Theory of laser-induced excitation transfer and atomic association. II. Resonances

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(Received 18 August 1988)

We have extended our previous analysis of diatom laser-induced excitation transfer, illustrated by several examples, to include modifications due to laser-induced resonances. Compact and rigorous final results have been obtained through the use of a projection-operator scheme in combination with the "symmetric-top" basis set and a full quantal treatment of the radiation field. The principal limitations on our analysis are a neglect of fine-structure coupling and a simplifying assumption that the ground electronic manifold supports no bound nuclear states. Simple order-of-magnitude estimates of the predicted resonant cross sections also are provided.

I. INTRODUCTION

The theory presented here is an extension and revision of our recent analysis[1] of laser-induced excitation transfer (LIET), hereafter referred to as I. Of primary concern in this paper are several prototypical processes in which the laser induces resonances as part of the excitation process. A schematic representation of the reactions considered here is given by the equations

$$A(1)+B(1)\rightarrow[A(1)\cdots B(1)] \overset{\hbar\omega}{\rightarrow}[A(2)\cdots B(2)]\rightarrow \begin{cases} A(2)+B(2) \\ A(1)+B(1)+\hbar\omega \end{cases}, \tag{1.1}$$

$$A(1)+B(1)\rightarrow[A(1)\cdots B(1)] \overset{\hbar\omega}{\rightarrow}[A(2)\cdots B(2)] \overset{\hbar\omega}{\rightarrow}[A(3)\cdots B(3)] \rightarrow A(3)+B(3)\ . \tag{1.2}$$

The numbers 1, 2, and 3 denote composite electronic states of the atoms. The intermediate states $[A(j)\cdots B(j)]$ will be specified more fully in what follows. It is assumed that the laser frequency ω is not resonant with any electronic transition of the atoms, A or B, and that the laser intensity is low enough ($<10^{10}$ W/cm^2) so that dressed-state effects are unimportant.[2] The presence of photons is therefore important only during the brief interval during which the atoms interact.

Our study differs from previous, related work[3–6] both in the details of the processes being considered and in the way we shall treat the (surprisingly important) effects of spontaneous radiation. Any theory of reactions such as (1.1) and (1.2) must incorporate the coupling between the collision dynamics and the radiation-matter interaction. In addition, a systematic treatment including the effects of spontaneous emission must treat the radiation field as a quantal object. Related studies include those of Julienne and Mies[3] and Regenorter and Feaurier,[4] who have studied the fluorescence produced by the *products* of collision systems. Lam and George[5] have published a theory of the collision-induced fluorescence events

$$A(2)+B(2)\rightarrow[A(2)\cdots B(2)] \rightarrow[A(1)\cdots B(1)]+\hbar c|\boldsymbol{\kappa}| \rightarrow A(1)+B(1)+\hbar c|\boldsymbol{\kappa}|\ , \tag{1.3}$$

where "2" denotes an excited electronic manifold and "1" the ground-state manifold. This reaction is not too different from the ones we are considering and Lam and George's treatment incorporates a quantal treatment of the radiation field. There are, however, two drawbacks to their approach. First, the collision dynamics are regarded as semiclassical; indeed, no real prescription for computing the collision trajectories is given. Second, the treatment of the radiation field is very complicated and results in final formulas that cannot readily be interpreted.

Hutchinson and George[6] also have investigated the reaction

$$A(1)+B(1)\rightarrow[A(1)\cdots B(1)] \overset{\hbar\omega'}{\leftrightarrow}[A(2)\cdots B(2)] \overset{\hbar\omega}{\leftrightarrow} A(1)+B(1)\ , \tag{1.4}$$

in which two quasibound states in the excited electronic manifold are coupled by an infrared laser with the frequency ω'. Although this process again bears a great similarity to (1.1) and (1.2), effects due to spontaneous radiation were not considered. The presence of spontaneous emission certainly complicates the mathematical analysis, but its practical implications are significant and deserve systematic treatment. Our aim then is to provide a fully quantal theory of (1.1) and (1.2) that yields simple and readily interpretable final results. Our previous treatment[1] of reactions (1.1) and (1.2) produced more complicated and less rigorous results than those reported here. Furthermore, the role of resonances described below, in Secs. II and III, was not properly accounted for in the earlier paper.

The simplest of the examples to be considered in this paper is depicted by Fig. 1(a). Although this first example may not be of great intrinsic interest, it is needed here as a reference point for the two other examples that follow. Furthermore, a consideration of this "conventional" case allows us to present computations and results in

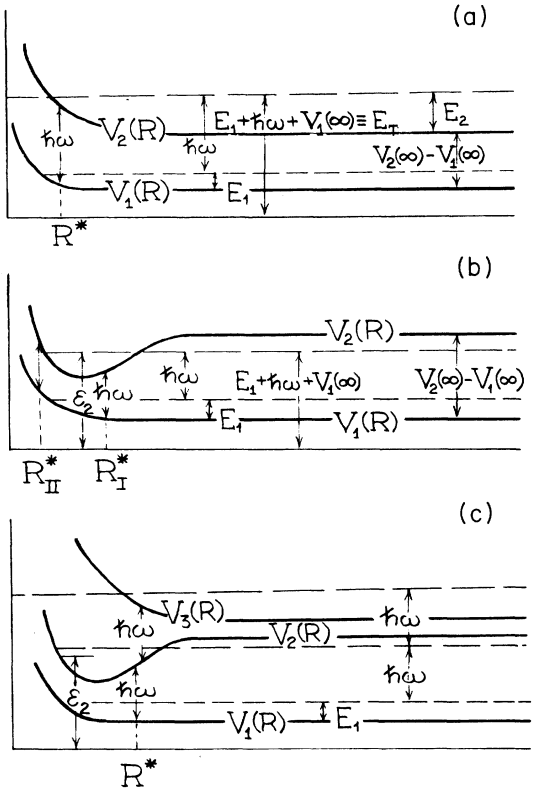

FIG. 1. (a) Neither electronic state ($x=1,2$) supports bound nuclear states. (b) Excited state can support at least one bound state with energy ε_2. (Channel 2 may or may not be open.) (c) A two-photon process. State 2 supports bound states but 1 and 3 do not.

their simplest forms, unobscured by decorations due to resonances. In our example two adiabatic electronic states are involved, neither of which supports bound electronic states. A collision begins with the reactant atoms approaching one another subject to the potential energy $V_1(R)$. In the midst of collision the system is transferred from the initial electronic state $[A(1)\cdots B(1)]$ to the final electronic state $[A(2)\cdots B(2)]$ by a laser photon. The event draws to an end with the atoms separating from one another on the potential energy surface $V_2(R)$, characteristic of the excited electronic state.

The theory establishes that the photoabsorptive event is only likely to occur near the internuclear separation(s) R^* satisfying the "resonance condition"

$$V_2(R^*)-V_1(R^*)=\hbar\omega\ . \tag{1.5}$$

If there is no value of R satisfying this condition, the cross section for the process will be very small.

Conservation of energy leads to the second, more rigorous condition

$$E_1+V_1(\infty)+\hbar\omega=E_2+V_2(\infty)\ , \tag{1.6}$$

with E_1 and E_2 denoting the pre- and postcollisional relative kinetic energies of the two atoms. When $E_1+V_1(\infty)+\hbar\omega<V_2(\infty)$, the channels associated with the excited electronic state are closed and reaction cannot occur. In this subthreshold regime all that can happen is elastic scattering in manifold 1 and this will be affected imperceptibly by the laser.

In the case just discussed the duration of the encounter is far too small (e.g., $\sim 10^{-13}$ sec for thermal atoms) for spontaneous emission to accompany the collision and it is extremely unlikely that stimulated emission will occur subsequent to photoexcitation. However, this is not so for the situation illustrated by Fig. 1(b). In this second example the potential V_1 is the same as before, but the excited-state potential V_2 is now capable of supporting bound nuclear states. [The symbol ε_2 appearing in Fig. 1(b) denotes the energy of one such state.] It is these bound states that can give rise to resonances.

There will be no significant differences between this and the previous example provided that the channels of manifold 2 are *open*, i.e., provided that $E_1+V_1(\infty)+\hbar\omega>V_2(\infty)$. The differences are most profound in the subthreshold regime with manifold 2 *closed* and the scattering restricted to manifold 1. Thus, even though there is insufficient energy to form unbound excited products, the radiation field will couple the two manifolds and this coupling can result in an intensity-dependent change of the manifold 1 scattering. To understand how this can come about, suppose that as the atoms approach one another on V_1, photoexcitation (from $[A(1)\cdots B(1)]$ to $[A(2)\cdots B(2)]$) occurs at a separation R^* satisfying the resonance condition (1.5). [Figure 1(b) shows two separations R^*_I and R^*_{II} at which this condition is satisfied, but R^*_{II} is "classically inaccessible" under the conditions indicated in the figure.] The atom then will be confined to a bound state of V_2 (with energy ε_2) until a photoemissive transition returns the system to V_1. If the event that restores the system to manifold 1 is a laser-stimulated emission, the atoms will fly apart with a kinetic energy equal to that with which they originally collided. This constitutes a two-photon elastic scattering event, with a phase differing from that of the comparable field-free collision by an amount dependent upon the intensity and polarization of the laser. However, if the decay back to manifold 1 occurs by *spontaneous* emission, the products of reaction will include a photon with a wave vector $\boldsymbol{\kappa}$ that can vary over a range of magnitudes and directions. In this second case the relative kinetic energy of the atomic products (E_1') will differ from that of the reactants (E_1) by an amount specified by the conservation equation

$$E_1+\hbar\omega=E_1'+\hbar c|\boldsymbol{\kappa}| \tag{1.7}$$

(manifold 2 closed). Since the total radiation field is altered by events of this second type, the scattering they produce will be coherent neither with field-free elastic scattering nor with that associated with the previously described absorption-plus-stimulated emission two-photon events.

Finally, since the excited bound state is coupled very weakly to the elastic scattering system, the energy of the

initial scattering system must be nearly coincident with ε_2 for there to be a significant probability of photoexcitation, i.e.,

$$E_1 + V_1(\infty) + \hbar\omega \doteq \varepsilon_2 \ . \tag{1.8}$$

Thus the mechanisms described here combine to produce a cross section that is strongly dependent on the laser frequency (for fixed E_1). Indeed, the laser-intensity-dependent portion of the cross section will be important only when this equation is satisfied; the cross section will exhibit a series of resonances at laser frequencies given by (1.8). This is in accordance with Feshbach's[7] general analysis of bound-continuum coupling. The theory presented here closely resembles his, the main difference stemming from our need to handle spontaneous radiation and its effects on the shapes and strengths of resonances.

The third and last example we consider involves three distinct electronic states, such as those depicted in Fig. 1(c). In this case our main interest is a two-photon process consisting of photoexcitation from manifold 1 to manifold 2 followed by photoexcitation from 2 to 3. As before, conservation of energy fixes the value of E_3 (the relative kinetic energy of the atomic products) in terms of the initial kinetic energy of the reactants, the electronic energies of the initial and final states, and the laser frequency,

$$E_3 + (N-2)\hbar\omega + V_3(\infty) = E_1 + N\hbar\omega + V_1(\infty) \ . \tag{1.9}$$

Also, by analogy with the previous examples, it is clear that there are two "resonance conditions,"

$$\begin{aligned} \hbar\omega &= V_2(R^*) - V_1(R^*) \ , \\ \hbar\omega &= V_3(R^{*\prime}) - V_2(R^{*\prime}) \ , \end{aligned} \tag{1.10}$$

that must be satisfied (for at least one R^* and one $R^{*\prime}$) if the cross section for the two-photon process is to be of significant magnitude. However, this cross section normally is found to be very small even when the conditions (1.10) are satisfied. This comes as no surprise, for if the single-photon events of the earlier examples are rare events, then the two-photon processes should be even more so. The one exception to this is the case where manifold 2 supports bound states *and* the laser frequency satisfies the additional resonance condition (1.8). In these circumstances absorption of the first photon populates the metastable bound state $[A(2)\cdots B(2)]$. If the lifetime of this state is sufficiently great, then absorption of the first photon almost certainly will be followed by absorption of a second. Consequently, under optimal circumstances the cross section for the two-photon process (1.2) will be comparable to that of a one-photon process such as (1.1). This "resonance enhancement" is familiar from experiments involving the multiphoton ionization of atoms and molecules. Here spontaneous radiation again plays a role since it limits the lifetime of the metastable state $[A(2)\cdots B(2)]$ and thus the effectiveness of the resonance enhancement. The theory for this process is outlined in Sec. IV, along with a discussion of the dependence of its cross section of the parameters of the system.

II. GENERALITIES, DEFINITIONS, AND NOTATION

We consider two crossed atomic beams, one of species A and one of B. Focused on the collision region is a single-mode laser. The (center-of-mass) Hamiltonian of the system is taken to be

$$H = T_n + H_{\rm el} + H_r + H_{\rm int} \ . \tag{2.1}$$

Here T_n is the relative kinetic energy of the two atomic nuclei. The operator $H_{\rm el}$ is the sum of the electronic kinetic energies and of the Coulombic interactions among the nuclei and electrons. $H_r = \sum_j \hbar\omega_j a_j^\dagger a_j$ is the energy of the free radiation field, with $a_j^\dagger$ and a_j denoting creation and annihilation operators for photons with angular frequency ω_j, momentum $\hbar\boldsymbol{\kappa}_j$, and linear polarization $\hat{\boldsymbol{\alpha}}_j$. Finally, $H_{\rm int}$ is the energy of interaction between the charged particles and the laser. In the applications considered here this operator is taken to be the electric dipole interaction between the laser and the electrons. Furthermore, it is assumed that the intensity and frequency of the laser are such that it does not interact with the atoms unless they are in the midst of collision. In practice, this requires that the laser frequency ω be detuned from all atomic transitions and that its intensity be "low," i.e., $I \lesssim 10^{10}$ W/cm^2.[4] Thus the part ($H_{\rm int}$) of the Hamiltonian responsible for LIET is a short-ranged operator, suitable for analysis by conventional scattering theory.

Spin-orbit interactions deliberately have been neglected throughout this paper, in order to reduce complexity and to expose any identifiable characteristics of the photocollisional processes. However, we recognize that fine structure must be reintroduced in subsequent, more detailed studies in order to provide an adequate representation of the quasimolecular states.

Our considerations will be confined to a limited number of electronic subspaces, to each of which is assigned a single value S of electron spin, a single value of $|\Lambda|\hbar$ (the magnitude of the component of total electronic orbital angular momentum along the internuclear axis) and the single, corresponding potential energy surface. It is thereby assumed that the dynamics of interest are represented adequately by kets having projections on only a few electronic states. These may be adiabatic (ABO) or diabatic (DBO) Born-Oppenheimer states as appropriate. The electronic kets associated with these states are denoted by symbols $|1a\mathbf{R}\rangle$, $|2b\mathbf{R}\rangle$, and (in Sec. IV) $|3c\mathbf{R}\rangle$. The labels 1, 2, and 3 identify the potential energy curves connected with the states and $\mathbf{R} = \mathbf{X}_A - \mathbf{X}_B$ is the vector extending from nucleus B to nucleus A. The identification of the electronic states is completed (and all residual degeneracies resolved) by the composite labels a, b, and c. These sets of quantum numbers include (1) the projection of total electronic spin (in units of $\hbar$) Ω_{1a} (Ω_{2b}, Ω_{3c}) along the lab z axis, and (2) the projection of total electronic orbital angular momentum (in units of $\hbar$) Λ_{1a} (Λ_{2b}, Λ_{3c}) along $\mathbf{R}$. The incoming channel for scattering is designated as subspace 1, $a \equiv 0$: the corresponding electronic ket is $|10\mathbf{R}\rangle$.

In much of what follows it is convenient to treat all electronic kets at once, regardless of the potential curves

to which they are related. Accordingly, electronic kets will be denoted by generic symbols $|xl\mathbf{R}\rangle$, with $x=1,2,\ldots,$ and $l=a$ (for $x=1$), b (for $x=2$), and c (for $x=3$). In this generic notation and the extensions of it that follow, it must be remembered that the meanings of quantum numbers such as l depend on the labels x with which they are associated.

With this rejoinder in mind, let us proceed to other definitions and notation. The potential energy function

$$V_x(R)=V_{xl}(R)\equiv\langle xl\mathbf{R}|H_{\rm el}|xl\mathbf{R}\rangle = \int d\xi\,\phi^*_{xl}(\xi|R\hat{\mathbf{z}})H_{\rm el}\phi_{xl}(\xi|R\hat{\mathbf{z}}) \tag{2.2}$$

is the expectation value of the electronic Hamiltonian operator common to all states $|xl\mathbf{R}\rangle$ with a specified value of x. The last of these formulas expresses the energy of the BO state in terms of its coordinate wave function,

$$\langle\mathbf{r}|xl\mathbf{R}\rangle=\phi_{xl}(\mathbf{r}|\mathbf{R})=\phi_{xl}(\xi|R\hat{\mathbf{z}})\ . \tag{2.3}$$

Here $\mathbf{r}$ and $\mathbf{R}$ are electronic and nuclear coordinates referred to a laboratory frame of reference, the polar axis of which points in the direction of $\hat{\mathbf{z}}$. The symbol ξ denotes the "molecular frame" coordinates, specifying the positions of the electrons relative to a frame that has its polar axis directed along the internuclear axis.

We associate with each electronic state $|xl\mathbf{R}\rangle$ a product state

$$|xl\mathbf{R}\rangle\!\rangle\equiv|xl\mathbf{R}\rangle|\mathbf{R}\rangle\ . \tag{2.4}$$

Here $|\mathbf{R}\rangle$ denotes an eigenket of the nuclear coordinate operator $\mathbf{R}_{\rm op}$ so normalized that $\langle\mathbf{R}|\mathbf{R}'\rangle=\delta(\mathbf{R}-\mathbf{R}')$. The scattering theory is then formulated in terms of the electron-photon subspaces spanned by orthogonal projection operators

$$P_x\equiv\sum_l\sum_n\int d\mathbf{R}|xl\mathbf{R}n\rangle\!\rangle\langle\!\langle xl\mathbf{R}n|\ , \tag{2.5}$$

$$P_xP_{x'}=\delta_{xx'}P_x\ , \tag{2.6}$$

which, in turn, are defined in terms of the product states

$$|xl\mathbf{R}n\rangle\!\rangle\equiv|xl\mathbf{R}\rangle\!\rangle|n\rangle\ . \tag{2.7}$$

The object $|n\rangle$ appearing in (2.7) is an eigenket of the free radiation field Hamiltonian operator H_r. The set of photon states associated with a projection operator P_x depends upon the value of x,

$$\begin{aligned} &x=1,\quad n=N\ \text{ and }\ (N-1,\kappa\mu)\ ;\\ &x=2,\quad n=N-1\ ;\\ &x=3,\quad n=N-2\ . \end{aligned} \tag{2.8}$$

In the first line of (2.8) $n=N$ denotes a photon state having N photons in the original linearly polarized laser mode, while $(N-1,\kappa\mu)$ denotes $N-1$ photons in the laser mode plus *one* with differing momentum $\hbar\kappa$ and (linear) polarization μ. The states $(N-1,\kappa\mu)$ are included to account for spontaneous radiation, the effects of which are important in Secs. III and IV.

As mentioned previously, we use the few-channel approximation, thereby limiting attention to the space spanned by a selected set of kets $|xl\mathbf{R}n\rangle\!\rangle$. It therefore is implicit in what follows that each operator $\hat{0}$ is replaced with $\hat{1}\hat{0}\hat{1}$, where

$$\hat{1}\equiv\sum_{x\ (\text{finite})}P_x\ .$$

Thus, for example, the Schrödinger equation $(H-E_T)|\psi\rangle\!\rangle=0$ becomes

$$(H_{ii}-E_T)|\psi_i\rangle\!\rangle=-\sum_j H_{ij}|\psi_j\rangle\!\rangle,\quad i=1,2,\ldots,I \tag{2.9}$$

with

$$H_{ij}=P_iHP_j,\quad |\psi_i\rangle\!\rangle=P_i|\psi\rangle\!\rangle\ . \tag{2.10}$$

Because the issues that concern us here are not sensitively dependent upon Born-Oppenheimer couplings, these will be disregarded. Consequently, each diagonal element of the Hamiltonian matrix can be written in the form

$$H_{xx}\equiv P_xHP_x\doteq\sum_l P_{xln}HP_{xln}=\sum_l H_{ll}(xn)\ , \tag{2.11}$$

with $P_{xln}=\int d\mathbf{R}|xl\mathbf{R}n\rangle\!\rangle\langle\!\langle xl\mathbf{R}n|$ and where

$$H_{ll}(xn)=P_{xln}\left[T_R+\frac{1}{2\mu R^2}(K^2-\hbar^2\Lambda_{xl}^2)+V_x(R)+\langle n|H_r|n\rangle\right]P_{xln}\ . \tag{2.12}$$

Here $T_R\equiv-(\hbar^2/2\mu)R^{-2}\partial_R(R^2\partial_R)$ is the radial kinetic energy operator and $\mathbf{K}$ is the total orbital angular momentum operator, equal to the sum of the electronic orbital angular momentum and that associated with the relative motion of the two nuclei. Accordingly, we introduce a ket $|xlKMqn\rangle\!\rangle$ that satisfies the single-channel wave equation

$$(H_{xx}-E_T)|xlKMqn\rangle\!\rangle=(\sum_l H_{ll}(xn)-E_T)|xlKMqn\rangle\!\rangle =0 \tag{2.13}$$

and additionally is an eigenket of $\mathbf{K}$ and of the component of $\mathbf{K}$ along the lab z axis; K and M are the corresponding quantum numbers.

We write the coordinate wave function of this ket in the form

$$\langle\!\langle\mathbf{r},\mathbf{R}|xlKMqn\rangle\!\rangle =F_{xlK}(q,R)N_KD^K_{\Lambda_{xl},M}(\hat{\mathbf{R}})\phi_{xl}(\xi|R\hat{\mathbf{z}})|n\rangle\ . \tag{2.14}$$

Here $\hat{\mathbf{R}}=(\phi,\theta)$ is a unit vector in the direction of the internuclear axis and the functions $D^K_{\Lambda,M}(\hat{\mathbf{R}})\equiv D^K_{\Lambda,M}(\phi,\theta,0)$ are representation coefficients of the rotation group[8] 0_3^+ which satisfy the orthonormality conditions

$$\int d\hat{\mathbf{R}}[N_KD^K_{\Lambda,M}(\hat{\mathbf{R}})]^*[N_{K'}D^{K'}_{\Lambda,M'}(\hat{\mathbf{R}})]=\delta_{KK'}\delta_{MM'}\ , \tag{2.15}$$

with $N_K=[(2K+1)/4\pi]^{1/2}$.

It follows from (2.11)–(2.14) that the radial amplitude

F_{xlK} is a solution of the one-dimensional Schrödinger equation

$$\left[T_R+\frac{\hbar^2}{2\mu R^2}[K(K+1)-\Lambda_{xl}^2]+V_x(R)-E_x(Kq)\right]F_{xlK}(q,R)=0\ . \quad (2.16)$$

When channel xl is *closed* this is an eigenvalue equation with $E_x(Kq)=E_T-\langle n|H_r|n\rangle$ discrete, q a vibrational quantum number, and $F_{xlK}(q,R)$ a real, square-integrable function satisfying the orthonormality condition

$$\int_0^\infty dR\ R^2F_{xlK}(q,R)F_{xlK}(q',R)=\delta_{qq'}\ . \quad (2.17)$$

When xl is *open*, $E_x(Kq)=\hbar^2q^2/2\mu$ is the relative kinetic energy of the separated atoms and $F_{xlK}(q,R)$ is a continuum wave function which we choose to be regular at the origin, δ-function normalized in the manner

$$\int_0^\infty dR\ R^2F_{xlK}(q,R)F_{xlK}(q',R)=\delta(q-q')\ , \quad (2.17')$$

and subject to the asymptotic boundary condition

$$F_{xlK}(q,R)\underset{k\to\infty}{\sim}(2/\pi)^{1/2}R^{-1}\sin(qR+\eta_{xK})\ . \quad (2.18)$$

Consequently, the kets $|xlKMqn\rangle\rangle$ satisfy the conditions

$$\langle\langle xl'K'M'q'n'|xlKMqn\rangle\rangle=\delta_{l'l}\delta_{K'K}\delta_{M'M}\delta_{n'n}\delta(q',q)\ , \quad (2.19)$$

with $\delta(q',q)$ indicating the Kronecker or Dirac δ, depending on which is appropriate.

With the neglect of Born-Oppenheimer couplings, the only remaining contributor to the off-diagonal elements of the Hamiltonian matrix is the laser-electron interaction operator $H_{\rm int}$,

$$H_{xx'}\equiv P_xHP_{x'}\doteq P_xH_{\rm int}P_{x'}\ \ (\text{for } x'\neq x)\ . \quad (2.20)$$

The matrix elements of these operators can be written in the form

$$\langle\langle x'l'\mathbf{R}'n'|H_{\rm int}|xl\mathbf{R}n\rangle\rangle=\delta(\mathbf{R}'-\mathbf{R})V_{x'l'n',xln}(\mathbf{R},\omega)\ , \quad (2.21)$$

with

$$V_{x'l'n',xln}(\mathbf{R},\omega)=i\rho^{1/2}(\omega;n'|n)w_{x'x}(R)\langle x'l'\mathbf{R}|\hat{\boldsymbol{\alpha}}_\mu\cdot\mathbf{d}|xl\mathbf{R}\rangle \quad (2.22)$$

and

$$w_{x'x}(R)=(\hbar\omega)^{-1}[V_{x'}(R)-V_x(R)]\ . \quad (2.23)$$

Here, $\mathbf{d}$ is the electronic dipole moment and $\hat{\boldsymbol{\alpha}}_\mu$ the linear polarization axis of the emitted or absorbed photon. In the event of absorption or stimulated emission, $\hat{\boldsymbol{\alpha}}_\mu=\hat{\boldsymbol{\alpha}}$ is the polarization axis of the laser and

$$\rho(\omega;N-1|N)=\rho(\omega;N|N-1)=2\pi(I/c\omega^2)\ . \quad (2.24)$$

The symbol $I=\hbar\omega c(N/\Omega)$ denotes the flux of laser energy and Ω is the photon-field quantization volume.

If the photon is emitted spontaneously $[n=(N-1,\boldsymbol{\kappa}\mu)]$, there will be two polarizations $\hat{\boldsymbol{\alpha}}_\mu$ $(\mu=1,2)$, each of which is perpendicular to the photon wave vector $\boldsymbol{\kappa}$. The corresponding value of ρ is

$$\rho(\omega;N-1,\boldsymbol{\kappa}\mu|N-1)=2\pi\hbar/\Omega c|\boldsymbol{\kappa}|\ . \quad (2.25)$$

The electronic matrix element appearing in the formula (2.22) can be written more explicitly as

$$\langle x'l'\mathbf{R}|\hat{\boldsymbol{\alpha}}\cdot\mathbf{d}|xl\mathbf{R}\rangle=(4\pi/3)^{1/2}\delta(\Omega_{x'l'},\Omega_{xl})\times\sum_{m=0,\pm1}(-1)^mY_{1m}(\hat{\boldsymbol{\alpha}})D^1_{\Delta\Lambda,m}(\hat{\mathbf{R}})\times\{x'l'R|d_{\Delta\Lambda}|xlR\}\ , \quad (2.26)$$

with $\Delta\Lambda=\Lambda_{x'l'}-\Lambda_{xl}$ (values $0,\pm1$) and where $\Omega_{x'l'}$ and Ω_{xl} denote the electron spin projection quantum numbers of the two states. The symbol $\{\cdots|d_\nu|\cdots\}$ indicates the body-frame matrix element of a spherical component $(\nu=0,\pm1)$ of the electronic dipole moment operator and $Y_{1m}(\hat{\boldsymbol{\alpha}})=Y_{1m}(\phi_\alpha,\theta_\alpha)$ is a spherical harmonic referred to the lab frame.

III. PROCESSES INVOLVING TWO ELECTRONIC STATES

In this section we treat the first and second of the three processes described in the introduction.

A. Neither electronic state supports bound nuclear states

This is the situation depicted by Fig. 1(a). The appropriate Schrödinger equation is $(H-E_T)|\psi^+_{10kN}\rangle\rangle=0$. The state vector $|\psi^+_{10kN}\rangle\rangle$ appearing here is specific to the initial electronic state $|10\mathbf{R}\rangle$, to an initial heavy-particle relative momentum $\hbar\mathbf{k}$, and to a radiation field of N laser photons. The plus superscript refers to the conventional "radiative" or "expanding-wave" boundary condition of scattering theory and E_T is the total energy of the system in the center-of-mass frame. When it is not likely to cause confusion, we shall replace the symbol $|\psi^+_{10kN}\rangle\rangle$ with $|\psi\rangle\rangle$.

It is assumed that there are no significant dynamic contributions from electronic states other than the two with energy expectation values $V_1(R)$ and $V_2(R)$. Furthermore, because the collision times are so brief we disregard the possibility of spontaneous emission and thereby limit our attention to the two laser states $n_1=N$ and $n_2=N-1$. Subject to these restrictions, the "relevant" components of the state vector are governed by the two coupled equations

$$(H_{11}-E_T)|\psi_1\rangle\rangle=-H_{12}|\psi_2\rangle\rangle\ , \quad (3.1)$$

$$(H_{22}-E_T)|\psi_2\rangle\rangle=-H_{21}|\psi_1\rangle\rangle\ . \quad (3.2)$$

The desired solutions of these equations may be expressed formally as follows:

$$|\psi_1\rangle\rangle = |\Phi_1\rangle\rangle + G_1^+ H_{12}|\psi_1\rangle\rangle \ , \tag{3.3}$$

$$|\psi_2\rangle\rangle = G_2^+ H_{21}|\psi_1\rangle\rangle \ , \tag{3.4}$$

where G_1^+ and G_2^+ are the Green operators

$$G_x^+ = \lim_{\epsilon\to 0+} [E_T - H_{xx} + i\epsilon]^{-1} \tag{3.5}$$

and $|\Phi_1\rangle\rangle \equiv |\Phi_{10\mathbf{k}N}^+\rangle\rangle$ is a solution of the homogeneous equation

$$[H_{00}(1N) - E_T]|\Phi_{10\mathbf{k}N}^+\rangle\rangle = 0 \ , \tag{3.6}$$

with a coordinate representative that is equal asymptotically to the sum of the plane-wave state $\phi_{10}(\xi|R\hat{\mathbf{z}})|N\rangle\exp(i\mathbf{k}\cdot\mathbf{R})$ and outward-bound spherical waves. This ket can be written as a linear combination

$$|\Phi_{10\mathbf{k}N}^+\rangle\rangle = \sum_{K,M} C_{KM}(\mathbf{k})|10KMkN\rangle\rangle \tag{3.7}$$

of the kets $|xlKMqn\rangle\rangle$ defined in Sec. II, cf. (2.13)–(2.19). The requisite asymptotic behavior is then obtained by selecting the coefficients $C_{KM}(\mathbf{k})$ according to the prescription[9]

$$C_{KM}(\mathbf{k}) = (8\pi^3)^{1/2} k^{-1} [N_K D^K_{\Lambda_{10},M}(-\mathbf{k})]^* e^{i\eta_{1K}} \ . \tag{3.8}$$

To lowest order in the laser intensity, the solutions (3.3) and (3.4) becomes $|\psi_1\rangle\rangle \doteq |\Phi_1\rangle\rangle$ and

$$|\psi_2\rangle\rangle \doteq G_2^+ H_{21}|\Phi_1\rangle\rangle = \lim_{\epsilon\to 0+} \sum_{K',M',b} \int_0^\infty dq \frac{|2bK'M'q,N-1\rangle\rangle\langle\langle 2bK'M'q,N-1|H_{\rm int}|\Phi_1\rangle\rangle}{E_T - E_2(q) + i\epsilon} \ , \tag{3.9}$$

respectively, with

$$E_2(q) \equiv \hbar^2 q^2/2\mu + V_2(\infty) + (N-1)\hbar\omega \ . \tag{3.10}$$

It then is straightforward[10] but tedious to show that the asymptotic ($R\to\infty$) form of the wave function $\langle\langle 2b\mathbf{R}N-1|\psi_2\rangle\rangle$ equals the product of $R^{-1}\exp(iq_0R)$ with the *inelastic scattering amplitude*

$$f_{2b}^+(\hat{\mathbf{R}},\hat{\boldsymbol{\alpha}}) = -(2\pi)^{1/2}\frac{\mu}{\hbar^2 q_0} \sum_{Q,M} [N_Q D^Q_{\Lambda_{2b},M}(\hat{\mathbf{R}})] e^{i\eta_{2Q}} \langle\langle 2bQMq_0,N-1|H_{\rm int}|\Phi_1\rangle\rangle \ . \tag{3.11}$$

The wave number q_0 appearing in these formulas is the solution of the energy-conservation condition $E_T = E_2(q_0)$ or, equivalently, $\hbar^2 q_0^2/2\mu = \hbar^2 k^2/2\mu + V_1(\infty) - V_2(\infty) + \hbar\omega$.

By inserting the formula (3.7) for $|\Phi_1\rangle\rangle$ into this last expression one can relate the inelastic scattering amplitude to the matrix elements of $H_{\rm int}$ given by (2.22). The simplest form of the resulting expression is obtained by selecting the lab z axis to coincide with the direction of the initial relative momentum $\hbar\mathbf{k}$. Thus it follows[8] that $D^K_{\Lambda,M}(-\hat{\mathbf{k}}) \to D^K_{\Lambda,M}(-\hat{\mathbf{z}}) = D^K_{\Lambda,M}(\pi+\phi,\pi-\theta,0) = (-1)^K\delta(M,-\Lambda)$ and

$$f_{2b}^+(\hat{\mathbf{R}},\hat{\boldsymbol{\alpha}}) = -\frac{\pi\mu}{\hbar^2 q_0 k} \sum_{Q,K,M} \{[(2K+1)(2Q+1)]^{1/2}(-1)^K \exp[i(\eta_{1K}+\eta_{2Q})]\}$$
$$\times D^Q_{\Lambda_{2b},M}(\hat{\mathbf{R}}) \langle\langle 2bQMq_0,N-1|H_{\rm int}|10K,-\Lambda_{10},k,N\rangle\rangle \ . \tag{3.12}$$

From this, (2.22), and (2.26) it easily is established that

$$f_{2b}^+(\hat{\mathbf{R}},\hat{\boldsymbol{\alpha}}) = \delta(\Omega_{2b},\Omega_{10}) \left[-\frac{i\pi\mu}{\hbar^2 q_0 k} \left[\frac{32}{3}\right]^{1/2} \left[\frac{I}{c\omega^2}\right]^{1/2} \right]$$
$$\times \sum_{K,Q,M} [D^Q_{\Lambda_{2b},M}(\hat{\mathbf{R}}) Y_{1,-M-\Lambda_{10}}(\hat{\boldsymbol{\alpha}})] \left[(2Q+1) \begin{pmatrix} Q & 1 & K \\ -M & M+\Lambda_{10} & -\Lambda_{10} \end{pmatrix} \chi_{QK} \right] \ , \tag{3.13}$$

wherein

$$\chi_{QK}(\omega,k,b) = (2K+1)(-1)^{K+\Lambda_{2b}-\Lambda_{10}}$$
$$\times \begin{pmatrix} Q & 1 & K \\ -\Lambda_{2b} & \Lambda_{2b}-\Lambda_{10} & \Lambda_{10} \end{pmatrix}$$
$$\times F(2bQq_0|10Kk) \tag{3.14}$$

and

$$F(x'l'K'k'|xlKk)$$
$$= \int_0^\infty dR\, R^2 F_{x'l'K'}(k',R) F_{xlK}(k,R)$$
$$\times w_{x'x}(R)\{x'l'R|d_{\Lambda_{x'}-\Lambda_x}|xlR\} \ . \tag{3.15}$$

The function $f_{2b}^+(\hat{\mathbf{R}},\hat{\boldsymbol{\alpha}})$ is the scattering amplitude of an event which (1) begins with two atoms in the electronic state $|10\mathbf{R}\rangle$, colliding with a relative kinetic energy $\hbar^2 k^2/2\mu$; (2) involves the absorption of a laser photon of frequency ω and linear polarization $\hat{\boldsymbol{\alpha}} = (\phi_\alpha,\theta_\alpha)$; and (3) ends in the excited electronic state $|2b\mathbf{R}\rangle$ with the atoms receding from one another along the direction of $\hat{\mathbf{R}} = (\phi,\theta)$. Because several vectors are involved, a geometric depiction of the situation is provided by Fig. 2. Finally, it should be pointed out that the Franck-Condon condition [cf. (1.5)], $V_{x'}(R^*) - V_x(R^*) = \hbar\omega$, is a direct consequence of evaluating the integral $F(x'l'K'k'|xlKk)$ by the stationary phase approximation.[1]

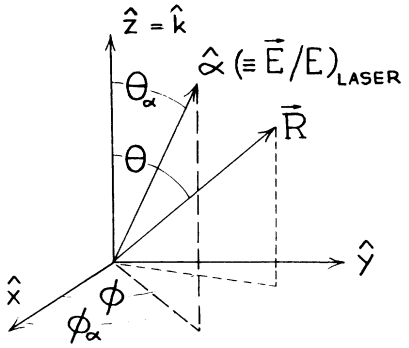

FIG. 2. Vectors and coordinates involved in f_{2b}^{+} and σ_{2b}.

It is possible, given the relatively simple structure of (3.13), to predict some things about the functional dependence of f_{2b}^{+} on experimental parameters such as I and $\hat{\alpha}$. The well-known fact that f_{2b}^{+} is proportional to $I^{1/2}$ is manifest in (3.13). The question of how f_{2b}^{+} depends on the laser polarization $\hat{\alpha}$ is in general more subtle, but some conclusions nonetheless can be made. Thus let us examine inelastic scattering into a product state with $\Lambda_{2b}=0$ (Σ term). In particular, let us focus upon the $\hat{\alpha}$ dependence of that scattering in the *threshold regime.* Under these conditions, only $Q=0$ contributes to the value of f_{2b}^{+} and the scattering amplitude is independent of $\hat{\mathbf{R}}$. From (3.13) we see that if $\Lambda_{10}=0$, f_{2b}^{+} will *decrease* from a maximum at $\theta_\alpha=0$ to a minimum of zero at $\theta_\alpha=\pi/2$. If $\Lambda_{10}=\pm 1$, just the opposite will be observed. Finally, when the magnitude of Λ_{10} is greater than 1, the scattering amplitude vanishes identically in the threshold region, a reflection of a single photon's inability to transfer two units of angular momentum to the matter system.

The integral cross section associated with the inelastic scattering amplitude f_{2b}^{+} is given by the formula

$$\sigma_{2b}\equiv\frac{q_0}{k}\int d\hat{\mathbf{R}}|f_{2b}^{+}(\hat{\mathbf{R}},\hat{\alpha})|^2$$
$$=\left[\delta(\Omega_{10},\Omega_{2b})\frac{32\pi^2\mu^2}{\hbar^4 q_0 k^3}\left[\frac{I}{c\omega^2}\right]\right]\left[\sum_J(-1)^J(2J+1)\begin{bmatrix}1&1&J\\0&0&0\end{bmatrix}P_J(\cos\theta_\alpha)\right.$$
$$\left.\times\sum_Q(2Q+1)(-1)^{Q+\Lambda_{10}}\sum_{K,K'}\begin{Bmatrix}1&K&Q\\K'&1&J\end{Bmatrix}\begin{bmatrix}K'&K&J\\\Lambda_{10}&-\Lambda_{10}&0\end{bmatrix}\chi_{QK}\chi^{*}_{QK'}\right] \quad (3.16)$$

or

$$\sigma_{2b}=\left[\delta(\Omega_{10},\Omega_{2b})\frac{32\pi^2\mu^2}{\hbar^4 q_0 k^3}\left[\frac{I}{c\omega^2}\right]\right]\times[A_0+A_2P_2(\cos\theta_\alpha)], \quad (3.17)$$

wherein

$$A_0=-\frac{1}{\sqrt{3}}\sum_Q(2Q+1)(-1)^{Q+\Lambda_{10}}\times\sum_K\begin{Bmatrix}1&K&Q\\K&1&0\end{Bmatrix}\begin{bmatrix}K&K&0\\\Lambda_{10}&-\Lambda_{10}&0\end{bmatrix}\times|\chi_{QK}|^2, \quad (3.18)$$

$$A_2=\frac{2}{\sqrt{30}}\sum_Q(2Q+1)(-1)^{Q+\Lambda_{10}}\times\sum_{K,K'}\begin{Bmatrix}1&K&Q\\K'&1&2\end{Bmatrix}\begin{bmatrix}K'&K&2\\\Lambda_{10}&-\Lambda_{10}&0\end{bmatrix}\times\chi_{QK}\chi^{*}_{QK'}. \quad (3.19)$$

These formulas show that the inelastic integral cross section can be represented as a single unbounded sum over total angular momentum quantum numbers and that its polarization dependence has the simple functional form $[a+b\cos^2\theta_\alpha]$. Indeed, under the threshold conditions mentioned in the previous paragram ($\Lambda_{2b}=0$), we obtain the very simple results

$$A_0+A_2P_2(\cos\theta_\alpha)=\tfrac{1}{9}\cos^2\theta_\alpha \quad (3.20)$$

for $\Lambda_{10}=0$, and

$$A_0+A_2P_2(\cos\theta_\alpha)=\tfrac{1}{6}\sin^2\theta_\alpha \quad (3.21)$$

in the case that $\Lambda_{10}=1$. Thus the angular distribution serves as a signature of the Λ selection rule of the electric-dipole transition, at least when $\Lambda_{2b}=0$. These results may be of use in providing an experimental tool for determining the magnitude of Λ_{10}, something of considerable value when several initial molecular states are possible contributors to the reaction.

Finally, the magnitude of σ_{2b} can be gauged by using sensible estimates for the objects appearing in Eqs. (3.16)–(3.19). In particular, we can decompose the matrix element χ_{QK} into the product of a factor $[(ea_0)\omega/k]$, containing the Bohr radius a_0, with a dimensionless quantity $\bar{\chi}_{QK}$, the magnitude of which is expected to be of the order of unity. The cross section of (3.16) is then connected by the formula

$$\sigma_{2b}=\delta(\Omega_{2b},\Omega_{10})\frac{32\pi^2\mu^2}{\hbar^4 q_0 k^3}\left[\frac{I}{c\omega^2}\right]\frac{(ea_0)^2\omega^2}{k^2}\bar{\sigma}_{2b} \quad (3.22)$$

to a dimensionless object

$$\bar{\sigma}_{2b}=\sum_{J,Q}\sum_{K,K'}(2Q+1)(2K+1)\begin{bmatrix}1 & 1 & J\\ 0 & 0 & 0\end{bmatrix}P_J(\cos\theta_\alpha)\times\begin{bmatrix}K & J & K'\\ \Lambda_{10} & 0 & -\Lambda_{10}\end{bmatrix}(-1)^{Q+\Lambda_{10}+K+K'}\times\begin{Bmatrix}1 & K & Q\\ K' & 1 & J\end{Bmatrix}\bar{\chi}_{QK}\bar{\chi}^{*}_{QK'}\,, \tag{3.23}$$

the value of which should be on the order of unity. As an example, let us consider Na $\cdots$ Na collisions with $k=q_0=10^{-8}$ cm^{-1}, in which case the only significant contributions to the cross section are from K and K' with values of 20 or less. Then, with $\omega=2\times10^{15}$ sec^{-1}, $\mu=4\times10^{-23}$ g, and $\bar{\sigma}_{2b}\approx1$ we find that σ_{2b} (cm^2)$=10^{-27}I$ (W/cm^2). Thus σ_{2b} is small, but not unobservably so, being about $10^{-11}I$ (W/cm^2) times the geometric cross section. The smallness of this number verifies that a perturbative treatment is adequate for this process.

To complete the picture we turn now to the elastic scattering. Thus, from (2.18), (3.7), (3.8), and the identity

$$\delta(\hat{\mathbf{R}}-\hat{\mathbf{k}})=\sum_{K,M}N_K^2D^K_{\Lambda,M}(\hat{\mathbf{R}})D^K_{\Lambda,M}(\hat{\mathbf{k}})^*\,, \tag{3.24}$$

it follows that

$$\langle\langle\xi,\mathbf{R}|\Phi_{10\mathbf{k}N}\rangle\rangle\underset{R\to\infty}{\sim}[e^{i\mathbf{k}\cdot\mathbf{R}}+(e^{ikR}/R)f^{+}_{10}(\hat{\mathbf{R}})]\times\phi_{10}(\xi|R\hat{\mathbf{z}})|N\rangle\,, \tag{3.25}$$

with

$$f^{+}_{10}(\hat{\mathbf{R}})=\frac{2\pi}{ik}\sum_{K,M}N_K^2D^K_{\Lambda_{10},M}(\hat{\mathbf{R}})[D_{\Lambda_{10},M}(-\hat{\mathbf{k}})^*e^{2i\eta_{1K}}-D_{\Lambda_{10},M}(\hat{\mathbf{k}})^*]\,. \tag{3.26}$$

While the object $f^{+}_{10}(R)$ is formally a scattering amplitude, it does not have an immediate interpretation in terms of a physically observable cross section. However, the appropriate elastic scattering amplitude can be identified without great difficulty. Let us recall that the basis scattering states used here are specific to a fixed value of Λ_{10}. Although this is convenient and sensible for modest values of the total angular momentum quantum number K, in an actual collision the electronic orbitals of the atoms will not maintain fixed values of Λ_{10} for *large* values of K. Since scattering through any significant angle is associated with those values of K for which Λ_{10} is "locked" to its initial value, this discrepancy should have no effect upon the physical predictions of the theory.

We shall see that because Λ_{10} is fixed for all values of K, the scattering state obtained when $V_{10}(R)$ is set equal to its asymptotic value $V_{10}(\infty)$ is *not*, in general, quite a plane wave. To identify the portion of the scattering associated with $V_{10}(R)$ we must subtract from the full elastic scattering wave function that which would result if $V_{10}(R)$ were everywhere equal to $V_{10}(\infty)$. In the specific case of $\Lambda_{10}=0$ the latter is a simple plane wave and the procedure for extracting the scattering amplitude is the standard one. In the general case we proceed by introducing an auxiliary function $f^{+0}_{10}(R)$ which is obtained from Eq. (3.26) by replacing η_{1K}, the phase shift associated with the radial wave function $F_{10K}(k,R)$ [cf. Eqs. (3.14), (2.16), (2.17′), and (2.18)], with η^0_{1K}, the phase shift obtained when Eq. (2.16) is solved with the electronic energy $V_1(R)$ set equal to its asymptotic value $V_1(\infty)$. The solution of this modified form of (2.16) can be written as $F^0_{10K}(k,R)=k(kR)^{-1/2}J_\lambda(kR)$, with $\lambda\equiv[(K+\frac{1}{2})^2-\Lambda^2_{10}]^{1/2}$ and where $J_\lambda(y)$ denotes the Bessel function which satisfies the equation[11]

$$y^2Q''(y)+yQ'(y)+(y^2-\lambda^2)Q(y)=0\,, \tag{3.27}$$

is bounded at the origin, and has the asymptotic form (cf. p. 526 of Ref. 11)

$$J_\lambda(y)\underset{y\to\infty}{\sim}(2/\pi y)^{1/2}\cos(y-\lambda\pi/2-\pi/4)\,. \tag{3.28}$$

Consequently, $F^0_{10K}(k,R)$ has the requisite asymptotic form,

$$F^0_{10K}(k,R)\underset{R\to\infty}{\sim}(2/\pi)^{1/2}R^{-1}\sin(kR+\eta^0_{1K})\,, \tag{3.29}$$

with

$$\eta^0_{1K}=\pi/4-\lambda\pi/2=-\pi K/2+(K+\tfrac{1}{2})\left\{1-\left[1-\left[\frac{\Lambda_{10}}{K+\frac{1}{2}}\right]^2\right]^{1/2}\right\}. \tag{3.30}$$

When $\Lambda_{10}=0$, $F^0_{10K}(k,R)$ is proportional to the spherical Bessel function $j_K(k,R)$, η^0_{1K} equals $-\pi K/2$, and $f^{+0}_{10}(\hat{\mathbf{R}})$ vanishes identically. When $\Lambda_{10}\neq0$, we rewrite (3.22) in the form

$$f^{+}_{10}(\hat{\mathbf{R}})=f^{+0}_{10}(\hat{\mathbf{R}})+\delta f^{+}_{10}(\hat{\mathbf{R}})\,, \tag{3.31}$$

with $f^{+0}_{10}(\hat{\mathbf{R}})\neq0$ and where

$$\delta f^{+}_{10}(\hat{\mathbf{R}})=\frac{2\pi}{ik}\sum_{K,M}N_K^2D^K_{\Lambda_{10},M}(\hat{\mathbf{R}})D^K_{\Lambda_{10},M}(-\hat{\mathbf{k}})^*\times(e^{2i\eta_{1K}}-e^{2i\eta^0_{1K}})\,. \tag{3.32}$$

When $\hat{\mathbf{z}}$ is chosen equal to $\hat{\mathbf{k}}$ this becomes

$$\delta f^{+}_{10}(\hat{\mathbf{R}})=k^{-1}\sum_K(2K+1)[d^{(K)}_{\Lambda_{10},-\Lambda_{10}}(\theta)e^{i\Lambda_{10}\phi}]\times(e^{2i(\eta^0_{1K}+\pi K/2)})(e^{i\delta_{1K}}\sin\delta_{1K})\,, \tag{3.33}$$

with $\delta_{1K}\equiv\eta_{1K}-\eta^0_{1K}$. The object $d^{(K)}_{\Lambda,-\Lambda}(\theta)\equiv D^K_{\Lambda,-\Lambda}(0,\theta,0)$ appearing here is the regular solution of an ordinary second-order differential equation, cf. p. 65 of Ref. 8.

The term $f^{+0}_{10}(\hat{\mathbf{R}})$ is a contribution from the asymptotic part of the continuum wave function that arises from the dynamic constraint that the component of orbital angular momentum along the internuclear axis have a fixed value $\Lambda_{10}\hbar$. Associated with this constraint is the long-

ranged contribution $-\hbar^2\Lambda_{10}^2/2\mu R^2$ to the effective potential which governs the radial wave function $F_{10K}(k,R)$. Consequently, the asymptotic form of the wave function $\langle\langle \xi,\mathbf{R}|\Phi^+_{10kN}\rangle\rangle$ differs from the plane-wave state

$$\exp(i\mathbf{k}\cdot\mathbf{R})\phi_{10}(\xi|R\hat{\mathbf{z}})|N\rangle$$

even if the channel potential $V_1(R)$ is equal to its asymptotic value $V_1(\infty)$ at all internuclear separations.

The function $\delta f^+_{10}(\hat{\mathbf{R}})\equiv f^+_{10}(\hat{\mathbf{R}})-f^{+0}_{10}(\hat{\mathbf{R}})$ can be identified with the elastic scattering amplitude characteristic of the potential $V_1(R)$. The corresponding integral cross section is

$$\sigma^{\rm el}_{10}=\int d\hat{\mathbf{R}}|\delta f^+_{10}(\hat{\mathbf{R}})|^2$$
$$=\frac{4\pi^2}{k^2}\sum_{K,M}N_K^2|D^K_{\Lambda_{10},M}(-\hat{\mathbf{k}})|^2\,|e^{2i\eta_{1K}}-e^{2i\eta^0_{1K}}|^2$$
$$=\frac{4\pi}{k^2}\sum_K(2K+1)\sin^2\delta_{1K}\ . \qquad (3.34)$$

This result (3.34) is formally identical to the usual partial-wave expression for the elastic cross section.[12] Furthermore, it converges in the same sense as does the usual series, because δ_{1K} rapidly approaches zero as K rises to values so large [e.g., $K(K+1)>R_c^2k^2$] that the associated wave function does not penetrate into the region where $V_1(R)\neq V_1(\infty)$.

B. Excited electronic state supports one or more bound nuclear states

The electronic energy $V_1(R)$ of this second example is the same as that of the first. However, $V_2(R)$ has been changed; it now can support one or more bound nuclear states, although only one is indicated in Fig. 1(b). Let us first assume that the total center-of-mass energy of the system is greater than the threshold energy of the excited electronic state, i.e., that $E_T>V_2(\infty)+(N-1)\hbar\omega$. Then, provided that the atomic collision is accompanied by absorption of a laser photon, the electronically excited products of reaction will separate from one another with a relative kinetic energy $E_2=E_1+V_1(\infty)-V_2(\infty)+\hbar\omega>0$, dictated by the conservation of energy. (Of course, it is possible in principle for the spontaneous or stimulated emission of a photon to return the collision complex to its initial electronic state, but the occurrence of such an event is extremely unlikely.) Although the Green operator G_2^+ of (3.9) now includes bound-state as well as continuum contributions, the former are not contributors to the asymptotic form of $|\psi_2\rangle\rangle$. Therefore the inelastic scattering amplitude will be given by the same formula as before. Its numerical value will, of course, be altered somewhat by the change of $V_2(R)$. Similar remarks apply to elastic scattering.

Indeed, it is only in the subthreshold regime $E_T<V_2(\infty)+(N-1)\hbar\omega$ that the situation becomes truly interesting. In this case the products of the collision cannot separate from one another in the excited electronic state even though this state may be fleetingly occupied. Only two postcollisional, final states of the radiation field are accessible. Thus the collision may terminate in the photon state $n_1=N$, either because the atomic collision is a field-free elastic process or because it is a collision-induced two-photon event involving the absorption and subsequent *stimulated* emission of laser photons. However, it also is possible for the final state to be $n_1'=(N-1,\kappa\mu)$, consisting of $N-1$ laser photons together with a single *spontaneously* emitted photon of momentum $\hbar\boldsymbol{\kappa}$ and polarization $\hat{\boldsymbol{\alpha}}_\mu$ ($\hat{\boldsymbol{\alpha}}_\mu\cdot\boldsymbol{\kappa}=0$, $\mu=1,2$).

The dynamics of these subthreshold scattering events are governed by the same two coupled equations, (3.1) and (3.2), as before. However, the solution of the second of these no longer is given by the open-channel, expanding-wave formula (3.4). To obtain the equation which determines $|\psi_2\rangle\rangle$ we substitute $|\psi_1\rangle\rangle=|\Phi_1\rangle\rangle+G_1^+H_{12}|\psi_2\rangle\rangle$ from (3.3) into (3.2). The result of this is the linear inhomogeneous equation

$$(H^+_{22}-E_T)|\psi_2\rangle\rangle=-H_{21}|\Phi_1\rangle\rangle\ . \qquad (3.35)$$

Here, $H^+_{22}\equiv H_{22}+H_{21}G_1^+H_{12}$ is a non-Hermitian operator descriptive of transitory bound nuclear motion on the energy surface $V_2(R)$, coupled by the operator $H_{\rm int}$ to the open channel 1. The right-hand side of (3.35) represents the photoabsorptive excitation of the colliding atoms that initially populates the decaying state $|\psi_2\rangle\rangle$.

To compute the Green operator associated with H^+_{22} we use the first-order perturbative estimates

$$|2bQMq,N-1;\pm\rangle\rangle=|2bQMq,N-1\rangle\rangle+\cdots \qquad (3.36)$$

and

$$\varepsilon_2(bQMq)=[E_2(Qb)+(N-1)\hbar\omega]+\langle\langle 2bQMq,N-1|H_{21}G_1^+H_{12}|2bQMq,N-1\rangle\rangle+\cdots \qquad (3.37)$$

to the eigenkets and eigenvalues of the equations

$$[H^+_{22}-\varepsilon_2(bQMq)]|2bQMq,N-1;+\rangle\rangle=0\ ; \qquad (3.38)$$

$$[H^-_{22}-\varepsilon_2^*(bQMq)]|2bQMq,N-1;-\rangle\rangle=0\ ,$$
$$H^-_{22}=H_{22}+H_{21}G_1^-H_{12}\ . \qquad (3.39)$$

The kets $|2bQMq,N-1;+\rangle\rangle$ and their adjoints $|2bQMq,N-1;-\rangle\rangle$ are "bi-orthogonal" in the sense

$$\langle\langle 2bQMq,N-1;+|2bQ'M'q',N-1;-\rangle\rangle$$
$$=\delta_{QQ'}\delta_{MM'}\delta(q-q')\ . \qquad (3.40)$$

The quantity $E_2(Qb)<V_2(\infty)$ appearing in (3.37) is the "internal energy" of the undressed quasibound state, the numerical value of which can be obtained from the energy-conservation condition $E_2(Qb)+(N-1)\hbar\omega$

$=E_1+V_1(\infty)+N\hbar\omega$. The first-order perturbative approximation to the energy of the corresponding resonance is

$$E_2(Qb)+\mathrm{Re}\langle\langle 2bQMq,N-1|H_{21}G_1^+H_{12}|2bQMq,N-1\rangle\rangle;$$

this can be identified with ε_2 of Fig. 1(b).

At the subthreshold energies considered here the unbound, continuum states should not be important contributors to the Green operator $(E_T-H_{22}^+ +i\epsilon)^{-1}$. Consequently, they are disregarded. Then, by using the perturbative estimates of (3.36) and (3.37), we can express the solution of (3.35) in the form

$$|\psi_2\rangle\rangle=\sum_{b,Q,M,q} W_2^{-1}(bQMq)|2bQMq,N-1\rangle\rangle \times\langle\langle 2bQMq,N-1|H_{21}|\Phi_1\rangle\rangle\ , \tag{3.41}$$

with

$$W_2(bQMq)=E_T-E_2(Qq)-(N-1)\hbar\omega-\langle\langle 2bQMq,N-1|H_{21}G_1^+H_{12}|2bQMq,N-1\rangle\rangle$$
$$=E_1+V_1(\infty)+\hbar\omega-[E_2(Qq)+\Delta]+i\frac{\pi}{2}\Gamma\ . \tag{3.42}$$

In the second line of (3.42) the symbols Δ and $-i(\pi/2)\Gamma$ have been substituted for the real and imaginary parts of the matrix element

$$\langle\langle 2bQMq,N-1|H_{21}G_1^+H_{12}|2bQMq,N-1\rangle\rangle\ .$$

Finally, from (3.3) we see that the entrance-channel component of the state vector can be related to $|\psi_2\rangle\rangle$ of (3.41) by the formula

$$|\psi_1\rangle\rangle=|\Phi_1\rangle\rangle+\lim_{\epsilon\to 0+}\left[\sum_{K',M',a'}\sum_n\int dk'\frac{|1a'K'M'k'n\rangle\rangle\langle\langle 1a'K'M'k'n|}{E_T-E(1k')-\langle n|H_r|n\rangle+i\epsilon}\right]H_{\mathrm{int}}|\psi_2\rangle\rangle\ , \tag{3.43}$$

Here, the sum over states of the radiation field includes $n_1=N$ and $n_1'=(N-1,\kappa\mu)$, with the latter implying a sum over the polarizations $\hat{\alpha}_\mu$ and an integral over the wave vector κ of the spontaneously emitted photon; $E(1k')\equiv\hbar^2k'^2/2\mu+V_1(\infty)$.

From the first term on the right-hand side of (3.43) we obtain the potential scattering amplitude $f_{10}^+=f_{10}^{+0}+\delta f_{10}^+$ of (3.31). The scattering amplitude associated with the remainder of (3.43) is

$$f_{10n}^+(\hat{\mathbf{R}})=-(2\pi)^{1/2}\frac{\mu}{\hbar^2k_n'(k,\kappa)}\sum_{K',M'}N_{K'}D^{K'}_{\Lambda_{10},M'}(\hat{\mathbf{R}})e^{i\eta_{1K'}}\langle\langle 10K'M'k_n'(k),n|H_{\mathrm{int}}|\psi_2\rangle\rangle\ , \tag{3.44}$$

with $k_n'(k,\kappa)$ the solution of $E_T=E(1k')+\langle n|H_r|n\rangle$. To obtain a more explicit expression for this portion of the elastic scattering amplitude we substitute for $|\psi_2\rangle\rangle$ from (3.41), with $|\Phi_1\rangle\rangle$ given by (3.7). Finally, the axis of laser polarization is selected to be coincident with the laboratory z axis, i.e., $\hat{\alpha}=\hat{\mathbf{z}}$. The result of these manipulations is the formula

$$f_{10n}^+(\hat{\mathbf{R}})=-32\pi^2(\mu/\hbar^2k)\sum_{\substack{K,K',m,M'\\ b,Q,q}}N_KN_{K'}D^K_{\Lambda_{10},M}(-\hat{\mathbf{k}})^*D^K_{\Lambda_{10},M'}(\hat{\mathbf{R}})L_{MM'}(QKK')$$
$$\times W_2^{-1}(bQMq)e^{i(\eta_{1K}+\eta_{1K'})}[\delta(n|n_1)\mathcal{F}(n_1)+\delta(n|n_1')\mathcal{F}(n_1')]\ , \tag{3.45}$$

with

$$\mathcal{F}(N)=k^{-1}(2\pi I/c\omega^2)F^*(2bQq,10K'k)F(2bQq,10Kk)\delta_{MM'} \tag{3.46}$$

$$\mathcal{F}(N-1,\kappa\mu)=k'(k,\kappa)^{-1}(2\pi\hbar/\Omega c\kappa)(2\pi I/c\omega^2)^{1/2}F^*(2bQq,1aK'k'(k,\kappa))F(2bQq,10Kk)[(4\pi/3)^{1/2}Y^*_{1,M'-M}(\hat{\alpha}_\mu)] \tag{3.47}$$

and where $\kappa=|\boldsymbol{\kappa}|$ in (3.47) denotes the wave number of the spontaneously emitted photon. Finally, $k'(k,\kappa)$ is given by the solution of $\hbar^2k'^2/2\mu+\hbar c\kappa=\hbar^2k^2/2\mu+\hbar\omega$ and

$$L_{MM'}(QKK')\equiv(2Q+1)N_KN_{K'}\begin{pmatrix}Q & 1 & K'\\ -\Lambda_2 & \Lambda_2-\Lambda_{10} & \Lambda_{10}\end{pmatrix}^2\begin{pmatrix}Q & 1 & K'\\ -M & M-M' & M'\end{pmatrix}\begin{pmatrix}Q & 1 & K\\ -M & M-M' & M'\end{pmatrix}\ . \tag{3.48}$$

The term $f_{10n_1}^+(\hat{\mathbf{R}})$ interferes with δf_{10}^+ of (3.32), whereas $f_{10n_1'}^+$ does not. Therefore the integral cross section associated with $|\psi_1\rangle\rangle$ of (3.43) is the sum of two parts,

$$\sigma_{10}^{\mathrm{el-st}}=\sum_{K',M'}\Big|2\pi i k^{-1}N_{K'}D^{K'}_{\Lambda_{10},M'}(-\hat{\mathbf{k}})^*(e^{2i\eta_{1K'}}-e^{2i\eta^0_{1K'}})$$
$$-[32\pi^2(\mu/\hbar^2k^2)(2\pi I/c\omega^2)]\sum_K e^{i(\eta_{1K}+\eta_{1K'})}N_K[D^K_{\Lambda_{10},M}(-\hat{\mathbf{k}})]^*$$
$$\times\sum_{b,Q,q}L_{MM'}(QKK')W_2^{-1}(bQMq)F^*(2bQq,10K'k)F(2bQq,10Kk)\Big|^2, \tag{3.49}$$

which accounts for field-free elastic and two-laser-photon events [absorption follows by *stimulated* (st) emission], and

$$\sigma_{10}^{\mathrm{sp}}=(2\pi)^{-3}I\sum_{K',M'}\int_0^\infty d\kappa\,\kappa k'(k,\kappa)k^{-1}\Big|\sum_{\Delta M=0,\pm1}\sum_{K,Q,b,q}W_2^{-1}(bQMq)P(K,K',M'+\Delta M,M';bQq;a)\Big|^2, \tag{3.50}$$

with

$$P(K,K',M,M';bQq;a)=4^{-|M-M'|}\left[\frac{\mu}{\hbar^2kk'(k,\kappa)}\right]\left[\frac{3\pi\hbar}{c^2\omega^2}\right]^{1/2}\left[\frac{256}{3\pi^3}\right]N_Ke^{i(\eta_{1K}+\eta_{1K'})}$$
$$\times D^K_{\Lambda_{10},M}(-\hat{\mathbf{k}})^*L_{MM'}(QKK')F(2bQq,10Kk)F^*[2bQq,1aK'k'(k,\kappa)], \tag{3.51}$$

which accounts for absorption followed by *spontaneous* (sp) emission.

The reason that these cross sections depend on the direction ($\hat{\mathbf{k}}=\mathbf{k}/k$) of the initial relative momentum of the two atoms is that the lab $\hat{\mathbf{z}}$ axis has been chosen to coincide with the direction $\hat{\boldsymbol{\alpha}}$ of laser polarization, cf. Fig. 3.

The final step in the development is the presentation of an explicit expression for the matrix element

$$\langle\langle 2bQMq,N-1|H_{21}G_1^+H_{12}|2bQMq,N-1\rangle\rangle=\lim_{\epsilon\to0+}\sum_{a',K',M',n}\int dk'\frac{|\langle\langle 2bQMq,N-1|H_{\mathrm{int}}|1a'K'M'k'n\rangle\rangle|^2}{E_T-E(1k')-\langle n|H_r|n\rangle+i\epsilon}$$
$$=\Delta_{12}^{\mathrm{sp}}+I\Delta_{12}^{\mathrm{st}}-i\frac{\pi}{2}(\Gamma_{12}^{\mathrm{sp}}+I\Gamma_{12}^{\mathrm{st}}) \tag{3.52}$$

that contributes to $W_2(bQMq)$, cf. (3.42). The quantities $\Delta_{12}^{\mathrm{sp}}$ and $I\Delta_{12}^{\mathrm{st}}$ appearing here are level shifts associated with the processes of spontaneous (sp) and stimulated (st) photoemission. $\Gamma_{12}^{\mathrm{sp}}$ and $I\Gamma_{12}^{\mathrm{st}}$ are the corresponding level widths given by the formulas

$$\Gamma_{12}^{\mathrm{sp}}=\left[\frac{2\mu}{\hbar^2}\frac{16}{3}2\pi\hbar\right](2Q+1)\sum_{K,a}(2K+1)\delta(\Omega_{2b},\Omega_{1a})\left|\begin{bmatrix}Q & 1 & K\\ -\Lambda_{2b} & \Lambda_{2b}-\Lambda_{10} & \Lambda_{10}\end{bmatrix}\begin{bmatrix}Q & 1 & K\\ -M & 0 & M\end{bmatrix}\right|^2$$
$$\times\left[\frac{1}{(2\pi)^3}\int d\kappa\frac{\kappa^2}{k'(k,\kappa)}|F(2bQq,1aK,k'(k,\kappa)|^2\right] \tag{3.53}$$

and

$$\Gamma_{12}^{\mathrm{st}}=\left[\frac{2\mu}{\hbar^2}\frac{2}{\pi}\frac{2\pi}{c}\right](2Q+1)\sum_{K,a}(2K+1)\delta(\Omega_{2b},\Omega_{1a})\left|\begin{bmatrix}Q & 1 & K\\ -\Lambda_2 & \Lambda_{2b}-\Lambda_{10} & \Lambda_{10}\end{bmatrix}\right|^2$$
$$\times\sum_{M'}\left|\begin{bmatrix}Q & 1 & 1\\ -M & M-M' & M'\end{bmatrix}\right|^2\left[\frac{1}{k}|F(2bQq,10Kk)|^2\right], \tag{3.54}$$

respectively.

The equations presented above provide explicit formulas for the integral cross section, specific to the case when the excited electronic channel is closed. To aid in the interpretation of these results we shall express $\sigma_{10}=\sigma_{10}^{\mathrm{el-st}}+\sigma_{10}^{\mathrm{sp}}$ in a more compact and traditional "resonance" cross section form. Thus by combining a few of the preceding formulas we can write the integral cross section appropriate to subthreshold conditions in the form

$$\sigma_{10}=\sum_{K',M'}\left[\left|A^{K'M'}+I\sum_{b,K,Q,q}\frac{B^{K'M'}_{bKQq}}{U_{bQq}+IV_{bQq}}\right|^2\right.$$
$$+I\int_0^\infty d\kappa\,\kappa[k'(k,\kappa)/k]$$
$$\left.\times\left|\sum_{b,K,Q,q}\frac{C^{K'M'}_{bKQq}}{U_{BQq}+IV_{bQq}}\right|^2\right], \tag{3.55}$$

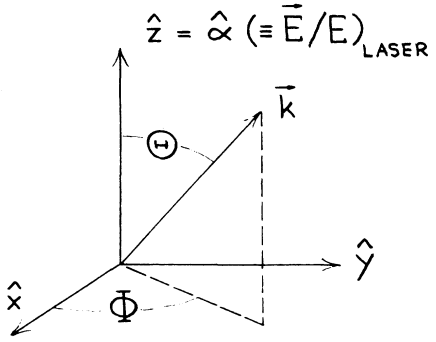

FIG. 3. Vectors and coordinates involved in $\sigma_{10}^{el\text{-}st}$ and σ_{10}^{sp}.

where A, B, C, U, and V are functions of k; A, B, and C are functions of $\hat{\mathbf{k}}=\mathbf{k}/k$ as well (Fig. 3 is relevant in this context); and $U=U'-iU''$ and $V=V'-iV''$, with U'' and V'' proportional to Γ_{12}^{sp} and Γ_{12}^{st}, respectively. $U'+V'$ is equal to the difference between the total energy of the system and the sum of the level-shifted bound state plus $(N-1)\hbar\omega$.

To extract the essence from this result it is useful once again to introduce estimates for the quantities it involves and then to suppress numerical factors of the order of unity. Thus, by introducing the order-of-magnitude estimates

$$F(2bQq,1aKk)\sim\begin{cases}(ea_0)\omega/k & \text{unbound excited state}\\ (ea_0)\omega/k^{1/2} & \text{bound excited state}\end{cases}, \tag{3.56}$$

ignoring all but one resonant state, and assuming that $\kappa=\omega/c$, it is found that

$$\sigma_{10}\approx\left|\frac{1}{k}+\frac{IA(1/k)}{\Delta E-iA\left[\dfrac{\hbar\omega^3\Delta\omega}{c^3}+\dfrac{I}{c}\right]}\right|^2 +I\frac{\omega}{c}\frac{\Delta\omega}{c}\left|\frac{A(\omega^2/k)(\hbar/c^2\omega^2)^{1/2}}{\Delta E-iA\left[\dfrac{\hbar\omega^3\Delta\omega}{c^3}+\dfrac{I}{c}\right]}\right|^2 . \tag{3.57}$$

Here, $A=(\mu/\hbar^2k^2)(ea_0)^2$ and, as in the preceding section, a_0 denotes the Bohr radius. The symbol $\Delta\omega$ indicates a characteristic *range* of spontaneous photon frequencies which generally will depend in a complex way upon the shapes of the relevant potential energy curves. One would expect the value of $\Delta\omega$ to be less than that of ω but possibly not by more than one order of magnitude. Finally, by discarding the level shifts (which are not essential to the present, qualitative arguments) we can identify ΔE with $E_T-E_2(Qq)-(N-1)\hbar\omega$.

Despite its obvious inadequacies the simple formula (3.57) is a useful tool for generating crude numerical estimates. Thus, with $k=10^8$ cm^{-1}, $\omega=2\times10^{15}$ sec^{-1}, $\Delta\omega=10^{14}$ sec^{-1}, and $\mu=4\times10^{-23}$ g, it predicts a resonance width (in eV) of

$$\Gamma\simeq3\times10^{-7}+3\times10^{-19}I\ (\text{W/cm}^2) \tag{3.58}$$

and an integral cross section (in cm^2) of

$$\sigma_{10}\simeq\frac{1}{k^2}\left|1+\frac{10^{-8}I}{\Delta E-i\Gamma}\right|^2 +\frac{1}{k^2}[(2.2\times10^9)I]\left|\frac{2\times10^{-17}}{\Delta E-i\Gamma}\right|^2 . \tag{3.59}$$

It can be seen from this example that, although the resonances are very narrow, they are capable of producing contributions to the inelastic cross section that are comparable to and possibly even greater than typical elastic cross sections. It also is noteworthy that estimates of the resonance width which fail to take account of spontaneous emission could be very much in error. More elaborate calculations than these are, of course, required to determine with precision the magnitudes of the effects predicted here. However, two points about the present results deserve mention. First, our estimate of the resonance width corresponds to a very reasonable lifetime of about 10^{-9} sec. Secondly, the *maximum* values of the resonant portions of σ_{10} are nearly independent of our crude estimates (3.56) for $F(2bQq,1aKk)$ because, at resonance, there is a cancellation of the numerator and denominator factors of A.

IV. PROCESSES INVOLVING THREE ELECTRONIC STATES

The processes considered here differ from those treated previously in that they directly involve a third quasimolecular electronic state. To be specific we assume that the adiabatic (diabatic) energy curves associated with the two lower-lying states are identical with those of Sec. III B; compare Figs. 1(b) and 1(c). The additional state, labeled 3, is purely repulsive. The symmetries of these states are taken to be such that the transitions $1\rightarrow2$ and $2\rightarrow3$ are dipole allowed. Therefore, direct single-photon transitions from 1 to 3 cannot occur. The coupled equations (2.9) appropriate to this case are

$$(H_{11}-E_T)|\psi_1\rangle\rangle=-H_{12}|\psi_2\rangle\rangle\ , \tag{4.1}$$

$$(H_{22}-E_T)|\psi_2\rangle\rangle=-H_{21}|\psi_1\rangle\rangle-H_{23}|\psi_3\rangle\rangle\ , \tag{4.2}$$

$$(H_{33}-E_T)|\psi_3\rangle\rangle=-H_{32}|\psi_2\rangle\rangle\ . \tag{4.3}$$

Just as in the second of the examples treated in Sec. III one proceeds differently depending upon the value of the energy. If $E_T<V_2(\infty)+(N-1)\hbar\omega$, then as before *single*-photon collision-induced transitions cannot produce separated products in state 2. Similarly, when $E_T<V_3(\infty)+(N-2)\hbar\omega$, it is energetically impossible to populate state 3, even if two photons were to be absorbed. There are two situations of interest. In the first of these $E_T>V_2(\infty)+(N-1)\hbar\omega$ *and* $E_T>V_3(\infty)+(N-2)\hbar\omega$, so that channel 2 is open to single-photon excitation *and* absorption of two photons can produce products in channel 3. The second situation differs from the first in that channel 2 is closed, that is, $E_T<V_2(\infty)+(N-1)\hbar\omega$. The products of collision than either will separate from

one another in state 3 (after the absorption of two laser photons) or in the ground state 1. We now proceed to the analysis of these two cases.

A. Channel 2 is accessible by single-photon absorption

In this situation $V_1(\infty)+\hbar\omega > V_2(\infty)$, cf. Fig. 1(c), and it is furthermore assumed that $V_1(\infty)+2\hbar\omega > V_3(\infty)$. The boundary conditions appropriate to this case are incorporated into the coupled equations (4.1)–(4.3) by rewriting them in the forms

$$|\psi_1\rangle\rangle = |\Phi_1\rangle\rangle + G_1^+ H_{12}|\psi_2\rangle\rangle \ , \tag{4.4}$$

$$|\psi_2\rangle\rangle = G_2^+ H_{21}|\psi_1\rangle\rangle + G_2^+ H_{23}|\psi_3\rangle\rangle \ , \tag{4.5}$$

$$|\psi_3\rangle\rangle = G_3^+ H_{32}|\psi_2\rangle\rangle \ . \tag{4.6}$$

To lowest order in the radiative couplings these become $|\psi_1\rangle\rangle \doteq |\Phi_1\rangle\rangle$, $|\psi_2\rangle\rangle \doteq G_2^+ H_{21}|\Phi_1\rangle\rangle$, and $|\psi_3\rangle\rangle \doteq G_3^+ H_{32} G_2^+ H_{21}|\Phi_1\rangle\rangle$. With this approximation the scattering amplitude and cross section for channel 2 are the same as those given in Sec. III. The scattering amplitude associated with channel 3 is (with the choice $\hat{\alpha}=\hat{\mathbf{z}}$ of Fig. 3)

$$f_{3c}^+(\hat{\mathbf{R}}) = \frac{8\mu}{\pi\hbar^2 k s_0}\left[\frac{I}{c\omega^2}\right] \times \sum_{K',K,M} D^K_{\Lambda_{3c},M}(\hat{\mathbf{R}}) D^{K'}_{\Lambda_{10},M}(-\hat{\mathbf{k}})^* N_{KK'M} \ , \tag{4.7}$$

with

$$N_{KK'M} = \sum_{b,Q} C^b_{QKK'M}(-i\pi^2\mu/\hbar^2 q_0) F^*(2bQq_0|3cK's_0) \times F(2bQq_0|10Kk) \tag{4.8}$$

and where

$$C^b_{QKK'M} = (-1)^{\Lambda_{3c}+\Lambda_{2b}} e^{i(\eta_{1K}+\eta_{3K'})}\delta(\Omega_{3c},\Omega_{2b})\delta(\Omega_{2b},\Omega_{10})(2Q+1)(2K+1)(2K'+1) \times \begin{bmatrix} Q & 1 & K \\ -M & 0 & M \end{bmatrix}\begin{bmatrix} Q & 1 & K' \\ -M & 0 & M \end{bmatrix}\begin{bmatrix} Q & 1 & K \\ -\Lambda_{2b} & \Lambda_{2b}-\Lambda_{3c} & \Lambda_{3c} \end{bmatrix}\begin{bmatrix} Q & 1 & K' \\ -\Lambda_{2b} & \Lambda_{3c}-\Lambda_{2b} & \Lambda_{3c} \end{bmatrix} . \tag{4.9}$$

The wave numbers q_0 and s_0 appearing in these formulas are solutions of $E_T=\hbar^2 q_0^2/2\mu + V_2(\infty)+(N-1)\hbar\omega$ and $E_T=\hbar^2 s_0^2/2\mu + V_3(\infty)+(N-2)\hbar\omega$, respectively.

No contributions from spontaneous emission appear in (4.7) and (4.8), for the collisional event is far too brief to permit the quasimolecule to radiate spontaneously. Beyond this, two features of f_{3c}^+ deserve mention. First, this scattering amplitude is proportional to the laser intensity I and so the corresponding cross section will be proportional to I^2. Secondly, f_{3c}^+ will be very small for the laser intensities ($I < 10^{10}$ W cm^{-2}) to which our theory is applicable. This is expected, for it already was found in Sec. III that single-photon free-free transitions are rare events. One therefore expects the comparable double transitions to be correspondingly more unlikely.

The integral cross section for this collision-induced, two-photon $1\rightarrow 3$ transition is given by the formulas

$$\begin{aligned}\sigma_{3c} &= \frac{s_0}{k}\int d\hat{\mathbf{R}}|f_{3c}^+|^2 \\ &= 4\pi\left[\frac{8\mu}{\pi\hbar^2}\right]^2 (k^3 s_0)^{-1}\left[\frac{I}{c\omega^2}\right]^2 \sum_{K',K'',M} D^{K'}_{\Lambda_{10},M}(-\hat{\mathbf{k}})^* D^{K''}_{\Lambda_{10},M}(-\hat{\mathbf{k}}) \sum_K (2K+1)^{-1} N_{KK'M} N^*_{KK''M} \\ &= 4\pi\left[\frac{8\mu}{\pi\hbar^2}\right]^2 (k^3 s_0)^{-1}\left[\frac{I}{c\omega^2}\right]^2 \sum_J (2J+1) B_J P_J(\cos\theta) \ ,\end{aligned} \tag{4.10}$$

with

$$B_J = \sum_{K',K'',M} (-1)^{\Lambda_{10}+M}\begin{bmatrix} K' & K'' & J \\ \Lambda_{10} & -\Lambda_{10} & 0 \end{bmatrix} \times \begin{bmatrix} K' & K'' & J \\ M & -M & 0 \end{bmatrix} \times \sum_K (2K+1)^{-1} N_{KK'M} N^*_{KK''M} \tag{4.11}$$

and where $\Theta=\cos^{-1}(\hat{\mathbf{k}}\cdot\hat{\alpha})$, cf. Fig. 3.

B. Channel 2 is closed

By substituting (4.4) and (4.6) into (4.2) we obtain for $|\psi_2\rangle\rangle$ an equation of the same form

$$(H_{22}^+ - E_T)|\psi_2\rangle\rangle = -H_{21}|\Phi_1\rangle\rangle \ , \tag{4.12}$$

as (3.31). However, the non-Hermitian operator

$$H_{22}^+ = H_{22} + H_{21}G_1^+ H_{12} + H_{23}G_3^+ H_{32} \tag{4.13}$$

appropriate to the present situation not only contains radiative couplings between states 2 and 1 but between 2 and 3 as well.

The solution of (4.12) is constructed following the procedure of Sec. III. This solution then can be used to compute $|\psi_3\rangle\rangle = G_3^+ H_{32}|\psi_2\rangle\rangle$ and the associated scattering amplitude [compare with (4.7)]

$$f_{3c}^{+}(\hat{\mathbf{R}})=\frac{8\mu}{\pi\hbar^2 k s_0}\left[\frac{I}{c\omega^2}\right] \times \sum_{K',K,M} D^{K}_{\Lambda_{3c},M}(\hat{\mathbf{R}})D^{K'}_{\Lambda_{10},M}(-\hat{\mathbf{k}})^* N_{KK'M}(I) , \tag{4.14}$$

with [compare with (4.8)]

$$N_{KK'M}(I)=\sum_{b,Q,q} C^{b}_{QKK'M}[W_2'(bQMq)]^{-1} \times F^*(2bQq|3cK's_0)F(2bQq|10Kk) \tag{4.15}$$

and [compare with (3.42) and (3.52)]

$$\begin{aligned} W_2'(bQMq)&=E_T-E_2(Qq)-(N-1)\hbar\omega-\left[\Delta'-i\frac{\pi}{2}\Gamma'\right] \\ &=E_1+V_1(\infty)+\hbar\omega \\ &\quad-[E_2(Qq)+\Delta^{\mathrm{sp}}_{12}+I(\Delta^{\mathrm{st}}_{12}+\Delta^{\mathrm{st}}_{23})] \\ &\quad+i\frac{\pi}{2}[\Gamma^{\mathrm{sp}}_{12}+I(\Gamma^{\mathrm{st}}_{12}+\Gamma^{\mathrm{st}}_{23})] . \end{aligned} \tag{4.16}$$

The level shift $\Delta^{\mathrm{st}}_{23}$ and width $\Gamma^{\mathrm{st}}_{23}$ are defined analogously to $\Delta^{\mathrm{st}}_{12}$ and $\Gamma^{\mathrm{st}}_{12}$, respectively.

The integral cross section appropriate to this case is given by (4.10) but with the factor B_J replaced with an analogous factor $B_J(I)$. This, in turn, is related to the intensity-dependent quantities $N_{KK'M}(I)$ by a formula identical to the connection (4.11) between B_J and $N_{KK'M}$.

An analysis similar to that appearing at the end of Sec. III (and using the same numbers that were employed in the example presented there) produces the estimate (in cm^2)

$$\sigma_{3c}\approx\frac{10^{-26}}{k^2}[I(\mathrm{W/cm}^2)]^2 \tag{4.17}$$

for the "nonresonant" two-photon cross section of (4.10). Here it has been assumed that $s_0=q_0=k$. Similarly, the maximum value of the resonant two-photon cross section of Sec. IV B is given approximately by the formula

$$\sigma^{\mathrm{reson}}_{3c}\approx\frac{10^{-22}}{k^2}[I(\mathrm{W/cm}^2)]^2 . \tag{4.18}$$

This dramatic increase is precisely analogous to the "resonance enhancement" observed in bound-state spectroscopy. Indeed, given a sufficiently powerful laser, this example indicates that the magnitude of the resonant *two*-photon cross section will not be far different from that of the corresponding nonresonant *one*-photon process. As it was with the previous examples, the accuracy of these estimates must be tested by performing more careful (and difficult) calculations. What these preliminary estimates indicate is that the cross sections probably are large enough and interesting enough to warrant a more detailed numerical examination.

V. CONCLUDING REMARKS

In closing, we identify the most important features of this investigation as well as the methods used to carry it out. One of our objectives has been to demonstrate that resonant cross sections for laser-induced excitation transfer processes can be handled with relative ease and rigor by using a projection-operator scheme. The principal limitations of our analysis are (1) a neglect of fine-structure effects and (2) the assumption that the ground electronic state is incapable of supporting bound nuclear states. While the first of these limitations almost certainly is of little concern, the second imposes severe restrictions upon the systems to which our analysis is applicable. The elimination of this restriction if a goal of our current research. Once this has been done we shall be able to extend the present theory to include the cross sections for formation of *bound* ground state *A-B* molecules by a laser-assisted collision process similar to that of Sec. III. Also of interest is the analysis of "two-color" experiments in which a "power" laser is used to excite the collision complex and a second "spectroscopic" laser probes the complex much as ordinary lasers are used to probe bound molecular species. We believe that the theory of these events can be treated though extensions of the formalism developed here.

Two features of our mathematical approach deserve additional consideration, since in their absence the rigor of the present work would be lost. A systematic and quantitative treatment of spontaneous radiation and its effects requires that the radiation field be treated as a quantal rather than a classical object. We have seen, particularly with regard to resonance lifetimes, that spontaneous radiation plays a critical role. This provides *a posteriori* justification for our decision to treat the radiation field quantally. Secondly, the difficulties normally attendant to such an approach have been overcome in part by the projection-operator scheme and in part by our use of the symmetry top basis set. It is the latter of these that has made the formal manipulations involving the various resonance widths both tractable and rigorous. It also has produced an overall simplification of the scattering formalism, in a fashion analogous to that which it has to the theory of associative ionization.[13] The use of this basis is commonplace in bound-state problems and so it should not be surprising that it is useful in collision problems as well. By combining these various elements we have shown that laser-induced resonant transitions and the effects of spontaneous radiation upon these processes can be systematically treated in systems composed of colliding atoms.

ACKNOWLEDGMENTS

This research was supported by a grant from the National Science Foundation.

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