as a function of the field-free Landau-Zener parameter p_0 for several values of $G(1, 2)/\omega$. The corresponding field-free inelastic transition probability $f_0 = 2e^{-2\pi p_0}(1 - e^{-2\pi p_0})$ is drawn in dashed line for comparison. The maxima of f are shifted toward larger p_0 for greater $G(1, 2)/\omega$. (a) For $G(1, 2) = G'(1, 2)$, $f \leq \frac{1}{2}$. (b) For $G(1, 2) = 10G'(1, 2)$, f can be greater than $\frac{1}{2}$.

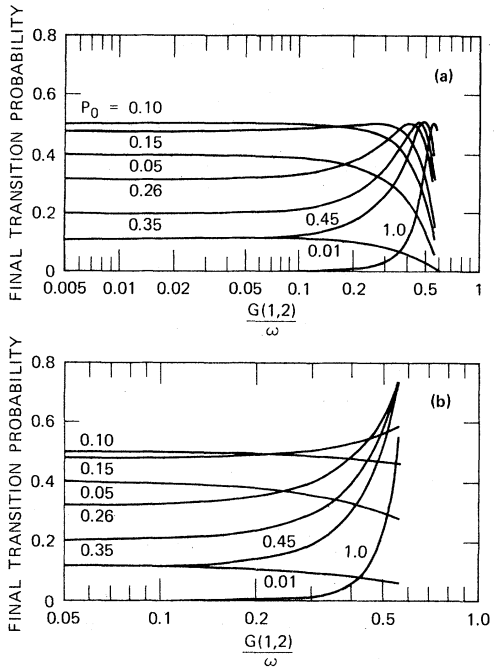

FIG. 5. For processes involving two Landau-Zener crossings with interactions $G(1,2)/\omega$ and $G'(1,2)/\omega$ respectively, the final inelastic transition probability f is given as a function of the interaction $G(1,2)/\omega$ for several values of p_0. The intercept at ordinate axis gives approximately the corresponding field-free value f_0. It is seen that for some values of p_0, f always decreases while for other p_0, f increases and (should) eventually decrease again. (a) For $G(1,2) = G'(1,2)$; (b) for $G(1,2) = 10\,G'(1,2)$.

and the expansion coefficients in the charge-field adiabatic eigenstate $\hat{\Psi}_{01}$,

$$\tilde{a}_0^{01}(1) = 1.0,$$

$$\tilde{a}_1^{01}(2) = \frac{G(1,2)}{\omega - W}, \quad \tilde{a}_{-1}^{01}(2) = \frac{-G(1,2)}{\omega + W}, \tag{5.2}$$

$$\tilde{a}_2^{01}(1) = \frac{G^2(1,2)}{2\omega(\omega - W)}, \quad \tilde{a}_{-2}^{01}(1) = \frac{G^2(1,2)}{2\omega(\omega + W)},$$

correct to second order in $G^2(1,2)/\omega^2$. The corresponding coefficients in the charge-field adiabatic states $\hat{\Psi}_{02}$ are given by

$$\tilde{a}_\nu^{02}(\alpha) = (-1)^\nu \tilde{a}_{-\nu}^{01}(\beta), \quad \beta \neq \alpha, \tag{5.3}$$

similar to Eq. (3.15).

A measure of the deviation from the perturbative assumption is the total probability in the sidebands, P_s. If the charge-field system is in the adiabatic state $\hat{\Psi}_{01}$, the probability in all the sidebands of $W_0(1)$ is given by

$$P_s \equiv \sum_{\substack{\nu \neq 0 \\ \alpha = 1,\,2}} |a_\nu^{01}(\alpha)|^2 = 1 - |a_0^{01}(1)|^2 .$$

The exact value of P_s is evaluated using the normalized $a_\nu(\alpha)$ given by the nonperturbative theory and is given in the last column of Table V.

The following quantities, which were defined earlier, are now evaluated using the perturbative results in Eqs. (5.1)–(5.3) and distinguished by a tilde (~) over them:

$$\tilde{D} = 1 - 4G^2(1,2)/(\omega^2 - W^2), \tag{5.4}$$

$$\tilde{r} = 1 - 2G^2(1,2)/(\omega^2 - W^2), \tag{5.5}$$

$$\tilde{q}_t = \tilde{r}^2/\tilde{D}, \tag{5.6}$$

$$\tilde{P}_s = G^2(1,2)/(\omega - W)^2 + G^2(1,2)/(\omega + W)^2, \tag{5.7}$$

$$\tilde{S}_t = e^{-2\pi p_0 \tilde{q}_t}. \tag{5.8}$$

The ratio of each quantity to the corresponding exact value is given in Table V and Table VI. It is seen that stationary perturbative theory overestimates r, P_s, and the shift δ, and hence underestimates D. Contrary to the correct limit $2\delta/W \leq 1$ expected in the nonperturbative theory, the stationary perturbation result gives the limit $2\delta/W > 1$ for large $G(1,2)/\omega$. Thus, D can be negative and this represents a complete breakdown of the stationary perturbation theory (see Table V).

The inaccuracy in the overestimated $\tilde{q}$ factor leads to values for $\tilde{S}_t$ which are too small, as shown in Table VI. Although this table is evaluated with values for the case $W/\omega = 0.1$, using values of any $W/\omega \leq 0.2$ gives approximately the same results, since the statements of Eqs. (3.23) and (3.24) are valid for the perturbative results as well. Since $\tilde{D} < D$, $\tilde{S}_a$, the inelastic transition probability for avoided crossing calculated using perturbative result, would be greater than the true value S_a.

From Table VI, we may conclude that the results of stationary perturbation theory applied to analyze nonresonant field modification of Landau-Zener crossings contain relative error less than 1% if both $G(1,2)/\omega < 0.1$ and $p_0 < 0.1$ apply. But as stated in the last section, this is also the parameter region where nonresonant field modification of inelastic processes is less than 1%.

Contrary to Eq. (3.33), the results of Eqs. (5.4) and (5.5) show that $\tilde{D} \neq \tilde{r}$. By further taking normalization of the $\tilde{a}_\nu(\alpha)$'s in Eq. (5.2) for the evaluation of $\tilde{r}$, we can improve the agreement between $\tilde{D} \approx \tilde{r} \approx 1 - 4G(1,2)/\omega^2$ valid for small W/ω. However, this result is in poor agreement with the exact values in Tables II and III. It is much inferior to the formula given by Eq. (3.35).

Inclusion of perturbative terms higher in order than $G^2(1,2)/\omega^2$ further *increases* the discrepancy

TABLE V. Ratios of results (denoted by ~) of stationary perturbation theory to exact results for various $G(1,2)/\omega$. δ is energy shift, $D \equiv 1 - 2\delta/W$, r is ratio of field-dressed nonadiabatic coupling to the field-free nonadiabatic coupling, $q_t \equiv r^2/D$ is the multiplicative factor representing the entire effect of the field on a true crossing, and P_s is the probability in all the sidebands of $W_0(1)$. The symbol "c.b." stands for "complete breakdown" of perturbation theory for $G(1,2)/\omega \gtrsim 0.5$.

$G(1,2)/\omega$	$\tilde{\delta}/\delta$	$\tilde{D}/D$	$\tilde{r}/r$	$\tilde{q}_t/q_t$	$\tilde{P}_s/P_s$	P_s
0.01	1.0001	1.0000	1.0002	1.0004	1.0001	0.206 08 (–3)
0.05	1.0026	0.9999	1.0052	1.0104	1.0029	0.514 09 (–2)
0.1	1.0105	0.9995	1.0210	1.0429	1.0115	0.204 26 (–1)
0.3	1.0987	0.9511	1.2261	1.5804	1.1062	0.171 45
0.4	1.1818	0.7804	1.4991	2.8795	1.1929	0.287 50
0.45	1.2353	0.5384	1.7563	5.7288	1.2475	0.351 50
0.50	1.2980	c.b.	2.2399	c.b.	1.3105	0.417 75
0.55	1.3710	c.b.	3.5958	c.b.	1.3828	0.484 97

between the perturbative results and the exact results. For example, the next higher order $[\propto G^4(1,2)/\omega^4]$ corrections to the energy shift $\tilde{\delta}$ in Eq. (5.1) and the ratio $\tilde{r}$ in Eq. (5.5) are both positive, thus higher-order perturbative theory *further* overestimates the shift δ and the ratio r. Thus, the conclusions of this section are not limited to second-order stationary perturbation theory but apply to higher order as well.

VI. CHARGE SYSTEMS WITH MORE-THAN-TWO LEVELS

We return to Sec. II to discuss a general n-level charge system where $n > 2$. At higher field intensity, radiative interactions $G(\alpha,\beta)$ between many more states become important. For charge systems with "even-odd" symmetry (like parity for atoms, gerade-ungerade symmetry for diatomics of equal nuclear charges), it was shown in Sec. III E that a two-level model excludes electric dipole interaction if there is nonzero nonadiabatic transition. It is expected that the effect on the two close-lying levels due to electric dipole interaction with other levels is in most cases more important than the higher-multipole interactions between two such levels.

Many simple relations for the two-level charge system no longer hold rigorously for $(n > 2)$ discrete levels.[3] Equations (3.12)–(3.15) are not valid so that both eigensolutions involved in the nonadiabatic transition have to be found explicitly as shown below. The general result in Eq. (2.12) indicates that the simple result for field-dressed nonadiabatic coupling $C_{01,\,02} = rC^0_{01,\,02}$ for a two-level charge system does not hold in general except when there is no effective radiative coupling between E_{01} and E_{02} *and* when one field-free nonadiabatic coupling $C^0_{01,\,02}$ dominates. However, many of the statements remain valid to first order. One exception is the formation of new avoided crossing analyzed below.

A. Formation of new crossings

For both the case of unequal nuclear charges and the case of equal nuclear charges, *a true crossing*

TABLE VI. Ratio of $\tilde{S}_t$, the result of perturbation theory, to the exact S_t calculated by nonperturbation theory. Perturbation theory underestimates S_t, the elastic probability for true crossing and hence overestimates the inelastic transition probability.

p_0 \ $G(1,2)/\omega$	0.05	0.1	0.3	0.45	0.49
0.01	0.999	0.997	0.976	0.905	0.582
0.05	0.997	0.987	0.886	0.608	0.665
0.10	0.994	0.974	0.784	0.369	0.443 (–2)
0.50	0.968	0.879	0.297	0.687 (–2)	0.170 (–11)
1.0	0.937	0.772	0.883 (–1)	0.472 (–4)	0.290 (–23)
3.0	0.824	0.460	0.688 (–3)	0.105 (–12)	0.245 (–70)
5.0	0.724	0.274	0.536 (–5)	0.235 (–21)	0.21 (–117)
7.5	0.616	0.144	0.124 (–7)	0.361 (–32)	0.30 (–176)
10.0	0.524	0.753 (–1)	0.287 (–10)	0.554 (–43)	0.42 (–235)

can become an avoided crossing. For example, a true crossing between a Σ^+ (Σ_g^+) level and a Π (Π_g) level becomes an avoided crossing due to electric dipole interaction with another Σ^+ (Σ_u^+) level. With formation of new crossing, the influence of the nonresonant field is significant at much lower intensity than those shown in Sec. IV.[21]

Unlike the case of a two-level model, two close-lying levels that are *both* interacting with other, but the same, levels should always be treated as nearly degenerate in the solution of the charge-field adiabatic eigenvalue problem.[3,6] In the notations of Refs. 3 and 6, we need to have ($E_{\rho\sigma}$, $\hat{\Psi}_{\rho\sigma}=\underline{a}^{\rho\sigma}$) and ($E_{\mu\tau}$, $\hat{\Psi}_{\mu\tau}=\underline{a}^{\mu\tau}$) where $\rho=\mu$. The simplifications now are that $\underline{T}_\nu$ and $\underline{T}'_\nu$ are found by recurrence relations without any interruption from $\nu=M$ to $\nu=\rho+1$ and from $\nu=-M$ to $\nu=\rho-1$ respectively. With known values of $d_\rho(\sigma)=1$ and $d_\rho(\tau)=0$, the other $(n-2)$ $d_\rho(\alpha)$'s with $\alpha\neq\sigma$, τ are obtained by solving the $(n-2)$ inhomogeneous linear equations with $\alpha\neq\sigma$, τ resulting from the $(\nu=\rho)$th set. Similar procedure can be carried out to find $s_\nu(\alpha)$'s with known values of $s_\rho(\sigma)=0$ and $s_\rho(\tau)=1$. Actually there is no need to find the $\underline{V}_\nu$ and $\underline{V}'_\nu$ separately, since $\underline{V}_\nu=\underline{T}_\nu$ for $M\geq\nu>\rho$ and $\underline{V}'_\nu=\underline{T}'_\nu$ for $-M\leq\nu<\rho$. The eigenenergies E_u and E_l have a separation,

$$E_u-E_l=\{[W'_\rho(\tau)-W'_\rho(\sigma)]^2+4G^2\}^{1/2}, \qquad (6.1)$$

where W' are the perturbed energy surfaces and G is the effective coupling. Thus, even when the unperturbed levels $W_\rho(\tau)$ and $W_\rho(\sigma)$ are degenerate (for example at the crossing point), the effective coupling G between the two states resulting from radiative interaction with other levels and between them [if $G(\sigma,\tau)\neq 0$] is nonzero and, therefore, a new avoided crossing is formed at any field strength. This analysis also shows that an avoided crossing will remain as an avoided crossing in the presence of the field. In the analysis of the transition probabilities across the field-dressed avoided crossing, we may use the perturbed states and energies W' as was done explicitly in Ref. 6, or preferably the field-dressed diabatic states and energies as shown in Sec. II above. New transition channels can be open due to formation of new avoided crossing.[21]

B. Suggested system for experiment: iodine

Molecular iodine (I_2) exhibits crossing phenomena[22] which are very sensitive to perturbing influences arising either from collisions or small internal couplings.[23] From the perspective of the previous analysis, we can regard an externally applied radiation field as simply another form of perturbation. An observable alteration of the fluorescence intensity in experiments[22] examining the effects of magnetically induced predissociation of I_2 was caused by state-mixing due to a static magnetic field of $\sim 10^3$ G. A magnetic field of this magnitude in an optical wave corresponds to an intensity of $\sim 10^8$ W/cm^2, a value achieved at 10 μm with CO_2 lasers. Also the work of Broyer *et al.*[23] suggests that an internal energy of ~ 1 eV is controlled by a small perturbation with a magnitude of $\sim 4\times 10^{-6}$ eV. We suggest here the possibility for observation of the optical analogue of these effects. Sidebands with relative intensities given by Eq. (2.36) and frequencies displaced $\pm\nu\omega$ from the main transitions can also be detected. For diatomics of equal nuclear charges, as well as for atoms, detection of sidebands with *odd* ν gives a measure of nonadiabaticity. To conclude, we point out that application of the laser fields would enable rapid switching of material properties in large volumes at a rate limited only by the speed of light.

Note added in proof. It is well known that some field-free true crossing becomes field-free avoided crossing with a small energy gap when higher-order interactions, hitherto neglected, are taken into account. In Sec. III D we conclude that when compared with their corresponding field-free values, the inelastic transition probability for a field-dressed avoided crossing is increased whereas for a field-dressed true crossing it is decreased. This may seem at first to suggest that our results depend critically on the true or avoided nature of the field-free crossing. In fact it is not so. As seen in both Figs. 2(a) and 2(b), starting with the same initial-value conditions at τ_0, the positive-time ($\tau>0$) asymptotic probabilities in the higher-energy state in *both* cases, $S_t=\exp(-2\pi p_0 q_t)$ for true crossing and $S_a=\exp(-2\pi p_0 q_a)$ for avoided crossing, are increased. Furthermore, our results in Eqs. (3.36) and (4.1)–(4.4) show that *quantitatively* the same final probability in the higher-energy state is obtained whether we analyze the same crossing as a true crossing or as an avoided crossing with a small energy gap. The conclusion in Sec. III D, still valid, is due to our labeling of $|B_u(\infty)|^2$ as the inelastic transition probability in both cases.

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[1]See, for example, C. F. Melius and W. A. Goddard III, Phys. Rev. A 10, 1541 (1974), and references therein.

[2]N. M. Kroll and K. M. Watson, Phys. Rev. A 13, 1018 (1976).

[3]A. M. F. Lau, Phys. Rev. A 13, 139 (1976).

[4]By "charge system" we refer to diatomic or polyatomic molecules or "quasimolecules." The latter is a simple and accurate description of the atoms and/or molecules in slow collision over the entire range of internuclear separations. See Ref. 1.

[5]For examples, penetration into otherwise inaccessible regions on the energy surfaces and the formation of quasibound molecules studied in Sec. V B of Ref. 3 are effects due to optical-Stark energy shift and polarization dependence, respectively.

[6]A. M. F. Lau, Phys. Rev. A 14, 279 (1976).

[7]The two unequal couplings can give rise to predominant transition at only one of the two crossings. See Sec. IV of Ref. 6. For only one crossing, inelastic transition probability (due to absorption or emission of photons) greater than $\frac{1}{2}$ is possible of course.

[8]Other analyses on collisions with real photon absorption or emission between a two-level charge system in one field mode are, for example, L. I. Gudzenko and S. I. Yakovlenko, Zh. Tekh. Fiz. 45, 234 (1975) [Sov. Phys. Tech. Phys. 20, 150 (1975)], V. S. Lisitsa and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. 68, 479 (1975) [Sov. Phys. JETP 41, 233 (1975)]; M. H. Mittleman, Phys. Rev. A 14, 586 (1976), and references therein; J. M. Yuan, T. F. George, and F. J. McLafferty, Chem. Phys. Lett. 40, 163 (1976).

[9]Some recent experiments, in which photoabsorption during collision in the presence of laser fields is involved, are: R. W. Falcone, W. R. Green, J. C. White, J. F. Young, and S. E. Harris, Phys. Rev. A 15, 1333 (1977); J. L. Carlsten and A. Szöke, J. Phys. B 9, L231 (1976), and references therein.

[10]See, for example, E. E. Nikitin, *Theory of Elementary Atomic and Molecular Processes in Gases* (Oxford University, London, 1974).

[11]See, for example, H. F. Schaefer III, *The Electronic Structure of Atoms and Molecules* (Addison-Wesley, Reading, Mass., 1972).

[12]This form is appropriate for the "$\vec{r}\cdot\vec{E}$" electric dipole interaction or the magnetic dipole interaction. For electric quadrupole interaction, the form $h' \equiv h''(a+a^+)$ is appropriate. Using $\hat{\Psi} \equiv \sum_{\nu\beta} a_\nu(\beta)\varphi_\beta \Omega(N-\nu)$ and $G(\alpha,\beta) \equiv N^{1/2}(\varphi_\alpha, h''\varphi_\beta)/\hbar$, we still get Eq. (2.5) and all subsequent expressions. Compare Ref. 3.

[13]More detailed statements can be made analogous to collisions in absence of laser fields: see for examples, J. B. Delos, W. R. Thorson, and S. K. Knudson, Phys. Rev. A 6, 709 (1972); and J. B. Delos and W. R. Thorson, *ibid.* 6, 720 (1972).

[14]The model and its results have well-defined conditions of validity, which should not be violated in using the results. Compare D. R. Bates, Proc. R. Soc. (London) A257, 22 (1960).

[15]C. Zener, Proc. R. Soc. A 137, 1696 (1932). See also Ref. 2 and Ref. 6.

[16]Characterizing the matrix element of U as $\cos\theta$ and $\pm\sin\theta$, one has $(\hat{\Phi}_1, d\hat{\Phi}_2/dt) = -d\theta/dt + (\hat{\Psi}_1, d\hat{\Psi}_u/dt)$. Thus, by choosing the still arbitrary $\theta(t)$ such that $d\theta/dt$ equals the known quantity $(\hat{\Psi}_1, d\hat{\Psi}_u/dt)$, Eq. (2.24) is satisfied.

[17]See Ref. 2. The differences in expressions given here are due to our use of the $\vec{r}\cdot\vec{E}$ interaction Hamiltonian, our choice of phases of φ_α and our use of the T_ν scalar recurrence relations. The odd-parity and even-parity solutions here are respectively the A and B solutions in Ref. 2.

[18]The variation is about 5% or less. The exact percentage can be found from values tabulated.

[19]See, for example, R. H. Garstang, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic, New York, 1962).

[20]See, for example, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1968), 3rd ed.

[21]A. M. F. Lau and C. K. Rhodes, to be published.

[22]E. O. Degenkolb, J. I. Steinfeld, E. Wasserman, and W. Klemperer, J. Chem. Phys. 51, 615 (1969).

[23]M. Broyer, J. Vigue, and J. C. Lehmann, J. Chem. Phys. 64, 4793 (1976).