Field-induced avoided crossing and new transition channels in atomic and molecular gases irradiated by lasers*†

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We show that the presence of an oscillating electromagnetic field can induce a new avoided crossing between true crossing electronic energy surfaces of molecules without actual absorption or emission of photons. This avoided-crossing energy gap and the field-dressed energies and states are functions of the field intensity, frequency, and polarization. Thus the elastic and inelastic probabilities across these energy regions can be controlled by tuning these field parameters. This mechanism can be used to enhance or suppress field-free transitions by orders of magnitude. More importantly, the field can open up new inelastic channels so that the field-induced transitions, free of any competing field-free transitions, can be readily detected. We apply these new effects to molecular dissociation and predissociation and to atomic (ionic) and molecular collisions. The field-induced probabilities of these processes are studied as functions of the (quasi) molecular electronic energies, relative velocity or vibrational energies, laser field frequency and intensity. It is shown that far-away nonresonant states can contribute significantly to the field-induced avoided crossing and transitions. We give approximate but accurate formulas which enable rapid calculation of all these effects. Our method of solution of the charge-field interaction includes the stationary perturbation theory in the weak-field limit. Our modified Landau-Zener formulas of transition probability include the time-dependent perturbation results, the adiabatic limit, and the field-free limit. Improvements over earlier methods of solving the adiabatic eigenvalue problem are given, especially for charge systems with definite "parities." It is shown that the radiative-induced predissociation of I_2 in the B $0^+u(^3\Pi)$ state into the repulsive $1u(^1\Pi)$ state can broaden its vibrational spectrum and quench its fluorescence. The same mechanism can be used to increase the enrichment of laser isotope separation of Br_2 involving the same states. Formulas for field-induced predissociation rate per second without or with tunneling are given. In these cases, the small laser-induced coupling controls the large internal energy flow as fluorescence or as kinetic energy. In other situations such as dissociation and collisions, the laser field is also a means of switching on the exchange of electronic or vibronic energies internally and/or externally as kinetic energy. All these are achieved at no expense of photon energy since no actual photo-absorption or -emission is involved in these nonresonant processes.

I. INTRODUCTION

In earlier publications[1] we studied the radiative control of collision-free and collisional processes in atomic and molecular gases without actual absorption or emission of photons from the applied laser fields (to be called "nonresonant"). One of the results shown is that if no other states are interacting with them, two degenerate states coupled by an *oscillatory* electromagnetic field remain degenerate at any strength of the field. Thus, unlike the case of static field interaction,[2] a true crossing[3] of electronic energy levels or surfaces of molecules remains as true crossing in the presence of the oscillatory field. We have also proved that radiative interaction through other states of the correct symmetries can, however, remove the degeneracy and thus lead to *new* avoided crossings. This new avoided crossing is a function of the field parameters (intensity, frequency and polarization) and can thus be varied by external control of the field parameters.

In the absence of the field, transition between the two states forming the true crossing may or may not be possible. Figures 1 and 2 illustrate the two cases respectively. If there is field-free transition possible through angular coupling,[4] we shall show that the addition of the oscillatory field induces formation of avoided crossing and can enhance or suppress the corresponding field-free transitions. This switching on and off of the inter- and intramolecular processes by varying the field parameters can lead to observation of phenomena previously too weak to detect or disappearance of undesirable strong transitions.

More interesting are the situations (e.g., Fig. 2) where in the absence of the field there was no transition possible between the two states, whether by angular or radial coupling. Without any actual absorption or emission of photons, the laser field can induce formation of avoided crossing and nonzero transition between these states. The significance of such a class of situations is that completely new transition channels are opened that were closed without the field. Thus, without any competing field-free transition into these channels, the effect of the field is significant even at relatively weak fields.

Our work is generally motivated by the use of laser radiation to initiate and to control nonreactive and reactive molecular processes and to direct energy-flow pathways, especially those that involve electronic transitions. We suggest here two specific systems illustrating the kind of situations analyzed in this paper. The first is the use of the electromagnetic radiation to control the predissociation of the B $0^+u(^3\Pi)$ state of iodine molecule into its $1u(^1\Pi)$ state. See Fig. 1(b). Spontaneous predissociation[5] and hyperfine predissociation[6] of this state into the same $1u$ state are already known to occur. Interference terms arising from the radiative-induced predissociation proposed here with the other field-free predissociations can also be observed. Predissociation involving the same states in Br_2 has been used as an extraction mechanism for isotopical-selectivity photoexcited Br_2.[7] We propose that it is possible to enhance the enrichment of the process by increasing the predissociation rate through nonresonant effects of the already present or additional laser field.

In this paper, we analyze the field-induced formation of avoided crossings and new transition channels opened by the field and apply them to (i) molecular dissociation and molecular collisions, (ii) atomic collisions, and (iii) predissociation, as examples of processes involving, respectively, one, two, and many field-induced avoided crossings. These are done in Secs. IV, V, and VI, respectively. For weak fields, the energy gap in the field-induced avoided crossing is small, and hence, the field-induced transition probability (per traversal of the crossing) to the other state is small. For predissociation, however, a small transition probability per oscillation in a molecular-vibrational state can lead to high probability of dissociation and tunnelling after many oscillations during its lifetime.[2,5,6]

The method of solution of the adiabatic (i.e., fixed internuclear frame R) eigenvalue problem for the charge-field system given in Sec. III is addressed to (quasi) molecules whose n states under consideration can be separated into two

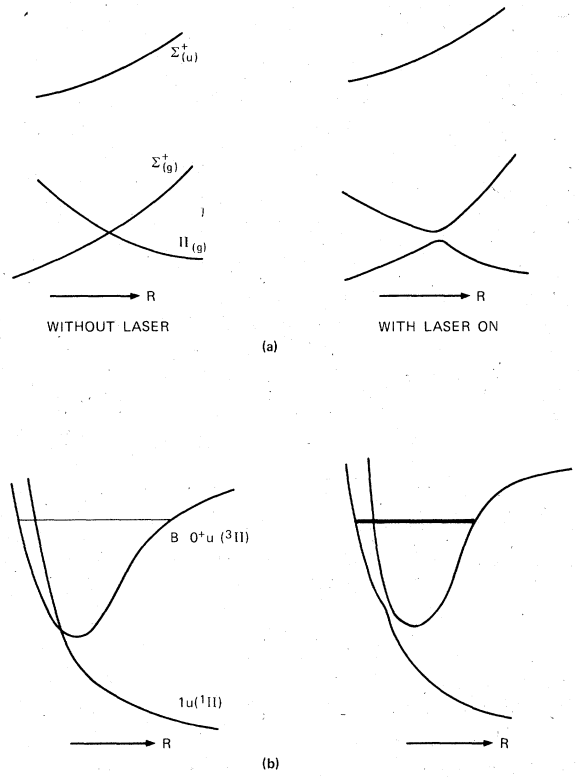

FIG. 1. Examples of situations where there is field-free nonadiabatic transition between the crossing states. With the laser field on, the field induces an avoided crossing whose energy gap is controlled by the field parameters like intensity and frequency. Thus the field-induced inelastic probability is controlled by the field and can be equal or become much larger than the field-free inelastic probability. (a) For diatoms of unequal or equal nuclear charges. (b) For iodine molecules, the corresponding energies for bromine molecules being similar. The vibrational spectrum is broadened due to field-induced predissociation.

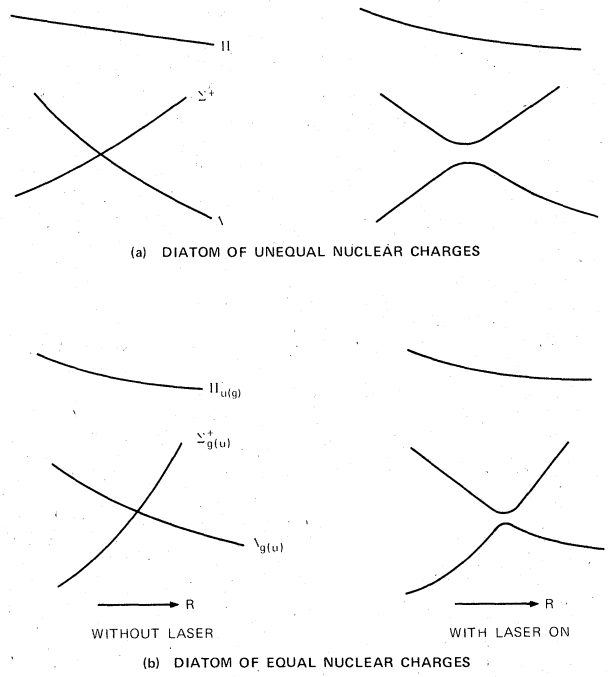

FIG. 2. Examples of situations where there is *no* field-free nonadiabatic transition between the crossing states because $\Delta\Lambda = \pm 2$. Thus even a small field-induced coupling (or energy gap) can produce inelastic transitions into the new channels that are readily detected.

groups such that states of one group interact only with states of the other group. For such charge systems of more than two states,[8] the method presented here is more efficient than the more general method developed by Lau[9,10] in the studies of single- and multiphoton transitions in atoms and molecules during or without collisions.[11] For strong radiative interactions, separate iterations to calculate the two new eigensolutions arising from degenerate charge-field levels are proposed to replace the earlier method.

Section II summarizes the general theory and shows the important separation of the effect of the field into avoided-crossing formation and residual radiative dressing of states. A modified Landau-Zener formula is given for the new situation and it has the correct field-free limit. A brief discussion is given in Sec. VII.

II. GENERAL THEORY

We follow the general theory and notations in Ref. 1. Essentially there are two parts in the theory. The first is the solution of the time-independent eigenvalue problem,[12]

$$H\hat{\Psi} = \hbar E \hat{\Psi} , \tag{2.1}$$

for the entire system of the field and the fast (e.g., electronic) motion of the charge system at a fixed (i.e., adiabatic) frame $\underline{R}$ of its slow (e.g., internuclear) motion. Section III is addressed to this problem. As the charge-field interactions go to zero, the labeling of the solution $\hat{\Psi}_{\rho\sigma}$ for one field mode is such that it approaches the photon number state $|N-\rho\rangle$ and the charge state φ_σ of the fast motion. N is the initial mean number of photons in the coherent electromagnetic field.

The second part of the theory is to calculate the transition probabilities between these eigenstates $\hat{\Psi}$ of H due to the slow motion. There are numerous classical, semiclassical, and quantum techniques developed in theories of field-free inter- and intramolecular processes to treat this slow motion.[13,4] They can be adopted by replacing the corresponding field-free quantities with the *new* quantities based on the solutions of Eq. (2.1). The classical trajectories or quantum energies and wave functions of this slow motion based on the new field-dependent eigenenergies E in Eq. (2.1) can be very different from its corresponding field-free values.[9,1]

It is adequate for many applications to treat the slow motion classically. Then we solve the time-dependent Schrödinger equation,

$$i\hbar \frac{d\Psi(t)}{dt} = H\Psi(t) , \tag{2.2}$$

where the general state $\Psi(t)$ is expanded in terms of the charge-field adiabatic eigenstates $\hat{\Psi}_{\rho\sigma}$. The resulting equations [Eqs. (2.10) in Ref. 1] are then solved analytically or numerically for the appropriate initial-value conditions to give the final transition probability and hence other quantities such as the cross section and transition rates.

The kinds of situations analyzed in this paper are illustrated in Fig. 3 where many notations are also defined. Without the radiation field, the energies, w_{σ_-} and w_{τ_-} of the fast-motion states φ_{σ_-} and φ_{τ_-} form a true crossing.[2] In the presence of the field, a new avoided crossing is induced between them through radiative interaction. In this sec-

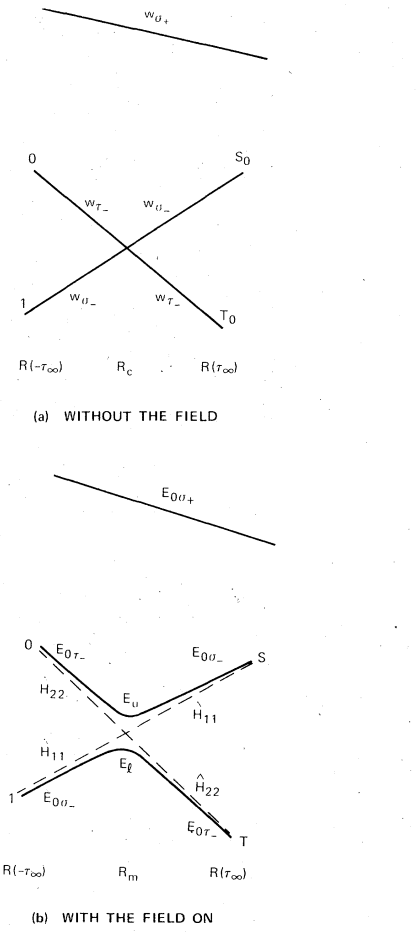

FIG. 3. Typical configurations with and without the field. Besides producing the new avoided crossing, the field also optical-Stark shifts the energy levels so that (a) the relative slope between the radiative diabatic levels $\hat{H}_{ii}$ is different from that of the field-free levels w_{τ_-} and w_{σ_-} (see Table VI); (b) the new energy minimum point R_m can be to the left or right of the original crossing point [see Eq. (3.62)]; (c) the new "center of levels" is shifted up or down depending on the nonresonant states φ_{σ_+} [see Eq. (3.58)]. S and T are the elastic and inelastic probability with the field on.

tion, the theory applies to cases where all states are radiatively coupled as well as to those that φ_{σ_-} and φ_{τ_-} do not radiatively interact via an electric dipole moment. Actually Fig. 3(b) gives the field-induced energy configuration for the states $\hat{\Psi}_{\rho\sigma_-}$ and $\hat{\Psi}_{\rho\tau_-}$ with $\rho = 0$ only. If $\Psi_{1\sigma_-}$ has been populated (e.g., by single-photon absorption earlier) before traversing the present field-induced avoided crossing, the same analysis applies to transition between $\hat{\Psi}_{1\sigma_-}$ and $\hat{\Psi}_{1\tau_-}$ as well. In this paper, we always consider transition between $\hat{\Psi}$'s of the same ρ because no real photon absorption or emission is involved.

Due to our convention of labeling the charge-field adiabatic states at each R, as explained below Eq. (2.1), the same eigenenergy and eigenstate may be labeled as $E_{0\tau_-}$ at one R and as $E_{0\sigma_-}$ at another R, as shown in Fig. 3(b). Near the crossing, the two states $\hat{\Psi}$'s contain roughly equal admixtures of φ_{σ_-} and φ_{τ_-}. Therefore in the entire region of transition, it is convenient to call the upper energy and its state E_u and $\hat{\Psi}_u$, respectively, and the lower one as E_l and $\hat{\Psi}_l$. Away from the crossing, they may also be called either $E_{0\tau_-}$ or $E_{0\sigma_-}$ depending on their weak-field limits.

Assuming that it is necessary to consider simultaneous transition between only two[14] charge-field adiabatic states, we let the general state $\Psi(t) = B_l(t)\hat{\Psi}_l + B_u(t)\hat{\Psi}_u$, and from Eq. (2.2) we obtain the coupled equation governing the time-development of the probability amplitude $B_l(t)$ in the state $\hat{\Psi}_l$,

$$i\frac{dB_l}{dt} = E_l B_l + C_{lu}B_u\,,$$
$$i\frac{dB_u}{dt} = E_u B_u + C_{ul}B_l\,, \tag{2.3}$$

where the nonadiabatic coupling C_{lu} between $\hat{\Psi}_l$ and $\hat{\Psi}_u$ has been defined and examined in Eqs. (2.10)–(2.12) of Ref. 1. We point out that for the present configuration, both sums in C_{lu} in Eq. (2.12) can be nonzero, and have to be evaluated explicitly in general.

A. Separation of the effect of the field into avoided-crossing formation and residual radiative dressing of states

We can (in some cases discussed below) circumvent the more tedious task of evaluating C_{lu} (and then integrating Eqs. (2.3)] by transforming to the radiative-dressed diabatic states $\hat{\Phi}_1$ and $\hat{\Phi}_2$. With the same notations, this was done in Eqs. (2.19)–(2.23) of Ref. 1 with a general unitary matrix $\underline{U}$. Being entirely equivalent to Eq. (2.3), a set of equations describing the coupling between the probability amplitudes $D_1(t)$ and $D_2(t)$ in the two radiative-dressed diabatic states are[12]

$$i\frac{dD_1}{dt} = \hat{H}_{11}D_1 + (\hat{H}_{12} + C''_{12})D_2\,,$$
$$i\frac{dD_2}{dt} = \hat{H}_{22}D_2 + (\hat{H}_{21} + C''_{21})D_1\,,$$

where

$$C''_{ij} \equiv -i\left(\hat{\Phi}_i\,,\ \frac{d\hat{\Phi}_j}{dt}\right)\,. \tag{2.4}$$

If we choose $\underline{U}$ to be real, then $\hat{H}_{12} = \hat{H}_{21}$ are real, as seen in its definition Eq. (2.20) of Ref. 1. Also C''_{ij} is pure imaginary,

$$C''_{ij} = -i\left(\underline{U}^{+}\ \frac{d}{dt}\ \underline{U}\right)_{ij} + (\underline{U}^{+}\underline{C}\underline{U})_{ij}\,, \tag{2.5}$$

since according to Eq. (2.12) of Ref. 1, $C_{ul} = C^{*}_{lu}$ are chosen to be pure imaginary.

As the field intensity becomes very weak, the field-induced avoided crossing becomes the field-free true crossing between w_{σ_-} and w_{τ_-}. In such case $\hat{\Psi}_l$ and $\hat{\Psi}_u$ approach ψ_l and ψ_u, respectively, where $\psi_l \equiv \{\varphi_{\sigma_-}$ for $R \le R_c$; φ_{τ_-} for $R > R_c\}$ and $\psi_u \equiv \{\varphi_{\tau_-}$ for $R \le R_c$; φ_{σ_-} for $R > R_c\}$. Also the unitary transformation $\underline{U}$ expressible in terms of the field-dressed quantities $\hat{H}_{ij}$ approaches $\underline{U}^0$ expressible in terms of the field-free quantities w_{σ_-}, w_{τ_-} and an aribitrarily small (fictitious) energy gap. Therefore we have $\hat{\Phi}_1 = U_{l1}\hat{\Psi}_l + U_{u1}\hat{\Psi}_u \to U^0_{l1}\psi_l + U^0_{u1}\psi_u$, which is φ_{σ_-}; and $\hat{\Phi}_2 = U_{l2}\hat{\Psi}_l + U_{u2}\Psi_u \to U^0_{l2}\psi_l + U^0_{u2}\psi_u$, which is φ_{τ_-}. Hence in the field-free limit,

$$C''_{12} \to C^0_{\sigma_-,\tau_-} \equiv -i\left(\varphi_{\sigma_-}\,,\ \frac{d\varphi_{\tau_-}}{dt}\right). \tag{2.6}$$

Thus when the field-free nonadiabatic coupling $C^0_{\sigma_-,\tau_-}$ is significant,[4] C''_{12} should not be taken to be negligible for the correct weak-field behavior of Eq. (2.4) and of its solutions.

From the above, it is also seen that $\hat{H}_{11}$ and $\hat{H}_{22}$ become w_{σ_-} and w_{τ_-}, respectively, in the field-free limit. It is reasonable then to require $(\hat{H}_{22} - \hat{H}_{11})^2$ to vanish at some point R_m, which in general is not R_c. According to Eq. (2.23) of Ref. 1, this occurs at the minimum, $(E_u - E_l)_{\min}$, of the field-induced avoided crossing (see also below). The value of $\hat{H}_{12}$ is given by

$$\hat{H}^2_{12} = \tfrac{1}{4}(E_u - E_l)^2_{\min}\,. \tag{2.7}$$

Hence $\hat{H}_{12}$ goes to zero as the field vanishes.

The physical meaning of the coupling term, $\hat{H}_{12} + C''_{12}$, in Eq. (2.4) is now clear. The coupling $\hat{H}_{12}$ between $\hat{\Phi}_1$ and $\hat{\Phi}_2$ is due to the formation of the avoided crossing (i.e., nonzero energy gap) produced by the effective radiative coupling between $\hat{\Phi}_1$ and $\hat{\Phi}_2$. On the other hand, the coupling C''_{12} is the residual nonadiabatic coupling between $\hat{\Phi}_1$ and

$\hat{\Phi}_2$ with the effect of the energy gap subtracted out. With the field on, the difference $C''_{12} - C^0_{\sigma_-,\tau_-}$ is due to radiative dressing of states of $\hat{\Phi}_i$.

When the field-free nonadiabatic coupling $C^0_{\sigma_-,\tau_-}$ *is not negligible*, it is useful to think in terms of several cases. In case (a) of the "weak-field" domain, characterized by

$$\text{(a) } C''_{12} = C^0_{\sigma_-,\tau_-} \text{ and } |C^0_{\sigma_-,\tau_-}|^2 \gg |\hat{H}_{12}|^2 , \tag{2.8a}$$

we can simply ignore the effect of the field and analyze the transition probability identically as the field-free case, since now $\hat{H}_{11} = w_{\sigma_-}$ and $\hat{H}_{22} = w_{\tau_-}$ also. In case (b) or the "moderate-field" domain, characterized by

$$\text{(b) } C''_{12} = C^0_{\sigma_-,\tau_-} \text{ and } |C^0_{\sigma_-,\tau_-}|^2 \text{ comparable to } |\hat{H}_{12}|^2 , \tag{2.8b}$$

we need not calculate C''_{12} by Eq. (2.5) but have to take both $\hat{H}_{12}$ and $C^0_{\sigma_-,\tau_-}$ into account. The calculation $\hat{H}_{12}$ from the *energies* E_u and E_l is simple. In case (c) or the "strong-field" domain, defined by the failure of $C''_{12} = C^0_{\sigma_-,\tau_-}$ to be a good approximation, i.e.,

$$\text{(c) } C''_{12} \neq C^0_{\sigma_-,\tau_-} \text{ and } |C^0_{\sigma_-,\tau_-}|^2 \text{ comparable to } |\hat{H}_{12}|^2 , \tag{2.8c}$$

C''_{12} has to be calculated as in Eq. (2.5) after $\underline{C}$ is evaluated and an explicit function of the unitary matrix elements are chosen. In this case, the more tedious task of differentiation of the coefficients $a^u_\nu(\beta)$ may have to be performed in evaluating C_{lu}. If so, the computational advantage of separating out the effect associated with the field-induced energy gap and the effect of the residual radiative-dressing of states is lost and it may be simpler to integrate the original Eq. (2.3) instead. Finally in case (d) or the "very-strong-field" domain, defined by

$$\text{(d) } C''_{12} \neq C^0_{\sigma_-,\tau_-} \text{ and } |C''_{12}|^2 \ll |\hat{H}_{12}|^2 , \tag{2.8d}$$

we do not have to evaluate C''_{12} for each calculation but a typical value can be estimated or checked. In this case, C''_{12} can be neglected in Eq. (2.4) and the calculation is again simple.

When the nonadiabatic transition between φ_{σ_-} *and* φ_{τ_-} *is negligible in the absence of the laser field,* we have $C^0_{\sigma_-,\tau_-} = 0$. It is then physically correct to choose the unitary transformation such that

$$\text{(e) } C''_{12} = 0 . \tag{2.8e}$$

Then any *nonadiabatic* transition induced by the nonresonant field is due to the formation of avoided crossing, $\hat{H}_{12} \neq 0$, and is free of any field-free competing effect. Thus the field opens up new channels of transitions that can be readily detected and identified.

B. A modified Landau-Zener model for the field-induced crossing

In order to study the effect of the field on a true crossing by a simple formula, we use a modified Landau-Zener model. Like the usual Landau-Zener model for the field-free crossing, we assume in Eq. (2.4)

$$\hat{H}_{22} - \hat{H}_{11} = -\alpha\tau , \tag{2.9}$$

where α is a constant and

$$\hat{H}_{12} = \text{const} , \tag{2.10}$$

$$C''_{12} = \text{const} , \tag{2.11}$$

in the entire transition region $(-\tau_\infty, \tau_\infty)$ such that $\tau_\infty^2 \gg |\alpha|^{-1}$. For the *physical* reason discussed in the last subsection, we do not assume C''_{12} to be zero in general and this differs from the usual Landau-Zener model.

If the charge system in the absence of the field is prepared in the state φ_{σ_-} at $-\tau_\infty$, then after the field is turned on adiabatically, the *charge-field* system is in the state $\hat{\Psi}_{0\sigma_-}(= \hat{\Psi}_l$ at $-\tau_\infty)$. Note that due to *state-mixing*, $\hat{\Psi}_{0\sigma_-}$ contains probability amplitudes $a^{0\sigma_-}_\nu(\tau_-)$ in $\varphi_{\tau_-}\Omega(N-\nu)$, $a^{0\sigma_-}_\nu(\sigma_+)$ in $\varphi_{\sigma_+}\Omega(N-\nu)$, etc. Analysis of nonadiabatic transitions using $\hat{\Psi}_{0\sigma_-}$ and $\hat{\Psi}_{0\tau_-}$ then in effect considers simultaneously the array of transition between pairs of corresponding sidebands from $\hat{\Psi}_{0\sigma_-}$ and $\hat{\Psi}_{0\tau_-}$.[8-10,1]

For the initial-value conditions that $B_l(-\tau_\infty) = D_1(-\tau_\infty) = 1$ and that $B_u(-\tau_\infty) = D_2(-\tau_\infty) = 0$, the asymptotic solutions to Eq. (2.4) and hence also to Eq. (2.3) are

$$\begin{aligned} |B_u(\tau_\infty)|^2 &= |D_1(\tau_\infty)|^2 = e^{-2\pi p} \equiv S , \\ |B_l(\tau_\infty)|^2 &= |D_2(\tau_\infty)|^2 = 1 - e^{-2\pi p} \equiv T , \end{aligned} \tag{2.12}$$

where

$$p \equiv (\tfrac{1}{4}\Delta_m^2 + |C''_{12}|^2)/|\alpha| , \tag{2.13}$$

$$\alpha \equiv -\frac{d(\hat{H}_{22} - \hat{H}_{11})}{dt} = -\frac{d}{dt}(\Delta^2 - \Delta_m^2)^{1/2} , \tag{2.14}$$

$$\Delta \equiv E_u - E_l , \tag{2.15}$$

$$\Delta_m \equiv (E_u - E_l)_{\min} . \tag{2.16}$$

In writing Eqs. (2.13) and (2.14), we have made use of the fact that H_{12} is real, that C_{12} is purely imaginary, and of Eqs. (2.10) and (2.7) above and Eq. (2.23) of Ref. 1.

As the field intensity becomes zero, we recover the field-free results:

$$|B_u(\tau_\infty)|^2 = 1 - |B_l(\tau_\infty)|^2 \to e^{-2\pi p_0} \equiv S_0 \tag{2.17}$$

where

$$p_0 \equiv |C^0_{\sigma_-,\tau_-}|^2/|\alpha_0| , \tag{2.18}$$

$$C^0_{\sigma_-,\tau_-} = -i\frac{dR}{dt} \cdot (\varphi_{\sigma_-}, \underline{\nabla}\varphi_{\tau_-}) ,$$

$$\alpha_0 = -\frac{d}{dt}(w_{\tau_-} - w_{\sigma_-}) = -\frac{dR}{dt} \cdot \underline{\nabla}(w_{\tau_-} - w_{\sigma_-}) , \tag{2.19}$$

and S_0 is the field-free probability of the charge system staying in the state φ_{σ_-} [see Fig. 3(a)].

For small $2\pi p$ due to nonstrong-field and small field-free nonadiabatic coupling, the above Landau-Zener formula gives results in agreement with time-dependent perturbation theory,[3]

$$|B_u(\tau_\infty)|^2 = 1 - 2\pi p\,, \qquad |B_l(\tau_\infty)|^2 = 2\pi p\,. \tag{2.20}$$

In the adiabatic limit $2\pi p \gg 1$, $|B_u(\tau_\infty)|^2 = 0$ and $|B_l(\tau_\infty)|^2 = 1$.

For use in subsequent sections, we rewrite p in Eq. (2.13) as

$$p = q\,|\alpha_0|^{-1}\,, \tag{2.21}$$

where

$$q \equiv (\tfrac{1}{4}\Delta_m^2 + |C_{12}''|^2)\chi^{-1}\,, \tag{2.22}$$

and

$$\chi \equiv \frac{|\alpha|}{|\alpha_0|} = \frac{|d(\Delta^2 - \Delta_m^2)^{1/2}/dt)|}{|d(w_{\tau_-} - w_{\sigma_-})/dt|}\,. \tag{2.23}$$

Thus the entire effect of the field in this model is contained in the factor q, and χ is the ratio of the temporal relative slope between the radiative diabatic levels to that of the field-free true crossing. As the field vanishes, χ approaches unity. In general, it can be greater than or less than unity when the field is turned on.

The readers who are not so concerned with the theoretical methods of calculations in Sec. III may go directly to Sec. IV–VI for physical results.

III. EXACT EIGENSOLUTION FOR THE CHARGE-FIELD SYSTEM

A. New method of solution

Considerable simplifications of the previously given method[9,10] of eigensolution result when the charge states φ_α can be grouped into two groups, such that states of the same group do not radiatively interact with each other, but only with states of the other group. For electric-dipole interaction, examples of two such groups of states are states of even parity and states of odd parity in atoms, gerade electronic states, and ungerade electronic states of diatoms of equal nuclear charge, and {one $\Sigma^\pm$ state, and one Δ state} and {one π state} for diatoms of unequal nuclear charges.[15]

With the states of the two groups labeled by + and − and the number of states in each group denoted by n_+ and n_-, the eigensolutions $(E, \hat{\Psi})$ satisfy the following system of equations resulting from Eq. (2.1) [see Eq. (2.5) of Ref. 1][12]:

$$Ea_\nu(\alpha_+) = W_\nu(\alpha_+)a_\nu(\alpha_+) + \sum_{\beta_-=1}^{n_-} G(\alpha_+,\beta_-)[a_{\nu-1}(\beta_-) + a_{\nu+1}(\beta_-)]\,, \tag{3.1}$$

$$Ea_\nu(\alpha_-) = W_\nu(\alpha_-)a_\nu(\alpha_-) + \sum_{\beta_+=1}^{n_+} G(\alpha_-,\beta_+)[a_{\nu-1}(\beta_+) + a_{\nu+1}(\beta_+)]\,, \quad -M \le \nu \le M\,, \tag{3.2}$$

where M is some positive integer and where $a_\nu(\alpha_\pm)$ are the coefficients (probability amplitudes) in the expansion

$$\hat{\Psi} = \sum_{\nu\beta} a_\nu(\beta)\,\varphi_\beta \Omega(N-\nu)\exp(i\nu\pi/2)\,,$$

and $G(\alpha_+,\beta_-) = G(\beta_-,\alpha_+)$ are the radiative interaction matrix elements, which are chosen to be real. It is seen that $a_\nu(\alpha_+)$ of odd ν are coupled to $a_\nu(\alpha_-)$ of even ν only, whereas $a_\nu(\alpha_+)$ of even ν are coupled with $a_\nu(\alpha_-)$ of odd ν. Therefore any $\hat{\Psi}$ would contain nonzero coefficients of one set or the other.

Without loss of generality, suppose we want to calculate $\hat{\Psi}_{0\sigma_-} = \underline{a}^{0\sigma_-}$. Then the relevant set of equations in matrix notations is

$$\underline{D}_{\nu_0}\underline{a}_{\nu_0} = \underline{G}_0(\underline{a}_{\nu_0-1} + \underline{a}_{\nu_0+1})\,, \tag{3.3}$$

$$\underline{D}_{\nu_e}\underline{a}_{\nu_e} = \underline{G}_e(\underline{a}_{\nu_e-1} + \underline{a}_{\nu_e+1})\,, \tag{3.4}$$

where $\underline{a}_{\nu_0}$ and $\underline{a}_{\nu_e}$ are, respectively, an n_+- and n_--dimensional column vector; $D_{\nu_0}(\alpha_+,\alpha_+') \equiv [E - W_{\nu_0}(\alpha_+)]\delta_{\alpha_+,\alpha_+'}$ and $D_{\nu_e}(\alpha_-,\alpha_-') \equiv [E - W_{\nu_e}(\alpha_-)]\delta_{\alpha_-,\alpha_-'}$ are $n_+\times n_+$ and $n_-\times n_-$ diagonal matrices, respectively; and $G_0(\alpha_+,\alpha_-) \equiv G(\alpha_+,\alpha_-)$ and $G_e(\alpha_-,\alpha_+) \equiv G(\alpha_-,\alpha_+)$ are $n_+\times n_-$ and $n_-\times n_+$ matrices, respectively. Substitution of Eq. (3.3) into Eq. (3.4) yields

$$\underline{\hat{D}}_{\nu_e}\underline{a}_{\nu_e} = \underline{\hat{G}}_{\nu_e-1}\underline{a}_{\nu_e-2} + \underline{\hat{G}}_{\nu_e+1}\underline{a}_{\nu_e+2}\,, \tag{3.5}$$

where

$$\underline{\hat{D}}_{\nu_e} \equiv \underline{D}_{\nu_e} - \underline{G}_e\underline{D}_{\nu_e-1}^{-1}\underline{G}_0 - \underline{G}_e\underline{D}_{\nu_e+1}^{-1}\underline{G}_0\,,$$
$$\underline{\hat{G}}_{\nu_e-1} \equiv \underline{G}_e\underline{D}_{\nu_e-1}^{-1}\underline{G}_0\,,$$
$$\underline{\hat{G}}_{\nu_e+1} \equiv \underline{G}_e\underline{D}_{\nu_e+1}^{-1}\underline{G}_0\,,$$

are all $n_-\times n_-$ nondiagonal matrices. For $\nu_e \ge 2$, we define $\underline{\hat{T}}_{\nu_e}$ by

$$\underline{a}_{\nu_e} \equiv \underline{\hat{T}}_{\nu_e}\underline{a}_{\nu_e-2}\,. \tag{3.6}$$

$\underline{\hat{T}}_{\nu_e}$ satisfies recurrence relations obtained from Eq. (3.5),

$$\underline{\hat{T}}_{\nu_e} = (\underline{\hat{D}}_{\nu_e} - \underline{\hat{G}}_{\nu_e+1}\underline{\hat{T}}_{\nu_e+2})^{-1}\underline{\hat{G}}_{\nu_e-1}\,. \tag{3.7}$$

With G_m defined as the largest matrix element of $G(\alpha_+,\alpha_-)$, it has the limit

$$\underline{\hat{T}}_{\nu_e} \to \text{constant-in-}\nu_e\text{ matrix} \times G_m^2/\nu_e(\nu_e-1)\omega^2 \approx 0\,, \tag{3.8}$$

for a sufficiently large integer $\nu_e = M+2$ such that $\nu_e(\nu_e-1) \gg G_m^2/\omega^2$.[16] Similar recurrence relations and limit are obtained for $\underline{\hat{T}}_{\nu_e}$ defined by $\underline{a}_{\nu_e} \equiv \underline{\hat{T}}_{\nu_e}\underline{a}_{\nu_e+2}$ for $\nu_e \leq -2$.

The significance of this new method is this: To obtain $\underline{\hat{T}}_{\nu_e}$ from $\underline{\hat{T}}_{\nu_e+2}$ in Eq. (3.7), we have to invert *one* $n_- \times n_-$ nondiagonal matrix, $(\underline{\hat{D}}_{\nu_e} - \underline{\hat{G}}_{\nu_e+1}\underline{\hat{T}}_{\nu_e+2})$, whereas in applying the more general method[9,10] to the two groups of states treated together, one would invert *two* larger $(n_+ + n_-)$ by $(n_+ + n_-)$ nondiagonal matrices, $(\underline{D}_{\nu_e+1} - \underline{G}\underline{T}_{\nu_e+2})$ and $(\underline{D}_{\nu_e} - \underline{G}\underline{T}_{\nu_e+1})$, as given by Eq. (3.6a) of Ref. 9. Since this statement is true for each $M \geq \nu_e \geq 2$ and $-2 \geq \nu_e \geq -M$ within each iteration, the computational efficiency is significantly improved. For the same reason, if $n_+ < n_-$, we could substitute Eq. (3.4) into Eq. (3.3) to obtain recurrence relations for $\underline{\hat{T}}_{\nu_0}$ with a cutoff value $M = odd$ integer. In such recurrence relations, we would have to invert a smaller $n_+ \times n_+$ (instead of $n_- \times n_-$) nondiagonal matrix. This idea is used in Sec. III B; but in the rest of Sec. III A, we continue to assume Eqs. (3.5)–(3.8) to be adequately efficient, for example if $n_- \lesssim n_+$.

The nondegenerate case. When $\varphi_\sigma \Omega(N)$ is not degenerate with any other $\varphi_\alpha \Omega(N-\rho)$, the eigenvalue $E_{0\sigma_-}$ and the eigenvector $\underline{a}^{0\sigma_-}$ are determined by letting

$$a_\nu(\alpha) \equiv d_\nu(\alpha)\, a_0(\sigma_-)\,, \tag{3.9}$$

where $a_0(\sigma_-)$ is the normalization constant. Then from the $\nu = \pm 1$ set of Eq. (3.2), we find $\underline{d}_{\pm 1}$ by

$$\underline{d}_{\pm 1} = \underline{D}_{\pm 1}^{-1}\underline{G}_0(\underline{I} + \underline{\hat{T}}_{\pm 2})\underline{d}_0\,, \tag{3.10}$$

where $\underline{\hat{T}}_{\pm 2}$ are given by Eqs. (3.7)–(3.8) and the corresponding equations for $\nu_e \leq -2$, where $d_0(\sigma_-) = 1$ and where the other $d_0(\alpha_- \neq \sigma_-)$ are obtained from the $\nu = 0$ set of Eq. (3.2) whose $\alpha \neq \sigma_-$. Finally, the right-hand expression of the $(\nu = 0, \alpha = \sigma_-)$ equation (3.2),

$$E = W_0(\sigma_-) + \sum_{\beta_+} G(\sigma_-, \beta_+)\,[d_{-1}(\beta_+) + d_1(\beta_+)]\,, \tag{3.11}$$

is calculated iteratively to give a convergent value $E_{0\sigma_-}$. The initial trial value E may be $W_0(\sigma_-)$ for a weak field. Or it is obtained by an approximate analytic formula or appropriate extrapolation for a very strong field.

The degenerate case. The state $\varphi_{\sigma_-}\Omega(N)$ may be degenerate with another state $\varphi_{\tau_-}\Omega(N-\rho_e)$ of even ρ or another state $\varphi_{\sigma_+}\Omega(N-\rho_0)$ of odd ρ. Since we are not interested in photon absorption or emission, we shall consider $\rho_e = 0$ here. However, the cases with $\rho_e \neq 0$, or $\rho_0 \neq 0$ can also be given as before,[9,10] with modifications arising chiefly from considerations connected with Eqs. (3.1)–(3.8).

Due to our labeling convention of $\hat{\Psi}$ discussed following Eq. (2.1), the two charge-field eigensolutions at $w_{\sigma_-} \approx w_{\tau_-}$ are best called $(E_u, \hat{\Psi}_u)$ and $(E_l, \hat{\Psi}_l)$ rather than $(E_{0\sigma_-}, \hat{\Psi}_{0\sigma_-})$ and $(E_{0\tau_-}, \hat{\Psi}_{0\tau_-})$, because $\hat{\Psi}_u$ and $\hat{\Psi}_l$ contain approximately equal admixtures of φ_{σ_-} and φ_{τ_-} even at the weak-field limit. To obtain these eigensolutions, we let

$$a_\nu(\alpha) = d_\nu(\alpha)\, a_0(\sigma_-) + s_\nu(\alpha)\, a_0(\tau_-)\,, \tag{3.12}$$

which implies

$$d_0(\sigma_-) = 1, \quad d_0(\tau_-) = 0\,, \tag{3.13}$$

and

$$s_0(\tau_-) = 1, \quad s_0(\sigma_-) = 0\,. \tag{3.14}$$

With the relations (3.13), all other $d_\nu(\alpha)$ are found by substitution of $d_\nu(\alpha)\, a_0(\sigma_-)$, which are independent of $a_0(\tau_-)$, in place of $a_\nu(\alpha)$ in Eqs. (3.3)–(3.8). The resulting equations are solved without the two ($\nu = 0$, $\alpha_- = \sigma_-$, and τ_-) equations (3.2). Similarly all $s_\nu(\alpha)$ other than $s_0(\tau_-)$ and $s_0(\sigma_-)$ are found. Then the expressions for the roots of the characteristic equation resulting from the use of the ($\nu = 0$, $\alpha_- = \sigma_-$, and τ_-) equations are

$$E_u = \tfrac{1}{2}[W_0'(\tau_-) + W_0'(\sigma_-)] + \tfrac{1}{2}\{[W_0'(\tau_-) - W_0'(\sigma_-)]^2 + 4G^2\}^{1/2}, \tag{3.15}$$

and

$$E_l = \tfrac{1}{2}[W_0'(\tau_-) + W_0'(\sigma_-)] - \tfrac{1}{2}\{[W_0'(\tau_-) - W_0'(\sigma_-)]^2 + 4G^2\}^{1/2}, \tag{3.16}$$

where

$$W_0'(\sigma_-) \equiv W_0(\sigma_-) + \sum G(\sigma_-, \beta_+)\,[d_{-1}(\beta_+) + d_1(\beta_+)]\,,$$

$$W_0'(\tau_-) \equiv W_0(\tau_-) + \sum G(\tau_-, \beta_+)\,[s_{-1}(\beta_+) + s_1(\beta_+)]\,,$$

$$G \equiv \sum G(\sigma_-, \beta_+)\,[s_{-1}(\beta_+) + s_1(\beta_+)]\,,$$

$$= \sum G(\tau_-, \beta_+)\,[d_{-1}(\beta_+) + d_1(\beta_+)]\,. \tag{3.17}$$

Thus the minimum of $\Delta \equiv E_u - E_l$,

$$\Delta_m = (E_u - E_l)_{\min} + O(2G)\,, \tag{3.18}$$

is nonzero, and *the field induces a new avoided crossing between the two states of the same (parity) group.*

Separate iteration to obtain E_u and E_l. We shall calculate $(E_u, \hat{\Psi}_u)$ using Eq. (3.15) for iteration and obtain $(E_l, \hat{\Psi}_l)$ separately using Eq. (3.16) for iteration. This is a departure from earlier methods,[8–10] where only one expression, Eq. (3.15), is used for iteration to obtain E_u, $\underline{a}^u$, and hence the values W_u' and G_u for the W' and G. Then a value $E_{l(u)}$ is calculated from Eq. (3.16) using these W_u' and G_u. On

the other hand, if we use Eq. (3.16) for iteration, we obtain E_l, $\underline{a}^l$ and hence values W_l' and G_l for $W's$ and G. For very strong interaction, $E_{l(u)}$ differs significantly (but of the same order) from E_l owing to $G_u \neq G_l$, $W_u' \neq W_l'$. Hence formulation and calculation in terms of the less physical quantities W' and G lead to different results depending on which of the two sets of values $\{W_u's, G_u\}$ and $\{W_l's, G_l\}$ are used. This was noted in footnote 18 of Ref. 9. The formulation in terms of the more physical quantities $(E_u, \hat{\Psi}_u)$, $(E_l, \hat{\Psi}_l)$ here and of $(E_{\rho\sigma}, \hat{\Psi}_{\rho\sigma})$ in Ref. 1 removes this ambiguity, provided E_u and E_l are calculated separately by iterating, respectively, Eq. (3.15) and Eq. (3.16). The E_u and E_l thus calculated (and not $E_{l(u)}$ for example) are the true eigenvalues because each of them, being now nondegenerate, satisfies the nondegenerate solution Eqs. (3.3)–(3.10).

Therefore, analysis of transition probability across field-induced, field-dressed, or charge-field[17] avoided crossings should be formulated in terms of radiative diabatic states as in Sec. II B of Ref. 1, rather than in terms of the perturbed states of Ref. 9. The main difference is that the radiative-dressed diabatic energy difference $\hat{H}_{22} - \hat{H}_{11}$ and coupling $\hat{H}_{12}$ are calculated from unique values of E_u and E_l, whereas the $W's$ and G are given in the calculation of E_u or E_l.

We emphasize, however, that the difference in the results based on the two formulations differs only for very strong interaction (see below), and is not too significant for the range of interaction in the explicit numerical calculations of Ref. 9 and even less so for those in Ref. 10. To conclude this discussion, we point out that separate iterations for each expression of the eigenvalues should be carried out also for cases involving more than two near-degenerate levels, such as in the situation of double resonance discussed in Ref. 10.

The connection between the nondegenerate case and the degenerate case. The distinction between the two cases is not a sharp one. The degenerate case was needed to take into account the fact that when $w_{\tau_-} \approx w_{\sigma_-}$ and when the radiative interaction is small, the factors $E - W_0(\sigma_-)$ and $E - W_0(\tau_-)$ are approximately zero so that we cannot divide the two ($\nu = 0$, $\alpha_- = \sigma_-, \tau_-$) equations (3.2) by these factors. In computation this means that the method for the degenerate case provides stable and convergent iterations where the nondegenerate solution would diverge. Therefore the degenerate case is also useful to find eigenvalues of *nondegenerate* levels when the nondegenerate method diverges. The eigenvalue E_u or E_l, depending on the actual expression used for iteration, can be easily identified as $E_{0\sigma_-}$ or $E_{0\tau_-}$ due to the smooth variation of the latter with the interactions $G(\alpha, \alpha')$. It can always be tested by using E_u or E_l as a trial value in the nondegenerate solution to obtain $E_{0\sigma_-}$ or $E_{0\tau_-}$. This is possible because according to Eq. (3.11), the factor $E - W_0(\sigma_-) = \sum G(\sigma_-, \beta_+)[d_{-1}(\beta_+) + d_1(\beta_+)]$ for strong interaction [$G(\sigma_-, \beta_+)$ not small] is in fact not close to zero. Indeed, the correct "trial" value E_u or E_l (with relative error $< 10^{-10}$) always converges to the true value with the same accuracy upon the first iteration using the nondegenerate method.

The addition of an oscillatory radiation field does not induce an avoided crossing between two crossing levels w_{σ_-} and w_{σ_+} whose states φ_{σ_-} and φ_{σ_+} belong to different (parity) groups. The proof of this statement is that effective coupling G through other levels must involve even numbers of *virtual* photon emissions and absorptions and hence the opposite "parities" of the two states require that their radiative coupling must be identically zero. But the field does shift the two levels relative to each other, and dress the states. If the field-free states do not have parity symmetry such as gerade-ungerade symmetry, the terms $(\varphi_{\beta_-}, d\varphi_{\beta_+}/dt)$ are not necessarily zero. Then the field-dressed nonadiabatic coupling $C_{0\sigma_-, 0\sigma_+}$ [Eq. (2.12) of Ref. 1] is nonzero,

$$C_{0\sigma_-, 0\sigma_+} = -i \sum_{\beta_- \beta_+} \left(\sum_{\nu_e} a_{\nu_e}^{0\sigma_-}(\beta_-) a_{\nu_e}^{0\sigma_+}(\beta_+) - \sum_{\nu_0} a_{\nu_0}^{0\sigma_-}(\beta_+) a_{\nu_0}^{0\sigma_+}(\beta_-) \right) \left(\varphi_{\beta_-}, \frac{d\varphi_{\beta_+}}{dt} \right).$$

Thus we see that the field couples in the nonadiabatic transitions between states of $\beta_- \neq \sigma_-$ and $\beta_+ \neq \sigma_+$. However, when the states φ_{β_-} and φ_{β_+} have definite parities so that all $(\varphi_{\beta_-}, d\varphi_{\beta_+}/dt)$ are identically zero, then the field-dressed nonadiabatic coupling is zero also.

B. Prototype configuration for numerical study

We study the prototype field-free configuration, shown in Fig. 3(a), of a charge system consisting of three states φ_{σ_-}, φ_{τ_-}, and φ_{σ_+} whose energies are w_{σ_-}, w_{τ_-}, and w_{σ_+} and whose radiative interactions are $G_\sigma \equiv G(\sigma_-, \sigma_+) \neq 0$, $G_\tau \equiv G(\tau_-, \sigma_+) \neq 0$ and $G(\sigma_-, \tau_-) = 0$. Since $G(\sigma_-, \tau_-) = 0$, the formation of avoided crossing is necessarily due to radiative interaction through other states. Four dimensionless ratios characterize the adiabatic eigenvalue problem for such charge system interacting with one field of angular frequency ω. They are[18]

$$G_\sigma/\omega, \; G_\tau/\omega, \; W/\omega \equiv (w_{\tau_-} - w_{\sigma_-})/\omega, \text{ and } w_{\sigma_+}/\omega. \tag{3.19}$$

The field intensity I and the field polarization de-

pendences are contained in the radiative interaction $G_\beta(\beta=\sigma,\tau)$:

$$G_\beta/\omega = 5.8577\times10^{-8}\lambda\mu_\beta I^{1/2}, \tag{3.20}$$

where the wavelength λ is in μm, I is in W/cm^2, and μ_β in a.u. is

$$\mu_\beta \equiv -\langle\varphi_\beta|\sum q_i\vec{r}_i|\varphi_{\sigma_+}\rangle\cdot\hat{\epsilon}$$

for electric dipole transitions or possibly higher multipole moments.[9,10] Since we consider only the class of situations where no photon emission or absorption is involved, ranges of the parameters of interest to us are $|W|/\omega<2$; and $(w_{\sigma_+}-w_{\sigma_-})/\omega$ and $(w_{\sigma_+}-w_{\tau_-})/\omega$ are not close to an odd integer. In order to examine the effect of far-lying off-resonant states, the values of w_{σ_+}/ω considered may be large, e.g., 100.

The system of equations (3.1) and (3.2) appropriate for this case is

$$[E-W_{\nu_0+1}(\sigma_-)]a_{\nu_0+1}(\sigma_-) = G_\sigma[a_{\nu_0}(\sigma_+)+a_{\nu_0+2}(\sigma_+)], \tag{3.21}$$

$$[E-W_{\nu_0+1}(\tau_-)]a_{\nu_0+1}(\tau_-) = G_\tau[a_{\nu_0}(\sigma_+)+a_{\nu_0+2}(\sigma_+)], \tag{3.22}$$

$$[E-W_{\nu_0}(\sigma_+)]a_{\nu_0}(\sigma_+) = G_\sigma[a_{\nu_0-1}(\sigma_-)+a_{\nu_0+1}(\sigma_-)] + G_\tau[a_{\nu_0-1}(\tau_-)+a_{\nu_0+1}(\tau_-)], \tag{3.23}$$

$$-M_0\le\nu_0\le M_0,$$

where M_0 is an odd integer. Since we have only one state σ_+, we shall substitute expressions of $a_{\nu_0\pm1}(\sigma_-)$ and $a_{\nu_0\pm1}(\tau_-)$ obtained from Eqs. (3.21) and (3.22) into Eq. (3.23) and obtained recurrence relation for the scalar quantities T_{ν_0} defined by

$$a_{\nu_0+2}(\sigma_+)\equiv\hat{T}_{\nu_0+2}a_{\nu_0}(\sigma_+), \quad 3\le\nu_0\le M_0, \tag{3.24}$$

and

$$a_{\nu_0-2}(\sigma_+)\equiv\hat{T}_{\nu_0-2}a_{\nu_0}(\sigma_+), \quad -3\ge\nu_0\ge -M_0. \tag{3.25}$$

Such a procedure gives the following recurrence relations for $\hat{T}_{\nu_0}$:

$$\hat{T}_{\nu_0} = V_{\nu_0-1}/[E-W_{\nu_0}(\sigma_+)-V_{\nu_0-1}-V_{\nu_0+1}(1+\hat{T}_{\nu_0+2})], \quad 3\le\nu_0\le M_0, \tag{3.26}$$

and

$$\hat{T}_{\nu_0} = V_{\nu_0+1}/[E-W_{\nu_0}(\sigma_+)-V_{\nu_0+1}-V_{\nu_0-1}(1+\hat{T}_{\nu_0-2})], \quad -3\ge\nu_0\ge -M_0, \tag{3.27}$$

where

$$V_{\nu_0-1}\equiv\sum_{\beta=\sigma_-,\tau_-}\frac{G_\beta^2}{E-W_{\nu_0-1}(\beta)}, \tag{3.28}$$

$$V_{\nu_0+1}\equiv\sum_{\beta=\sigma_-,\tau_-}\frac{G_\beta^2}{E-W_{\nu_0+1}(\beta)}. \tag{3.29}$$

To examine the limiting values of $\hat{T}_{\nu_0}$, two cases are of interest to us. The first is when $(M_0+2)\omega/w_{\sigma_+}>1$ for chosen value of M_0 such that

$$(E-w_\beta)/[(M_0+1)\omega]\ll1, \tag{3.30}$$

and

$$G_\beta^2/[(M_0+2)(M_0+1)\omega^2]\ll1, \quad \beta=\sigma_-,\tau_-, \tag{3.31}$$

$\hat{T}_{M_0+2}$ has the limiting value

$$\hat{T}_{M_0+2}\sim\sum_\beta\frac{G_\beta^2}{(M_0+2)(M_0+1)\omega^2}\approx0, \tag{3.32}$$

and similarly,

$$\hat{T}_{-M_0-2}\approx0. \tag{3.33}$$

Depending on the accuracy desired and the values of G_β/ω, M_0 is usually an odd integer between 3 and 7. Another case is when $w_{\sigma_+}>(M_0+2)\omega$ for a chosen M_0 value; then if

$$(E-w_\beta)/[(M_0+1)\omega]\ll1, \tag{3.34}$$

and

$$G_\beta^2/[w_{\sigma_+}\omega(M_0+1)]\ll1, \quad \beta=\sigma_-,\tau_-, \tag{3.35}$$

then

$$\hat{T}_{M_0+2}\sim\sum_\beta\frac{-G_\beta^2}{w_{\sigma_+}\omega(M_0+1)}\approx0, \tag{3.36}$$

and similarly

$$\hat{T}_{-M_0-2}\approx0. \tag{3.37}$$

The nondegenerate case. Suppose $(E_{0\sigma_-},\hat{\Psi}_{0\sigma_-})$ is desired. Then letting $a_\nu(\alpha)=d_\nu(\alpha)a_0(\sigma_-)$ and using the remaining equations (3.21)–(3.23) with $\nu=\pm2$, ±1, and 0, we obtain

$$E = W_0(\sigma_-)+G_\sigma^2(D_{22}+D_{11}-2D_{12})/D, \tag{3.38}$$

where

$$D_{11}\equiv E-W_1(\sigma_+)-V_2(1+\hat{T}_3)+D_{12}, \tag{3.39}$$

$$D_{22}\equiv E-W_{-1}(\sigma_+)-V_{-2}(1+\hat{T}_{-3})+D_{12}, \tag{3.40}$$

$$D_{12}\equiv -G_\tau^2/(E-w_{\tau_-}), \tag{3.41}$$

$$D\equiv D_{11}D_{22}-D_{12}^2, \tag{3.42}$$

and $\hat{T}_{\pm3}$ are obtained from Eqs. (3.26) and (3.27). Equation (3.38) is iterated by starting with $\hat{T}_{M_0+2}=0$, $\hat{T}_{-M_0-2}=0$, and a trial value for E. The procedure gives both $E_{0\sigma_-}$ and $\hat{\Psi}_{0\sigma_-}=\underline{a}^{0\sigma-}$.

The degenerate case. The eigensolutions $(E_{0\tau_-},\hat{\Psi}_{0\tau_-}=\underline{a}^{0\tau-})$ for the configuration of Fig. 3 are obtained by writing Eqs. (3.12)–(3.14) and solving for the unknown d's and s's. Finally, Eqs. (3.15) and (3.16) are obtained. But by substituting ex-

plicit expressions for $d_{\pm1}$ and $s_{\pm1}$, the $W_0'(\sigma_-)$, $W_0'(\tau_-)$ and G are given by the following simple relationships:

$$\frac{W_0'(\sigma_-)-W_0(\sigma_-)}{G_\sigma^2}=\frac{W_0'(\tau_-)-W_0(\tau_-)}{G_\tau^2}=\frac{G}{G_\tau G_\sigma}=k\,, \tag{3.43}$$

where

$$k\equiv\frac{1}{E-W_{-1}(\sigma_+)-V_{-2}(1+\hat{T}_{-3})}+\frac{1}{E-W_1(\sigma_+)-V_2(1+\hat{T}_3)}\,, \tag{3.44}$$

with $\hat{T}_{\pm3}$ obtained from Eqs. (3.26)–(3.33). Thus once the single quantity k is determined either by numerical iteration or by analytic expressions given below, the other quantities $W_0'(\sigma_-)$, $W_0'(\tau_-)$, G, and hence E_u or E_l can be calculated from the given parameters. In fact from Eqs. (3.15), (3.16), and (3.43), letting $E_u>E_l$ we obtain

$$E_u=\tfrac{1}{2}[w_{\tau_-}+w_{\sigma_-}+k(G_\tau^2+G_\sigma^2)]+\tfrac{1}{2}\{[W+k(G_\tau^2-G_\sigma^2)]^2+4k^2G_\tau^2G_\sigma^2\}^{1/2} \tag{3.45}$$

and

$$E_l=\tfrac{1}{2}[w_{\tau_-}+w_{\sigma_-}+k(G_\tau^2+G_\sigma^2)]-\tfrac{1}{2}\{[W+k(G_\tau^2-G_\sigma^2)]^2+4k^2G_\tau^2G_\sigma^2\}^{1/2}\,. \tag{3.46}$$

At $W\equiv w_{\tau_-}-w_{\sigma_-}=0$, the above expressions simplify individually to

$$E_u=\tfrac{1}{2}(w_{\tau_-}+w_{\sigma_-})+\tfrac{1}{2}(k+|k|)(G_\tau^2+G_\sigma^2) \tag{3.47}$$

and

$$E_l=\tfrac{1}{2}(w_{\tau_-}+w_{\sigma_-})+\tfrac{1}{2}(k-|k|)(G_\tau^2+G_\sigma^2)\,. \tag{3.48}$$

Thus, without any calculation, one charge-field eigenvalue [call it $E_0\equiv\frac{1}{2}(w_{\tau_-}+w_{\sigma_-})$] and all those differing from it by $\pm2\nu\omega$ are known exactly.[9] At $W=-k(G_\tau^2-G_\sigma^2)$,

$$E_u=\tfrac{1}{2}(w_{\tau_-}+w_{\sigma_-})+\tfrac{1}{2}k(G_\tau^2+G_\sigma^2)+|k|\,|G_\tau G_\sigma|\,, \tag{3.49}$$

$$E_l=\tfrac{1}{2}(w_{\tau_-}+w_{\sigma_-})+\tfrac{1}{2}k(G_\tau^2+G_\sigma^2)-|k|\,|G_\tau G_\sigma|\,. \tag{3.50}$$

Note that the phases of φ_{σ_-} or φ_{τ_-} can always be chosen such that G_τ and G_σ are of the same sign. For the special case that $G_\tau=G_\sigma$,

$$W_0'(\sigma_-)-W_0(\sigma_-)=W_0'(\tau_-)-W_0(\tau_-)=G=G_\sigma^2k\,, \tag{3.51}$$

and expressions (3.45) and (3.46) simplify further.

In general, we calculate E_u and E_l (and their wave functions) by numerically iterating the expressions (3.45) and (3.46) separately. For initial trial values, we may use Eqs. (3.56) or Eqs. (3.53). Thus the values k_u of k appearing in Eqs. (3.45), (3.47), and (3.49), and k_l for k in Eqs. (3.46), (3.48), and (3.50), are different.

Some exact values of the ratio of the minimum energy gap[12] of the field-induced avoided crossing to the photon frequency ω are given in Table I.[18] It is seen that Δ_m/ω can be greater than 1. Nonadiabatic transition from the populated state $\hat{\Psi}_{\rho\sigma_-}$ to the unpopulated state $\hat{\Psi}_{\rho\tau_-}$ is highly probable. There is still no real photon absorption or emission associated with the transition in this energy-surface region. But state-mixing effect will produce significant probability amplitudes in various sidebands of φ_{τ_-} and φ_{σ_+} as well as of φ_{σ_-} in $\hat{\Psi}_{\rho\tau_-}$. It is seen from Table I that even very-far-away nonresonant states ($w_{\sigma_+}/\omega>5.5$) can produce significant field-induced energy gaps.

Analytic expression for k enabling direct evaluation without numerical iteration will be very useful since then all the above quantities can be easily calculated. If we write out the definition of Eq. (3.44) for k, we see that the only unknown quantity in the entire expression is E. However, at $w_{\tau_-}=w_{\sigma_-}$, according to Eqs. (3.47) or (3.48) one eigenvalue E_0 is known for any interaction strength and w_{σ_+}. Therefore *exact* values of k_0 can be calculated directly by substitution of this value into the definition of k, Eq. (3.44). We obtain[18]

$$k_0=\frac{1}{\omega-w_{\sigma_+}-(G_\sigma^2+G_\tau^2)(1+\hat{T}_3)/2\omega}-\frac{1}{\omega+w_{\sigma_+}-(G_\sigma^2+G_\tau^2)(1+\hat{T}_{-3})/2\omega}\,, \tag{3.52}$$

where $\hat{T}_3$ and $\hat{T}_{-3}$ are calculated from Eqs. (3.26) and (3.27) with the known value E_0.

TABLE I. The ratio of the minimum energy gap Δ_m of the field-induced avoided crossing to the photon frequency ω, given as a function of the radiative interaction $G_\sigma=G_\tau$ and the position of the nonresonant level w_{σ_+}, as illustrated in Fig. 3. There is no radiative interaction between the levels w_{σ_-} and w_{τ_-} forming the field-free true crossing, i.e., $G(\sigma_-,\tau_-)=0$. The values of Δ_m/ω for $G_\sigma/\omega<0.001$ can be obtained by scaling $\Delta_m/\omega\propto(G_\sigma/\omega)(G_\tau/\omega)$ for given ω and w_{σ_+}. The relation of G_β/ω to the transition moment, field intensity, and frequency is given in Eq. (3.20). No exact results are obtained for entries marked by "···".

G_σ/ω \ w_{σ_+}/ω	1.5	5.5	10	100
0.001	4.800(−6)	7.521(−7)	4.040(−7)	4.000(−8)
0.01	4.795(−4)	7.521(−5)	4.040(−5)	4.000(−6)
0.05	1.172(−2)	1.879(−3)	1.010(−3)	1.000(−4)
0.1	4.398(−2)	7.505(−3)	4.038(−3)	4.000(−4)
0.5	5.014(−1)	1.790(−1)	9.951(−2)	1.000(−2)
1.0	···	6.403(−1)	3.821(−1)	3.998(−2)
1.5	···	1.267	8.115(−1)	8.989(−2)
2.0	···	···	1.350	1.596(−1)

In general when $w_{\tau_-} \neq w_{\sigma_-}$ or when the other value of $k \neq k_0$ at $w_{\tau_-} = w_{\sigma_-}$ is desired, we obtain approximate formulas for k_u and k_l. By keeping terms in the *denominators* of the expression (3.44) correct to second order in G_σ and G_τ, we have[18]

$$k_u'' = \frac{1}{\omega - w_{\sigma_+} + \delta_u - V_u} - \frac{1}{\omega + w_{\sigma_+} - \delta_u + V_{-u}}, \tag{3.53a}$$

$$k_l'' = \frac{1}{\omega - w_{\sigma_+} + \delta_l - V_l} - \frac{1}{\omega + w_{\sigma_+} - \delta_l + V_{-l}}, \tag{3.53b}$$

where

$$\delta_u \equiv \tfrac{1}{2}k_u'(G_\tau^2 + G_\sigma^2) + \tfrac{1}{2}\{[W + k_u'(G_\tau^2 - G_\sigma^2)]^2 + 4k_u'^2 G_\tau^2 G_\sigma^2\}^{1/2}, \tag{3.54a}$$

$$\delta_l \equiv \tfrac{1}{2}k_l'(G_\tau^2 + G_\sigma^2) - \tfrac{1}{2}\{[W + k_l'(G_\tau^2 - G_\sigma^2)]^2 + 4k_l'^2 G_\tau^2 G_\sigma^2\}^{1/2}, \tag{3.54b}$$

and

$$V_{\pm u} \equiv \sum_{\beta=\sigma_-,\tau_-} \frac{G_\beta^2}{\frac{1}{2}|W| - w_\beta \pm 2\omega}, \tag{3.55a}$$

$$V_{\pm l} \equiv \sum_{\beta=\sigma_-,\tau_-} \frac{G_\beta^2}{-\frac{1}{2}|W| - w_\beta \pm 2\omega}, \tag{3.55b}$$

and

$$k_u' \equiv \frac{2(w_{\sigma_+} - \frac{1}{2}|W|)}{\omega^2 - (w_{\sigma_+} - \frac{1}{2}|W|)^2}, \tag{3.56a}$$

$$k_l' \equiv \frac{2(w_{\sigma_+} + \frac{1}{2}|W|)}{\omega^2 - (w_{\sigma_+} + \frac{1}{2}|W|)^2}. \tag{3.56b}$$

Clearly k_u' and k_l' are simply the weak-field limit of k_u'' and k_l'', respectively.

By making a second-order approximation in the denominators rather than in the power series expansion of the terms in Eq. (3.44), the values k_u'' and k_l'' are much more accurate than second-order in G_σ and G_τ. Table II compares k_u'' with the corresponding exact value of k_u.[18] Table III makes a similar comparison for k_l''. It is for convenience of tabulation that we give the results for the special case $G_\sigma = G_\tau$. It is seen that both k_u'' and k_l'' are accurate (<1%) even for strong interaction, $G_\sigma/\omega \lesssim 0.5$, in the case of close-lying nonresonant levels, $w_{\sigma_+}/\omega = 1.5$. Therefore accurate values of E_u and E_l are obtained by substituting k_u'' and k_l'' into Eqs. (3.45) and (3.46), respectively, with the approximation lying only in k_u'' and k_l''.

We have not tried to compute E_u or E_l with G_σ/ω and/or G_τ/ω having values greater than 2.0. It is noticed from Tables II and III that with other parameters being the same, iteration with E_u is convergent at stronger interaction G_σ/ω than that with E_l. This is due to the fact that in all cases shown, $w_{\sigma_+} > \omega$ and therefore [see Eq. (3.57) below] k_u and k_l are both negative. Then for values of W/ω not close to unity, Eqs. (3.47) and (3.48) hold approximately and therefore $E_u - \frac{1}{2}(w_{\tau_-} + w_{\sigma_-})$ is (much) smaller than $E_l - \frac{1}{2}(w_{\tau_-} + w_{\sigma_-})$. Incidently the exact values of these two quantities can be obtained by using the analytic values k_u'' and k_l'' and the errors shown in these tables.

The accuracy of k_u' and k_l', which are even simpler to use, is given in Table IV.[18]

Level separation for the field-induced avoided crossing. In those ranges of interaction G_β and w_{σ_+} for which the differences in k_u and k_l are negligible, separate iteration of Eqs. (3.45) and (3.46) is not required. Then E_l can be calculated from

TABLE II. Comparison of the approximate values k_u'' of Eq. (3.53a) with exact values k_u calculated by numerical solution. The relative error, defined as $(k_u''/k_u)-1$, is given as a function of the energy difference $W \equiv w_{\tau_-} - w_{\sigma_-}$ between the true-crossing levels w_{τ_-} and w_{σ_-}, of the third level w_{σ_+}, and of the radiative interaction $G_\sigma = G_\tau$. The entries marked "w.s." mean k_u'' has the wrong sign compared to the exact k_u value. The entries marked "···" mean that the numerical iteration to obtain the exact k_u was not convergent. It is seen that k_u'' remains accurate (<1%) up to strong interactions and that its accuracy is only weakly dependent on W.

w_{σ_+}/ω	W/ω \ G_σ/ω	0.01	0.05	0.1	0.5	1.0	1.5	2.0
1.5	0.4	−1.5(−6)	−8.0(−4)	−8.03(−3)	4.89(−2)	0.712	w.s.	w.s.
	0.04	−2.4(−7)	−8.6(−5)	−1.53(−4)	5.56(−2)	0.786	4.040	w.s.
5.5	0.4	−3.0(−9)	−2.0(−7)	−3.1(−6)	−1.67(−3)	−2.42(−2)	−0.174	···
	0.04	−3(−10)	−2.1(−7)	−3.4(−6)	−2.74(−3)	−3.52(−2)	−0.197	···
10	0.4	−1(−10)	−9.9(−8)	−1.6(−7)	−1.49(−4)	−4.52(−2)	−3.68(−2)	−0.256
	0.04	−2(−11)	−1.5(−8)	−2.7(−7)	−5.03(−4)	−9.33(−3)	−5.64(−2)	−0.271
10^2	0.4	1(−14)	1(−11)	1(−10)	2.69(−8)	−3.53(−6)	−5.12(−5)	−3.07(−4)
	0.04	−1(−15)	−1(−12)	−6(−11)	−7.76(−7)	−4.15(−5)	−3.29(−4)	−1.26(−3)

TABLE III. Comparison of the approximate values k_l'' of Eq. (3.53b) with exact values k_l calculated by numerical solution. The relative error defined as $(k_l''/k_l)-1$ is given as a function of the energy difference $W \equiv w_{\tau_-} - w_{\sigma_-}$ between the true-crossing levels w_{τ_-} and w_{σ_-}, of the third level w_{σ_+}, and of the radiative interaction $G_\sigma = G_\tau$. The entries marked "w.s." mean k_l'' has the wrong sign compared to the exact k_l value. The entries marked "$\cdots$" mean that the numerical iteration to obtain the exact k_l was not convergent. It is seen that k_l'' remains accurate (<1%) up to strong interaction and that its accuracy is only weakly dependent on W.

w_{σ_+}/ω	W/ω \ G_σ/ω	0.01	0.05	0.1	0.5	1.0	1.5	2.0
1.5	0.4	−4.9(−8)	−3.1(−5)	−5.04(−4)	−6.09(−2)	$\cdots$	$\cdots$	$\cdots$
	0.04	−1.8(−7)	−1.5(−4)	−3.53(−3)	−1.86(−1)	$\cdots$	$\cdots$	$\cdots$
5.5	0.4	−3(−10)	−2.3(−7)	−3.58(−6)	−1.57(−3)	−7.85(−3)	1.79(−3)	$\cdots$
	0.04	−3(−10)	−2.1(−7)	−3.26(−6)	−9.52(−4)	−1.84(−3)	1.60(−2)	$\cdots$
10	0.4	−3(−11)	−1.9(−8)	−3.04(−7)	−1.06(−4)	1.15(−3)	1.59(−2)	6.55(−2)
	0.04	−2(−11)	−1.5(−8)	−2.06(−7)	2.05(−4)	5.26(−3)	2.82(−2)	8.96(−2)
10^2	0.4	−7(−15)	−5(−12)	1.2(−11)	8.83(−8)	5.41(−6)	6.01(−5)	3.25(−4)
	0.04	0	−1(−12)	2.1(−11)	7.51(−7)	4.11(−5)	3.27(−4)	1.24(−3)

the k_u obtained in iterating the expression E_u. In this domain, many interesting results can be derived. To give a representative indication of this domain, the ratio k_l/k_u as a function of $G_\tau = G_\sigma$ and w_{σ_+} is given in Table V.[18]

It can be seen from Eqs. (3.53)–(3.55) that the inequality of k_u'' and k_l'' is due to the inequality between δ_u and δ_l. We note that the difference, $\delta_u - \delta_l$, is of the same order of magnitude as δ_u and δ_l. Therefore the same value is obtained for k_u and k_l only if δ_u and δ_l are negligible compared to w_{σ_+}. That $|\delta_u/w_{\sigma_+}|$ and $|\delta_l/w_{\sigma_+}|$ are small also implies that $|W/w_{\sigma_+}|$ and $|(G_\tau^2+G_\sigma^2)/(\omega^2-w_{\sigma_+}^2)|$ are small. In this domain, an approximate expression for $k_u \cong k_l$ is[18]

$$k_1 = \frac{2w_{\sigma_+}}{\omega^2 - w_{\sigma_+}^2} . \tag{3.57}$$

Thus if w_{σ_+} is positive, $k_1 \gtrless 0$ for $\omega \gtrless w_{\sigma_+}$.

Thus employing Eqs. (3.45) and (3.46) *together*, the following relations useful in subsequent sections are derived. The new "center of levels" at each R [or equivalently $W(R)$] is shifted up or down relative to the field-free center according to whether k is positive or negative,

$$\tfrac{1}{2}(E_u + E_l) - \tfrac{1}{2}(W_{\tau_-} + W_{\sigma_-}) = \tfrac{1}{2}k(G_\tau^2 + G_\sigma^2) . \tag{3.58}$$

The new level separation is given by

$$\Delta \equiv E_u - E_l = \{[W + k(G_\tau^2 - G_\sigma^2)]^2 + 4k^2 G_\tau^2 G_\sigma^2\}^{1/2} , \tag{3.59}$$

where k, G_τ, and G_σ are evaluated at each W. At $W = 0$,

TABLE IV. Comparison of the approximate values k_u' and k_l' of Eqs. (3.56) with exact values of k_u and k_l, respectively. The relative errors $\xi_u' \equiv k_u'/k_u - 1$ and $\xi_l' \equiv k_l'/k_l - 1$ are given as a function of the third-level position w_{σ_+} and of the radiative interaction $G_\sigma = G_\tau$. The dependence of ξ_u' and ξ_l' on W is again very weak for $W/\omega \leq 0.4$ and is not shown. The entries marked "$\cdots$" mean that the numerical iteration to obtain the exact values k_u or k_l was not convergent. It is seen that k_u' and k_l' are accurate in a large domain of parameters. They are simpler to use than k_u'' and k_l'' although they are not so accurate, as expected.

w_{σ_+}/ω		G_σ/ω 0.01	0.05	0.1	0.5	1.0	1.5	2.0
1.5	ξ_u'	1.4(−3)	3.3(−2)	0.118	1.12	3.48	2.82	8.70
	ξ_l'	3.4(−4)	8.5(−3)	3.4(−2)	0.895	$\cdots$	$\cdots$	$\cdots$
5.5	ξ_u'	1.3(−5)	3.3(−4)	1.3(−3)	2.4(−2)	2.1(−2)	−0.21	$\cdots$
	ξ_l'	1.5(−5)	3.8(−4)	1.5(−3)	3.8(−2)	1.5(−1)	3.0(−1)	$\cdots$
10	ξ_u'	3.2(−6)	8.0(−5)	3.2(−4)	6.5(−3)	7.5(−3)	−5.1(−2)	−0.343
	ξ_l'	5.0(−6)	1.3(−4)	5.0(−4)	1.2(−2)	4.9(−2)	1.1(−1)	1.8(−1)
10^2	ξ_u'	−6(−14)	−1.6(−6)	−6.4(−6)	−1.7(−4)	−7.6(−4)	−2.1(−3)	−4.7(−3)
	ξ_l'	1(−7)	3.6(−6)	1.4(−5)	3.5(−4)	1.3(−3)	2.8(−3)	4.6(−3)

the level separation is

$$\Delta_0 \equiv (E_u - E_l)_0 = |k|(G_\sigma^2 + G_\tau^2). \tag{3.60}$$

The minimum value of the energy difference of the field-induced avoided crossing is given by

$$\Delta_m \equiv (E_u - E_l)_{\min} = 2|kG_\tau G_\sigma| \tag{3.61}$$

and occurs at

$$W = -k(G_\tau^2 - G_\sigma^2). \tag{3.62}$$

Thus this minimum occurs to the left or right of the field-free crossing point depending on the sign of k and the relative magnitude of G_τ^2 and G_σ^2. For low intensity, the field-dependence of k is negligible. From Eq. (3.20), it is seen that the minimum Δ_m scales linearly with field intensity I and the product of transition moments $\mu_\sigma\mu_\tau$. Results (3.61) and (3.62) satisfy the requirement $\Delta_0 \geq \Delta_m$. From Eq. (3.62) and numerical results for very strong interactions, *the minimum of the field-induced avoided crossing always occurs at* $w_{\tau_-} = w_{\sigma_-}$ *if* $|G_\tau| = |G_\sigma|$.

Since $k = k_0$ is known exactly at $w_{\tau_-} = w_{\sigma_-}$, and since $\Delta_m = \Delta_0$ for the case $G_\tau = G_\sigma$, an exact result

$$\Delta_m = 2|k_0|G_\tau^2, \quad \text{if } G_\tau = G_\sigma, \tag{3.63}$$

is obtained in the domain $k_l = k_u$ without any iterative calculation. However, if in the general case $G_\tau \neq G_\sigma$, an approximate expression valid in this domain is

$$\Delta_m = 2|k_1 G_\tau G_\sigma|. \tag{3.64}$$

Comparison of the approximate values of Δ_m given by Eq. (3.64) for $G_\sigma/\omega \geq G_\tau/\omega$ with exact numerical values shows that the relative error is less than 1% (i) for $w_{\sigma_+}/\omega = 1.5$, if $G_\sigma/\omega \leq 0.05$; (ii) for $w_{\sigma_+}/\omega = 5.5$, if $G_\sigma/\omega < 0.3$; (iii) for $w_{\sigma_+}/\omega = 10$, if $G_\sigma/\omega < 0.5$; and (iv) for $w_{\sigma_+}/\omega = 10^2$, if $G_\sigma/\omega \leq 2$ and possibly higher values. An examination of Table V shows that this is also the domain in which the relative differences between k_l and k_u are less than 1%. Furthermore, this is also the domain in which the quantity χ satisfies Eq. (3.66) and Eq. (3.68) with a relative error less than 1% (see Table VI). From previous results,[1] it is reasonable to assume that the relative difference between C_{12}'' and $C^0_{\sigma_-,\tau_-}$ is also less than 1%. Therefore to use the formula Eqs. (2.12) and (2.21), the only effect of the field is the transition associated with the energy gap Δ_m given by Eq. (3.64).

Values of the ratio χ can be calculated exactly according to the definition in Eqs. (2.23) and by using definitions (2.15) and (2.16) for Δ and Δ_m. A simple approximation to χ can be given (i) if the relative kinetic energy is high enough or the optical Stark shifts are small enough so that the field-free trajectory s of the relative motion is not affected significantly by the field, and (ii) if the R dependence of $(w_{\tau_-} + w_{\sigma_-})/\omega$, w_{σ_+}, G_σ, and G_τ are weak compared to that of W. Condition (ii) can be satisfied for some molecular systems since the "region of transition" around the crossing is relatively "narrow." Condition (i) also implies that the velocity with the field on is approximately the same as the field-free velocity. This is of course consistent with the classical-motion approximation. Then the approximate formula for evaluating χ is

$$\chi \cong \frac{\partial(\Delta^2 - \Delta_m^2)^{1/2}}{\partial W}. \tag{3.65}$$

Using this formula to evaluate χ for given w_{σ_+}, G_τ, and G_σ, we found that to an excellent approximation,

TABLE V. The ratio of the exact value k_l to the exact value k_u, given as a function of the radiative interaction $G_\sigma = G_\tau$ and of the third-level w_{σ_+} at the true-crossing point $W = 0$. Deviation of the ratio from 1 indicates the extent of the necessity for separate iteration to obtain E_u and E_l. When this ratio is close to 1, many simple results in Eqs. (3.58)–(3.64) are valid.

G_σ/ω \ ω_{σ_+}/ω	1.5	5.5	10	100
0.01	0.999	1.000	1.000	1.000
0.05	0.980	1.000	1.000	1.000
0.1	0.932	0.999	1.000	1.000
0.3	0.718	0.987	0.996	1.000
0.5	0.594	0.963	0.989	1.000
1.0	...	0.848	0.946	0.999
1.5	...	0.587	0.840	0.998
2.0	...	...	0.557	0.995

TABLE VI. Typical values of χ, the ratio of the relative slope of the radiative-dressed diabatic levels to that of the true-crossing levels in the absence of the laser field, given as function of the position of the third level and of the radiative interaction $G_\sigma = G_\tau$. The number of significant figures shown gives an indication of the extent of constancy of χ as a function of W. Those entries marked with "*" mean there are values of χ at some W/ω that deviate from the values shown by 1% to 10%. The entries marked by "..." mean no exact values are computed. For $G_\sigma/\omega = G_\tau/\omega < 0.01$, $\chi = 1$.

G_σ/ω \ w_{σ_+}/ω	1.5	5.5	10	100
0.01	1.000	1.000	1.000	1.000
0.05	0.990	1.000	1.000	1.000
0.1	0.966	0.999	1.000	1.000
0.3	0.865	0.993	0.998	1.000
0.5	0.784	0.982	0.994	1.000
1.0	...	0.92	0.973	1.000
1.5	...	0.75*	0.916	0.999
2.0	...	...	0.75*	0.998

$$\chi = \text{constant}, \tag{3.66}$$

as a function of W/ω varying from 0.4 to −0.4. *If the statement (3.66) holds, then the dressed diabatic energy levels have constant relative slope* ($\alpha = \text{const}$) *if the field-free true crossing does* ($\alpha_0 = \text{const}$).

Examination of the analytic expression for χ shows that if

$$\left| \frac{w_{\sigma_+} G_\beta^2}{\omega^2 - w_{\sigma_+}^2} \right| \ll |W|, \quad \beta = \sigma, \tau, \tag{3.67}$$

then

$$\chi = 1 \tag{3.68}$$

for a wide range of W/ω. Condition (3.67) says the physically expected result that W at each R does not change in the weak-field limit or a far-away third level in the strong-field limit. Note in connection with Eq. (3.67) that $\omega^2 = w_{\sigma_+}^2$ is ruled out for this study on nonresonant effect and that for evaluation of χ, W has nonzero values.

For G_τ/ω and $G_\sigma/\omega \leq 0.05$, we found that both Eq. (3.66) and Eq. (3.68) are satisfied to an accuracy of four significant figures over the parameter ranges $W/\omega = 0.4$ to −0.4 and for $w_{\sigma_+}/\omega = 0$ to 100. For higher values of G_τ/ω and G_σ/ω, Table VI gives the values of χ for different w_{σ_+} values and also notes the extent of deviation from constancy with respect to variation in W.

To conclude this section, we emphasize the importance of knowing the accuracy of various quantities Δ_m, χ, etc. to be used in calculating the transition probabilities. In the modified Landau-Zener model, Eqs. (2.12)–(2.16) and (2:21)–(2.23), any error δ in the values p is magnified by a factor of 2π in the exponent [i.e., ratio of inaccurate value of $|B_u(\tau_\infty)|^2$ to its exact value $= \exp(-2\pi\delta)$]. This sensitivity of the transition probability on the energy differences and coupling between states is expected to be independent of models but to hold generally.

IV. MOLECULAR COLLISION AND DISSOCIATION

During the course of molecular collisions and molecular dissociations in the presence of the laser field, one field-induced avoided crossing may be traversed. After the crossing, the final elastic and inelastic probabilities in the *field-dressed* states such as $\hat{\Psi}_{0\sigma\_}$ and $\hat{\Psi}_{0\tau\_}$ forming such a crossing are, respectively,

$$S = e^{-2\pi p} \text{ and } T = 1 - S \tag{4.1}$$

in the modified Landau-Zener model [see Eq. (2.12) and Fig. 3].

If the charge-field system is probed for probability $P(\tau\_)$ in the charge state $\varphi_{\tau\_}$ at the positive asymptotic time t_i, the value of $P(\tau\_)$ is $Tp_{0\tau\_}(\tau\_) + Sp_{0\sigma\_}(\tau\_)$, where $p_{0\tau\_}(\tau\_)$ is the probability of finding the charge system in the state $\varphi_{\tau\_}$ and its sidebands if the charge-field system is in the state $\hat{\Psi}_{0\sigma}$.[1] If the charge-field system is probed after the field is turned off, $p_{0\tau\_}(\tau\_) \Rightarrow 1$, whereas $p_{0\sigma\_}(\tau\_) \Rightarrow 0$, so that the probabilities of populating the states $\varphi_{\tau\_}$ and $\varphi_{\sigma\_}$ are simply T and S, respectively. Measurements of fluorescence from excited atomic and molecular species after irradiation with laser pulses of time duration short compared to radiative lifetime(s) fall into this category.

We define a quantity Γ, whose physical meaning depends on the cases to be discussed in Secs. IV A and IV B:

$$\Gamma \equiv 1 - \exp\left[-\tfrac{1}{2}\pi(\Delta_m/\omega)^2 \underline{\chi}^{-1}(|\alpha_0|/\omega^2)^{-1}\right] \geq 0. \tag{4.2}$$

Note that the explicitly written ω factors in the exponent actually cancel out, but they are used for convenience of dimensionless representation of the minimum energy gap Δ_m and the field-free parameter $|\alpha_0|$. Compare this with Eqs. (2.12) and (2.21). The dimensionless ratio $|\alpha_0|/\omega^2$ is given by

$$|\alpha_0|/\omega^2 = 8.0915 \times 10^{-8} \lambda^2 v F, \tag{4.3}$$

in terms of the wavelength λ (in μm) of the laser field, the relative velocity v (in cm/sec) at the crossing region, and the force difference (in eV/a_0) $F \equiv \hat{s} \cdot \nabla(w_{\tau\_} - w_{\sigma\_})$ along the trajectory $\underline{s}$. The experimentally interesting range of values is 10^{-6}–10^3. Figures 4 and 5 plot the exact values of Γ as a function of the radiative interactions and the $|\alpha_0|/\omega^2$ parameter. The case $G_\sigma = G_\tau$ is chosen for presentation.

The quantity Γ has the field-free limit of zero since then the energy gap of the field-induced avoided crossing vanishes, $\Delta_m \Rightarrow 0$. At high intensities that are achievable at laboratories, Γ reaches its maximum value 1. The intensity at which the saturation behavior sets in depends on the quantity $|\alpha_0|$. It is seen that lower intensity is required to induce the same value Γ for smaller values of $|\alpha_0|$, i.e., smaller relative velocity and smaller force difference between the true crossing energies.

In the intermediate domain described below Eq. (3.64), in which k_1 is a good approximation to obtain Δ_m, we have

$$\Delta_m/\omega = 2\left|(\omega k_1)(G_\tau/\omega)(G_\sigma/\omega)\right|, \tag{4.4}$$

where

$$\omega k_1 = \frac{2(w_{\sigma_+}/\omega)}{1 - (w_{\sigma_+}/\omega)^2}, \tag{4.5}$$

Therefore when the exponent in Eq. (4.2) is small,

$$\Gamma = 2\pi \left(\omega k_1 \frac{G_\tau}{\omega} \frac{G_\sigma}{\omega} \right)^2 \Big/ \left(\frac{\alpha_0}{\omega^2} \right) ,$$

$$= 3.6570 \times 10^{-21} \frac{\lambda^2 I^2 \mu_\tau^2 \mu_\sigma^2}{vF} \times \left(\frac{w_{\sigma_+}/\omega}{1-(w_{\sigma_+}/\omega)^2} \right)^2 , \tag{4.6}$$

where the various quantities and their units are defined in connection with Eqs. (3.20) and (4.3). We see that $\Gamma \propto I^2$ and v^{-1}. For $(w_{\sigma_+}/\omega)^2 \approx O(1)$, $\Gamma \propto \lambda^4$; but for $(w_{\sigma_+}/\omega)^2 \gg 1$, Γ is independent of λ. It is also seen from Eq. (4.6) that Γ is proportional to the fourth power of the field amplitude, explaining the linear slope of 4 in Figs. 4 and 5.

In Figs. 4 and 5, we plot Γ for the cases $w_{\sigma_+}/\omega = 1.5$ and 5.5 only. In the domain before saturation sets in (e.g., the linear portions in Figs. 4 and 5) and for

$$(w_{\sigma_+}/\omega)^2 \gg 1, \tag{4.7}$$

it is seen from Eqs. (4.5) and (4.6) that[18]

$$\Gamma \propto (w_{\sigma_+})^{-2} . \tag{4.8}$$

Therefore plots of Γ for $w_{\sigma_+}/\omega > 5.5$ have not been given. In any case they can be easily calculated from the values of χ (e.g., Table VI) and the analytic formulas for k_u'' and k_l'' (or k_u' and k_l') which according to Tables II and III remain accurate (error < 1%) up to $G_\sigma/\omega = G_\tau/\omega = 1.5$ for $w_{\sigma_+}/\omega = 10$ to 10^2. From these results or Fig. 5, it is seen that even very-far-away nonresonant states can produce important field-induced transitions.

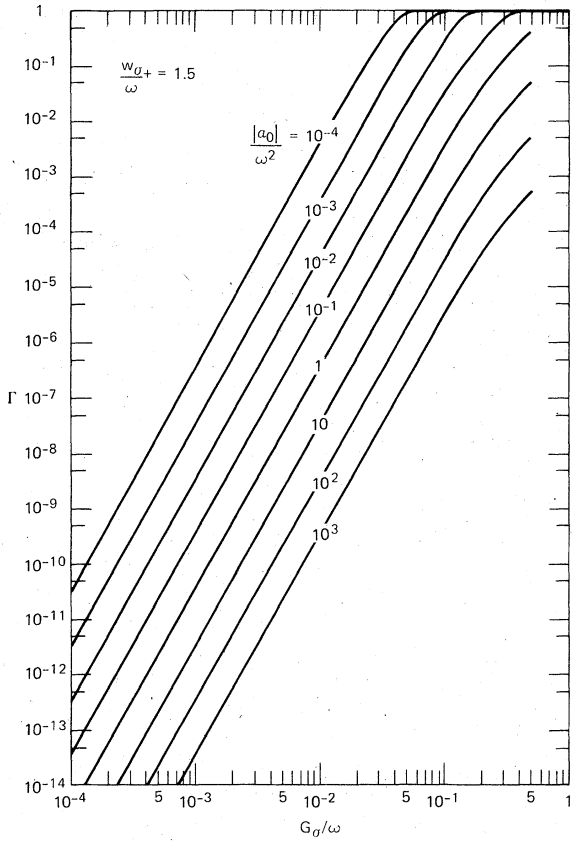

FIG. 4. Plots of Γ defined in Eq. (4.2) as a function of the radiative interaction ratio G_σ/ω [see Eq. (3.20)] and the field-free parameter $|\alpha_0|/\omega$ [see Eq. (4.3)] for the prototype configuration of Fig. 3 and Sec. III B with $G_\tau = G_\sigma$, $w_{\sigma_+}/\omega = 1.5$. For a new transition channel opened up by the laser field, Γ is the inelastic transition probability after one traversal of the field-induced avoided crossing. For cases with significant field-free inelastic transitions, Γ is the fractional *decrease* of the elastic channel probability due to the presence of the field [see Eq. (4.9)].

A. New transition channel opened by field

For the case of the new transition channel represented by Eq. (2.8e), the inelastic probability T is simply Γ of Eq. (4.2). Small transition probability

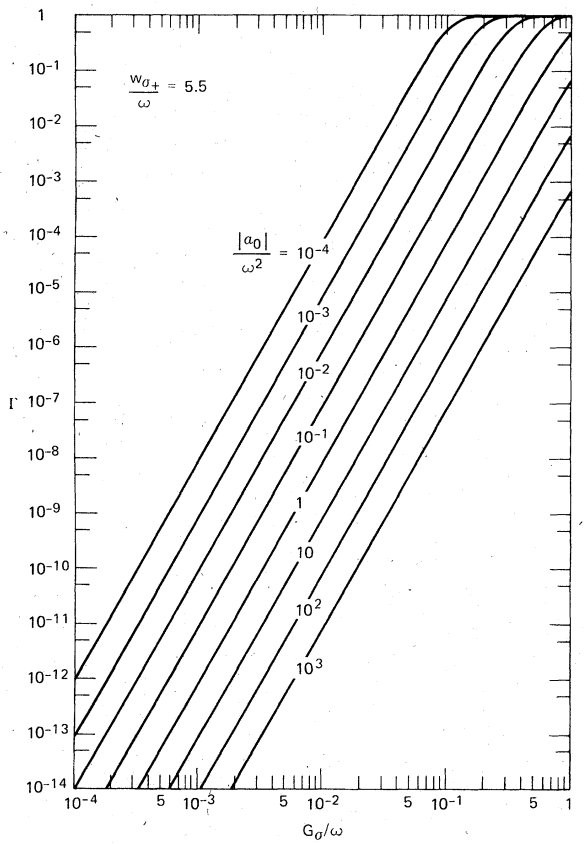

FIG. 5. Plots of Γ as mentioned in Fig. 4 except now $w_{\sigma_+}/\omega = 5.5$. In both Figs. 4 and 5, saturation of the inelastic channel or equivalently the complete depletion of the elastic channel is shown possible. For larger w_{σ_+}/ω, $\Gamma \propto w_{\sigma_+}^{-2}$. Therefore very far-away nonresonant levels can be significant for field-induced transitions.

induced by a field of moderate intensity can still be readily detected since there is no competing field-free transition into this new channel. Depending on the parameter $|\alpha_0|/\omega^2$, sufficiently intense field can nonresonantly redirect all transitions into this new channel.

B. Cases with non-negligible field-free inelastic transition

For these cases, the quantities that best characterize the effect of the field on the field-free elastic and inelastic probabilities S_0 and T_0 are the fractional *decrease* of elastic probability,

$$(S_0 - S)/S_0 = 1 - S/S_0 , \tag{4.9}$$

and the fractional *increase* of inelastic probability

$$(T - T_0)/T_0 = (1 - S/S_0) S_0/T_0 . \tag{4.10}$$

This last expression states that the significance of field effect on the inelastic channel is a product of the fractional decrease of elastic probability and the ratio of the field-free elastic probability S_0 to the field-free inelastic probability T_0. For example, for a small depletion of the elastic probability $1 - S/S_0 = 10^{-3}$, transition probability into the inelastic channel is increased tenfold if the field-free ratio S_0/T_0 has a value of 10^4. For this case, experimental detection of the field-induced change of events (e.g., fluorescence) associated with the inelastic channel can be more readily demonstrated than those with the elastic channel. On the other hand, if S_0/T_0 equals 10^{-4}, even though there is complete depletion of the elastic channel (i.e., $1 - S/S_0 = 1$), the fractional increase of probability in the inelastic channel is only 10^{-4}. Assuming the original field-free signal of the elastic channel is strong enough, experimental demonstration of the field-induced effect should detect the change in the elastic channel.

In the domain of a moderately intense field as characterized by Eqs. (2.8b) and (3.68) [see also discussion following Eq. (3.64)], then, the fractional decrease of elastic probability defined in Eq. (4.9) is simply equal to Γ if the modified Landau-Zener model in Eqs. (2.12)–(2.19) is used,

$$1 - S/S_0 = \Gamma. \tag{4.11}$$

Some cases are plotted in Figs. 4 and 5. It is seen that the characterization of the field-induced effect by Eqs. (4.9) and (4.10) is independent of S_0 and T_0 and is therefore rather general.

To conclude this section, it is seen from Eq. (4.2) that Γ is always positive in the presence of the field. Therefore *the addition of the field always decreases the field-free elastic probability* (i.e., $S < S_0$) *and increases the inelastic probability* (i.e., $T > T_0$). *Furthermore, these dependences are monotonic.* The physical explanation is that as the field intensity is increased, the dominant effect is the increase of the field-induced energy gap so that the process becomes more adiabatic *along the new charge-field adiabatic eigenenergy* E_1.

V. ATOMIC COLLISIONS

In atomic collisions, the same true crossing is traversed twice in one encounter, once during the incoming transit and once on the outgoing one. The same holds true for the corresponding field-induced avoided crossing. However, because of the rotation of the nuclear frame with respect to the space-fixed polarization of the field, the radiative interactions at the two crossings are different. Thus, effectively two different field-induced avoided crossings are involved. The final probability in the initially unpopulated channel is given simply in the Landau-Zener model by

$$f = e^{-2\pi p}(1 - e^{-2\pi p'}) + e^{-2\pi p'}(1 - e^{-2\pi p}) , \tag{5.1}$$

aside from an interference term that averages out in the integration over impact parameter to find the total cross sections. The p and p' for the two crossings are defined in Eq. (2.13). Again note that f is the inelastic probability in a field-dressed state (say, $\hat{\Psi}_{0\tau_-}$) if the measurement is taken in the presence of field. Otherwise it is the final probability in the charge state (say, φ_{τ_-}).

A. New transition channels

For the case of Eq. (2.8e), we have

$$p = \Delta_m^2/4\chi|\alpha_0| \text{ and } p' = \Delta_m'^2/4\chi'|\alpha_0| . \tag{5.2}$$

Again we note that the effect of the field is more readily detectable for smaller values of $|\alpha_0|$. In the domain described following Eq. (3.64) and if $2\pi p \ll 1$ and $2\pi p' \ll 1$ are valid, then

$$\begin{aligned} f &= 2\pi k_1^2 [G_\tau^2 G_\sigma^2 + G_\tau'^2 G_\sigma'^2] |\alpha_0|^{-1} , \\ &= 3.6570 \times 10^{-21} \frac{\lambda^2 I^2}{vF} \left(\frac{w_{\sigma_+}/\omega}{1 - (w_{\sigma_+}/\omega)^2} \right)^2 \\ &\quad \times (\mu_\tau^2 \mu_\sigma^2 + \mu_\tau'^2 \mu_\sigma'^2) \end{aligned} \tag{5.3}$$

in the same notations and units defined in Eqs. (3.20) and (4.3). The dependence of f on various quantities in this region is similar to that of Γ in Eq. (4.6). Outside this region, the dependence of f on various parameters is exponential. For $2\pi p \gg 1$, and $2\pi p' \gg 1$, $f = e^{-2\pi p} + e^{-2\pi p'}$.

The maximum value of f is in general found by graphical method. But for the special symmetrical case that $p = p'$, the maximum of f occurs for the value of Δ_m:

$$\Delta_m = (2\chi\,|\alpha_0|\ln 2)^{1/2}/\pi^{1/2}\,. \tag{5.4}$$

In the domain described below Eq. (3.64), the above equation implies that the intensity I_m at which the maximum of f occurs is given by

$$I_m = 1.3767\times10^{10}\,\frac{(vF)^{1/2}}{\lambda\mu_\sigma\mu_\tau}\left(\frac{w_{\sigma_+}/\omega}{1-(\omega_{\sigma_+}/\omega)^2}\right)^{-1}, \tag{5.5}$$

where the quantities and their units have been defined in Eqs. (3.20) and (4.3).

Figures 6 and 7 plot f as a function of the dimensionless parameters G_β/ω and $|\alpha_0|/\omega^2$ for the respective cases $w_{\sigma_+}/\omega = 1.5$ and 5.5 of the prototype configuration. For a given $|\alpha_0|/\omega^2$ value, f initially increases as a fourth power in G_σ/ω_0, reaches a maximum, and ultimately drops exponentially ($\approx$ a fourth power of G_σ/ω *in the exponents*). The maxima of f are also indicated for these cases where $p \neq p'$.

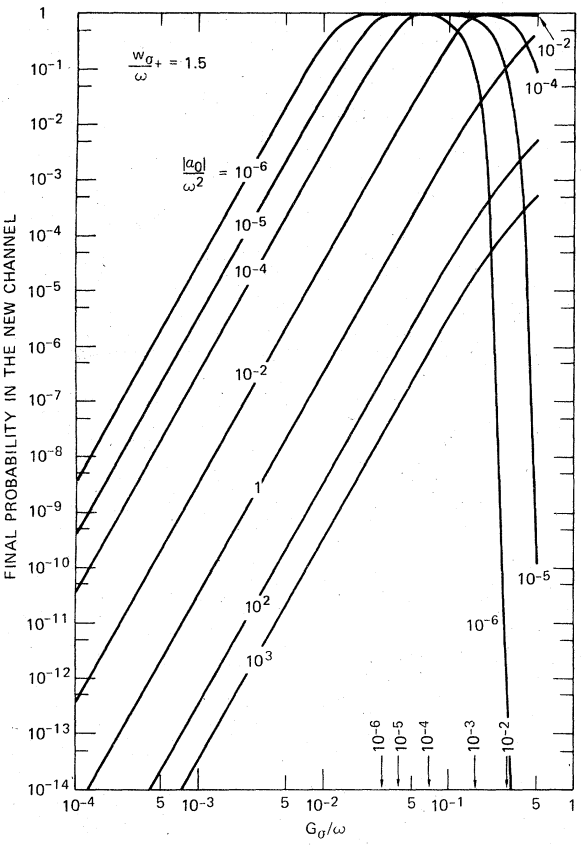

FIG. 6. Plots of the inelastic probability f [Eq. (5.1)] *in the new channel opened by the laser field* after two field-induced avoided crossings, as in atomic collisions. The numerical values of f are calculated for the prototype configuration of Fig. 3 and Sec. III B with $G_\sigma = G_\tau = 10\,G'_\sigma = 10\,G'_\tau$ and $w_{\sigma_+}/\omega = 1.5$. The dimensionless ratios G_σ/ω and $|\alpha_0|/\omega^2$ are given in terms of intensity, velocity, etc. by Eqs. (3.20) and (4.3). The position of the maximum of each curve is marked by arrows labeled $|\alpha_0|/\omega^2$. That f can be greater than $\frac{1}{2}$ is due to $G_\sigma \neq G'_\sigma$ and/or $G_\tau \neq G'_\tau$. Unlike the case of one crossing, further increase of field intensity after the maximum can lead to rapid decrease of inelastic probability due to adiabatic behavior associated with two increasing energy gaps.

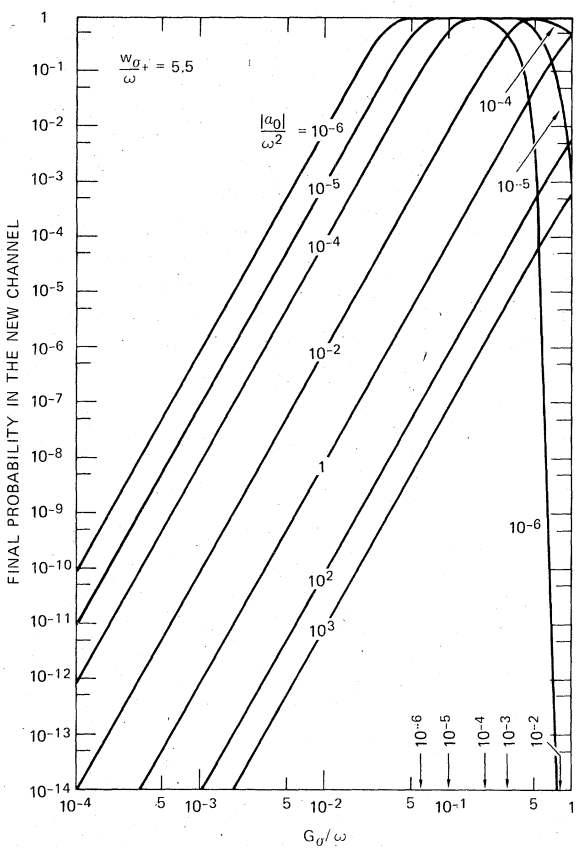

FIG. 7. Plots of the inelastic probability f [Eq. (5.1)] *in the new channel opened by the laser field* after two field-induced crossings. See caption of Fig. 6. Here $w_{\sigma_+}/\omega = 5.5$ and it shows that significant field-induced transition can arise due to coupling through far-away nonresonant levels.

B. Cases with non-negligible field-free inelastic transitions

We shall study these cases for the domain characterized by Eq. (2.8b) and that $\chi = \chi' = 1$. Then it is best to write p and p' in Eq. (5.1) as

$$p = \Delta_m^2/4|\alpha_0| + p_0 \tag{5.6}$$

and

$$p' = \Delta_m'^2/4|\alpha_0| + p_0\,, \tag{5.7}$$

where p_0 is defined in Eq. (2.18). As the field vanishes, Δ_m and Δ'_m approach zero so that f becomes the field-free function,

$$f_0 = 2e^{-2\pi p_0}(1 - e^{-2\pi p_0}). \tag{5.8}$$

We know that f_0 is a function that peaks at $p_0 = 0.1103$. As seen in Eqs. (5.6) and (5.7), *the field-induced energy gap is in effect to increase the size of the exponents*.

Therefore one expects that for $p_0 < 0.1103$ (see, for example, Fig. 8), adding on a field would at least initially increase the inelastic probability ($f > f_0$). Further increase in intensity increases f until the new maximum for f is reached. For the $p = p'$ case, these maxima are given by $p = 0.1103$. Furthermore, since p_0 can be small in this domain, sufficiently intense field can produce the conditions

$$\Delta_m^2/4|\alpha_0| \gg p_0 \text{ and } \Delta_m'^2/4|\alpha_0| \gg p_0 . \tag{5.9}$$

If so, f becomes independent of p_0, but depends on $\Delta_m^2/4|\alpha_0|$ and $\Delta_m'^2/4|\alpha_0|$ only. Its values are essentially the same as those of the new transition channel ($p_0 = 0$). This explains the ultimate merging of f curves for various p_0 (but of the same $|\alpha_0|/\omega^2$) into one curve in Fig. 8. One notes also that for smaller p_0 values, the field-induced contribution is significant relative to the field-free value at smaller field intensity. This is in addition to the greater sensitivity of the field-induced effect for a smaller $|\alpha_0|$ value. See Eqs. (5.6) and (5.7).

The new maximum of f for a nonzero field intensity always occurs at a p_0 value < 0.1103. Therefore, for all cases $p_0 \geq 0.1103$, f must decrease with increasing field intensity. Furthermore, since $f \Rightarrow f_0$ as the field vanishes, the inelastic probability in the presence of the field must be less than its field-free value ($f < f_0$). For "large" p_0 values such that $e^{-2\pi p_0} \ll 1$,

$$\frac{f}{f_0} \cong \frac{1}{2}\left[\exp\left(-\frac{\pi}{2}\frac{\Delta_m^2}{|\alpha_0|}\right) + \exp\left(-\frac{\pi}{2}\frac{\Delta_m'^2}{|\alpha_0|}\right)\right], \tag{5.10}$$

so that the relative significance of the field is insensitive to p_0. Figure 9 illustrates the above

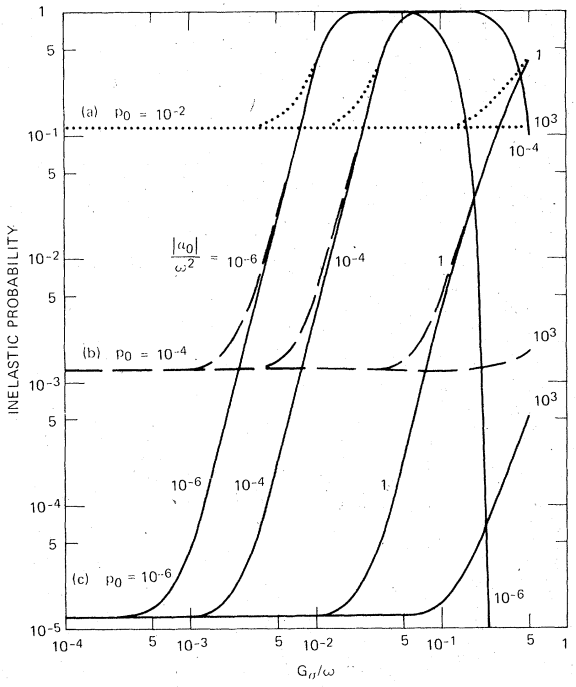

FIG. 8. Plots of the inelastic probability f [Eq. (5.1)] after two field-induced avoided crossings in atomic collisions for *cases with non-negligible field-free inelastic transitions* [$p_0 \neq 0$ in Eqs. (5.6) and (5.7)]. The actual numerical values of f are calculated for the prototype configuration of Fig. 3 and Sec. III B, with $G_\sigma = G_\tau = 10\,G_\sigma' = 10\,G_\tau'$ and $w_{\sigma+}/\omega = 1.5$. This figure illustrates the cases $p_0 < 0.1103$ for which the addition of the field always initially increases the inelastic probability until the new maximum is reached. Many behaviors of the curves are explained in the text below Eq. (5.8).

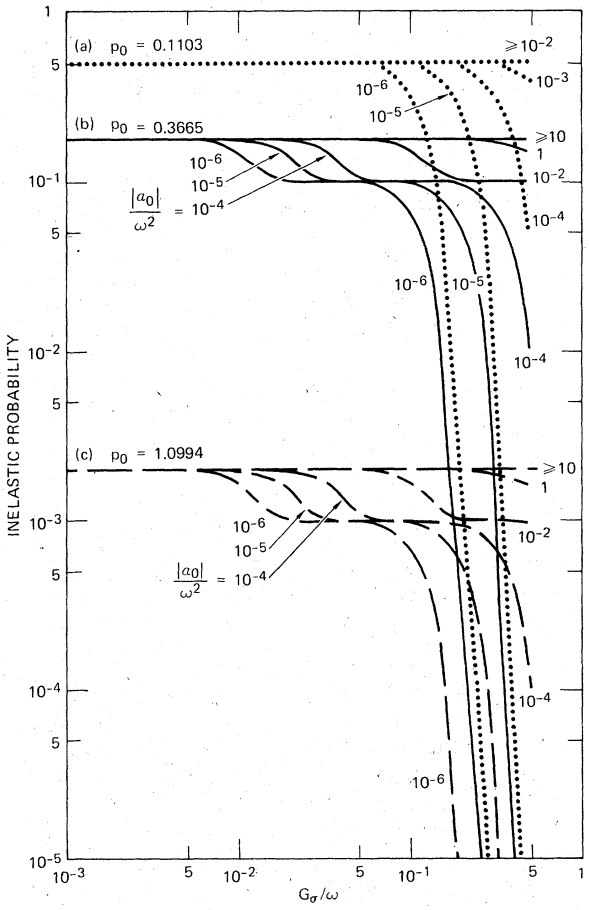

FIG. 9. Plots of the inelastic probability f as in Fig. 8 but for $p_0 \geq 0.1103$. For these cases, addition of the field always decrease the inelastic probability. See text near Eq. (5.10).

points. The appearance of flat "shoulders" on some curves in Fig. 9 is due to the two exponentials in Eq. (5.10). Since we assumed $G_\sigma = 10G'_\sigma$, there is a region of G_σ such that the first exponential vanishes whereas the second is still close to unity.

VI. RADIATIVE-CONTROLLED PREDISSOCIATION

Due to the large number ν_i of oscillations per second in the ith vibrational state, even very small field-induced inelastic transition probability per oscillation, $2\Gamma_i$, can lead to a significant field-induced predissociation rate per second, $\gamma(i)$. Therefore only very moderate field intensity is needed to produce observable field-induced effect. The domain of field intensity characterized by Eq. (2.8b) and the discussion following Eq. (3.64) is adequate for analysis. When the field is so intense that field-induced predissociation is probable with one or a few transits of the crossing, then considerations are similar to those of Secs. IV and V.

Predissociation induced by *static* fields has been studied, for example by Zener,[2] whose analysis and results using WKB approximation for the internuclear motion we follow and use by analogy.

If $\gamma_0(i)$ denotes the field-free predissociation rate for the ith vibrational state, then the total predissociation rate is

$$\gamma_t(i) = \gamma(i) + \gamma_0(i), \tag{6.1}$$

where for $\Gamma_i \ll 1$,

$$\Gamma_i = 2.6422 \times 10^{-27} \frac{\lambda^2 I^2}{[\Delta E(i)/m_r]^{1/2} F} \times \left(\mu_\tau \mu_\sigma \frac{w_{\sigma_+}/\omega}{1-(w_{\sigma_+}/\omega)^2} \right)^2, \tag{6.2}$$

$$\gamma(i) = 2\nu_i \Gamma_i = 1.2777 \times 10^{-12} \frac{\lambda^2 I^2 E_v(i)}{[\Delta E(i)/m_r]^{1/2} F} \times \left(\mu_\tau \mu_\sigma \frac{w_{\sigma_+}/\omega}{1-(w_{\sigma_+}/\omega)^2} \right)^2. \tag{6.3}$$

In these equations, the laser intensity I in W/cm^2, its wavelength λ in μm, the force difference F in eV/a_0, the transition matrix elements μ in a.u. and the dimensionless ratio of the off-resonant energy w_{σ_+} to the photon energy ω have already been defined [see Eqs. (3.20) and (4.3)]. $E_v(i)$ in eV is the vibrational energy of the ith vibrational state. $\Delta E(i)$ in eV is the magnitude of energy difference between the ith vibrational energy and the energy at which the attractive and repulsive electronic energies cross. See Fig. 10. The reduced mass m_r of the vibrating particles is in units of proton mass.

The quantity Γ_i is the inelastic probability for one transit of the field-induced crossing and is therefore very much like Γ of Eq. (4.2). Defining an equivalent velocity v_i in cm/sec at the crossing by

$$v_i = 1.3841 \times 10^6 [\Delta E(i)/m_r]^{1/2}, \tag{6.4}$$

the correspondence of Γ_i and Γ of Eq. (4.6) for $\Gamma \ll 1$ is most transparent.

Our writing of Eq. (6.1) as a sum of two rates without interference term is based on the results of Eq. (2.13) under the assumption of real wave functions and linear polarization of the field. In general, one may expect interference terms due to different competing processes (i.e., the hyperfine and the spontaneous as well as the field-induced predissociation from the B state to the $1u$ state of the iodine molecules).

For field-induced predissociation rate $\gamma(i)$ small compared to $1/\tau_i$, where τ_i (in sec) is the field-free lifetime of the ith vibrational state, *broadening* of the vibrational spectrum is expected to be proportional to the square of the intensity. In the extreme case, for a molecule in the ith vibrational state with energy $E_v(i) > E_c$, the field-induced predissociation is certain if $\gamma_i \tau_i = 1$. The field in-

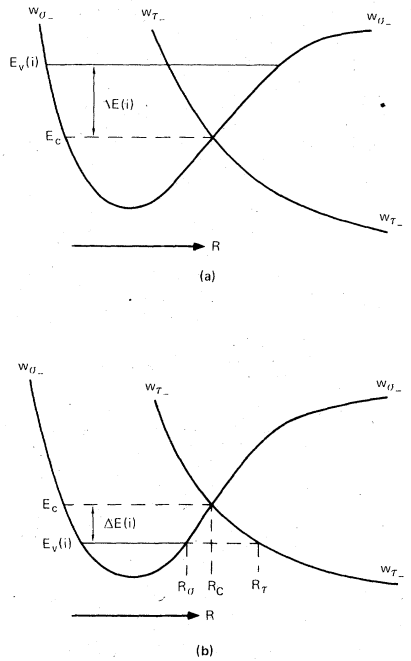

FIG. 10. Radiative-induced predissociation of vibrational states with energy $E_v(i)$ of the attractive electronic states φ_{σ_-} into the repulsive state φ_{τ_-}. (a) $E_v(i) > E_c$. (b) $E_v(i) < E_c$. With the laser field turned on, the new electronic-field potential surfaces corresponding to these true crossings would exhibit avoided crossings.

tensity I_i (in W/cm^2) at which this complete predissociation occurs is given by

$$I_i = 8.8468\times10^5 \times \frac{F^{1/2}[\Delta E(i)/m_r]^{1/4}}{\lambda E_v^{1/2}(i)\tau_i^{1/2}\mu_\tau\mu_\sigma(w_{\sigma_+}/\omega)/[1-(w_{\sigma_+}/\omega)^2]} \cdot \quad (6.5)$$

All vibrational states j with energy $E_v(i) \gtrsim E_v(j) \gtrsim w_x$ are also expected to predissociate with certainty at this intensity. Fluorescence from these states are expected to be quenched. In the iodine molecule, the g states closest to the crossing between the B $0^+u(^3\pi)$ state and the $1u$ state are the $1g(^3\pi)$ and $0g^+(^3\pi)$ states.[19] Our rough estimate (due to the lack of knowledge of the μ's) of the intensity I_i for the vibrational states around $i=25$ is of the order 10^8 W/cm^2. At this intensity $\gamma_{25} = O(10^6/\text{sec})$ and is therefore about the same to four orders of magnitude larger than the hyperfine predissociation rate and spontaneous predissociation rate, depending on the rotational angular momentum J.

For the vibrational states whose energy $E_v(i)$ lies $\Delta E(i)$ *below* the predissociation energy E_c [see Fig. 10(b)], the probability of predissociation per oscillation is given[2] as $t_i\Gamma_i$, where Γ_i is the same electronic transition probability defined before for the vibrational state whose energy is by the same amount $\Delta E_v(i)$ *above* E_c; and t_i is the tunneling probability given by[12]

$$t_i = \exp\left(-2\int_{R_\sigma}^{R_c} k_\sigma\, dR - 2\int_{R_c}^{R_\tau} k_\tau\, dR\right),$$

$$k_\beta = \{2m_r[E_v(i) - w_\beta(R)]/\hbar\}^{1/2}, \quad \beta = \sigma, \tau. \quad (6.6)$$

Therefore the *field-induced predissociation rate* per sec *with tunneling* is given by

$$\gamma(i) = \nu_i t_i \Gamma_i = 6.3885\times10^{-13} \frac{\lambda^2 I^2 E_v(i) t_i}{[\Delta E(i)/m_r]^{1/2} F} \times\left(\mu_\tau\mu_\sigma \frac{w_{\sigma_+}/\omega}{[1-(w_{\sigma_+}/\omega)^2]}\right)^2 . \quad (6.7)$$

VII. DISCUSSION

We have analyzed a new situation where the oscillatory coherent radiation field provided by modern lasers induces avoided crossing and opens up new channels of transition in atomic and molecular gases. Not all the field-free true-crossings[3] become avoided crossings in the presence of the field. Only those true-crossing states that radiatively couple to each other through other intermediate states by an even number of virtual photons do form avoided crossings for their field-dressed levels. See the end of Sec. III A. It is shown that the field induces significant transition probability so that the cross sections for such collisions and predissociation rates can be large.

Our theory given in Secs. II and III A, and the formulas in Secs. IV, V, and VI are quite generally applicable to deal with collision-free and collisional processes of (quasi)diatom or (quasi)polyatoms. The solution of the field-interaction with a finite but large number of discrete charge states is exact as long as the numerical iteration converges. This in turn enables us to give approximate formulas and determine their validity region, such as those for the k values of the prototype configuration in Sec. III B. Although the numerical results shown are limited to the prototype configuration (so as to elicit the various parameter dependences), the theory and many formulas are not. In fact, in the moderate field region expressed in Eq. (2.8b) and discussed following Eq. (3.64), the radiative interaction of many (say, n_+) φ_{σ_+} states with the two crossing states φ_{σ_-} and φ_{τ_-} can be considered as additive contributions. This is reasonable because to the lowest order, the states φ_{σ_+} do not couple among themselves but each separately with φ_{σ_-} and φ_{τ_-}. In this case, many of the formulas in Secs. III A to VI are directly applicable if the following implicit summation is taken over σ_+:

$$\mu_\tau\mu_\sigma \frac{w_{\sigma_+}/\omega}{1-(w_{\sigma_+}/\omega)^2} \rightarrow \sum_{\sigma_+=1}^{n_+} \mu(\tau_-,\sigma_+)\mu(\sigma_-,\sigma_+)\frac{w_{\sigma_+}/\omega}{1-(w_{\sigma_+}/\omega)^2} . \quad (7.1)$$

This agrees with results[20] based on stationary perturbative theory valid in this domain of moderate field intensities.

In conclusion, *the significance of the field-induced effects on matters without actual absorption or emission of photons is that material properties in large volume can be rapidly switched on at no expense of photon energy*. In field-induced molecular predissociation, the flow of internal electronic-vibrational energy as fluorescence, or alternatively as kinetic energy, can be controlled by the laser-field parameters. For atomic and molecular collisions,

$$A + B + \Delta E \rightleftharpoons A + B^*,$$

$$AB + C \rightleftharpoons AC + B + \Delta E,$$

and in molecular dissociation, association, and inverse predissociation,

$$AB \rightleftharpoons A + B + \Delta E,$$

the laser field can be used to trigger the desired rate of exchange of electronic-vibrational energies *internally* and/or *externally* as kinetic energy *at no expense of laser photon energy*.

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[1]A. M. F. Lau and C. K. Rhodes, Phys. Rev. A 15, 1570 (1977). See also A. M. F. Lau and C. K. Rhodes, Bull. Am. Phys. Soc. 22, 90 (1977); *ibid.* 22, 451 (1977).

[2]For example, see C. Zener, Proc. R. Soc. A 140, 660 (1933).

[3]It is understood that when finer interactions are taken into consideration, the so-called true crossing may be a small avoided crossing. Even for these cases, the distinction between such a "true" crossing in the absence of the external field and the field-induced avoided crossing has a practical meaning when the field-induced energy gap is larger than the small field-free energy gap.

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[8]All the situations dealt with in this paper involve more than two states. For a two-state model, there is obviously no need in the adiabatic eigensolution to distinguish between systems with or without "parities": see N. M. Kroll and K. M. Watson, Phys. Rev. A 13, 1018 (1976).

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

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[11]A recent discussion and experiment is given by J. Carlsten, A. Szoke, and M. Raymer, Phys. Rev. A 15, 1029 (1977).

[12]All energies and interactions are given in angular frequency in this paper, unless explicitly stated otherwise.

[13]See, for general references, N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University, London, 1965); K. Smith, *The Calculation of Atomic Collision Processes* (Wiley, New York, 1971); E. E. Nikitin, *Theory of Elementary Atomic and Molecular Processes in Gases* (Oxford University, London, 1974); M. S. Child, *Molecular Collision Theory* (Academic, New York, 1974); *Dynamics of Molecular Collisions*, edited by W. H. Miller (Plenum, New York, 1976), Parts A and B.

[14]This should not be confused with the larger number $n(\geq 2)$ of charge states φ that we use to obtain $\hat{\Psi}_{\rho\sigma}$ through the solution of Eq. (2.1). For treatment of simultaneous transitions between three or more *charge-field* adiabatic states, see Sec. V of Ref. 10.

[15]By "*one* Π or Δ state," we include the doubly degenerate $\pm\Lambda$ states. Choosing the reflection plane defined by the internuclear axis and the linear polarization of the field, only the positive component of Π is coupled to Σ^+ and to the positive component of Δ.

[16]Since the final results use $\hat{T}_{\pm 2}$ calculated through Eq. (3.8), even a large error in calculating $\hat{T}_{M\pm 2}$ gives very accurate values of $\hat{T}_{\pm 2}$.

[17]By "field-induced" avoided crossing, we refer to the new avoided crossing formed between two originally true-crossing levels, as considered in this paper. An original avoided crossing being modified by the field is called "field-dressed" (Ref. 1). A "charge-field" avoided crossing is that formed between charge-field levels with resonant absorption or emission of photons (Refs. 8–10).

[18]If the energies w_{σ_+}, w_{τ_-}, or w_{σ_-} do not occur in the expressions as energy difference with some other relative energy, the convention that they are measured from $\frac{1}{2}[w_{\sigma_-}(R)+w_{\tau_-}(R)]$ at each R is already used. In such case w_{τ_-} or w_{σ_-} are equal to $\pm\frac{1}{2}|w_{\tau_-}-w_{\sigma_-}|$ depending on whether $w_{\tau_-} \gtrless w_{\sigma_-}$.

[19]R. S. Mulliken, J. Chem. Phys. 55, 288 (1971).

[20]A. M. F. Lau (unpublished).