Inelastic atom-atom scattering within an intense laser beam*

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An analysis is given of multiphoton transitions between discrete quasimolecular states during the near-adiabatic collision of atoms and/or molecules. The variation of level spacing with changing internuclear separation can permit resonance absorption of one or more photons. Sufficiently intense laser beams can also significantly distort the molecular structure to modify potential surfaces, change activation energies, and so on. Through these two mechanisms specific chemical reactions in gases can be made to occur with rates that depend on laser power.

I. INTRODUCTION

The intense electromagnetic fields that are achievable with lasers can cause multiphoton[1-4] transitions to occur in atoms and molecules with a significant probability. These fields can also appreciably distort the structure of atoms and molecules, leading to types of transitions that would not be observed for the undistorted particle.[5]

In the present paper we restrict ourselves to the study of radiative transitions between discrete states of particles that are in a very intense laser beam. If the beam has an angular frequency ω and the energy separation of a pair of states is $\Delta\epsilon$, energy conservation requires that

$$\Delta\epsilon = n\hbar\omega , \tag{1.1}$$

where n is a positive integer.[6] To satisfy the condition that n be an integer, three possibilities come immediately to mind. Perhaps the most obvious is that of tuning the laser frequency; this will not be studied here. The other two possibilities involve changing $\Delta\epsilon$. If the level separation $\Delta\epsilon$ is that of a quasimolecule formed during a collision of two molecules, then $\Delta\epsilon$ varies as the internuclear separation varies and Eq. (1.1) can be satisfied at certain positions on the potential surfaces. We shall see that, with the proper conditions, transitions can occur with high probability as the "resonance condition" Eq. (1.1) is satisfied. The final possibility considered here for satisfying Eq. (1.1) depends on the fact that $\Delta\epsilon$ depends on the laser-beam power P, so that $\Delta\epsilon(P) = n\hbar\omega$ can be satisfied, in general, for certain discrete values of P.

When two atoms (or molecules)[7] collide, then, in an intense laser beam, the adiabatic molecular potential curves (or surfaces)[7] $E_\lambda(R,P)$ depend not only on the internuclear separation R but also on the power flux P of the beam. Thus, the shape of potential surfaces, including potential barriers, may be varied by changing the laser power. This, along with the stimulated absorption and/or emission of photons, may provide a useful tool for controlling chemical reactions in gases or molecular beams, possibly stimulating lasing transitions, and so on.

Our treatment does not use perturbation theory for the electromagnetic field, but is restricted to a finite number of modes for the electromagnetic field and a finite number of discrete states for the quasimolecule. In fact, we shall study in detail here only the simple case of two molecular states and a single field mode.[8] A considerable literature exists describing radiation between two molecular states into a discrete set of cavity eigenmodes of the field.[9] This has been extended to a description of radiation of N identical two-level atoms into a discrete set of field modes.[10] These treatments have used the "rotating-wave approximation," which is quite inadequate for our present applications.

In Sec. II we formulate a general theory of radiative transitions between discrete states of two particles colliding in the focal spot of a laser beam.[11] Such a situation could be realized, for example, by doing an atomic-beam scattering experiment with a laser beam focused in the region of collision. The analysis of atomic structure in the laser beam is given in Sec. III and the analysis of transitions in the "resonance region," defined by Eq. (1.1), will be described in Sec. IV. Several numerical results are presented in Sec. V. Finally, in Sec. VI, the case is studied in which the laser power is varied to satisfy Eq. (1.1).

II. ATOMIC COLLISIONS WITHIN A FOCUSED LASER BEAM

We consider the slow, or near-adiabatic, collision of two atoms[7] within the focal volume of a laser beam. The beam is assumed to be uniform in space and time for the distances and times over which the collision occurs.

A. Cavity eigenmode description

We consider first the idealized case in which the collision occurs in a resonant (to the electromagnetic field) cavity of volume $\mathcal{V}$, whose dimensions are very large compared with the Bohr radius a_0. Only a small number N_c of cavity modes are excited.

For the detailed calculations of this paper we shall further restrict ourselves to the case of $N_c=1$ (only a single cavity mode is excited). It will be supposed that there is initially a *very large* number N_γ of photons in this mode. We shall see that this case leads to the same equations and transition probabilities as that of a purely classical, sinusoidal electromagnetic field.

The adiabatic molecular Hamiltonian for the two colliding atoms (or "quasimolecule") is written as h. The molecular states $\phi_\alpha=\phi_\alpha(\xi;R)$ are then solutions to the eigenvalue equation

$$h\phi_\alpha=w_\alpha(R)\phi_\alpha\,. \tag{2.1}$$

Here ξ refers to the electron coordinates and $\vec{\mathrm{R}}$ to the internuclear separation. This latter quantity is assumed to be a known function of the time t, having been calculated as classical motion on the appropriate molecular potential surfaces.

The Hamiltonian for the free radiation field is

$$K_\gamma=\sum_{\lambda=1}^{N_c}\hbar\,\omega_\lambda a_\lambda^\dagger a_\lambda\,, \tag{2.2}$$

where λ refers to the cavity eigenmode, ω_λ is the frequency, and a and $a^\dagger$ are photon annihilation and creation operators. Keeping only electric dipole transitions, that part of the Hamiltonian describing the interaction of the radiation field with a quasimolecule is

$$V_\gamma=-\vec{\mathcal{P}}\cdot\vec{\mathrm{A}}\,, \tag{2.3}$$

where A is the vector potential,

$$\vec{\mathrm{A}}=\sum_{\lambda=1}^{N_c}\left(\frac{2\pi\hbar c^2}{\omega_\lambda\mathcal{V}}\right)^{1/2}(a_\lambda^\dagger+a_\lambda)\hat{e}_\lambda\,, \tag{2.4}$$

and

$$\vec{\mathcal{P}}=\sum_j\frac{e_j}{m_jc}\vec{\mathrm{p}}_j\,. \tag{2.5}$$

Here e_j, m_j, and $\vec{\mathrm{p}}_j$ are the charge, mass, and momentum of the jth charged particle in the quasimolecule. The A^2 term has been neglected as giving a contribution only to the dielectric constant of the cavity.[12]

The Schrödinger equation is then[13]

$$H\psi=i\frac{\partial\psi}{\partial t}\,, \tag{2.6}$$

where

$$H=h+K_\gamma+V_\gamma\,. \tag{2.7}$$

Adiabatic eigenstates (with $\vec{\mathrm{R}}$ considered a parameter) of H satisfy the equation

$$H\Phi_\lambda=E_\lambda(\vec{\mathrm{R}})\Phi_\lambda\,. \tag{2.8}$$

Equation (2.6) represents the starting point for our analysis. Since we are treating the orbits of the two colliding atoms classically, the distance of separation $\vec{\mathfrak{R}}(t)$ is determined for the appropriate potential surface $E_\lambda(\vec{\mathrm{R}})$.

The Schrödinger equation (2.6) is to be integrated subject to the following boundary conditions: In the remote past the interaction V_γ has not been "turned on" and the quasimolecule is in the state $\alpha=1$. The relative velocity of the two atoms is V, directed parallel to the z axis, and the impact parameter is b. We have, then, prior to the collision,

$$z=Vt\,,\quad R^2=z^2+b^2\,. \tag{2.9}$$

The laser-beam interaction is slowly turned on and then the two particles collide. Following the collision the beam interaction is slowly turned off and the final quasimolecular state of the now separated atoms observed. The initial and final kinetic energies will, in general, be different, the difference being determined by over-all energy conservation (with the laser on). In the near-adiabatic limit, transitions between adiabatic states will occur only when two energy levels are very close to each other—called a "pseudo-level-crossing" here.

In preparation for our solving Eq. (2.6) let us expand ψ in states of the quasimolecule [Eq. (2.1)]:

$$\psi=\sum_\alpha\Gamma_\alpha(t)\phi_\alpha\,, \tag{2.10}$$

where Γ_α contains the dependence on photon occupation numbers. Substitution into Eq. (2.6) then gives us

$$ih\dot{\Gamma}_\alpha-\left(w_\alpha+\sum_{\nu=1}^{N_c}\hbar\,\omega_\nu a_\nu^\dagger a_\nu\right)\Gamma_\alpha=\sum_{\beta(\neq\alpha)}\langle\phi_\alpha|\vec{\mathcal{P}}\phi_\beta\rangle\cdot\vec{\mathrm{A}}\Gamma_\beta-\sum_{\beta(\neq\alpha)}\hbar i\langle\phi_\alpha|\dot{\phi}_\beta\rangle\Gamma_\beta\,. \tag{2.11}$$

The phases of the ϕ_α have been taken to be independent of $\vec{R}$, so that the term corresponding to $\alpha=\beta$ in the second term on the right vanishes.

The matrix elements of $\mathcal{P}$ may be evaluated in conventional form[14] in terms of the oscillator strengths $f_{\alpha\beta}$ for the transition $\beta\to\alpha$. This lets us write (2.11) in the form

$$i\hbar\dot{\Gamma}_\alpha-\left(w_\alpha+\sum_{\nu=1}^{N_c}\hbar\omega_\nu a_\nu^\dagger a_\nu\right)\Gamma_\alpha$$
$$=\sum_\beta\sum_{\nu=1}^{N_c}g_{\alpha\beta}^\nu e^{i\phi_{\alpha\beta}}(a_\nu+a_\nu^\dagger)\Gamma_\beta-\sum_{\beta(\neq\alpha)}i\hbar\langle\phi_\alpha|\dot{\phi}_\beta\rangle\Gamma_\beta, \tag{2.12}$$

and the nonradiative term has been dropped, where

$$g_{\alpha\beta}^\nu=g_{\beta\alpha}^\nu=\hbar\omega_\nu\left[2\pi\left(\frac{e^2}{\hbar c}\right)\frac{|w_\alpha-w_\beta|}{\hbar\omega_\nu}|f_{\alpha\beta}|\left(\frac{\mathrm{Ry}}{\hbar\omega_\nu}\right)\right.$$
$$\left.\times\frac{a_0^2}{\hbar\omega_\nu^2}\left(\frac{\hbar\omega_\nu c}{v}\right)\right]^{1/2}, \tag{2.13}$$

and $\phi_{\alpha\beta}=-\phi_{\beta\alpha}$ is the phase of the matrix element of $\vec{\mathcal{P}}\cdot\hat{e}_\nu$.

In the remainder of this paper we shall restrict ourselves to the two-state approximation for the quasimolecule, corresponding (say) to $\alpha=1,2$. Then the phase $\phi_{\alpha\beta}$ can be eliminated and g^ν can be written for $g_{12}^\nu=g_{21}^\nu$. We may also take $i\langle\phi_1|\dot{\phi}_2\rangle$ real, in which case $i\langle\phi_1|\dot{\phi}_2\rangle=i\langle\phi_2|\dot{\phi}_1\rangle$. Then, with

$$\underline{\Gamma}\equiv\begin{pmatrix}\Gamma_1\\ \Gamma_2\end{pmatrix},$$

we have

$$i\hbar\dot{\underline{\Gamma}}=\left(\tfrac{1}{2}(w_1+w_2)+\tfrac{1}{2}\sigma_z(w_1-w_2)+\sum_{\lambda=1}^{N_c}\hbar\omega_\lambda a_\lambda^\dagger a_\lambda\right)\underline{\Gamma}$$
$$+\left(\sum_{\lambda=1}^{N_c}g^\lambda(a_\lambda+a_\lambda^\dagger)\right)\sigma_x\underline{\Gamma}-i\hbar\langle\phi_1|\dot{\phi}_2\rangle\sigma_x\underline{\Gamma}, \tag{2.14}$$

where $\sigma_x\sigma_z$ are the Pauli spin matrices. This is formally equivalent to a finite set of harmonic oscillators with linear coupling to a spin-$\frac{1}{2}$ system.

Equation (2.14) may be further simplified for the case of a single, strongly driven cavity eigenmode. In this case, let there be N_γ photons initially present in this mode and let $\Omega(N_\gamma-\sigma)$ be a cavity eigenfunction corresponding to $N_\gamma-\sigma$ photons in the cavity. We may then write

$$\Gamma_1=\left(\sum_{\nu\ \mathrm{even}}A_\nu\Omega(N_\gamma-\nu)+\sum_{\nu\ \mathrm{odd}}B_\nu\Omega(N_\gamma-\nu)\right)$$
$$\times\exp\left(-i\int^t(w_1+N_\gamma\hbar\omega)\,dt'\right),$$
$$\Gamma_2=\left(\sum_{\nu\ \mathrm{odd}}A_\nu\Omega(N_\gamma-\nu)+\sum_{\nu\ \mathrm{even}}B_\nu\Omega(N_\gamma-\nu)\right)$$
$$\times\exp\left(-i\int^t(w_1+N_\gamma\hbar\omega)\,dt'\right). \tag{2.15}$$

Because we have considered the laser field to be very intense, we can suppose that $N_\gamma\gg|\nu|$ above and write (we drop the mode subscript now)

$$a\Omega(N_\gamma-\nu)\cong(N_\gamma)^{1/2}\Omega(N_\gamma-\nu-1),$$
$$a^\dagger\Omega(N_\gamma-\nu)\cong(N_\gamma)^{1/2}\Omega(N_\gamma-\nu+1).$$

At this point it is convenient to put Eq. (2.14) into dimensionless form with the variables

$$Y\equiv Vt/a_0,\quad G\equiv(a_0/\hbar V)(N_\gamma)^{1/2}g,$$
$$G_x\equiv(ia_0/V)\dot{\vec{R}}\cdot\langle\phi_1|\nabla_R\phi_2\rangle,\quad F\equiv a_0\omega/V,$$
$$W\equiv(a_0/\hbar V)(w_2-w_1),$$
$$W_\nu\equiv W-\nu F,\quad \nu\ \text{an odd integer},$$
$$\equiv-\nu F,\quad \nu\ \text{an even integer},$$
$$W_\nu'\equiv W_{\nu-1}-F. \tag{2.16}$$

With these definitions and the use of Eqs. (2.15) we can write Eqs. (2.14) for the case of a single strongly driven mode as

$$i\dot{A}_\nu-W_\nu A_\nu=G[A_{\nu+1}+A_{\nu-1}]+G_xB_\nu, \tag{2.17a}$$

$$i\dot{B}_\nu-W_\nu'B_\nu=G[B_{\nu+1}+B_{\nu-1}]+G_xA_\nu, \tag{2.17b}$$

where ν runs over all integers, including zero, and (henceforth)

$$\dot{A}_\nu\equiv\frac{dA_\nu}{dY},\quad \dot{B}_\nu\equiv\frac{dB_\nu}{dY}. \tag{2.18}$$

In the adiabatic limit the G_x terms are to be neglected, since G_x/G, G_x/F, and G_x/W all vanish in this limit.

Under some conditions the energy of the colliding particles may be sufficiently high that a straight-line trajectory may be used. Then we have

$$R^2=Y^2+b^2 \tag{2.19}$$

(all distances are measured in units of a_0) and integration of Eqs. (2.17) is considerably simplified.

To make our discussion in the remainder of this paper appear specific, we shall discuss the case that

$$W>0\,, \tag{2.20}$$

or $w_2>w_1$, so a transition from state 1 to state 2 will extract energy from the radiation field. Our results also apply directly to the case that $W<0$, or electronic energy is transferred to the radiation field.

The derivation of Eqs. (2.17) for the case of a purely classical electromagnetic field is given in Appendix A.

B. Numerical relations

The dimensionless coefficient G in Eqs. (2.17) may be written in the form

$$G=F\left[\frac{2\pi e^2}{\hbar c}\left(\frac{\mathrm{Ry}}{\hbar\omega}\right)p_0\frac{a_0^2U_L}{\hbar\omega^2}\right]^{1/2}. \tag{2.21}$$

Here

$$p_0\equiv W(\infty)/F \tag{2.22}$$

represents the ratio of the level separation at $Y=\infty$ to the photon energy. The quantity U_L is

$$U_L\equiv\frac{w_2(Y)-w_1(Y)}{w_2(\infty)-w_1(\infty)}\,|f_{12}|P_L\,, \tag{2.23}$$

where

$$P_L=N_\gamma\hbar\omega c/\mathcal{V} \tag{2.24}$$

is the laser power flux. Since we do not wish to specify the Y dependence of f_{12}, we shall treat U_L as a constant in our analysis. (This simplification is in no way essential for our method, but is convenient for this exploratory study.)

If we express U_L in MW/cm^2 and the wavelength of the radiation λ in micrometers, then

$$G/F=(5.0\times10^{-8}p_0U_L\lambda^3)^{1/2}. \tag{2.25}$$

This is plotted as a function of U_L in Fig. 1 for several wavelengths.

The dimensionless frequency parameter F can be written as

$$F=10/\lambda V\,, \tag{2.26}$$

where again λ is in μm and V is in cm/μsec.

If the reactions which we are studying occur in a gas it may be desirable to keep the laser-beam power level below that at which cascade ionization develops. To illustrate this, we consider the breakdown threshold in air, which is[15]

$$P_B=3.2\times10^5/\lambda^2\ \mathrm{MW/cm^2}. \tag{2.27}$$

If we write $U_L=|f_{12}|P_B$ and substitute this into Eq. (2.25), there results

$$G/F\,|_B=0.13(|f_{12}|p_0\lambda)^{1/2} \tag{2.28}$$

as the value of the coupling strength at breakdown.

III. ADIABATIC STATES

We first consider the integration of Eqs. (2.17) in the adiabatic approximation. As described in Sec. II, we suppose that in the remote past ($t\to-\infty, Y\to-\infty$) the atoms are separated and in the quasimolecular state 1, so

$$\lim_{y\to-\infty}A_0=1,\quad A_\nu=0\ \text{ for }\nu\neq0\,. \tag{3.1}$$

The adiabatic approximation to Eqs. (2.17) is obtained on writing

$$A_\nu(Y)=\exp\left(-i\int^Y\mathcal{E}_\lambda(Y')\,dY'\right)A_\nu^{(\lambda)}(Y)\,, \tag{3.2a}$$

$$B_\nu(Y)=\exp\left(-i\int^Y\mathcal{E}'_\lambda(Y')\,dY'\right)B_\nu^{(\lambda)}(Y)\,, \tag{3.2b}$$

and introducing the approximate relations

$$i\dot{A}_\nu\cong\mathcal{E}_\lambda A_\nu\,,\quad i\dot{B}_\nu\cong\mathcal{E}'_\lambda B_\nu\,,\quad G_x=0$$

into Eqs. (2.17). There results the set of eigenvalue equations

$$(\mathcal{E}_\lambda-W_\nu)A_\nu^{(\lambda)}=G(A_{\nu+1}^{(\lambda)}+A_{\nu-1}^{(\lambda)})\,, \tag{3.3a}$$

$$(\mathcal{E}'_\lambda-W'_\nu)B_\nu^{(\lambda)}=G(B_{\nu+1}^{(\lambda)}+B_{\nu-1}^{(\lambda)})\,, \tag{3.3b}$$

where λ labels a particular eigenfunction $A_\nu^{(\lambda)}$ (or $B_\nu^{(\lambda)}$) and eigenvalue $\mathcal{E}_\lambda$ (or $\mathcal{E}'_\lambda$), both depending parametrically on Y. Using the relation $W'_\nu=W_{\nu-1}-F$ and setting $\mathcal{E}'_\lambda=\mathcal{E}_\lambda-F$, $B_\nu^{(\lambda)}=A_{\nu-1}^{(\lambda)}$, Eq. (3.3b) is seen to reduce to (3.3a). Hence it will be sufficient to discuss (3.3a).

No transitions occur in the adiabatic approximation, of course. The system remains in the eigenmode that corresponds to the boundary condition (3.1) as first $Y\to-\infty$ then $G\to0$. As $Y\to+\infty$, and $G\to0$, following the scattering, we again have

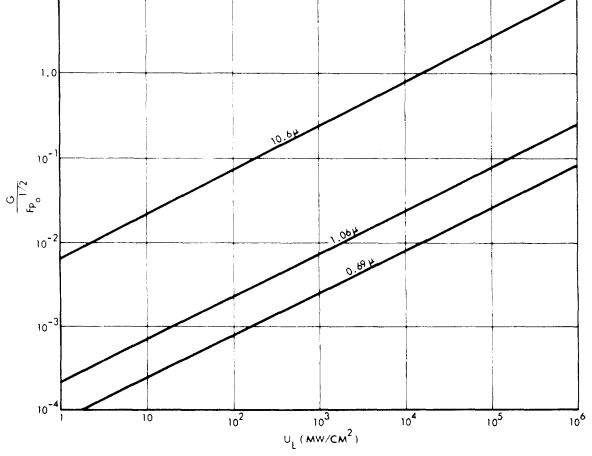

FIG. 1. Coupling constant $(G/F)p_0^{-1/2}$ shown as a function of the laser power parameter U_L [Eq. (2.25)].

$A_\nu = \delta_{\nu,0}$, just as in Eq. (3.1) with no photon absorption or state transition. Thus, to study transitions, we must evaluate Eq. (2.17) in an approximation that includes nonadiabatic corrections. This will be done in Sec. IV and will be formulated in terms of transitions between eigenmodes. Before doing this, we need to study some properties of the eigenfunction $\vec{A}^{(\lambda)}$.

In passing, we note that the eigenfunctions of H [Eq. (2.8) with R fixed] are

$$\Phi_\lambda = \sum_{\alpha,\nu} \phi_\alpha \Omega(N_\gamma - \nu) A_\nu^{(\lambda)} . \tag{3.4}$$

The corresponding eigenvalues are

$$E_\lambda = w_1 + (\hbar V/a_0)\mathcal{E}_\lambda + N_\gamma \hbar\omega . \tag{3.5}$$

For sufficiently small G, Eqs. (3.3) may be replaced by

$$(\mathcal{E}_\lambda - W_\nu) A_\nu^{(\lambda)} = 0 , \tag{3.6}$$

with the solutions

$$A_\nu^{(\lambda)} = \delta_{\nu\lambda} , \tag{3.7}$$

$$\mathcal{E}_\lambda = W_\lambda . \tag{3.8}$$

These correspond, of course, to adding (or subtracting) the energy of λ photons from the two basic quasimolecular states $(0, W)$. For $G \neq 0$, we index the eigenvalues $\mathcal{E}_\lambda(G)$ and eigenmodes $A_\nu^{(\lambda)}(G)$ by the requirement that $\mathcal{E}_\lambda(G) \to W_\lambda$, $A_\nu^{(\lambda)}(G) \to \delta_{\nu\lambda}$ as $G \to 0$.

All solutions of Eq. (3.3) can be constructed from any single solution by means of a simple algebraic procedure. To see this, let us assume that $\mathcal{E}_\sigma$ and $A_\nu^{(\sigma)}$ are known for some σ. Then we assert that

$$\mathcal{E}_{\sigma+2n} = \mathcal{E}_\sigma - 2nF , \tag{3.9}$$

$$A_\nu^{(\sigma+2)} = A_{\nu-2n}^{(\sigma)} , \tag{3.10}$$

as may be directly verified by substitution. Equation (3.10) exhibits the relation between solutions of the same parity in λ.

To relate a λ-odd to a λ-even eigensolution, consider $\lambda = 0$ and $\lambda = \sigma$, σ odd. Then,

$$\mathcal{E}_\sigma = W_\sigma - \mathcal{E}_0 , \tag{3.11}$$

$$A_{\sigma-\nu}^{(\sigma)} = (-1)^\nu A_\nu^{(0)} , \tag{3.12}$$

as may also be verified by substitution.

The eigenvalues $\mathcal{E}_\lambda$ are *even* functions of G. The energy $\mathcal{E}_0$ is even in F and odd in W.

Before presenting some numerical analysis of the eigenvalue equation (3.3), let us describe several qualitative features of its solutions. To be specific, let us consider a situation for which $W(Y)$ [Eq. (2.16)] has a Landau-Zener minimum at $Y = Y_m$, as is illustrated in Fig. 2. At this point we set

$$W(Y_m) \cong F p_m , \tag{3.13a}$$

where p_m is the ratio of energy gap at Y_m to the single-photon energy. For $Y \to \infty$, W is a constant, having the value

$$W(\infty) = F p_0 . \tag{3.13b}$$

The behavior of the unperturbed eigenvalue spectrum [Eq. (3.8)] is illustrated in Fig. 3. The two sets of curves are obtained from the two basic curves of Fig. 2 by displacing these by integral multiples of $2F$. With the perturbation G "turned on," two things happen. The levels in Fig. 3 are distorted and they are also rearranged so no crossings occur. This is illustrated in Fig. 4. Thus, the adiabatic perturbed curves involve a

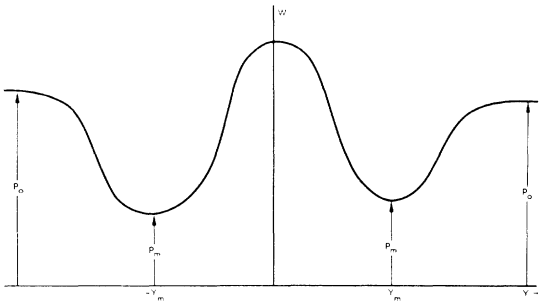

FIG. 2. Level spacing function W [Eq. (2.16)] shown as a function of position Y along the trajectory.

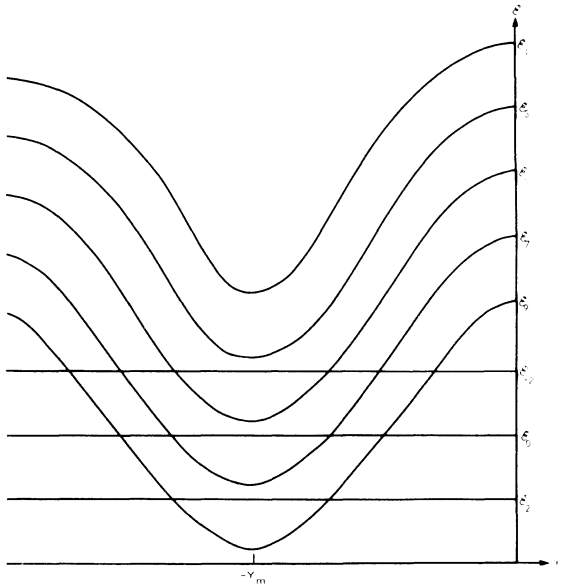

FIG. 3. Some curves of the unperturbed eigenvalue spectrum, Eq. (3.9). (Only the $Y<0$ part is shown.)

"switching" between the unperturbed modes of Eq. (3.6).

In accordance with the mode-indexing convention adopted above [just following Eq. (3.8)], the mode index ρ along a particular adiabatic curve switches as each "pseudocrossing" (henceforth referred to as a PC) is passed. The particular values of Y at which the index change occurs is indicated in Fig. 4. At these values of Y every curve experiences an index switch. While this convention may seem unnatural from the point of view of the adiabatic states, it leads ultimately to simpler bookkeeping.[16]

In addition to the solutions of Eq. (3.3a), illustrated in Fig. 3 and 4, there is a set of B modes obtained by displacing the A-mode energies down by F. Thus, there are (A,B) crossings between the (A,A) and (B,B) pseudocrossings. Since Eqs. (3.3a) and (3.3b) are uncoupled, the (A,B) crossings are true rather than pseudocrossings.

Now let us consider a typical scattering event. For large negative Y the system is in the state $\lambda = 0$ and moving in from the left along the 0 curve in Fig. 4. We shall see in Sec. IV that for sufficiently small G and G_x the system always remains on this horizontal curve, corresponding to a straight line in Fig. 4. However, if G is finite and the velocity small enough, the system will always remain on the same adiabatic curve, moving from curve 0 to curve 9, from curve 9 to curve 2, and then, after passing through 9 again, ultimately back to 0. In both of these cases *no transition occurs*, since the final state corresponds to curve 0. Only when the probability of curve jumping lies between zero and unity can a transition occur. The detailed analysis of these transitions will be given in Sec. IV.

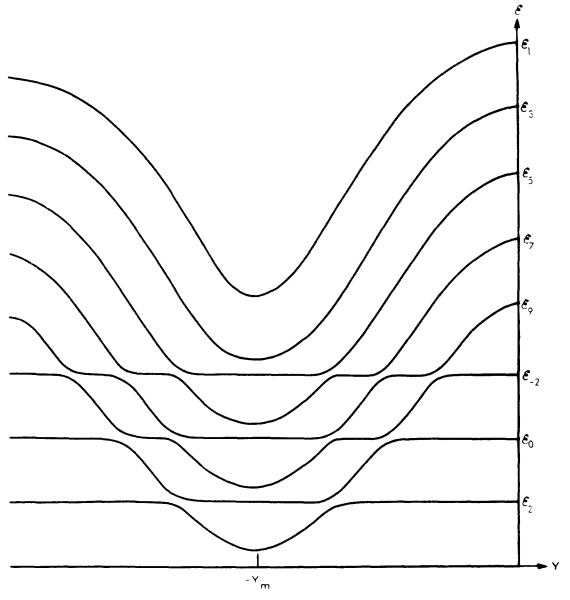

FIG. 4. Modification of the levels of Fig. 3 when the perturbation is "turned on."

The eigenvalue equation (3.3) was studied numerically with a vector A_ν of maximum dimensionality of 121 corresponding to $-60 \le \nu \le 60$. For Y not near a pseudocrossing, the following technique was used:

Equation (3.3) is written as

$$A_\nu = g_\nu (A_{\nu+1} + A_{\nu-1}), \qquad g_\nu = G/(\mathcal{E} - W_\nu). \tag{3.14}$$

For $\nu > 0$, we write

$$A_\nu = g_\nu H_\nu A_{\nu-1} \tag{3.15}$$

and obtain from Eq. (3.14)

$$H_\nu = 1/(1 - g_\nu g_{\nu+1} H_{\nu+1}). \tag{3.16}$$

Letting the maximum value of ν be M, we determine H_M from the postulate that

$$H_M = 1/(1 - g_M g_{M+1} H_M). \tag{3.17}$$

Having H_M we can calculate from Eq. (3.16) $H_{M-1}, H_{M-2}, \ldots, H_1$. Now,

$$A_1 = g_1 H_1 A_0. \tag{3.18a}$$

For $\nu < 0$, a similar procedure gives

$$A_{-1} = g_{-1} H_{-1} A_0. \tag{3.18b}$$

Finally, using the equations

$$A_0 = g_0 (A_1 + A_{-1})$$

and

$$g_0 = G/\mathcal{E},$$

we obtain

$$\mathcal{E} = G(g_1 H_1 + g_{-1} H_{-1}). \tag{3.19}$$

If an initial value is assumed for $\mathcal{E}$, Eq. (3.19) gives a next estimate. By iteration of this procedure the eigenvalue of $\mathcal{E}$ was found. The eigenvectors were obtained (when needed) from Eq. (3.15) and the corresponding set for $\nu < 0$. The eigenvector $\vec{A}$ was then normalized to unity by a suitable choice of A_0.

The above procedure usually converged in a few iterations. The mode to which it converges depends on the original choice of $\mathcal{E}$ with which one begins the iterations. Continuous variation of $\mathcal{E}$ with G gave assurance that $\mathcal{E}_0$ was being determined.

Near the pseudocrossing the level separation was generally very small and a different procedure was required. Let us suppose the pseudocrossing

of interest occurs at $Y = Y_\sigma$, the levels corresponding to $\lambda = 0$ and $\lambda = \sigma$ (σ a positive odd integer; recall that we can generate all other levels from this pair). For $\nu > \sigma$, we use the procedure outlined in Eqs. (3.15)–(3.17) to calculate $A_{\sigma+1}$, $A_{\sigma+2}, \ldots, A_M$ in terms of $\mathcal{E}$ and A_σ. For example,

$$A_{\sigma+1} = g_{\sigma+1} H_{\sigma+1} A_\sigma . \tag{3.20}$$

For $\nu < 0$, we also calculate as before A_{-1}, $A_{-2}, \ldots, A_{-M}$ in terms of A_0, the first expression being (3.18b).

In the interval $0 < \nu < \sigma$, we write

$$A_\nu = \Gamma_\nu^+ A_0 + \Gamma_\nu^- A_\sigma , \tag{3.21}$$

where Γ_ν^+ and Γ_ν^- are independent of A_0 and A_σ. To evaluate Γ_ν^+, we set $A_\sigma = 0$. Then, from Eqs. (3.14), we obtain

$$A_{\sigma-1} = g_{\sigma-1} A_{\sigma-2} \quad \text{or} \quad \Gamma_{\sigma-1}^+ = g_{\sigma-1} \Gamma_{\sigma-2}^+ . \tag{3.22}$$

Also, we introduce the relations

$$\Gamma_\nu^+ = g_\nu H_\nu \Gamma_{\nu-1}^+ , \tag{3.23}$$

with

$$H_{\sigma-1} = 1 , \quad \Gamma_0^+ = 1 . \tag{3.24}$$

The H's are seen to satisfy Eq. (3.16) for $\nu = \sigma - 2$, $\sigma - 3, \ldots, 1$. The Γ_ν^+'s are thus determined.

To evaluate the Γ_ν^-, we set $A = 0$ and then have

$$A_1 = g_1 A_2 \quad \text{or} \quad \Gamma_1^- = g_1 \Gamma_2^- . \tag{3.25}$$

In analogy to Eq. (3.23) we introduce the relations

$$\Gamma_\nu^- = g_\nu \hat{H}_\nu \Gamma_{\nu+1}^- , \tag{3.26}$$

with

$$\hat{H}_1 = 1 , \quad \Gamma_\sigma^- = 1 . \tag{3.27}$$

The $\hat{H}$'s are seen to satisfy the recurrence relations

$$\hat{H}_\nu = 1/(1 - g_\nu g_{\nu-1} \hat{H}_{\nu-1}) , \quad \nu = 2, 3, \ldots, \sigma - 1 . \tag{3.28}$$

The $\hat{H}_\nu$'s and Γ_ν^-'s are now determined. In particular, we have

$$\begin{aligned} A_1 &= g_1 H_1 A_0 + \Gamma_1^- A_\sigma , \\ A_{\sigma-1} &= \Gamma_{\sigma-1}^+ A_0 + g_{\sigma-1} \hat{H}_{\sigma-1} A_\sigma . \end{aligned} \tag{3.29}$$

With the definitions

$$\begin{aligned} &G' \equiv G \Gamma_{\sigma-1}^+ , \quad G'' \equiv G \Gamma_1^- , \\ &\Delta_0 \equiv G(g_1 H_1 + g_{-1} H_{-1}) , \\ &\Delta_\sigma \equiv W_\sigma + G(g_{\sigma+1} H_{\sigma+1} + g_{\sigma-1} \hat{H}_{\sigma-1}) , \end{aligned} \tag{3.30}$$

Eqs. (3.14) for $\nu = 0$ and $\nu = \sigma$ become

$$(\mathcal{E} - \Delta_\sigma) A_\sigma = G' A_0 , \quad (\mathcal{E} - \Delta_0) A_0 = G'' A_\sigma . \tag{3.31}$$

These two equations will be used to determine the pair of eigenvalues $\mathcal{E}_\pm$ [Eq. (3.35)] at the PC.

It is shown in Appendix B that when the levels $\lambda = 0$ and $\lambda = \sigma$ are much closer together than is either to a third level, we can set

$$G' = G'' \tag{3.32}$$

and

$$\Delta_\sigma + \Delta_0 = W_\sigma . \tag{3.33}$$

Thus,

$$\begin{aligned} &\Delta_\sigma - \Delta_0 = W_\sigma + \Delta W , \\ &\Delta W = -2G(g_1 H_1 + g_{-1} H_{-1}) . \end{aligned} \tag{3.34}$$

The eigenvalues, obtained from Eq. (3.31), are seen to be

$$\mathcal{E}_\pm = \tfrac{1}{2}\{W_\sigma \pm [(W_\sigma + \Delta W)^2 + 4G'^2]^{1/2}\} . \tag{3.35}$$

For all cases of interest to us $|G'| \ll 1$ and is a slowly varying function of $\mathcal{E}$. The point of closest approach is then given by

$$W_\sigma + \Delta W = 0 , \tag{3.36}$$

where the level splitting is $2|G'|$.

When G is sufficiently small that perturbation theory may be used, we have

$$\Delta W \cong \frac{4G^2 W}{W^2 - F^2} , \quad G' \cong G\left(\prod_{\lambda=1}^{\sigma-1} g_\lambda \right) . \tag{3.37}$$

At the point of closest approach of the levels,

$$\mathcal{E}_\pm = -\Delta W/2 \pm |G'| . \tag{3.38}$$

In the vicinity of the PC we evaluate ΔW and $|G'|$ with the mean value

$$\bar{\mathcal{E}} = -\Delta W(\bar{\mathcal{E}})/2 \tag{3.39}$$

rather than "self-consistently" with $\mathcal{E}_\pm$. This is justified because both quantities are smooth functions of $\mathcal{E}$, and because $|G'|$ is very small. The only Y dependence of $\mathcal{E}$ as given by Eq. (3.35) then results from the Y dependence of $W_\sigma(Y)$.

Near the PC's, numerical evaluation of G' and ΔW was performed as outlined above with trial values of $\mathcal{E}$. The root $\mathcal{E}_-$ was determined from Eq. (3.35) by iteration. Since W_σ is a known function, $\mathcal{E}_+$ can be obtained as $\mathcal{E}_+ = W_\sigma - \mathcal{E}_-$ consistent with Eq. (3.12). The point of closest approach was next determined by calculation for a sequence of Y values. At the point of closest approach, we have

$$\mathcal{E}_+ \cong \mathcal{E}_- \cong \bar{\mathcal{E}}$$

to an excellent approximation. For the time-dependent calculations of Sec. IV this fixed value of $\mathcal{E} \cong \bar{\mathcal{E}}$ was used to evaluate ΔW and G' near the PC.

For some illustrative calculations of the eigen-

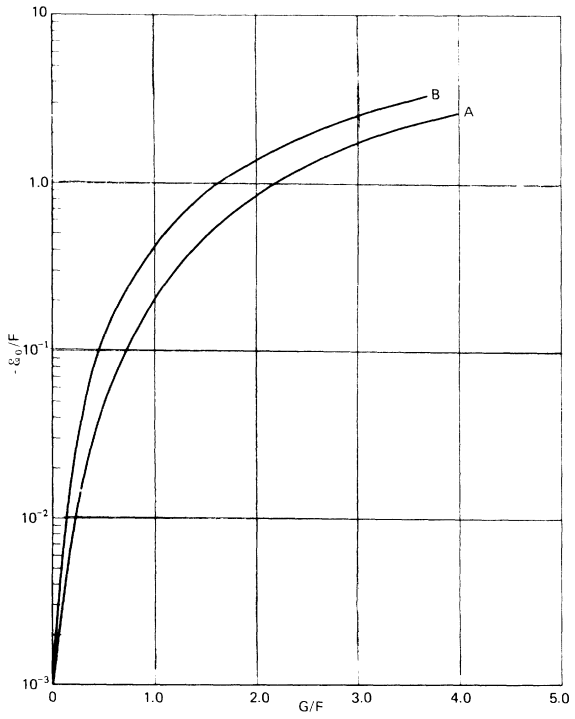

FIG. 5. Eigenvalue $\mathcal{E}_0/F$ as a function of coupling constant for cases A and B [Eqs. (3.41)].

values the following form was chosen for $W(Y)$ [Eq. (2.16)]:

$$W(Y)=F[p_0-2R_0^2(p_0-p_m)(1/R^2-R_0^2/2R^4)]\,, \tag{3.40}$$

with $R^2=Y^2+b^2$. At $R=R_0$, W has its minimum value Fp_m, while for $R\to\infty$, $W\to Fp_0$ (see Fig. 2).

We describe now two typical numerical examples. The parameters chosen were

$$\begin{aligned} &R_0=1\,,\quad b=0.1\,,\\ &p_0=14.1\,,\quad p_m=8.2\,,\quad \text{case A}\\ &p_0=8.1\,,\quad p_m=4.1\,,\quad \text{case B}\,. \end{aligned} \tag{3.41}$$

The eigenvalue $\mathcal{E}_0/F$ is shown as a function of G/F in Fig. 5 for $R(Y_m)=1$, or $W=Fp_m$. For small G/F, we have just the value from perturbation theory [see Eq. (3.37)]:

$$\mathcal{E}_0=-2F\frac{(G/F)^2p_m}{p_m^2-1}\,. \tag{3.42}$$

For the odd levels at $R(Y_m)=1$, we have from Eq. (3.11)

$$\mathcal{E}_\sigma=F(p_m-\sigma+2\mathcal{E}_0/F)\,,\quad \sigma\ \text{odd}\,. \tag{3.43}$$

When G/F is small we have PC's for $\sigma=9,11,13$ photons for case A and $\sigma=5,7$ photons for case B. There are, in addition, true crossings for $\sigma=10$, 12, 14 photons for case A and $\sigma=6$, 8 photons for case B. For larger G, displacement of the levels changes the photon numbers at which PC's occur. This is illustrated in Table I. For example, for case A with small G the minimum number of photons to give a transition is 9. When $G\approx 4$, at least 15 photons are required.

The quantity $|G'|/F$ is shown for case A in Fig. 6 as a function of G/F at the PC's. The curves are labeled by the number of photons required for the transition (compare with Table I). The value of G/F at which a PC disappears is indicated by a circle at the termination of the curve. An arrow is shown to indicate that the curves were not evaluated for G/F beyond the range shown. From Eq. (3.38) we recall that $|G'|/F$ is just one-half the level separation (divided by F) at the PC. As we have indicated, this tends to be small compared with unity.

Since we are primarily interested in situations in which F/W is small, an attempt was made to develop an analytic approximation for $\mathcal{E}_0$ suggested by the static-field Stark effect. A good approximation is provided by the expression

$$\mathcal{E}_0=\frac{W}{2}\left[1-\frac{2}{\pi}\left(1+\frac{16G^2}{W^2-F^2}\right)^{1/2}E(k)\right]\,, \tag{3.44}$$

where

$$E(k)\equiv\int_0^{\pi/2}d\theta\,(1-k^2\sin^2\theta)^{1/2}$$

TABLE I. Numbers of photons for which PC's occur [see Eq. (3.41)].

Case A		Case B	
G/F interval	Number of photons	G/F interval	Number of photons
$0 < G/F < 1.5$	9, 11, 13	$0 < G/F < 1.1$	5, 7
$1.5 < G/F < 2.3$	11, 13	$1.1 < G/F < 1.4$	7
$2.3 < G/F < 2.6$	11, 13, 15	$1.4 < G/F < 2.1$	7, 9
$2.6 < G/F < 3.3$	13, 15	$2.1 < G/F < 2.5$	9
$3.3 < G/F < 3.8$	13, 15, 17	$2.5 < G/F < 3.0$	9, 11
$3.8 < G/F \leq 4$	15, 17	$3.0 < G/F < 3.3$	11

is the complete elliptic integral of the second kind, and

$$k^2 = 16G^2/(W^2 - F^2 + 16G^2) .$$

Equation (3.44) is exact in the limit of either F/W or G/W small, and is consistent with the symmetry properties noted just after Eq. (3.12). It is within 3% of the correct value for the range shown in Fig. 5, and appears to become more accurate at the largest values of G (within 0.5%).

IV. TRANSITION PROBABILITIES

In Sec. III we discussed the eigenmodes of Eqs. (2.17) in the adiabatic limit—that is, solutions of Eq. (3.3). It was observed that when the internuclear separation Y changes at a finite rate, transitions can occur at the PC's. We now study these.

To do this we assume that transitions between only *two levels* at a time need be considered. For this assumption to be valid, we require that the separation between this pair of levels be much less than that between either level and a third level. To be specific, let us consider the PC that occurs at $Y = Y_\sigma$ for levels 0 and σ (where σ is a positive, odd integer). According to Eq. (3.35), the level separation at Y_σ is

$$\Delta\mathcal{E}_{0\sigma}(Y_\sigma) = 2|G'| ,$$

whereas the spacing between other levels tends to be about $2F$. Reference to Fig. 7 suggests that

$$|G'|/F \ll 1 ,$$

so our assumed condition that only one pair of levels need be considered at a PC has a considerable range of validity. Of course, for large enough velocity V, transitions between more distant levels can occur.

To integrate through the PC at $Y = Y_\sigma$, we return to Eqs. (2.17). For $\nu = 0$ and $\nu = \sigma$ we have

$$i\dot{A}_0 - \Delta_0 A_0 = G'A_\sigma , \quad i\dot{A}_\sigma - \Delta_\sigma A_\sigma = G'A_0 . \tag{4.1}$$

Here we have used the adiabatic approximations (3.29) as the solution to the less-singular components of Eqs. (2.17), corresponding to $\nu \neq 0, \sigma$. Equations (4.1) reduce, of course, to Eqs. (3.31) in the adiabatic limit. Near the PC we assume that[17]

$$\Delta_\sigma - \Delta_0 \cong -\alpha t , \quad t \equiv Y - Y_\sigma , \tag{4.2}$$

and introduce the relation

$$A_\sigma = \exp\left(-i\int^Y \Delta_0 dY'\right) e^{i(\alpha/4)t^2} U(t) . \tag{4.3}$$

Elimination of A_0 from Eqs. (4.1) then gives us the equation for U,

$$\frac{d^2U}{dt^2} + \left(G'^2 + i\frac{\alpha}{2} + \frac{\alpha^2 t^2}{4}\right)U = 0 . \tag{4.4}$$

It suffices to consider $\alpha > 0$, since α is real and, if a solution $U(t, |\alpha|)$ is found, then

$$U(t, -|\alpha|) = U^*(t, |\alpha|) . \tag{4.5}$$

On writing

$$p \equiv \frac{G'^2}{|\alpha|} , \quad n = ip , \quad Z = (|\alpha|)^{1/2} t e^{-i\pi/4} , \tag{4.6}$$

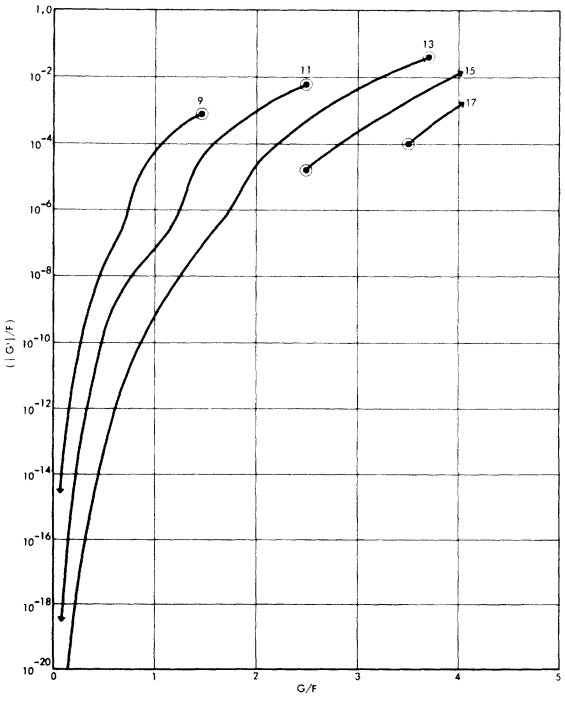

FIG. 6. Quantity $|G'|/F$ as a function of coupling constant and photon number σ. Case A [Eqs. (3.41)] is illustrated.

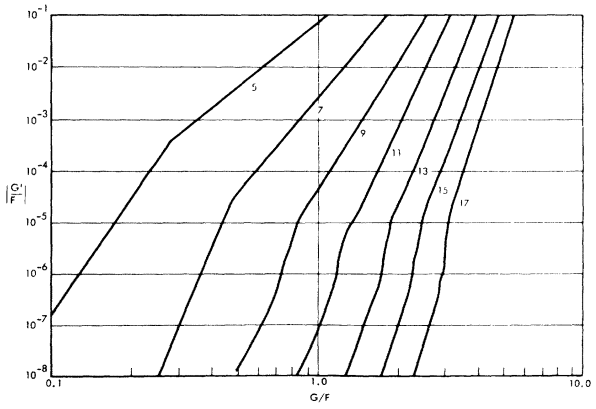

FIG. 7. Values of $|G'/F|$ as a function of G/F for several photon numbers.

we obtain Weber's equation[18] for U. Solutions of this are, in the notation of Ref. 18, $D_n(\pm Z)$ and $D_{-n-1}(\pm iZ)$. The solution that corresponds to the eigenmode 0 for negative t is $D_{-n-1}(-iZ)$.

The connection formula given in Ref. 18 gives the asymptotic solution for positive, large values of t. From this, A_σ and A_0 may be calculated. Comparison with the eigenmodes obtained from Eqs. (3.31) gives the connection formula across the PC. The calculation is straightforward, but a little tedious. For the initial condition that $\vec{A}=\vec{A}^{(0)}$ for $Y \ll Y_\sigma$, the result is

$$\vec{A}=e^{-\pi p}\vec{A}^{(0)}+e^{i\phi}(1-e^{-2\pi p})^{1/2}\vec{A}^{(\sigma)} \quad \text{for } Y \gg Y_\sigma . \tag{4.7}$$

Here ϕ is a phase factor that we shall not need explicitly. If the eigenmode lables 0 and σ are interchanged in Eqs. (4.7), corresponding to an initial eigenmode σ, then only the phase factor changes.

The probability for a transition $0 \to \sigma$ is seen to be $1-e^{-2\pi p}$. When the coupling constant G is sufficiently small, $p \simeq 0$ and the system remains on the $\mathcal{E}_0$ curve of Fig. 3. When $p \gg 0$, on the other hand, the motion is adiabatic, with the system remaining on one of the curves of Fig. 4.

The criterion of validity for Eqs. (4.8) is that we reach the asymptotic form of D functions for values of t small enough that the linear approximation (4.2) is still valid. If $p \lesssim 1$, then the asymptotic form of $D_{-n-1}(-iZ)$ is reached when $|Z|^2 \gg 1$ or when $|\alpha|\,\delta Y^2 \gg 1$, where δY is the distance from the PC. Now,

$$|\alpha| = \left(\frac{d}{dY}[(w_\sigma - w_0)/\mathrm{Ry}]\right)\frac{e^2}{\hbar V} . \tag{4.8}$$

In the adiabatic regime, for which $e^2/\hbar = 2\times 10^8$ cm/sec $\gg V$, we expect our Eqs. (4.8) to be useful. An exception occurs near those values of G/F at which a PC is lost and $|\alpha|$ is anomalously small, however.

We have seen in Table I and Fig. 6 that as G/F is increased we can lose PC's when W has a minimum value—say, at Y_m—as is the case for Eq. (3.40). This is illustrated in Fig. 8. As a PC approaches such a minimum from above, Eq. (4.8) no longer applies, both because of the failure of the linear approximation and because the two crossings on either side of the minimum are too close to be treated as independent. After the PC is lost (because of further increase in G/F), transitions between the indicated states 0 and σ may continue to occur as long as the level spacing remains sufficiently small.

To study this latter case we return to Eqs. (4.1) and, near $Y=Y_m$, we write

$$\Delta_\sigma - \Delta_0 \cong a + b(Y-Y_m)^2 , \tag{4.9}$$

where $a, b > 0$. If we write

$$Y - Y_m \equiv t + e^{i\pi/2}(a/b)^{1/2} , \tag{4.10}$$

then

$$\Delta_\sigma - \Delta_0 \cong i\alpha t , \quad \alpha \equiv 2(ab)^{1/2} . \tag{4.11}$$

On eliminating A_0 and making the transformation (4.3), we obtain once again Weber's equation. Now, however,

$$n = p - 1 , \quad Z = (\alpha)^{1/2} t , \tag{4.12}$$

where p is given in Eq. (4.6).

The connection formula may be obtained as before after a straightforward, but even more tedious calculation. The result, corresponding to Eq. (4.7), is, if $\vec{A}=\vec{A}^{(0)}$ for $Y \ll Y_m$, then

$$\vec{A}=e^{i\phi_1}\left\{\vec{A}^{(0)}+e^{i\phi_2}\frac{(2\pi p)^{1/2}}{\Gamma(1+p)}\exp\left[-\frac{2}{3}\left(\frac{a^3}{b}\right)^{1/2}\right]\vec{A}^{(\sigma)}\right\}$$

$$\text{for } Y \gg Y_m . \tag{4.13}$$

Here, ϕ_1 and ϕ_2 are phases not needed for our applications.

The validity of Eq. (4.13) requires that Eqs. (4.9) and (4.11) remain valid into the asymptotic regime of the D function. Also required for the matching is the condition

$$\exp[-\tfrac{2}{3}(a^3/b)^{1/2}] \ll 1 , \tag{4.14}$$

which is a requirement on the adiabatic approximation.

Near the value of G/F at which the PC is lost we have

$$\Delta_\sigma - \Delta_0 = \pm\,|a| + b(Y-Y_m)^2 , \tag{4.15}$$

where the plus sign refers to the condition of Eq. (4.8) and the minus sign to that of Eq. (4.13). In either case we have $|\alpha| = 2(|a|b)^{1/2}$. At just the value of G/F at which the PC is lost, $a=\alpha=0$ and our connection formulas are invalid. As the gap distance becomes large, the transition probability (4.13) becomes very small because of the exponential factor (4.14).

The preceding discussion applies unchanged to transitions between solutions of Eq. (3.3b) (B-B transitions) at pseudocrossings. To discuss the transitions that take place at a crossing of a solution of Eq. (3.3a) with a solution of Eq. (3.3b) (A-B transitions), we begin with

$$ih\dot{\underline{\Gamma}} = [\tfrac{1}{2}W(1-\sigma_z)+F(a^\dagger a - N_\gamma)]\underline{\Gamma}$$

$$+G\frac{a+a^\dagger}{(N_\gamma)^{1/2}}\sigma_x\underline{\Gamma}+G_x\sigma_x\underline{\Gamma} . \tag{4.16}$$

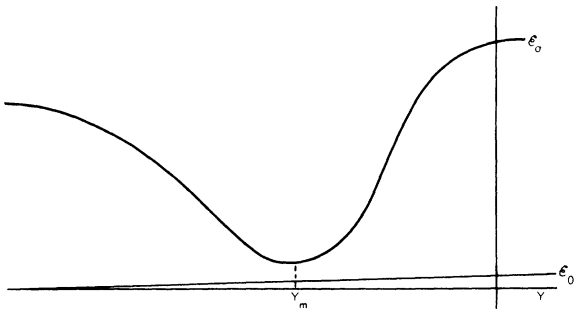

FIG. 8. Illustration of levels when a PC does not quite occur.

Equation (4.16) is the same as Eq. (2.14), specialized to a single cavity mode, expressed in terms of the variables and parameters defined in Eq. (2.16) (again a dot over a symbol means d/dY), and with the energy shifted by means of the time-dependent exponential factor appearing on the extreme right in Eq. (2.15). We now let $\underline{\Gamma}_a$ and $\underline{\Gamma}_b$ represent normalized adiabatic states determined by solutions of Eqs. (3.3a) and (3.3b), respectively. Explicitly [compare Eqs. (2.15) and (3.2)],

$$\underline{\Gamma}_a = \begin{pmatrix} \sum_{\nu \text{ even}} A_\nu^{(0)} \Omega(N_\gamma - \nu) \\ \sum_{\nu \text{ odd}} A_\nu^{(0)} \Omega(N_\gamma - \nu) \end{pmatrix}, \qquad \underline{\Gamma}_b = \begin{pmatrix} \sum_{\nu \text{ odd}} B_\nu^{\sigma} \Omega(N_\gamma - \nu) \\ \sum_{\nu \text{ even}} B_\nu^{\sigma} \Omega(N_\gamma - \nu) \end{pmatrix}, \tag{4.17}$$

where the $A_\nu^{(0)}$ and B_ν^{σ} satisfy Eqs. (3.3a) and (3.3b), respectively. Hence we have

$$[\tfrac{1}{2}W(1-\sigma_z) + F(a^\dagger a - N_\gamma)]\underline{\Gamma}_a + G\frac{a+a^\dagger}{(N_\gamma)^{1/2}}\sigma_x\underline{\Gamma}_a = \mathcal{E}_0\underline{\Gamma}_a\,, \tag{4.18}$$

$$[\tfrac{1}{2}W(1-\sigma_x) + F(a^\dagger a - N_\gamma)]\underline{\Gamma}_b + G\frac{a+a^\dagger}{(N_\gamma)^{1/2}}\sigma_x\underline{\Gamma}_b = \mathcal{E}'_\sigma\underline{\Gamma}_b\,.$$

In addition we assume $A_0^{(\sigma)}$ and $B_\sigma^{(\sigma)}$ real, in which case all the $A_\nu^{(\sigma)}$, $B_\nu^{(\sigma)}$ are real. Taking into account the normalization condition, we find

$$(\Gamma_a, \dot{\Gamma}_a) = (\Gamma_b, \dot{\Gamma}_b) = 0\,, \tag{4.19a}$$

and from Eq. (4.17) we can deduce (by inspection)

$$(\underline{\Gamma}_a, \dot{\underline{\Gamma}}_b) = (\underline{\Gamma}_b, \dot{\underline{\Gamma}}_a) = 0\,. \tag{4.19b}$$

We now assume that significant coupling occurs only between mode pairs with nearly equal energy and we write

$$\underline{\Gamma} = \alpha(Y)\underline{\Gamma}_a + \beta(Y)\underline{\Gamma}_b\,. \tag{4.20}$$

Substituting in Eq. (4.16), taking the inner product with $\underline{\Gamma}_a$ and $\underline{\Gamma}_b$, respectively, and using Eq. (4.19) and the equations

$$(\underline{\Gamma}_a, \sigma_x\underline{\Gamma}_a) = (\underline{\Gamma}_b, \sigma_x\underline{\Gamma}_b) = 0\,, \tag{4.21}$$

we find

$$\begin{aligned} i\dot{\alpha}(Y) - \mathcal{E}_\sigma(Y)\alpha(Y) &= G_x(\underline{\Gamma}_\alpha, \sigma_x\underline{\Gamma}_\beta)\beta(Y)\,, \\ i\dot{\beta}(Y) - \mathcal{E}'_\sigma(Y)\beta(Y) &= G_x(\underline{\Gamma}_\beta, \sigma_x\underline{\Gamma}_\alpha)\alpha(Y)\,. \end{aligned} \tag{4.22}$$

From the discussion following Eq. (3.3), crossing occurs only for odd σ, in which case the crossing condition $\mathcal{E}'_0 = \mathcal{E}_0$ is the same as $W - \mathcal{E}_0 = \mathcal{E}_0 + (\sigma+1)F$, corresponding to a transition with absorption of $\sigma+1$ photons. Furthermore,

$$\begin{aligned} G'_x &= G_x(\underline{\Gamma}_\beta, \sigma_x\underline{\Gamma}_\alpha) = G_x(\underline{\Gamma}_\alpha, \sigma_x\underline{\Gamma}_\beta) \\ &= G_x\sum_{\nu=-\infty}^{\infty} A_\nu^{(0)}B_\nu^{(0)} = G_x\sum(-1)^\nu A_\nu^{(1)}A_{\sigma+1-\nu}^{(0)}\,. \end{aligned} \tag{4.23}$$

Equation (4.22) is identical in form to Eq. (4.1) so that the previously derived formulas for the transition probability can be applied immediately. The ratio G'_x/G_x can be obtained from the solutions to the adiabatic states, and in the perturbation-theory limit is given by

$$(-1)^{(\sigma-1)/2}\frac{2}{[1\cdot3\cdot5\cdots\sigma]^2}\left(\frac{G_x}{F}\right)^{\sigma+1}\,.$$

We do not, however, have a satisfactory estimate of G_x. Presumably it is highly dependent on molecular structure and may well be small in many cases. The cross sections computed in the following sections omit the contribution from the A-B transitions. Inclusion of these transitions would yield larger excitation cross sections than those we shall compute, but we would not expect large increases.

V. EVALUATION OF THE CROSS SECTION

For a given impact parameter b the probability of a transition to the upper level of the quasimolecule is

$$P_2(b) = \lim_{Y\to\infty}\sum_{\nu \text{ odd}}|A_\nu|^2\,. \tag{5.1}$$

The probability that the system remains in the lower state is

$$P_1(b) = \lim_{Y\to\infty}\sum_{\nu \text{ even}}|A_\nu|^2 = 1 - P_2(b)\,. \tag{5.2}$$

The cross section for a transition to the upper level is then

$$\sigma_t = 2\pi \int db\, b P_2(b) . \tag{5.3}$$

It is expected that the integration over impact parameters will lead to phase oscillations that remove interference effects, so that we need calculate only transition probabilities and not amplitudes.

To obtain $P_2(b)$ we have the following prescription, based on the results of Secs. III and IV: With $\mathcal{E}_0$ determined numerically, as described in Sec. III, the adiabatic energy eigenvalues (2.8) are

$$\begin{aligned} E_\sigma(R) &= w_1 + (\hbar V/a_0)\mathcal{E}_0 + (N_\gamma - \sigma)\hbar\omega , \quad \sigma \text{ even} , \\ E_\sigma(R) &= w_2 - (\hbar V/a_0)\mathcal{E}_0 + (N_\gamma - \sigma)\hbar\omega , \quad \sigma \text{ odd} , \end{aligned} \tag{5.4}$$

except very near a PC. Removal of the field energy from these expressions gives us the adiabatic potential surfaces for levels 1 and 2 of the quasimolecule:

$$\begin{aligned} \mathcal{E}_{\text{ad}}^{(1)}(R) &= w_1(R) + (\hbar V/a_0)\mathcal{E}_0(R) , \\ \mathcal{E}_{\text{ad}}^{(2)}(R) &= w_2(R) - (\hbar V/a_0)\mathcal{E}_0(R) . \end{aligned} \tag{5.5}$$

[In using these expressions, we recall that G/F and $W/F = (w_2 - w_1)/\hbar\omega$ are independent of the asymptotic velocity V.] The classical motion for molecular state 1 is obtained from the equation

$$\frac{dR}{dt} = V\left[1 - \frac{\mathcal{V}_1(R)}{\epsilon} - \left(\frac{b}{R}\right)^2\right]^{1/2} , \tag{5.6}$$

where $\epsilon = MV^2/2$ and

$$\mathcal{V}_1(R) = \mathcal{E}_{\text{ad}}^{(1)}(R) - \mathcal{E}_{\text{ad}}^{(1)}(\infty) . \tag{5.7}$$

There are, of course, similar expressions for the motion in state 2. The PC's occur at those points R_σ(σ positive, odd integer) satisfying

$$\mathcal{E}_{\text{ad}}^{(2)}(R_\sigma) - \mathcal{E}_{\text{ad}}^{(1)}(R_\sigma) = \sigma\hbar\omega , \tag{5.8}$$

where R_σ is greater than the classical turning point at $dR/dt = 0$.

Returning to the "time" variable

$$Y = Vt/a_0 ,$$

we label the PC's as occurring at $Y_1, Y_2, \ldots, Y_N$, where $Y_1 < Y_2 < \cdots < Y_N$. Let $Q_\alpha(j)$, $\alpha = 1, 2$, be the probability that the system is in the quasimolecular level α when Y is in the interval $Y_j < Y < Y_{j+1}$, and let the starting condition be

$$Q_1(0) = 1 , \quad Q_2(0) = 0 , \tag{5.9}$$

corresponding to the assumption that the system is initially in level 1.

Recurrence relations for the Q's are

$$\begin{aligned} Q_1(j+1) &= T_n(j)Q_1(j) + T_t(j)Q_2(j) , \\ Q_2(j+1) &T_t(j)Q_1(j) + T_n(j)Q_2(j) , \end{aligned} \tag{5.10}$$

where from Eq. (4.8) we have

$$T_n(j) = e^{-2\pi p(j)} , \quad T_t(j) = 1 - T_n(j) \qquad j = 1, 2, \ldots, N . \tag{5.11}$$

Here $p(j)$ is the quantity (4.6) evaluated at the jth PC, as is illustrated in Fig. 9. Now,

$$p(j) = \left.\frac{G'^2}{|\alpha|}\right|_{R = R(Y_j)}$$

and

$$|\alpha| = \frac{F^2}{\omega}\left|\frac{dR}{dt}\frac{d}{dR}\left(\frac{\mathcal{E}_{\text{ad}}^{(2)} - \mathcal{E}_{\text{ad}}^{(1)}}{\hbar\omega}\right)\right| , \tag{5.12}$$

evaluated at $R(Y_j)$ [obtained from Eq. (5.8)]. The quantity dR/dt is obtained from Eq. (5.6) and $(G'/F)^2$ from Fig. 7. [Note that for the case with spherical symmetry discussed here, integration of the orbit equation (5.6) is unnecessary.]

The probability of a transition between a pair of levels at the point Y_m of closest approach (illustrated by the curves labeled $\mathcal{E}_7$ and $\mathcal{E}_0$ in Fig. 9) is obtained from Eq. (4.13) and taken into account in Eqs. (5.10).

Finally, the expressions (5.1) and (5.2) are reevaluated as

$$P_2(b) = Q_2(N) , \quad P_1(b) = Q_1(N) . \tag{5.13}$$

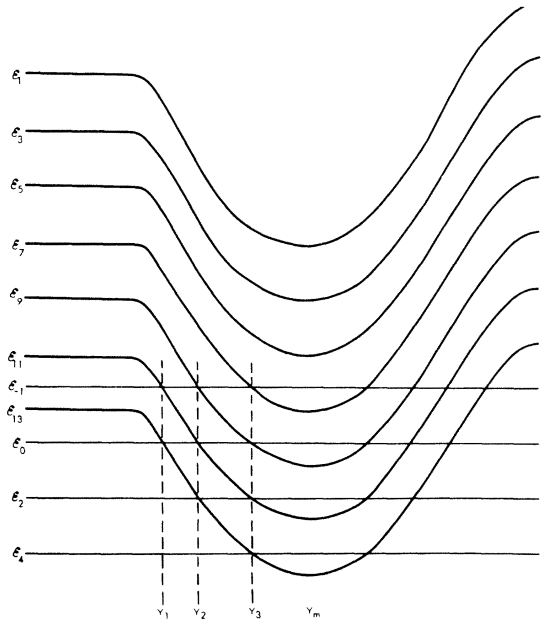

FIG. 9. Illustration of PC's occurring for the evaluation of Eq. (5.11).

VI. EXAMPLES

In this section we apply the techniques described in Sec. V to several examples.

For the first example we consider a single-photon transition, so $G' \cong G$. The wavelength is assumed to be $\lambda = 5$ μm and the oscillator strength $|f_{12}| = 0.1$. The laser beam is assumed to be just at the breakdown threshold, so Eq. (2.28) gives

$$G/F = 0.09 .$$

If $V = 0.1$ cm/μsec, we obtain from Eq. (2.26)

$$F = 20 , \quad G = 1.8 ,$$

and from Eq. (5.12) $|\alpha| \cong 20$. Then

$$2\pi p \simeq 1 ,$$

and we see from Eqs. (5.11) that the transition probability is of order 1.

For the same wavelength, laser power, oscillator strength, and velocity, a two-photon transition has a substantially reduced probability. In this case $p_0 = 2$, $G \cong 2.6$, and

$$G' \cong G^2/F = 0.3 .$$

The transition probability during a single atomic collision is now approximately

$$4\pi p \cong 0.04 .$$

To give another example, we evaluate the cross section, Eq. (5.3), for case A, Eq. (3.41), and a velocity $V = 3.1 \times 10^5$ cm/sec. For this example we assume the classical orbit to be a straight line and the kinetic energy to be large enough that the velocity is constant. The cross section (expressed in units of a_0^2) is shown in Fig. 10 as a function of G/F. The solid curve is the calculated cross section. The dotted curve shows the cross section that would result from neglecting the PC transitions and keeping only that resulting from Eq. (5.13). For small values of G/F this is seen to be the predominant contribution. The sharp peaks occur when PC's are lost. As was noted above, our matching equations (4.8) and (4.13) fail at these peaks, whose heights cannot be determined by our methods.[19]

The cross section (5.3) is shown in Fig. 11 for the parameters [see Eq. (3.40)]

$$R_0 = 1 , \quad p_0 = 22.5 ,$$
$$p_m = 3.2 , \quad V = 2.8 \times 10^5 \text{ cm/sec} . \tag{6.1}$$

The total cross section and the non-PC contributions are again displayed. Here again a simple straight-line trajectory approximation was assumed valid throughout the collision.

Our remaining examples take proper account of

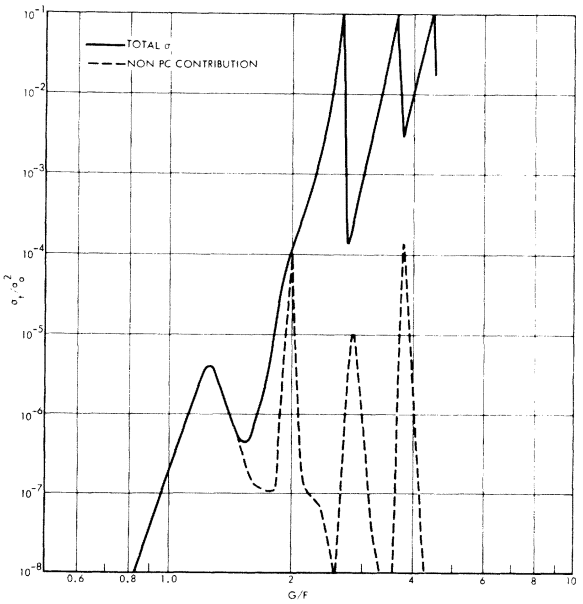

FIG. 10. Cross section [Eq. (5.3)] for case A [Eq. (3.41)] as a function of coupling constant G/F. The dotted curve represents the non-PC contribution [Eq. (5.13)], whereas the solid curve gives the total cross section.

the actual trajectory (5.6). The first of these is the reaction

$$\mathrm{H}(1s) + \mathrm{H}(1s)(b\,^3\Sigma_u^+) \rightarrow \mathrm{H}(1s) + \mathrm{H}(2p\sigma)(a\,^3\Sigma_g^+) . \tag{6.2}$$

The excitation energy required is 10.1 eV. If the initial kinetic energy ϵ is 9.0 eV, an absorbed energy of 1.1 eV is required from the laser beam. For $\lambda = 10.6$ μm, or $\hbar\omega = 0.117$ eV, at least 10 photons are required. The cross section as a

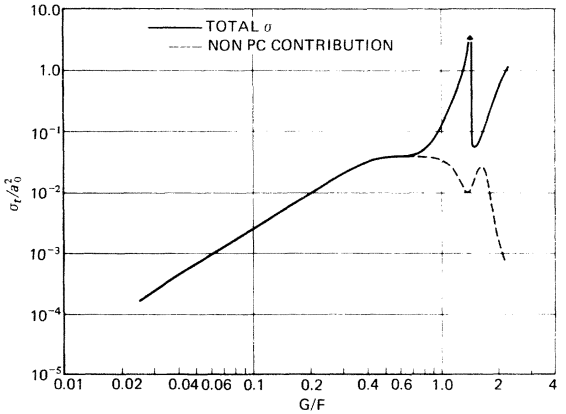

FIG. 11. Cross section [Eq. (5.3)] for the parameters given in Eq. (6.1).

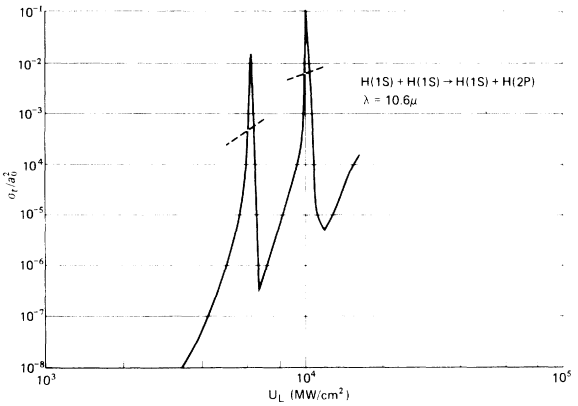

FIG. 12. Cross section [Eq. (5.3)] for the reaction described in Eq. (6.2) using 10.6-μm photons. Failure of the asymptotic connection formulas is indicated by the dashed lines.

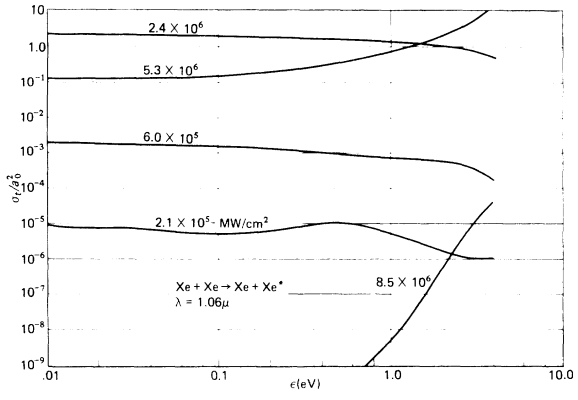

FIG. 14. Cross section [Eq. (5.3)] for the process given in Eq. (6.3) as a function of the initial relative energy ϵ (in eV) of the two Xe atoms. The curves are labeled by the laser power parameter U_L expressed in MW/cm^2.

function of the "laser power" U_L [defined by Eq. (2.32)] is shown in Fig. 12. The dashed lines through the peaks indicate the regions of failure of Eqs. (4.8).

For $\lambda = 1.06$ μm and a kinetic energy ϵ of 9.0 eV, a single absorbed photon can cause the reaction (6.2) to occur. The resulting cross section, calculated in the same manner, is shown in Fig. 13.

A second example studied was the reaction[20]

$$\mathrm{Xe} + \mathrm{Xe}(^1\Sigma_g^+) \rightarrow \mathrm{Xe} + \mathrm{Xe}(^3\Sigma_u^+). \tag{6.3}$$

The molecular potential curves were taken from the work of Mulliken.[21] The potential curve for the $^1\Sigma_u^+$ state is very similar to that for the $^3\Sigma_u^+$ state. (Spin selection rules are ineffective here because the configuration is somewhat intermediate between L-S and j-j coupling.)

For large internuclear separation the reaction (6.3) requires 8.4 eV, or about seven photons at 1.06-μm wavelength. In Fig. 14 we show the cross section σ_t for the process (6.3) with $\lambda = 1.06$ μm as a function of the relative kinetic energy of the colliding Xe atoms for several values of the "laser power" U_L. The largest cross section calculated was that for $U_L = 5.6 \times 10^6$ MW/cm^2. At this power level, $\sigma_t \cong 10 a_0^2$ for $1.0 < \epsilon < 4$ eV. For $U_L = 2 \times 10^5$ MW/cm^2, $\sigma_t \cong 10^{-7} a_0^2$.

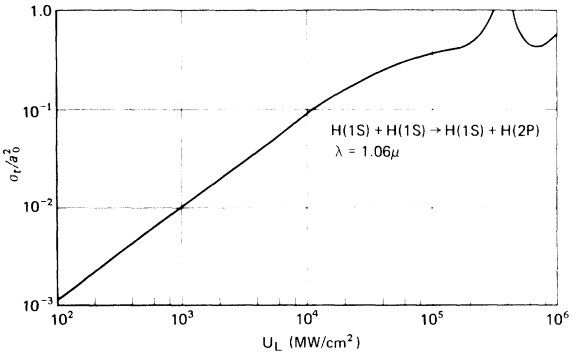

FIG. 13. Cross section [Eq. (5.3)] for the reaction described in Eq. (6.2) using 1.06-μm photons.

VII. TRANSITIONS RESULTING FROM LASER POWER VARIATIONS

It was mentioned in the Introduction that variation of the laser power can result in resonant absorption between two levels of an atom or molecule due to the shifting of these levels. Our discussion is easily adapted to this case.

Let the level separation be $W \equiv p_0 F$ before the laser is turned on. With the laser on, the pair of levels is separated by an amount

$$\Delta\mathcal{E} = W - \sigma F - 2\mathcal{E}_0 \equiv F(p_0 - \sigma - 2\epsilon_0/F) \tag{7.1}$$

except very near the PC. Here we shall use Eq. (3.44) to write

$$\frac{\mathcal{E}_0}{F} = \frac{p_0}{2}\left[1 - \frac{2}{\pi}\left(1 + \frac{16(G/F)^2}{p_0^2 - 1}\right)^{1/2} E(k)\right], \tag{7.2}$$

with

$$k^2 = \frac{16(G/F)^2}{p_0^2 - 1 + 16(G/F)^2}$$

and G/F given by Eq. (2.34).

As the PC occurs, the probability of a transition is, according to Eq. (4.8),

$$T = 1 - e^{-2\pi p}, \tag{7.3}$$

where [see Eq. (4.6)]

$$p=\left(\frac{\omega a_0}{v}\right)^2\frac{(G'/F)^2}{\alpha}\ . \tag{7.4}$$

Now, from Eq. (4.2) we have

$$\alpha=\frac{d}{dY}(2\mathcal{E}_0)=2\left(\frac{\omega a_0}{V}\right)\frac{d(\mathcal{E}_0/F)}{dt}\frac{a_0}{V}\equiv\omega\left(\frac{a_0}{V}\right)^2\frac{2\mathcal{E}_0/F}{\tau_r}\ , \tag{7.5}$$

where τ_r is the effective rise time of the pulse power. Combining results, we see that

$$p=\omega\tau_r\frac{(G'/F)^2}{2\mathcal{E}_0/F}\ . \tag{7.6}$$

Since $\mathcal{E}_0/F$ and G'/F are independent of F, the (in this case) fictitious velocity V has been eliminated.

In general, $\omega\tau_r$ will be quite large, which can lead to a substantial probability of transition. For example, let us use case A of Table I, setting $p_0=8.2$ and assuming $\lambda=10.6\ \mu$m, $\tau_r\sim10^{-9}$ sec. Then $\omega\tau_r\sim10^6$. At $U_L\cong3\times10^4$ MW/cm^2, or $G/F\simeq1.5$, we obtain a PC with 9 photons. From Fig. 7 we see that $G'/F\simeq10^{-3}$ and from Fig. 6 that $2\mathcal{E}_0/F\simeq0.4$. Thus,

$$p\simeq0.1\ . \tag{7.7}$$

In this case, T as given by Eq. (7.3) is comparable to unity.

ACKNOWLEDGMENTS

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APPENDIX A: CLASSICAL RADIATION FIELD

To discuss the case of a coherent, or classical, radiation field, we return to Eq. (2.6) and write

$$\Psi=e^{iK_yt}\hat{\Psi}\ ,$$

so

$$[h-\vec{\mathcal{P}}\cdot\vec{\mathrm{A}}(t)]\hat{\Psi}=i\dot{\hat{\Psi}}\ , \tag{A1}$$

and write

$$\vec{\mathrm{A}}(t)=\hat{e}(c/\omega)\mathcal{E}_0\cos(\omega t-\phi_0)\ , \tag{A2}$$

where ϕ_0 is a constant phase. Equation (A2) is equivalent, for our purposes, to the assumption that the electromagnetic field has a coherence time long compared with the collision time.

We adopt the two-state model and introduce the expression

$$\hat{\Psi}=\sum_{\alpha=1,2}c_\alpha(t)\phi_\alpha\exp\left[-i\int^t w_\alpha\,dt'/\hbar\right] \tag{A3}$$

into Eq. (A1) to obtain

$$\begin{aligned}i\dot{c}_1&=[2G\cos(FY-\phi_0)+G_x]e^{-i\Phi}c_2\ ,\\ i\dot{c}_2&=[2G\cos(FY-\phi_0)+G_x]e^{i\Phi}c_1\ .\end{aligned} \tag{A4}$$

Here

$$\Phi\equiv\int^Y W(Y')\,dY'\ , \tag{A5}$$

$\dot{c}_1=dc_1/dY$, etc., and the dimensionless variables of Eqs. (2.25) are used.

To put Eqs. (A4) into the form of Eqs. (2.17) we introduce the expansions

$$\begin{aligned}c_1&=\sum_{\nu\ \mathrm{even}}e^{-i\nu(FY-\phi_0)}A_\nu+\sum_{\nu\ \mathrm{odd}}e^{-i\nu(FY-\phi_0)}B_\nu\ ,\\ c_2&=\sum_{\nu\ \mathrm{odd}}e^{i(\Phi-\nu FY+\nu\phi_0)}A_\nu+\sum_{\nu\ \mathrm{even}}e^{i(\Phi-\nu FY+\nu\phi_0)}B_\nu\ .\end{aligned} \tag{A6}$$

We substitute these expressions into Eqs. (A4) and further define the A_ν, B_ν by requiring that the coefficient of each factor $e^{-i\nu FY}$ vanish. The equations that emerge are precisely Eqs. (2.17). The solutions of Eqs. (A4) are uniquely determined by specifying initial values of c_1 and c_2, while those of Eqs. (2.17) are determined by specifying initial values of the A_ν, B_ν. While there are clearly an infinite number of specifications of initial values that lead to the same solutions of Eqs. (A6) for c_1 and c_2, we shall choose the initial values for the classical formulation in the same way as for the cavity eigenmode formulation (see Sec. III). The connection between the two formulations is then most transparent.

In a strict sense, the interpretation of the A_ν's differs in the eigenmode and classical cases. For the former case, $|A_\nu|^2$ is the probability that the quasimolecule has absorbed ν photons. The probability that the quasimolecule is in the upper level 2 is

$$\sum_{\nu\ \mathrm{odd}}|A_\nu|^2+\sum_{\nu\ \mathrm{even}}|B_\nu|^2\ . \tag{A7}$$

This is not in general the same as $|c_2|^2$, the corresponding probability for the classical-field case. If our observation is averaged over a macroscopic interval of time and/or space, however, the interfering terms in $|c_2|^2$ vanish and this becomes equal to Eq. (A7).

APPENDIX B: PROOF OF EQ. (3.32)

At the PC for the curves $\mathcal{E}_0$ and $\mathcal{E}_\sigma$, we have $G'=G''$ if the curves at this point (Y_σ) are much closer to each other than to any other of the adiabatic eigenvalue curves. To see this, we set

$$\mathcal{E}_0 \cong \mathcal{E}_\sigma \cong \tfrac{1}{2}W_\sigma, \quad W_\sigma = -\Delta W, \tag{B1}$$

using Eq. (3.35). Then we obtain [Eqs. (3.14)]

$$g_{\sigma-\lambda} = -g_\lambda . \tag{B2}$$

Comparison of Eqs. (3.16) and (3.28) then gives

$$\hat{H}_{\sigma-\lambda} = H_\lambda , \quad H_{\sigma+1} = H_{-1} .$$

The desired result then follows from Eqs. (3.23), (3.26), and (3.30).

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*The work described in this paper was presented as an invited paper at both the 1973 Gordon Conference on Laser Beam Interactions and the 1974 Winter Meeting of the AAAS in San Francisco.

[1]Several reviews of multiphoton transitions are given in *Physics of Quantum Electronics*, edited by P. L. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill, New York, 1966).

[2]H. B. Bebb and A. Gold, Phys. Rev. 143, 1 (1966).

[3]L. V. Keldish, Zh. Eksp. Teor. Fiz. 47, 1945 (1964) [Sov. Phys.-JETP 20, 1307 (1965)].

[4]D. E. Evans and J. Katzenstein, Rep. Prog. Phys. 32, 207 (1969).

[5]V. Chalmeton, J. Phys. (Paris) 30, 687 (1969). Chalmeton has observed interesting anomalies in ionization produced by a laser. Although we do not here suggest a mechanism for these, it was this paper that provided the initial stimulus for the present work.

[6]Strictly speaking, Eq. (1.1) need not be precisely satisfied, because of line broadening. For applications of interest to us, natural broadening is negligible. Collisional broadening will be studied in this paper.

[7]For simplicity of notation, we shall refer to the two particles as "atoms," although either or both might be molecules, and the "potential curves" in our description are more generally "potential surfaces."

[8]The case of three molecular states and two field modes has been studied by A. F. M. Lau, Phys. Rev. A 13, 139 (1976), as a possible chemical laser.

[9]E. T. Jaynes and F. W. Cummings, Proc. IEEE 51, 89 (1963); J. A. Fleck, Phys. Rev. 149, 309 (1966); D. F. Walls and R. Barakat, Phys. Rev. A 1, 447 (1970).

[10]S. Swain, J. Phys. A 5, L3 (1972); 5, 1587 (1972).

[11]Since this paper was submitted for publication another paper with a similar objective has been published: N. F. Perel'man and V. A. Kovarskii, Zh. Eskp. Teor. Fiz. 63, 831 (1972) [Sov. Phys.-JETP 36, 436 (1973)].

[12]Exponential factors involving the photon momentum has been neglected in Eq. (2.4b). There is a dipole transition contribution from the A^2 term arising from the expansion of these exponentials. This is smaller than that arising from the linear term by a factor of $h\omega/mc^2$.

[13]We keep Planck's constant in our equations only where we wish to emphasize units.

[14]See, for example, M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964), Chap. 8.

[15]See, for example, N. Kroll and K. Watson, Phys. Rev. A 5, 1883 (1972).

[16]Compare M. Barat and W. Lichten, Phys. Rev. A 6, 211 (1972).

[17]We are following rather closely the analysis of pseudocrossings given by C. Zener, Proc. R. Soc. A 137, 1696 (1932).

[18]See, for example, E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge U.P., Cambridge, England, 1965), Chap. 16.

[19]Note that for $b < R_0$ [Eq. (3.40)] the value of p_m is fixed. Thus one loses a PC at a particular value of G/F for a whole range of impact parameters.

[20]We are indebted to Dr. Charles K. Rhodes for calling this reaction to our attention. See, for example, B. Krawetz and C. K. Rhodes, in Proceedings Symposium on High Power Molecular Lasers, Quebec City, 1972 (unpublished).

[21]R. S. Mulliken, J. Chem. Phys. 52, 5170 (1970).