Theory of laser-induced excitation transfer and atomic association

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Formulas are derived for the differential and integral cross sections associated with laser-induced excitation transfer. The theory is patterned closely after our recent treatment of laser-induced chemi-ionization. It is found that cross sections specific to single-photon absorption are proportional to the square of the cosine of the angle between the laser polarization and the initial relative velocity of the two colliding atoms. The distortion by a laser of the cross section for an elastic scattering event also is treated. Finally, a cross-section formula is derived for a collision-induced two-photon absorption, mediated by a single intermediate electronic state.

I. INTRODUCTION

The theory presented here is an extension to nonionizing events of our recent analysis[1,2] of laser-induced chemi-ionization. It is applicable to the atomic collisional processes represented schematically by the equation

$$A^*+B\rightarrow[(A^*\cdots B)\xrightarrow{\hbar\omega}(A\cdots B^*)]\rightarrow\begin{Bmatrix} AB^*, & \text{LIA} \\ A+B^*, & \text{LIET}\end{Bmatrix} \tag{1.1}$$

and called laser-induced association (LIA) and laser-induced excitation transfer (LIET), respectively. The laser frequency ω is assumed not to be resonant with any electronic transition of the two reactant atoms A^* and B. Consequently, photoabsorption or simulated emission as indicated in (1.1) only can occur during the brief interval when the electronic state of the A^*-B pair is undergoing a collisional distortion. Although events falling into the category LIET can take place during large impact parameter collisions, our principal concern is with situations where the interactional distortions of one or both of the colliding atoms are too large to be treated perturbatively.

Figure 1 shows three typical situations. In each case $R_r(\omega)$ denotes the internuclear separation at which the "resonance condition," $\hbar\omega=E_f(R)-E_i(R)$, is satisfied. In the first of these examples either LIA or LIET can occur, depending on whether the total energy

$$E^{\text{tot}}=N\hbar\omega+E_i(\infty)+E(\equiv\vec{p}\,^2_{ni}/2\mu)=\begin{cases}(N-1)\hbar\omega+E_f(\infty)+E_{n'}^{L'} \\ (N-1)\hbar\omega+E_f(\infty)+E'(\equiv\vec{p}\,^2_{nf}/2\mu)\end{cases} \tag{1.2}$$

for LIA and LIET, respectively, is equal to E_1^{tot} or E_2^{tot}. It also is possible for collision-induced stimulated emission to occur, thereby transforming a colliding A-B^* pair with relative kinetic energy E_2' into the product species A^* and B with a final relative kinetic energy equal to E_2.

The pair of electronic energy curves depicted of Fig. 1(b) provides an example where only LIET and the inverse, stimulated emission event can occur. Finally, the

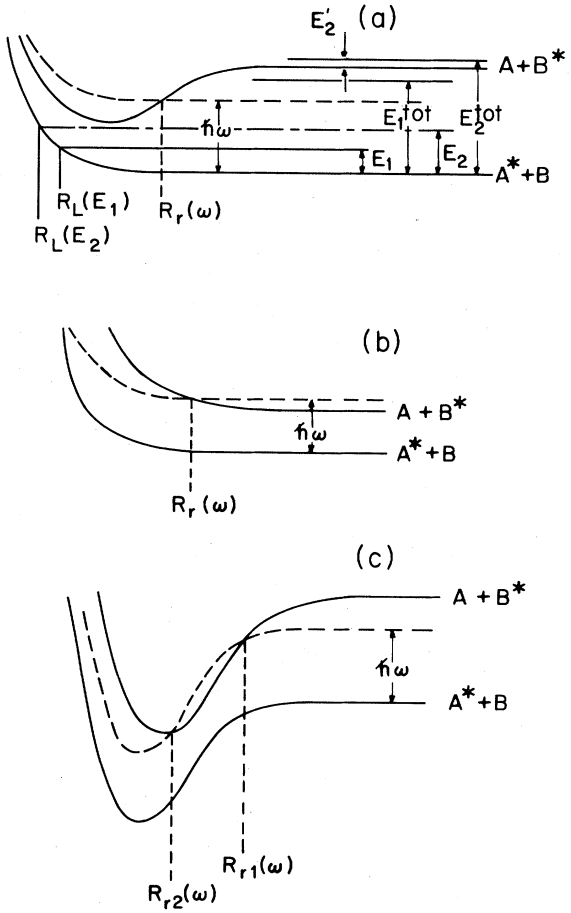

FIG. 1. Three examples of situations where laser-induced excitation transfer and/or laser-induced association could occur. E_1 and E_2 of (a) indicate two different values for the relative kinetic energy of A^* and B: $E_1^{\text{tot}}=E_1+\hbar\omega$ and $E_2^{\text{tot}}=E_2+\hbar\omega$ are the corresponding total energies. $R_L(E_1)$ and $R_L(E_2)$ are the classical turning points associated with the two different energies, specific to the relative orbital angular momentum L. Finally, $R_r(\omega)$ denotes the internuclear separation at which the Bohr condition $\hbar\omega=E_f(R)-E_i(R)$ is satisfied.

curves in Fig. 1(c) are shaped so that the "photoresonance condition" can be satisfied at two distinct internuclear separations. The theory presented in Sec. II is applicable to single-photon events occurring at either of these points. Curves similar to those of Fig. 1(c) are commonplace, familiar examples being the ionic and covalent potential energy curves of the hydrogen halides and the two lowest lying singlet states of H_2. When the curves are shaped as they are in Fig. 1(c), multiple-photon processes also can occur, with sequential absorptions and stimulated emissions taking place at R_{r1} and R_{r2}. A classical path theory already has been developed for events such as these:[3] its quantal analog is presented in Sec. III. A second multiphoton process treated in Sec. III is the sequential absorption of two photons, proceeding through an intermediate state.

II. COLLISION-INDUCED, SINGLE-PHOTON EVENTS

We consider two crossed atomic beams, one of species A and one of B. Focused on the collision region are one or more single-mode lasers. The Hamiltonian of this system is taken to be of the form

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

Here $T_n = \vec{\rm p}_n^{\,2}/2\mu$ is the relative kinetic energy of the two atomic nuclei, no distinction being made between the nuclear center of mass and that of the entire system. The operator $H_{\rm el}$ is the sum of the electronic kinetic energies and of all the Coulombic interactions among the nuclei and electrons. Spin-orbit interactions are neglected. $H_r = \sum_j \hbar\omega a_j^\dagger a_j$ is the energy of the free radiation field(s), with $a_j^\dagger$ and a_j denoting creation and annihilation operators for photons with angular frequency ω_j and linear polarization $\hat{\alpha}_j$. Finally, $H_{\rm int}$ is the energy of interaction between the charged particles and the laser(s). In all of the applications considered here this operator is limited to the electric dipole interaction between the laser(s) and the electrons.

A collision begins with the reactants in an electronic state (belonging to a single irreducible representation of $C_{\infty v}$) represented by the ket $|\phi_i\rangle = |\phi_{A^*B}\rangle$. The coordinate representatives of the wave function and energy of this state are given by the expressions $\phi_i(\vec{r}\,|\,\vec{R}) = \langle\langle \vec{r},\vec{R}\,|\,\phi_i\vec{R}\rangle\rangle = \langle\langle \vec{r},\vec{R}\,|\,\phi_i(\vec{R})\rangle\rangle$ and

$$E_i(R) = \langle\langle \phi_i(\vec{R})\,|\,H_{\rm el}\,|\,\phi_i(\vec{R})\rangle\rangle = \int d\vec{r}\,\phi_i^*(\vec{r}\,|\,\vec{R})H_{\rm el}\phi_i(\vec{r}\,|\,\vec{R}) \ , \tag{2.2}$$

respectively. Here and henceforth, $\vec{R}$ denotes the internuclear vector separation and $\vec{r}$ the aggregate of electronic spin and position variables. Single brackets ($|\ \rangle$ and $\langle\ |$) signify electronic or nuclear configurations whereas double brackets ($|\ \rangle\rangle$ and $\langle\langle\ |$) refer to the composite.

The electronic state subsequent to photoexcitation is represented by the ket $|\phi_f\rangle = |\phi_{AB^*}\rangle$. The associated wave function and energy are $\phi_f(\vec{r}\,|\,\vec{R})$ and $E_f(R) = \langle\langle \phi_f(\vec{R})\,|\,H_{\rm el}\,|\,\phi_f(\vec{R})\rangle\rangle$.

Our analysis will be limited to the (electron$\times$photon) subspace spanned by the orthogonal projection operators

$$Q = |\phi_i,N\rangle\langle\phi_i,N| \quad (|\phi_i,N\rangle \equiv |\phi_i\rangle\otimes|N\rangle) \ , \qquad P = |\phi_f,N'\rangle\langle\phi_f,N'| \ , \tag{2.3}$$

with the photon number N' equal either to $N-1$ (photoexcitation) or $N+1$ (stimulated emission). The position representative of the relevant photon matrix elements of $H_{\rm int}$ are

$$\langle\vec{R}\,|\,\langle\phi_f,N\pm1\,|\,H_{\rm int}\,|\,\phi_i,N\rangle\,|\,\vec{R}\,'\rangle = \delta(\vec{R}-\vec{R}\,')V_{fi}(\vec{R},\vec{\omega}) \tag{2.4a}$$

with

$$V_{fi}(\vec{R},\vec{\omega}) = i(2\pi I\hbar\omega/c)^{1/2}w_{fi}(R,\omega) \times \langle\langle \phi_f(\vec{R})\,|\,\hat{\alpha}\cdot\vec{d}\,|\,\phi_i(\vec{R})\rangle\rangle \ . \tag{24b}$$

Here I is the laser intensity, $\vec{\omega} = (\omega,\hat{\alpha})$, and $\vec{d} = -\sum_i e\vec{r}_i$ is the electronic dipole moment operator. Finally, $w_{fi}(R,\omega)$ is the function $[E_f(R)-E_i(R)]/\hbar\omega$ which inadvertently was equated to its "resonance value" of unity in the Appendix (and text) of Ref. 1.

The dipole matrix element in (2.4b) can be written more explicitly as

$$\langle\langle \phi_f(\vec{R})\,|\,\hat{\alpha}\cdot\vec{d}\,|\,\phi_i(\vec{R})\rangle\rangle = (4\pi/3)^{1/2}\sum_{m=0,\pm1} Y_{1m}^*(\hat{\alpha})_{\hat{R}}\langle\langle \phi_f(\vec{R})\,|\,d_m\,|\,\phi_i(\vec{R})\rangle\rangle$$
$$= (4\pi/3)^{1/2}(-1)^\mu \sum_{m'} Y_{lm'}(\hat{\alpha})\mathscr{R}^{(1)}_{m',-\mu}(\hat{R})\langle\langle \phi_f(\vec{R})\,|\,d_\mu\,|\,\phi_i(\vec{R})\rangle\rangle \tag{2.5}$$

with $Y_{1m}(\hat{\alpha})_{\hat{R}}$ and $Y_{1m}(\hat{\alpha})$ denoting spherical harmonics referred to the internuclear axis ($\hat{R} = \vec{R}/R$) and to a laboratory frame, respectively. $d_m = \hat{e}_m\cdot\vec{d}$ indicates one of the body-frame, spherical components of the electric dipole moment operator and $\mathscr{R}^{(j)}_{m,m'}(\hat{R}) = \mathscr{R}^{(j)}_{m,m'}(\phi,\theta,0)$ is a representation coefficient of O(3), as defined by Messiah.[4] Finally, $\mu = \mu_{fi} = \Lambda_f - \Lambda_i$ is the difference between the final and initial values of the quantum number which specifies the component of electronic orbital angular momentum parallel to the internuclear axis. The matrix elements given by (2.5) can differ from zero only if μ equals 0 or ±1.

The cross sections for LIET are related to the T matrix

$$T_{fi}(\vec{E}\,'\,|\,\vec{E}) = \langle\langle \Phi_P^-(\vec{E}\,')\,|\,PHQ\,|\,\Psi^+(\vec{E})\rangle\rangle = \int d\vec{R}\,\Phi_P^-(\vec{E}\,'\,|\,\vec{R})^* V_{fi}(\vec{R},\vec{\omega})\Psi_Q^+(\vec{E}\,|\,\vec{R}) \tag{2.6}$$

wherein $\vec{E} = (E,\hat{K}_i)$ and $\vec{E}\,' = (E',\hat{K}_f)$. The functions $\Phi_P^-(\vec{E}\,'\,|\,\vec{R})$ and $\Psi_Q^+(\vec{E}\,|\,\vec{R})$ appearing in this expression

are the position representatives of the two nuclear kets $\langle\phi_f,N\pm1\,|\,\Phi_P^+(\vec{E}')\rangle\rangle$ and $\langle\phi_i,N\,|\,\Psi_Q^+(\vec{E})\rangle\rangle \equiv\langle\phi_i,N\,|\,Q\Psi^+(\vec{E})\rangle\rangle$, respectively. $|\,\Phi_P^-\rangle\rangle$ is the solution of the single-channel equation $(E_T-PHP)\,|\,\Phi_P\rangle\rangle=0$, with $E_T=E^{\rm tot}$, which satisfies conventionally defined "in" boundary conditions: $\Phi_P^-(\vec{E}'\,|\,\vec{R})$ is the correspondingly conditioned solution of the partial differential equation

$$\left[E'-\left[-\frac{\hbar^2}{2\mu}\nabla_R^2+T_{ff}^{\rm BO}(\vec{R})+V_f(R)\right]\right]\Phi_P(\vec{E}\,|\,\vec{R})=0 \quad (2.7)$$

wherein $V_f(R)\equiv E_f(R)-E_f(\infty)$ and $E'=E-[E_f(\infty)-E_i(\infty)]+\hbar\omega$. $T_{ff}^{\rm BO}(\vec{R})$ is a diagonal element of the Born-Oppenheimer coupling operator

$$T_{mn}^{\rm BO}(\vec{R})=-\frac{\hbar^2}{2\mu}(\langle\phi_m\,|\,\nabla_R^2\,|\,\phi_n\rangle+2\langle\phi_m\,|\,\vec{\nabla}_R\,|\,\phi_n\rangle\cdot\vec{\nabla}_R)\,. \quad (2.8)$$

We henceforth discard all elements of this operator.

The function $\Psi_Q^+(\vec{E}\,|\,\vec{R})$ satisfies the integral equation

$$\Psi_Q^+(\vec{E}\,|\,\vec{R})=\Phi_Q^+(\vec{E}\,|\,\vec{R})+\int d\vec{R}'\langle\langle\phi_i(\vec{R})\,|\,G_Q^+(E)QHPG_P^+(E')PHQ\,|\,\phi_i(\vec{R}')\rangle\rangle\Psi_Q^+(\vec{E}\,|\,\vec{R}') \quad (2.9)$$

with $G_Q^+(E)=[Q(E_T^+-H)Q]^{-1}$, $G_P^+(E')=[P(E_T^+-H)P]^{-1}$, and $E_T^+=E_T+i0$. Finally, $\Phi_Q^+(\vec{E}\,|\,\vec{R})$ denotes the regular solution of the differential equation

$$\left[E-\left[-\frac{\hbar^2}{2\mu}\nabla_R^2+V_i(R)\right]\right]\Phi_Q(\vec{E}\,|\,\vec{R})=0 \quad (2.10)$$

which satisfies "out-type" boundary conditions. The notation introduced here will be retained throughout the paper, with the symbol $\Phi_{P_j}^{\pm}$ used for a single, uncoupled channel and with $\Psi_{P_j}^{\pm}=P_j\Psi^{\pm}$ designating a projection of the "complete," several-channel motion.

The partial wave expansions of the two nuclear wave functions appearing in the T-matrix formula (2.6) can be written as

$$\Psi_Q^+(\vec{E}\,|\,\vec{R})=\sum_{L,M}Y_{LM}^*(\hat{K}_i)Y_{LM}(\hat{R})i^Le^{i\bar{\eta}_i^L}R^{-1}\bar{F}_i^L(E\,|\,R)\,, \quad (2.11a)$$

$$\Phi_P^-(\vec{E}'\,|\,\vec{R})=\sum_{L',M'}Y_{L'M'}^*(\hat{K}_f)Y_{L'M'}(\hat{R})i^{L'}e^{-i\eta_f^{L'}}R^{-1}F_f^{L'}(E'\,|\,R)\,, \quad (2.11b)$$

with radial amplitudes $F_f^{L'}$ and $\bar{F}_i^L$ (overbars are used to draw attention to certain complex valued functions) which are regular at the origin and exhibit the asymptotic forms

$$\bar{F}_i^L(E\,|\,R)\sim(2\mu/\pi\hbar^2K)^{1/2}\sin(KR-\tfrac{1}{2}\pi L+\bar{\eta}_i^L)\,, \quad (2.12a)$$

$$F_f^{L'}(E'\,|\,R)\sim(2\mu/\pi\hbar^2K')^{1/2}\sin(K'R-\tfrac{1}{2}\pi L'+\eta_f^{L'})\,, \quad (2.12b)$$

with $K=(2\mu E/\hbar^2)^{1/2}$ and $K'=(2\mu E'/\hbar^2)^{1/2}$. In terms of these functions the transition matrix becomes

$$T_{fi}(\vec{E}'\,|\,\vec{E})=\sum_{\substack{LM,\\L',M'}}\sum_{m'}Y_{L'M'}(\hat{K}_f)Y_{LM}^*(\hat{K}_i)i^{L-L'}e^{i(\bar{\eta}_i^L+\eta_f^{L'})}[(4\pi/3)^{1/2}Y_{1m'}(\hat{\alpha})]\langle F_f^{L'}(E')\,|\,V_\mu\,|\,\bar{F}_i^L(E)\rangle$$
$$\times(-1)^{\mu+M'}\left[\frac{2L+1}{4\pi}\frac{2L'+1}{4\pi}\right]^{1/2}\sum_J(2J+1)\begin{pmatrix}L & L' & J\\ -M & M' & -m'\end{pmatrix}$$
$$\times\begin{pmatrix}L & L' & J\\ 0 & 0 & 0\end{pmatrix}\int d\hat{R}\,\mathscr{R}_{m',0}^{(J)}(\hat{R})\mathscr{R}_{m',-\mu}^{(1)}(\hat{R})\Bigg]\,. \quad (2.13)$$

The quantity $V_\mu=V_\mu(R,\omega)$ appearing here is defined by the same formula (2.4b) as $V_{fi}(\vec{R},\vec{\omega})$ but with $\hat{\alpha}\cdot\vec{d}$ replaced with $d_\mu=\hat{e}_\mu\cdot\vec{d}$. Also,

$$\langle F\,|\,V_\mu\,|\,G\rangle\equiv\int_0^\infty dR\,F^*(R)V_\mu(R,\omega)G(R)\,.$$

We now select the direction of the laboratory polar axis to coincide with that of $\vec{K}=K\hat{K}_i$ and introduce the (Franck-Condon related) approximation,

$$i^Le^{i\bar{\eta}_i^L}\langle F_f^{L'}\,|\,V_\mu\,|\,\bar{F}_i^L\rangle\doteq i^{L'}e^{-i\bar{\eta}_i^{L'}}\langle F_f^{L'}\,|\,V_\mu\,|\,\bar{F}_i^{L'}\rangle\,, \quad (2.14)$$

that the heavy-particle orbital angular momentum is unaltered by the photoabsorptive event. [Previous studies[5,6] have shown that the heavy-particle angular momentum is strictly conserved only for laser intensities below certain critical values, typically of the order of 10 GW/cm^2. This is not of great concern to us here, however, because the present theory loses its appropriateness at field intensities which are sufficiently large to produce significant distortions of the electronic states; cf. Sec. IV.] The T matrix then assumes the much simpler form

$$T_{fi}(\vec{\mathrm{E}}'\,|\,\vec{\mathrm{E}})=\frac{1}{4\pi}u_\mu\cos\theta_\alpha\sum_L\left[\frac{2L+1}{4\pi}\right]^{1/2}Y_{L0}(\hat{K}_f)\langle F_f^L(E')\,|\,V_\mu\,|\,\bar{F}_i^L(E)\rangle\exp i(\bar{\eta}_i^L+\eta_f^L) \tag{2.15}$$

with $\cos\theta_\alpha=\hat{K}_i\cdot\hat{\alpha}$ and

$$u_\mu=(-1)^\mu\sum_J(2J+1)\int d\hat{R}\,\mathscr{R}^{(J)}_{0,0}(\hat{R})\mathscr{R}^{(1)}_{0,-\mu}(\hat{R}) \tag{2.16}$$

The differential cross section for LIET now can be written as

$$\frac{d\sigma_{fi}(E)}{d\hat{K}_f}=g_i\frac{(2\pi)^4}{K^2}\,|\,T(\vec{\mathrm{E}}'\,|\,\vec{\mathrm{E}})\,|^2$$
$$=g_i\left[\frac{\pi^2\,|\,u_\mu\,|^2}{K^2}\right]$$
$$\times\left[\sum_{l=0}^{\infty}(2l+1)B_l(E)P_l(\cos\theta_f)\right]\cos^2\theta_\alpha \tag{2.17}$$

with g_i denoting the statistical weight of the initial state and where θ_f is defined by $\cos\theta_f=\hat{K}_f\cdot\hat{K}_i$. The energy (and $\vec{\omega}$)-dependent coefficients B are given by the formula

$$B_l(E)=(1+\delta_{l0})^{-1}\sum_{L=0}^{\infty}[F_l(L,L+l)+F_l(L+l,L)] \tag{2.18}$$

with

$$F_l(L,L')=\left|\begin{pmatrix}L & L' & l\\ 0 & 0 & 0\end{pmatrix}\right|^2 q^L(E',E)q^L(E',E)^* \tag{2.19a}$$

and

$$q^L(E',E)=(2L+1)\langle F_f^L(E')\,|\,V_\mu\,|\,\bar{F}_i^L(E)\rangle$$
$$\times\exp i(\bar{\eta}_i^L+\eta_f^L)\,. \tag{2.19b}$$

The corresponding integral cross section for LIET is

$$\sigma_{fi}(E)=4\pi g_i\left[\frac{\pi^2\,|\,u_\mu\,|^2}{K^2}\right]B_0(E)\cos^2\theta_\alpha\,. \tag{2.20}$$

Before we examine these results more closely let us consider LIA as well. Thus the transition matrix element specific to laser-induced association into the *bound* molecular state with energy $E_{n'}^{L'}$ and wave function

$$\Phi_P^{M'}(E_{n'}^{L'}\,|\,\vec{\mathrm{R}})=Y_{L'M'}(\hat{R})R^{-1}F_f^{L'}(E_{n'}^{L'}\,|\,R) \tag{2.21}$$

is

$$T_{fi}(E_{n'}^{L'}\,|\,\vec{\mathrm{E}})=\delta_{M'0}\frac{1}{4\pi}u_\mu\cos\theta_\alpha\left[\frac{2L'+1}{4\pi}\right]^{1/2}i^{L'}e^{i\bar{\eta}_i^{L'}}\langle F_f^{L'}(E_{n'}^{L'})\,|\,V_\mu\,|\,\bar{F}_i^{L'}(E)\rangle \tag{2.22}$$

and the associated cross section is

$$\sigma_{n'L'M'}(E)=\delta_{M'0}q_i\left[\frac{\pi^2\,|\,u_\mu\,|^2}{4\pi K^2}\right](2L'+1)\,|\,\langle F_f^{L'}(E_{n'}^{L'})\,|\,V_\mu\,|\,\bar{F}_i^{L'}(E)\rangle\,|^2\exp[-2\mathrm{Im}(\bar{\eta}_i^{L'})]\cos^2\theta_\alpha\,. \tag{2.23}$$

The radial wave function $F_f^{L'}(E_{n'}^{L'}\,|\,R)$ and the corresponding energy $E_{n'}^{L'}$ are determined by the eigenvalue problem

$$\left[E_{n'}^{L'}-\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+\frac{\hbar^2L'(L'+1)}{2\mu R^2}+V_f(R)\right]\right]F_f^{L'}(E_{n'}^{L'}\,|\,R)=0\,. \tag{2.24}$$

We have argued above that the collision-induced photoabsorptive and photoemissive events only occur at internuclear separations which satisfy the Bohr-like frequency condition $\hbar\omega=E_f(R)-E_i(R)$. However, it is clear from our analysis that the photoelectronic process is not the source of this condition, as was implied in Ref. 3. Instead, the requirement that $\hbar\omega$ be equal to the difference of adiabatic electronic energies is a Franck-Condon condition arising from the fact that (in the semiclassical limit) the product of nuclear wave functions occurring in the matrix elements $\langle F_f^L(E')\,|\,V_\mu(R,\omega)\,|\,\bar{F}_i^L(E)\rangle$ and $\langle F_f^L(E_n^L)\,|\,V_\mu(R,\omega)\,|\,\bar{F}_i^L(E)\rangle$ has a point of stationary phase at the internuclear separation for which $\hbar\omega=E_f(R)-E_i(R)$.[2] When the circumstances are such that no point of stationary phase exists, the resonance concept fails and the value of the corresponding nuclear matrix element [of $V_\mu(R,\omega)$] is likely to be very small. Transitions occurring at separations which do not conform to the resonance conditions are accompanied by changes of the nuclear kinetic energy.

The wave function $\Psi_Q^+(\vec{\mathrm{E}}\,|\,\vec{\mathrm{R}})$ and the associated set of radial amplitudes $\bar{F}_i^L(E\,|\,R)$ are dependent on the laser in-

tensity and on its polarization as well. This dependence could be explored by working with the Schrödinger equations (analogs of those derived by Bieniek[7] and by Saha, Dahler, and Nielsen[1] for field-free and laser-induced chemi-ionization) satisfied by these functions. These Schrödinger equations involved nonlocal operators descriptive of the effect of the laser on the projection of the nuclear motion in the incident channel.[8] Instead, we use the integral equation (2.9) and obtain from (2.6) the formula

$$T_{fi}(\vec{E}'|\vec{E})=T_{fi}^{\mathrm{DW}}(\vec{E}'|\vec{E})+\delta T_{fi}(\vec{E}'|\vec{E}) \tag{2.25}$$

with

$$T_{fi}^{\mathrm{DW}}(\vec{E}'|\vec{E})=\langle\langle \Phi_P^-(\vec{E}')|PHQ|\Phi_Q^+(\vec{E})\rangle\rangle \tag{2.26}$$

and

$$\delta T_{fi}(\vec{E}'|\vec{E})=\langle\langle \Phi_P^-(\vec{E}')|(PHQ)G_Q^+(QHP)G_P^+(PHQ)|\Psi_Q^+(\vec{E})\rangle\rangle\ . \tag{2.27}$$

The "distorted-wave" (DW) transition matrix T_{fi}^{DW} is exact to the lowest order ($I^{1/2}$) in the laser intensity. It only involves nuclear wave functions which satisfy single-channel wave equations with local potentials. All of the higher-order effects contained in δT_{fi} can be computed iteratively (but probably not convergently), order by order in I. Thus

$$\delta T_{fi}(\vec{E}'|\vec{E})=\int\int d\vec{E}_1' d\vec{E}_2'(E'-E_1'+i0)^{-1}(E-E_2'+i0)^{-1} \times T_{fi}^{\mathrm{DW}}(\vec{E}'|\vec{E}_1')\tilde{T}_{fi}^{\mathrm{DW}}(\vec{E}_1'|\vec{E}_2')\tilde{T}_{fi}^{\mathrm{DW}}(\vec{E}_2'|\vec{E})+O(I^{5/2})\ , \tag{2.28}$$

where the tilde attached to a T matrix such as

$$\tilde{T}_{fi}^{\mathrm{DW}}(\vec{E}'|\vec{E})=\int dR\ \Phi_P^+(\vec{E}'|\vec{R})^* V_{fi}(\vec{R},\vec{\omega})\Phi_Q^+(\vec{E}|\vec{R}) \tag{2.29}$$

indicates that *both* nuclear wave functions are conditioned by "out" boundary conditions. The classical interpretation of the term displayed explicitly in (2.28) is of a collision during which there occur two photoabsorptions and one stimulated emission. The phase of this contribution to δT_{fi} will differ from that of T_{fi}^{DW} and so can produce an interference term of order I^2 in the cross section.

III. EXAMPLES OF COLLISION-INDUCED, TWO-PHOTON PROCESSES

It has just been demonstrated (at the end of the preceding section) that the theory of this paper is applicable to processes involving the absorption and/or stimulated emission of several photons. Here two further examples of multiphoton processes will be examined: (i) pairs of absorptive and emissive events which result in laser-induced distortions of cross sections for elastic scattering and (ii) a sequential, two-photon absorption facilitated by an intermediate electronic state.

A. Field effects on elastic scattering

It was mentioned earlier in connection with Fig. 1(c) that it is possible, from a classical point of view, for (an alternating sequence of) resonant absorptions and stimulated emissions to occur at two distinct internuclear separations, the net effect being an elastic collisional encounter. It also is possible for a pair of these photoevents to occur near a single resonance separation, the first as the particles approach one another and the second as they fly apart. In either case it is to be expected that these paired photoevents will produce changes of the elastic cross section which are dependent on both the intensity and polarization of the laser.

To investigate this effect we retain the two-state model of the preceding section. The T matrix for elastic scattering then can be written in the form

$$T_{ii}(\vec{E}'|\vec{E})=T_{ii}^{\mathrm{FF}}(\vec{E}'|\vec{E})+\delta T_{ii}(\vec{E}'|\vec{E}) \tag{3.1}$$

where

$$T_{ii}^{\mathrm{FF}}(\vec{E}'|\vec{E})\int d\vec{R}\,\Phi_Q(\vec{E}'|\vec{R})^* V_i(R)\Phi_Q^+(\vec{E}|\vec{R}) \tag{3.2}$$

is the field-free (FF) value of the transition matrix for elastic scattering. Here $\Phi_Q(\vec{E}'|\vec{R})$ is the plane-wave function $(2\pi\hbar)^{-3/2}\exp(i\hbar\vec{K}'\cdot\vec{R})$ and, as before, $\Phi_Q^+(\vec{E}|\vec{R})$ denotes the wave function governed by the Hamiltonian operator $-(\hbar^2/2\mu)\nabla_R^2+V_i(R)$. The laser produces the additional T-matrix contribution

$$\delta T_{ii}(\vec{E}'|\vec{E})=\langle\langle \Phi_Q^-(\vec{E}')|(QHP)G_P^+(E_2')(PHQ)|\Psi_Q^+(\vec{E})\rangle\rangle = \int d\vec{E}''(E_2'-E''+i0)^{-1}T_{if}^{\mathrm{DW}}(\vec{E}'|\vec{E}'')\tilde{T}_{fi}(\vec{E}''|\vec{E}) \tag{3.3}$$

with $E_2'(E)=E-[E_f(\infty)-E_i(\infty)]+\hbar\omega$. Here $T_{\mathrm{if}}^{\mathrm{DW}}$ is defined as before, (2.26), and,

$$\tilde{T}_{fi}(\vec{E}''|\vec{E})=\int d\vec{R}\,\Phi_P^+(\vec{E}''|\vec{R})^* V_{fi}(\vec{R},\vec{\omega})\Psi_Q^+(\vec{E}|\vec{R}) \tag{3.4}$$

involves the wave function $\Psi_Q^+(\vec{E}|\vec{R})$ which satisfies the integral equation (2.9).

The lowest-order approximation (proportional to I) to δT_{ii} results from replacing $\tilde{T}_{fi}(\vec{E}''|\vec{E})$ in (3.3) with the

corresponding distorted-wave matrix $\tilde{T}_{fi}^{\mathrm{DE}}(\vec{\mathrm{E}}''\,|\,\vec{\mathrm{E}})$. The polarization dependence of the resulting cross section is the same as that for the case treated in Sec. III B and so will not be discussed separately here.

B. Sequential, two-photon absorption

The second example to be considered is a collision-induced two-photon absorption, facilitated by an intermediate electronic state. The analysis is reduced to its essentials by adopting a model consisting of three electronic states labeled 1, 2, and 3 in order of their increasing electronic energy. These energies can be imagined to vary with internuclear separation according to one or another of the two schematic representations of Fig. 2.

Although we shall treat the case of two lasers with frequencies and polarizations $\vec{\omega}'=(\omega,\hat{\alpha}')$ and $\vec{\omega}''=(\omega'',\hat{\alpha}'')$, the theory is equally applicable when the two absorbed photons are generated by a single laser. The critical feature is that state 1 comes into "radiative resonance" with 2 at a separation R_r' and 2 into resonance with 3 at R_r''. The Hamiltonian is the sum of $H=T_n+H_{\mathrm{el}}+H_r$ and $H'=H_{\mathrm{int}}$ with H_r and H_{int} both consisting of two parts, one specific to each of the two lasers.

In order that the two transitions $1\rightarrow 2$ and $2\rightarrow 3$ be dipole allowed, the parities of states 1 and 3 must be equal to one another and opposite to that of state 2. Thus a direct transition from 1 to 3 is dipole forbidden. The two allowed electric dipole transitions connect the (electron$\times$photon) subspaces associated with the three orthogonal projection operators

$$\begin{aligned} P_1&=|\,\phi_1,N',N''\rangle\langle\phi_1,N',N''\,|\equiv|\,1\rangle\langle 1\,|\ ,\\ P_2&=|\,\phi_2,N'-1,N''\rangle\langle\phi_2,N'-1,N''\,|\equiv|\,2\rangle\langle 2\,|\ ,\\ P_3&=|\,\phi_3,N'-1,N''-1\rangle\langle\Phi_3,N'-1,N''-1\,|\equiv|\,3\rangle\langle 3\,|\ . \end{aligned}\tag{3.5}$$

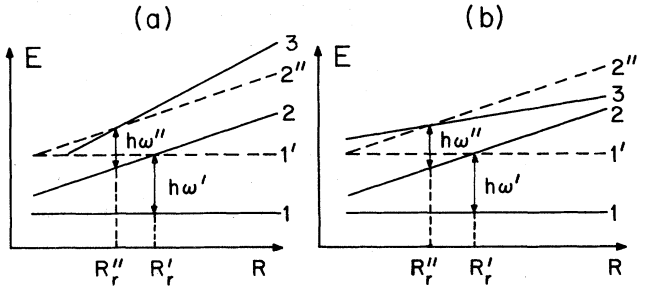

FIG. 2. Schematic depiction of the variations with internuclear separation of the energies of the three-state system considered in Sec. III B.

Accordingly, the state vector $|\,\Psi\rangle\!\rangle$ is the direct sum of three components $|\,\Psi_j\rangle\!\rangle=P_j\,|\,\Psi\rangle\!\rangle$ which satisfy the coupled equations

$$\begin{aligned} (E_T-H_{11})\,|\,\Psi_1\rangle\!\rangle&=H'_{12}\,|\,\Psi_2\rangle\!\rangle\ ,\\ (E_T-H_{22})\,|\,\Psi_2\rangle\!\rangle&=H'_{21}\,|\,\Psi_1\rangle\!\rangle+H'_{23}\,|\,\Psi_3\rangle\!\rangle\ ,\\ (E_T-H_{33})\,|\,\Psi_3\rangle\!\rangle&=H'_{32}\,|\,\Psi_{22}\rangle\!\rangle\ , \end{aligned}\tag{3.6}$$

wherein $H_{jj}=P_jHP_j$ and $H'_{jk}=P_jH'P_k$, $j\neq k$.

What we need are solutions of these equations, designated by the symbols $|\,\Psi_j^+(\vec{\mathrm{E}})\rangle\!\rangle$, specific to the initial electron-photon state $|\,1\rangle$ and to beam conditions characterized by the vector $\vec{\mathrm{E}}=(E,\hat{K})$. The corresponding value of E_T is $E+E_1(\infty)+N'\hbar\omega'+N''\hbar\omega''$. Let Q and P be defined as equal to P_1+P_2 and P_3, respectively. The T matrix for the collision-induced two-photon absorptive event then can be related to the solution $|\,\Psi^+(\vec{\mathrm{E}})\rangle\!\rangle$ by the formulas

$$\begin{aligned} T_{31}(\vec{\mathrm{E}}'\,|\,\vec{\mathrm{E}})&=\langle\!\langle\Phi_P^-(\vec{\mathrm{E}}')\,|\,PHQ\,|\,\Psi^+(\vec{\mathrm{E}})\rangle\!\rangle=\langle\!\langle\Phi_3^-(\vec{\mathrm{E}}')\,|\,H'_{32}\,|\,\Psi_2^+(\vec{\mathrm{E}})\rangle\!\rangle\\ &=\langle\!\langle\Phi_3^-(\vec{\mathrm{E}}')\,|\,H'_{32}[E_T^+-H_{22}-H'_{23}G_3^+(E')H'_{32}]^{-1}H'_{21}\,|\,\Psi_1^+(\vec{\mathrm{E}})\rangle\!\rangle\ . \end{aligned}\tag{3.7}$$

The last of these has been obtained by using Eq. (3.6) to relate $|\,\Psi_2^+\rangle\!\rangle$ to $|\,\Psi_1^+\rangle\!\rangle$. A second result that can be obtained from (3.6) is the integral equation

$$|\,\Psi_1^+(E)\rangle\!\rangle=|\,\Phi_1^+(\vec{\mathrm{E}})\rangle\!\rangle+G_1^+(E)H'_{12}[E_T^+-H_{22}-H'_{23}G_3^+(E')H'_{32}]^{-1}H'_{21}\,|\,\Psi_1^+(\vec{\mathrm{E}})\rangle\!\rangle\tag{3.8}$$

for $|\,\Psi_1^+(\vec{\mathrm{E}})\rangle\!\rangle$.

The two kets $|\,\Phi_1^+(\vec{\mathrm{E}})\rangle\!\rangle$ and $|\,\Phi_3^-(\vec{\mathrm{E}}')\rangle\!\rangle$ denote appropriately conditioned solutions of the single channel equations $(E_T-H_{jj})\,|\,\Phi_j\rangle\!\rangle=0$ which are specific to $\vec{\mathrm{E}}=(E,\hat{K})$ and $\vec{\mathrm{E}}'=(E',\hat{K}')$, respectively. The corresponding wave functions satisfy the two Schrödinger equations

$$\left[E-\left[-\frac{\hbar^2}{2\mu}\nabla_R^2+V_1(R)\right]\right]\Phi_1(\vec{\mathrm{E}}\,|\,\vec{\mathrm{R}})=0\tag{3.9a}$$

and

$$\left[E'-\left[-\frac{\hbar^2}{2\mu}\nabla_R^2+V_3(R)\right]\right]\Phi_3(\vec{\mathrm{E}}\,|\,\vec{\mathrm{R}})=0\tag{3.9b}$$

with $E'=E-[E_3(\infty)-E_1(\infty)]+\hbar\omega'+\hbar\omega''$.

The distorted-wave approximation to the T matrix of (3.7) can be written in either of the two forms

$$T_{31}^{\mathrm{DW}}(\vec{\mathrm{E}}'\,|\,\vec{\mathrm{E}})=\langle\langle\Phi_3^-(\vec{\mathrm{E}}')\,|\,H'_{32}G_2^+(E'')H'_{21}\,|\,\Phi_1^+(\vec{\mathrm{E}})\rangle\rangle$$
$$=\int d\vec{\mathrm{E}}'_2(E''-E'_2+i0)^{-1}T_{32}^{\mathrm{DW}}(\vec{\mathrm{E}}'\,|\,\vec{\mathrm{E}}'_2)\tilde{T}_{21}^{\mathrm{DW}}(\vec{\mathrm{E}}'_2\,|\,\vec{\mathrm{E}}) \tag{3.10}$$

with $E''(E)=E-[E_2(\infty)-E_1(\infty)]+\hbar\omega'$. This approximation to T_{31} is proportional to $I'^{1/2}I''^{1/2}$: the corrections of lowest order are proportional to $I'^{1/2}I''^{3/2}$ and $I'^{3/2}I''^{1/2}$.

The differential cross section for this two-photon absorptive process is directly proportional to $|\,T_{31}(\vec{\mathrm{E}}'\,|\,\vec{\mathrm{E}})\,|^2$ and this, in turn, is proportional to $\cos^2\theta'_\alpha\equiv(\hat{\alpha}'\cdot\hat{K})^2$. Its dependence on the polarization $\hat{\alpha}''$ is somewhat more complex. However, the corresponding *integral* cross section has the uncomplicated functional dependence

$$\int dK\,|\,T_{31}(\vec{\mathrm{E}}'\,|\,\vec{\mathrm{E}})\,|^2=a\cos^2\theta'_\alpha[b_1+(b_1-b_0)\cos^2\theta''_\alpha] \tag{3.11}$$

with $a=|\,u_{\mu_{21}}\,|^2/4(4\pi)^3$. To simplify the formulas for b_0 and b_1 as much as possible we assume that the single-photon T matrices appearing in (3.10) depend very weakly on the "intermediate-state" energy E'_2. The only significant contribution to the integral then will be that associated with the imaginary part $-i\pi\delta(E''-E'_2)$ of the propagator $(E''-E'_2+i0)^{-1}$. This approximation discards off-energy-shell contributions to T_{31}^{DW} and produces the formulas

$$b_j=\sum_L(2L+1)^{-1}\,|\,q_{32}^L(E'\,|\,E'')\,|^2\sum_{L',L''}q_{21}^{L'}(E''\,|\,E)q_{21}^{L''}(E''\,|\,E)^*a_j^L(L',L'') \tag{3.12a}$$

with

$$q_{ij}^l(E'\,|\,E)=(2l+1)\langle F_1^l(E')\,|\,V_{\mu_{ij}}\,|\,F_j^l(E)\rangle\exp[i(\eta_j^l-\eta_i^l)]\,, \tag{3.12b}$$

$$a_0^L(L',L'')=A_0^L(L')A_0^L(L'')\,, \tag{3.12c}$$

$$a_1^L(L',L'')=\tfrac{1}{2}[A_1^L(L')A_1^L(L'')^*+A_{-1}^L(L')A_{-1}^L(L'')^*]\,, \tag{3.12d}$$

and

$$A_M^L(L')=\sum_J(2J+1)\begin{bmatrix}L' & L & J\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}L' & L & J\\ 0 & M & -M\end{bmatrix}\int d\hat{R}\,\mathscr{R}_{M,0}^{(J)}(\hat{R})\mathscr{R}_{M,-\mu_{32}}^{(1)}(\hat{R})\,. \tag{3.12e}$$

The Franck-Condon principle (treated in Sec. II) leads us to expect that the cross section for this two-photon process will be large only if there are two separations R'_r and R''_r (as depicted in Fig. 2) which satisfy the resonance conditions $\hbar\omega'=E_2(R'_r)-E_1(R'_r)$ and $\hbar\omega''=E_3(R''_r)-E_2(R''_r)$. Among the many processes similar to that considered here is a three-photon absorption from one state to another (of opposite parity) which is enabled by *two* intermediate states.

IV. CLOSING REMARKS

In all of the examples examined in this paper our theory has proved itself capable of dealing quite efficiently with the contributions to the various cross sections which are of the lowest nontrivial order in the laser intensity. This is true for collision-induced two- and three-photon events as well as for collision processes which involve the absorption of but a single photon. However, the theory is not structured optimally to deal with higher-order terms in the laser intensity. This shortcoming is closely related to what might be identified as a second deficiency of the formalism, namely, that the cross sections have been defined in terms of transitions from one field-free electronic state to another. Both of these issues can be dealt with at once by recasting the theory in terms of the dressed states which actually exist within the laser spot, rather than in terms of the field-free, bare states used in this and two closely related papers[1,2] on laser-induced chemi-ionization. A dressed-state analog of the theory presented here has been developed and will be communicated separately.

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[1]H. P. Saha, J. S. Dahler, and S. E. Nielsen, Phys. Rev. A **28**, 1487 (1983).

[2]H. P. Saha and J. S. Dahler, Phys. Rev. A **28**, 2859 (1983).

[3]J. S. Dahler, R. E. Turner, and S. E. Nielsen, J. Phys. Chem. **86**, 1065 (1982).

[4]A. Messiah, *Quantum Mechanics* (Wiley, New York, 1962).

[5]P. L. DeVries and T. F. George, Mol. Phys. **38**, 561 (1979).

[6]P. S. Juliene and F. H. Mies, Phys. Rev. A **25**, 3399 (1982).

[7]R. J. Bieniek, Phys. Rev. A **18**, 392 (1978).

[8]The corresponding nonlocal interaction occurring in the theory of laser-induced chemi-ionization is associated with excitation to a continuum (ionized) state. In Sec. II of Ref. 1 a procedure was presented by which this nonlocal interaction could be replaced with an approximate local interaction $\Delta V-\frac{1}{2}\Gamma$ with ΔV and Γ, respectively, denoting the shift and width of the initial state. An analogous approximation is applicable to LIET and/or LIA provided that the electronic final state in question can be identified with a *set* of closely spaced Rydberg states. One then replaces the projection operator P of

(2.3) with

$$\sum_f |\phi_f,N'\rangle\langle\phi_f,N'| \doteq \int df\, |\phi_f,N'\rangle\langle\phi_f,N'|$$
$$= \int d\epsilon_f\, |\phi_f,N'\rangle\rho^{-1}(\epsilon_f)\langle\phi_f,N'| \ ,$$

where $\rho(\epsilon_f)=d\epsilon_f/df$ is the Rydberg analog of the density of continuum states that occurs in Ref. 1