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Radiative transitions in atom-atom scattering in intense laser fields[*]

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The quantum nonperturbative analysis of Kroll and Watson for a two-level system of near-adiabatic atom-atom scattering in an intense laser-field mode is extended to treat a general multilevel system interacting with intense single- or many-field modes. A procedure for rigorously solving the adiabatic eigenvalue problem for the whole charge-field system is given. A new transition-probability formula is derived. Cross sections are calculated for the processes $\mathrm{Li} + \mathrm{H}(X\,^1\Sigma^+) + \nu\hbar\omega \rightarrow \mathrm{Li} + \mathrm{H}(A\,^1\Sigma^+$ or $B\,^1\Pi)$ where $\nu \geq 1$. Analysis of transition in an atom due to intensity variation of a laser pulse shows that desired transition probability per pulse (e.g., 1/2) may be achieved by varying the pulse parameters. For this, numerical results of $\mathrm{Na}(3s) + 2\hbar\omega \rightarrow \mathrm{Na}(5s)$ and of $\mathrm{Li}(2s) + 8\hbar\omega \rightarrow \mathrm{Li}(3s)$ are given.

I. INTRODUCTION

In this paper, we analyze two physical situations: (i) near-adiabatic atom-atom[1] collisions in an intense laser beam; and (ii) an atom[1] being irradiated by a strong laser pulse. We are concerned with the calculation of the probability of single-photon or multiphoton bound-bound transitions in the atomic system. There have been many experiments on multiphoton transitions in atoms and molecules in intense laser field.[2-5] Resonant bound-bound transitions are often decisive in multiphoton ionization results.[2,4] Most theoretical analyses on this subject deal with isolated atoms or molecules.[6-9] There are comparatively fewer theoretical studies of atom-atom collision in an intense laser field.[10,11] In experiments with an atomic gas, radiative transitions during atom-atom collisions are significant compared to those of the isolated atoms.[5]

Kroll and Watson[10] (hereafter referred to as KW) have analyzed the interaction of a two-level "quasimolecule" (the atom-atom in near-adiabatic collision) with an intense radiation mode. With a similar approach, the present paper analyzes more general cases of a quasimolecule of finite number ($n \geqslant 2$) of discrete levels interacting with a finite number of intense field modes, thus providing treatment for a greater variety of physical phenomena. Approximating the real quasimolecule with more than two levels is useful since the roles of near-resonant intermediate states in determining the multiphoton transition probability and of nonresonant levels in determining the energy shift are important. The analysis does not make any perturbation expansion, nor does it make use of the rotating-wave approximation.[9] Further, it is not limited to the electric dipole approximation.

In Sec. II, we write down the time-dependent equation for near-adiabatic atom-atom collision in intense laser modes. Level shifts and coupling between states are found from solutions of the adiabatic molecular eigenvalue problem in Sec. III. In Sec. IV, a new formula for the transition probability between two shifted levels is derived. Section V contains two numerical studies. Finally in Sec. VI, we study transitions in an isolated atom that are due to intensity variation of the irradiating laser pulse.

II. TIME-DEPENDENT EQUATION

We consider near-adiabatic scattering of atoms in m field modes in a large cavity. The eigenvalues and eigenfunctions of the adiabatic molecular Hamiltonian h are written as w_α and ϕ_α, respectively, with parametric dependence on the fixed internuclear configuration $\vec{R}$.[12] Let the free-field Hamiltonian and the charge-field interaction Hamiltonian be h_γ and h', respectively.[13] We shall approximate the relative motion of the nuclei by classical orbits $\vec{R}(t)$. Then in the c.m. frame of the quasimolecule, the Hamiltonian describing the whole charge-field system is $H_c(t) = h + h_\gamma + h'$, where h and h' are functions of the orbit $\vec{R}(t)$.[10]

Since in scattering experiments the initial state of the quasimolecule is prepared before the charge-field interaction takes place, and the final state is observed after the interaction has occurred, we may expand the total wave function:

$$\psi = \sum_{\beta=1}^{n} c_\beta(t)\phi_\beta \,.$$

Substitution into the time-dependent Schrödinger equation for $H_c(t)$ gives

$$i\hbar \frac{dc_\alpha}{dt} = w_\alpha c_\alpha + h_\gamma c_\alpha + \sum_{\beta\neq\alpha} (\phi_\alpha, h'\phi_\beta) c_\beta \,, \qquad (2.1)$$

where the term $(\phi_\alpha, h'\phi_\alpha)$ for radiative transition between nuclear molecular states of the same electronic state and the term $i\hbar \sum_\beta c_\beta(\phi_\alpha, d\phi_\beta/dt)$ for collisional transition have been neglected.[10]

We now expand the c_α in terms of the photon number states $\Omega(N_\lambda - \nu_\lambda)$, where N_λ is the initial mean number of photons in the λth mode and $\nu_\lambda > 0$ (< 0) is the number of photons absorbed (emitted) by the quasimolecule. That is,

$$c_\alpha = \sum_{\{\nu_\lambda\}} i^{\Sigma_\lambda \nu_\lambda} b_{\{\nu_\lambda\}}(\alpha) \times \exp\left[-\frac{i}{\hbar}\int^t \left(w_p + \sum_\lambda \hbar\omega_\lambda N_\lambda\right) dt'\right] \times \prod_\lambda \Omega(N_\lambda - \nu_\lambda)\,, \tag{2.2}$$

where w_p is a particular w_α chosen for convenience of calculation, and $\{\nu_\lambda\}$ denotes a set of m integers, corresponding to m modes. Thus $b_{\{\nu_\lambda\}}(\alpha)$ is the probability amplitude that the charge-field system is in the electronic state α with $\{\nu_\lambda\}$ photons "absorbed." With the excellent approximation for intense field modes

$$N_\lambda - \nu_\lambda + 1 \approx N_\lambda - \nu_\lambda \approx N_\lambda\,,$$

we obtain from Eqs. (2.1) and (2.2)

$$i\frac{d}{dy} b_{\{\nu_\lambda\}}(\alpha) = W_{\{\nu_\lambda\}}(\alpha) b_{\{\nu_\lambda\}}(\alpha) + \sum_{\gamma=1}^{m} \sum_\beta G_\gamma^\pm(\alpha,\beta)\left[b_{\{\nu_\gamma -1\}}(\beta) \pm b_{\{\nu_\gamma+1\}}(\beta)\right], \tag{2.3}$$

where $y \equiv vt/a_0$ is a dimensionless time variable defined in terms of any convenient constant speed v and Bohr radius a_0,

$$W_{\{\nu_\lambda\}}(\alpha) \equiv \frac{a_0}{\hbar v}(w_\alpha - w_p) - \sum_\lambda \nu_\lambda F_\lambda$$

are the "unperturbed eigenlevels" of the noninteracting Hamiltonian $h + h_\gamma$, and

$$F_\lambda \equiv a_0\omega_\lambda / v$$

is the "photon energy." In the subscript set $\{\nu_\gamma \pm 1\}$ of the last term in Eq. (2.3), all the component indices are the same as those in the set $\{\nu_\lambda\}$ of the first and second terms except the γth, for which one has $\nu_\gamma \pm 1$ instead. The ± sign in Eq. (2.3) corresponds to the use of the electric dipole[14] interaction Hamiltonians,[15]

$$h'_+ \equiv -\sum_i q_i \vec{r}_i \cdot \vec{E}(0) \text{ and } h'_- \equiv -\sum_i \frac{q_i}{m_i c}\vec{p}_i \cdot \vec{A}(0)\,,$$

respectively. We have used both forms in our numerical calculations, though it is believed that the h'_+ is a better approximation in treatment where higher levels are neglected.[16] For plane-wave modes,

$$G_\lambda^\pm(\alpha, \beta \neq \alpha) \equiv \frac{a_0}{\hbar v}\left(\frac{2\pi I_\lambda}{c}\right)^{1/2} \left(\phi_{\alpha}, -\sum_i q_i \vec{r}_i \phi_\beta\right) \cdot \hat{\epsilon}_\lambda \left\{\begin{matrix} 1 \\ (w_\alpha - w_\beta)/\hbar\omega_\lambda \end{matrix}\right\},$$

$$G_\lambda^\pm(\alpha,\alpha) \equiv 0\,,$$

where $I_\lambda \equiv cN_\lambda \hbar\omega_\lambda / V$ is the intensity of the λth mode (cavity volume V). If the linear polarizations and a set of real ϕ_α are chosen, then G_λ^+ (G_λ^-) are real and symmetric (antisymmetric).

III. ADIABATIC EIGENVALUE PROBLEM

To calculate the transition probability, we use the level shifts and the coupling between states, obtained below by solution of the adiabatic eigenvalue problem. We write

$$b_{\{\nu_\lambda\}}(\alpha) \equiv \left[\exp\left(-i\int^y E(y')\,dy'\right)\right] a_{\{\nu_\lambda\}}(\alpha)\,, \tag{3.1}$$

where $(E(y), \underline{a})$ is the "adiabatic eigensolution" to be found. In the adiabatic limit,

$$\frac{d}{dy} a_{\{\nu_\lambda\}}(\alpha) = 0\,.$$

Use of these expressions in Eq. (2.3) gives

$$E a_{\{\nu_\lambda\}}(\alpha) = W_{\{\nu_\lambda\}}(\alpha) a_{\{\nu_\lambda\}}(\alpha) + \sum_{\gamma,\beta} G_\gamma^\pm(\alpha,\beta)\left[a_{\{\nu_\gamma -1\}}(\alpha) \pm a_{\{\nu_\gamma+1\}}(\beta)\right]. \tag{3.2}$$

With $(E_{\{\nu_\lambda\}\alpha}, \underline{a}^{\{\nu_\lambda\}\alpha})$ labeled such that as the interaction $G_\lambda^\pm(\alpha,\beta) \rightarrow 0$

$$E_{\{\nu_\lambda\}\alpha} \rightarrow W_{\{\nu_\lambda\}}(\alpha)\,,$$

it can be shown from Eq. (3.2) that if a particular $(E_{\{\rho_\lambda\}\alpha}, \underline{a}^{\{\rho_\lambda\}\alpha})$ is found, then $(E_{\{\rho_\lambda+\mu_\lambda\}\alpha}, a^{\{\rho_\lambda+\mu_\lambda\}\alpha})$ for the same α but any $\{\mu_\lambda\}$ can be obtained by

$$E_{\{\rho_\lambda+\mu_\lambda\}\alpha} = E_{\{\rho_\lambda\}\alpha} - \mu_\lambda F_\lambda$$

and

$$a_{\{\nu_\lambda\}}^{\{\rho_\lambda+\mu_\lambda\}\alpha}(\beta) = a_{\{\nu_\lambda-\mu_\lambda\}}^{\{\rho_\lambda\}\alpha}(\beta)\,.$$

We proceed to solve Eq. (3.2).

A. Single-field mode

Converting Eq. (3.2) into matrix notation and dropping the mode index, we let $\underline{G}^\pm$ be the $n\times n$ matrix $[G^\pm(\alpha,\beta)]$, $\underline{D}$ be the $n\times n$ diagonal matrix $[(E - W_\nu(\alpha))\delta_{\alpha\beta}]$ and $\underline{a}_\nu$ be the n-component column vector. Then Eq. (3.2) becomes

$$\underline{D}_\nu \underline{a}_\nu = \underline{G}^\pm(\underline{a}_{\nu-1} \pm \underline{a}_{\nu+1})\,, \tag{3.3}$$

for all ν.

At some point y, where an adiabatic level of interest (ρ, σ) is not in near resonance with any other levels, we let

$$a_\nu(\alpha) = d_\nu(\alpha) a_\rho(\sigma) \tag{3.4}$$

for all (ν, α). Thus $d_\rho(\sigma) = 1$. Upon substitution of Eq. (3.4), and factoring out $a_\rho(\sigma)$, Eq. (3.3) becomes

$$\underline{D}_\nu \underline{d}_\nu = \underline{G}^\pm (\underline{d}_{\nu-1} \pm \underline{d}_{\nu+1}) . \tag{3.5}$$

Defining $\underline{T}_\nu$ for $\nu > \rho$ by

$$\underline{d}_\nu = \underline{T}_\nu \underline{d}_{\nu-1} ,$$

we obtain directly from Eq. (3.4) the recurrence relation for $\underline{T}_\nu$,

$$\underline{T}_\nu = (\underline{D}_\nu \mp \underline{G}^\pm \underline{T}_{\nu+1})^{-1} \underline{G}^\pm . \tag{3.6a}$$

Since $D_\nu(\alpha, \beta)^{-1} \to (\nu F)^{-1} \delta_{\alpha\beta} \to 0$ as $\nu \to \infty$, $\underline{T}_\nu$ has the limit

$$\underline{T}_\nu \to (\nu F)^{-1} \underline{G}^\pm \to 0 . \tag{3.6b}$$

Similarly for $\nu < \rho$, we define $\underline{T}'_\nu$ by

$$\underline{d}_\nu \equiv \underline{T}'_\nu \underline{d}_{\nu+1}$$

and obtain, from Eq. (3.5),

$$\underline{T}'_\nu = \pm (\underline{D}_\nu - \underline{G}^\pm \underline{T}'_{\nu-1})^{-1} \underline{G}^\pm . \tag{3.7a}$$

As before,

$$\underline{T}'_\nu \to 0 \quad \text{as} \quad \nu \to -\infty . \tag{3.7b}$$

Alternatively, if $(\underline{G}^\pm)^{-1}$ exists, then defining $\underline{U}^\pm_\nu$, $\underline{H}_\nu$ and $\underline{H}'_\nu$ by

$$\underline{U}^\pm_\nu \equiv \underline{D}_\nu^{-1} \underline{G}^\pm ,$$

$$\underline{T}_\nu \equiv \underline{U}^\pm_\nu \underline{H}_\nu , \quad \nu > \rho$$

and

$$\underline{T}'_\nu \equiv \underline{U}^\pm_\nu \underline{H}'_\nu , \quad \nu < \rho ,$$

we obtain either directly from Eq. (3.5) or from Eqs. (3.6) and (3.7) the relations

$$\underline{H}_\nu = [\underline{I} \mp \underline{U}^\pm_{\nu+1} \underline{H}_{\nu+1} \underline{U}^\pm_\nu]^{-1} ,$$

with

$$\underline{H}_\nu \to \underline{I} \quad \text{as} \quad \nu \to \infty , \tag{3.8}$$

and

$$\underline{H}'_\nu = \pm [\underline{I} - \underline{U}^\pm_{\nu-1} \underline{H}'_{\nu-1} \underline{U}^\pm_\nu]^{-1} , \tag{3.9}$$

with $\underline{H}'_\nu \to \pm \underline{I}$ as $\nu \to -\infty$.

Thus with a cut-off value M, we let $\underline{T}_{M+1} = 0$ and $\underline{T}'_{-M-1} = 0$. Or if we take the approach using H matrices, we let $\underline{H}_{M+1} = \underline{I}$, $\underline{H}'_{-M-1} = \pm \underline{I}$.[17] For a given physical system, the smallest value of M is determined according to the accuracy desired by running a few numerical tests. Starting from these limits we can generate all other $\underline{T}_\nu$ $[-M < \nu(\neq\rho) < M]$ by the recurrence relations. Thus $\underline{d}_{\rho\pm1}$ can be expressed in terms of $\underline{d}_\rho$. With $d_\rho(\sigma) = 1$ known, all other $(n-1)$ d_ρ's $(\alpha \neq \sigma)$ are obtained by solving the $n-1$ inhomogeneous linear equations obtained from the $(\nu = \rho)$th set of Eq. (3.5) with $\alpha \neq \sigma$.

Finally, use of the $(\nu = \rho, \alpha = \sigma)$ equation of (3.5) gives

$$E = W_\rho(\sigma) + \sum_{\beta,\gamma} G^\pm(\sigma, \beta) [T'_{\rho-1}(\beta, \gamma) \pm T_{\rho+1}(\beta, \gamma)] d_\rho(\gamma) ,$$

where $d_\rho(\sigma) = 1$ has been used. This equation is used to find the adiabatic eigenvalue $E_{\rho\sigma}$ by successive iteration, starting with trial value $W_\rho(\sigma)$. The second term on the right-hand side is the shift of the unperturbed level $W_\rho(\sigma)$. For low intensity, it agrees with the value given by perturbation theory.

Near y, where two levels (ρ, σ) and (μ, τ) are nearly degenerate (see, for example, Fig. 1), we let

$$a_\nu(\alpha) = d_\nu(\alpha) a_\rho(\sigma) + s_\nu(\alpha) a_\mu(\tau) , \tag{3.10}$$

for all ν, α. It follows that

$$d_\rho(\sigma) = 1 = s_\mu(\tau), \quad d_\mu(\tau) = 0 = s_\rho(\sigma) . \tag{3.11}$$

To find $d_\nu(\alpha)$'s which are independent of $a_\mu(\tau)$, we substitute $d_\nu(\alpha) a_\rho(\sigma)$ in place of $a_\nu(\alpha)$ in Eq. (3.3) and obtain equations the same as (3.5). Thus, all the $\underline{d}_\nu$ can be found by the same procedure as before except for $\underline{T}_\mu$ (assuming $\tau > \sigma$ and $\mu > \rho$). For $\nu = \mu$, since we cannot use the "singular" equation $(\nu = \mu,\ \alpha = \tau)$ to find the d's, $\underline{T}_\mu$ is obtained (i) by filling its $(\alpha = \tau)$th row by zeros to satisfy $\underline{d}_\mu(\tau) = 0$; and (ii) by directly inverting the rest of the $n-1$ equations with $\nu = \mu$ to obtain the other $n-1$ rows. The $s_\nu(\alpha)$'s are found similarly by substituting $s_\mu(\alpha) a_\mu(\tau)$ in place of $a_\nu(\alpha)$ in Eq. (3.3). Defining $\underline{V}_\nu$ by $\underline{s}_\nu = \underline{V}_\nu \underline{s}_{\nu-1}$ for $\nu > \mu$ and $\underline{V}'_\nu$ by $\underline{s}_\nu = \underline{V}'_\nu \underline{s}_{\nu+1}$ for $\nu < \mu$, we note that $\underline{V}_\nu = \underline{T}_\nu$ for $\mu < \nu \leq M$ and $\underline{V}'_\nu = \underline{T}'_\nu$ for $-M \leq \nu < \rho$.

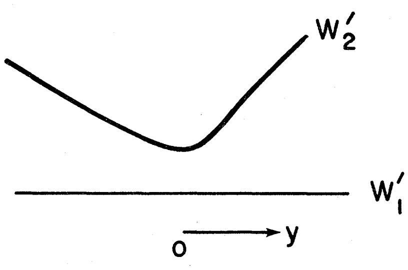

FIG. 1. Shifted level structure for which a transition probability formula is derived.

Finally, the characteristic equation resulting from the (μ, τ) and (ρ, σ) equations of (3.3) with substitution of Eq. (3.10) for $a_{\rho\pm 1}(\alpha)$ and $a_{\mu\pm 1}(\alpha)$ has roots

$$E_\mu = \tfrac{1}{2}(W'_\mu(\tau) + W'_\rho(\sigma) + \{[W'_\mu(\tau) - W'_\rho(\sigma)]^2 + 4G^2\}^{1/2}) ,$$
$$E_l = \tfrac{1}{2}(W'_\mu(\tau) + W'_\rho(\sigma) - \{[W'_\mu(\tau) - W'_\rho(\sigma)]^2 + 4G^2\}^{1/2}) , \tag{3.12}$$

where

$$W'_\rho(\sigma) \equiv W_\rho(\sigma) + \sum_\beta G^\pm(\sigma, \beta)[d_{\rho-1}(\beta) \pm d_{\rho+1}(\beta)],$$

$$W'_\mu(\tau) \equiv W_\mu(\tau) + \sum_\beta G^\pm(\tau, \beta)[s_{\mu-1}(\beta) \pm s_{\mu+1}(\beta)]$$

are the "shifted levels," and

$$G \equiv - \sum_\beta G^\pm(\sigma, \beta)[s_{\rho-1}(\beta) \pm s_{\rho+1}(\beta)]$$

$$= - \sum_\beta G^\pm(\tau, \beta)[d_{\mu-1}(\beta) \pm d_{\mu+1}(\beta)]$$

is the coupling constant. The last equality is based on hermiticity. We may use any one of the expressions of E_u and E_l for iteration to find $(E_u, \underline{a}^u)$ and/or $(E_l, \underline{a}^l)$. The minimum of the level separation $E_u - E_l$ is the "point of closest approach" around which we calculate the transition probability.

B. Many-field modes

For the sake of clarity, we will indicate the generalization of the above method to many-field modes using the case of two modes. We shall use this in the numerical example in Sec. V B. Equation (3.2) for two-field modes may be written in the form

$$\underline{D}_{\nu_2}\underline{a}_{\nu_2} = \underline{G}^\pm(\underline{a}_{\nu_2-1} \pm \underline{a}_{\nu_2+1}) , \tag{3.13}$$

where

$$D_{\nu_2}(\nu_1\alpha, \nu'_1\alpha') = (E + \nu_2 F_2)\delta_{\nu_1\nu'_1}\delta_{\alpha\alpha'} - W_{\nu_1}(\alpha)\delta_{\nu_1\nu'_1}\delta_{\alpha\alpha'}$$
$$- G_1^\pm(\alpha, \alpha')(\delta_{\nu_1\nu'_1+1} \pm \delta_{\nu_1\nu'_1-1}) ,$$

$$G^\pm(\nu_1\alpha, \nu'_1\alpha') \equiv \delta_{\nu_1\nu'_1}G_2^\pm(\alpha, \alpha') ,$$

and

$$a_{\nu_2}(\nu'_1\alpha') \equiv a_{\nu'_1\nu_2}(\alpha') .$$

For a transition where the photon number of only one mode changes, that mode should be assigned the role of mode 2 here. Equation (3.13) has the same form as Eq. (3.3) for one mode. Thus, the solution is similar as before, even though the $\underline{D}_{\nu_2}$ are not diagonal. For near resonance between levels $(\rho_1\rho_2\sigma)$ and $(\mu_1\mu_2\tau)$, for example, we write

$$a_{\nu_2}(\nu_1\alpha) \equiv d_{\nu_2}(\nu_1\alpha)a_{\rho_2}(\rho_1\sigma) + s_{\nu_2}(\nu_1\alpha)a_{\mu_2}(\mu_1\tau) , \tag{3.14}$$

for all α, $-M_1 \leqslant \nu_1 \leqslant M_1$, and $-M_2 \leqslant \nu_2 \leqslant M_2$, and use component equations $(\rho_1\rho_2\sigma)$ and $(\mu_1\mu_2\tau)$ to obtain the corresponding characteristic roots as in Eq. (3.12). The level shifts and the coupling constant contain additive contribution from each mode.

IV. TRANSITION PROBABILITY FORMULA

Suppose we have (near) resonance occurring between two levels "1" and "2" near $y = 0$. Then only the probability amplitudes b_1 and b_2 will vary significantly, while all other $b_\nu(\alpha)$'s in Eq. (2.3) may be approximated by their adiabatic counterparts, given by Eq. (3.1). We may use either $\underline{a}^u$ or $\underline{a}^l$, the resulting difference of such choice being small near the point of closest approach.[18] Substitution of Eqs. (3.1), (3.10), or (3.14) into the component equations for "1" and "2" of Eq. (2.3) gives

$$i\frac{db_1}{dy} - W'_1 b_1 = G b_2 , \quad i\frac{db_2}{dy} - W'_2 b_2 = G b_1 , \tag{4.1}$$

where W'_i and G are, respectively, the shifted levels and coupling constant defined before. The boundary conditions are that in the remote past $b_2 = 0$ and $|b_1| = 1$. Now we derive a new formula that is useful when the shifted levels have two well-defined relative slopes b and b',

$$W'_2 - W'_1 = \begin{cases} a - by, & y \leqslant 0 \\ a + b'y, & y > 0 , \end{cases}$$

where a is the minimum level separation (see Fig. 1). The only drawback in the above approximation is the introduction of discontinuity of slope of $W'_2 - W'_1$ at $y = 0$. However, the advantage is that, without further approximation, a transition probability formula can be derived rigorously and is applicable even when $a = 0$.

We introduce, with $k_1 \equiv \int_0^y W'_1(y')\,dy'$,

$$b_2(y) = U(y)e^{-ik_1}e^{-i(a/2)y}e^{i(b/4)y^2} \quad \text{for} \quad y \leqslant 0 ,$$
$$= U(y)e^{-ik_1}e^{-i(a/2)y}e^{-i(b'/4)y^2} \quad \text{for} \quad y > 0 ,$$

into Eq. (4.1) and obtain, neglecting the small dependence of G on y,[19]

$$\frac{d^2U}{dy^2} + \left[G^2 - \frac{ib}{2} + \frac{b^2}{4}\left(y - \frac{a}{b}\right)^2\right]U = 0 , \quad y \leqslant 0 ,$$

$$\frac{d^2U}{dy^2} + \left[G^2 + \frac{ib'}{2} + \frac{b'^2}{4}\left(y + \frac{a}{b'}\right)^2\right]U = 0 , \quad y > 0 .$$

We need to find only the solution $U(y; |a|, |b|, |b'|)$, since the solution $U(y; -|a|, -|b|, -|b'|)$

$= U^*(y, |a|, |b|, |b'|)$ as can be shown easily from the above equations.

Now, with the definitions

$$z_- \equiv (y - a/b) b^{1/2} e^{-i\pi/4} \equiv y_- b^{1/2} e^{-i\pi/4} ,$$

$$z_+ \equiv (y + a/b') b'^{1/2} e^{-i\pi/4} \equiv y_+ b'^{1/2} e^{-i\pi/4} ,$$

the above equations are reduced to the Weber equations[20]

$$\frac{d^2U(z_-)}{dz_-^2} + (n + \tfrac{1}{2} - \tfrac{1}{4}z_-^2)U(z_-) = 0, \quad y \leqslant 0 ,$$

$$\frac{d^2U(z_+)}{dz_+} + (n' + \tfrac{1}{2} - \tfrac{1}{4}z_+^2)U(z_+) = 0, \quad y > 0 ,$$

where

$$n \equiv ip, \quad n' = ip' - 1, \quad p \equiv G^2/b, \quad p' \equiv G^2/b' .$$

For $y < 0$, the solution satisfying the boundary condition $b_2 = 0$ and $|b_1| = 1$ in the "remote past" (i.e., $|b^{1/2}y - a/b^{1/2}| \gg 1$) is

$$U(z_-) = (|G|/b^{1/2}) e^{-\pi p/4} D_{-n-1}(-iz_-) .$$

A general solution for $y > 0$ is

$$U(z_+) = LD_{-n'-1}(-iz_+) + MD_{n'}(-z_+) ,$$

where L and M are coefficients to be determined by demanding continuity of b_2 and of its slope at $y = 0$. We obtain

$$L = N[n' e^{3i\pi/4} D_1 D_6 - (b/b')^{1/2}(n+1) e^{i\pi/4} D_2 D_5]/D ,$$

$$M = N[(a/b'^{1/2}) e^{i\pi/2} D_1 D_3 - (n'+1) e^{i\pi/4} D_1 D_4 + (b/b')^{1/2}(n+1) e^{i\pi/4} D_2 D_3]/D ,$$

where

$$N \equiv |G| b^{-1/2} e^{-\pi p/4} ,$$

$$D \equiv (a/b'^{1/2}) e^{i\pi/2} D_3 D_5 + n' e^{3i\pi/4} D_3 D_6 - (n'+1) e^{i\pi/4} D_4 D_5 ,$$

$$D_1 \equiv D_{-n-1}[(a/b^{1/2}) e^{i\pi/4}] ,$$

$$D_2 \equiv D_{-n-2}[(a/b^{1/2}) e^{i\pi/4}] ,$$

$$D_3 \equiv D_{-n'-1}[(a/b'^{1/2}) e^{-3i\pi/4}] ,$$

$$D_4 \equiv D_{-n'-2}[(a/b'^{1/2}) e^{-3i\pi/4}] ,$$

$$D_5 \equiv D_{n'}[(a/b'^{1/2}) e^{3i\pi/4}] ,$$

$$D_6 \equiv D_{n'-1}[(a/b'^{1/2}) e^{3i\pi/4}] .$$

For $|z_+| = b'^{1/2}y + a/b'^{1/2} \gg 1$, we obtain the asymptotic formula for $b_2(y)$

$$b_2(y) = \left(L e^{-3\pi p'/4} + M \frac{(2\pi)^{1/2}}{\Gamma(1 - ip')} e^{-\pi p'/4} \right) \times \exp\left[-i \int_0^y W_2' \, dy' - i \frac{p'}{2} \ln b' \left(y + \frac{a}{b'} \right)^2 - \frac{ia^2}{4b'} \right] ,$$

from which the transition probability is

$$|b_2|^2 = \left| L e^{-(3\pi/4)p'} + M \frac{(2\pi)^{1/2}}{\Gamma(1 - ip')} e^{-\pi p'/4} \right|^2 . \tag{4.2}$$

For the special case of $a/b^{1/2} \gg 1$ and $a/b'^{1/2} \gg 1$, we obtain

$$|b_2|^2 = [(2^{1/2}|G|/a)(1 - e^{-2\pi p'})]^2 ,$$

which has desirable behavior with respect to a, G and b', but is independent of b.

V. NUMERICAL EXAMPLES

The orbit of the relative motion of the colliding atoms enters into our calculations through (i) $G(\alpha, \beta)$ which depends on the orientation of the internuclear axis relative to the polarization vector $\hat{\epsilon}$, and (ii) the velocity dR/dt in the relative slopes

$$\alpha_{ij} = \frac{a_0}{v} \frac{d}{dR} (W_i' - W_j') \frac{dR}{dt} ,$$

that occur in the transition probability formulas. To take (i) into consideration, we integrate the differential orbit equation, using the unperturbed potential curves as a good approximation (though strictly speaking, the self-consistent shifted potential curves should be used). The evaluation of dR/dt, final transition probability, and cross section have been discussed in KW.

A. Li and H scattering

As examples, we consider scattering of Li with H in an intense field mode with $\lambda = 0.826$ μm in the geometry of Fig. 2 for relative speed $v_\infty = 5 \times 10^5$ cm/sec. Values of $w_\alpha(R)$ and $(\phi_\alpha, \sum_i \vec{r}_i \phi_\beta)$ for the lowest-lying singlet states $X\,^1\Sigma^+$, $A\,^1\Sigma^+$, and $B\,^1\Pi$ are taken from Docken and Hinze.[21] These three levels represent a fairly good approximation because, according to the less accurate calculation of Bender and Davidson,[22] the higher levels all lie at least about one-photon ($\hbar\omega \approx 1.5$ eV) in energy above the $B\,^1\Pi$ level. We assume that the

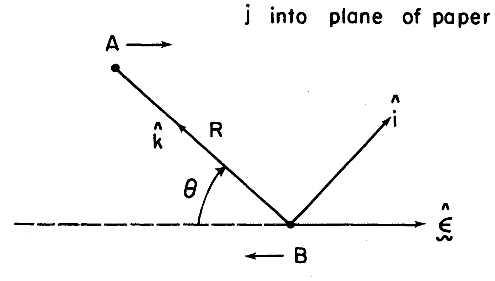

FIG. 2. Particular geometry for near-adiabatic scattering of two atoms in intense field. Internuclear axis is along $\hat{k}$ and the linear polarization $\hat{\epsilon}$ is in the $\hat{\imath}$-$\hat{k}$ plane.

atoms are initially in the electronic singlet ground state $X\,^1\Sigma^+$. There are one- and two-photon resonant transitions to $A\,^1\Sigma^+$ near internuclear separations $9.4a_0$ and $5.9a_0$, and $3.7a_0$, respectively, while two- and three-photon resonant transitions to $B\,^1\Pi$ occur at $5.1a_0$ and $3.1a_0$, respectively. Using a Landau-Zener–like formula,[10] we calculated the transition probabilities to these two excited states, and the cross sections are presented in Fig. 3. We observe that only for low enough intensity are the cross sections proportional to I and I^2 for transitions to $A\,^1\Sigma^+$ and $B\,^1\Pi$, respectively, as expected from perturbation theory.

B. Stimulated emission by field-dependent lowering of potential barrier

We shall consider here[23] colliding atoms with model adiabatic potential curves and dipole matrix elements illustrated in Fig. 4. Initially, the quasimolecule is in state 2, which has a potential barrier (e.g., arising from avoided crossing) at R_b. For $R > R_b$, the dipole transition to the state 1 is forbidden, while for $R < R_b$ it is allowed. For diatomics, the initial state 2 is achieved by some pumping. For polyatomics, however, no pumping is necessary because the potential surface 2 may represent ground state of one configuration of the quasimolecular complex, while potential surface 1 corresponds to a rearranged configuration. At thermal relative velocities, the potential barrier is too high for classical penetration (or too little quantum-mechanical tunneling) into region $R < R_b$. One way to overcome the barrier is to lower it by a sufficiently intense laser field with a photon energy smaller than the energy gap between levels 2 and 3 in the neighborhood of R_b. Once the quasimolecule penetrates into the $R < R_b$ region, it will most likely radiate near the classical turning point R_c at a second frequency. For the case depicted in Fig. 4, part of the electronic energy upon photoemission is converted into relative kinetic energy of the colliding particles.

For numerical study, we consider the following unperturbed potential energy curves $w_i(R)$ (in eV) and dipole matrix elements (in a.u) $M_{jk} = \langle j | \sum_i \vec{r}_i | k \rangle$ for a model diatomic colliding system (of reduced mass = 20 times the proton mass and relative speed = 10^5 cm/sec):

$$w_1(R) = 1.5\, e^{-5(R-3)},$$

$$w_2(R) = 2.9 + 0.1(1 - e^{-1.6(R-3.75)})^2 + 0.153 e^{-4.0(R-4.8)^2},$$

$$w_3(R) = 4.285 + 1.2 e^{-3(R-3)},$$

$$M_{12}(R) = 3.033 e^{-1.515(R-3.2)^2},$$

$$M_{23}(R) = 4 e^{-0.738(R-4.85)^2},$$

$$M_{13}(R) = 2.0,$$

for $R \geq 3.2a_0$. We assume electronic states 2 and

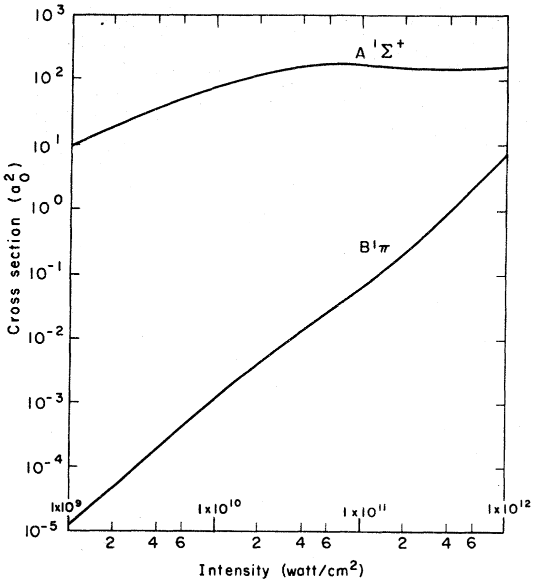

FIG. 3. Inelastic cross sections for the process $\text{Li} + \text{H}(X\,^1\Sigma^+) + \nu\hbar\omega \rightarrow \text{Li} + \text{H}(A\,^1\Sigma^+$ or $B\,^1\Pi)$ over a range of field intensity ($\lambda = 0.826\,\mu$).

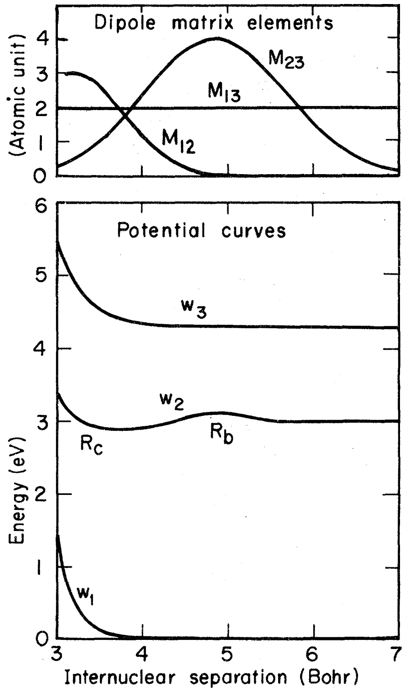

FIG. 4. Potential curves and dipole matrix elements of model quasimolecule for study of field-dependent lowering of potential barrier.

3 to have the same Λ quantum number while that of state 1 differs from theirs by 1. The scattering geometry is shown in Fig. 2, where $\hat{\epsilon}$ is the linear polarization $\hat{\epsilon}_1$ of the intense mode. The original barrier is 0.02 eV too high for classical penetration. With the high-intensity laser field wavelength chosen to be 1.0648 μm, the bump is lowered by about 0.04 eV at $I_1 = 10^{12}$ W/cm^2. The colliding atoms for a certain range of impact parameter ($b = 0$ to $b_{\max} = 1.97a_0$) can now penetrate into the $R < R_b$ region. The system has certain probability $P_{I_2}(b)$ to radiate near R_c by stimulated emission into the second mode $\lambda_2 \approx 0.486$ μm ($\hat{\epsilon}_2$ is chosen parallel to $\hat{\epsilon}_1$). The cross sections for stimulated emission into the second mode,

$$\sigma_{I_2} = 2\pi \int_0^{b_{\max}} db\, bP_{I_2}(b),$$

are given in Table I, $P_{I_2}(b)$ being approximated by formula (4.2). We assume that transition between the shifted levels 2 and 3 near R_b is negligible, because of the large off-resonance 0.06 eV. Raising the third level by 0.4 eV changes the amount of potential barrier down-shift by less than 10%. Thus, the selection of the third level (or high-intensity laser wavelength) is not severely restrictive.

An interesting effect occurs which is due to the fact that the coupling between the second and third levels depends on the angle between the internuclear axis of the colliding atoms and the space-fixed linear polarization $\hat{\epsilon}_1$. Thus, collisional systems with impact parameters $b = 1.46-1.97$ a_0 can get into the region $R < R_b$ but become bound owing to the change of this angle on the outgoing trip. Values for cross section for such "trapping,"

$$b_t = 2\pi \int_{1.46}^{1.97} db\, b[1 - P_{I_2}(b)],$$

are given in Table I. The trapped colliding system will become a "vibrating" molecule that keeps on rotating relative to $\hat{\epsilon}_1$. Following approximately the motion of the bound molecule in the intense beam shows that after five vibrations, the atoms are separated again. But while bound, they radiate predominantly near R_c, thus enhancing σ_{I_2} by an amount $\Delta\sigma$ indicated in the last column of Table I.

TABLE I. Cross sections of stimulated emission σ_{I_2}, of trapping σ_t, and of enhancement $\Delta\sigma$, as a function of the intensity of stimulated emission I_2.

I_2 (W/cm^2)	σ_{I_2} (a_0^2)	σ_t (a_0^2)	$\Delta\sigma$ (a_0^2)
1×10^7	1.14×10^{-3}	5.5	4.1×10^{-3}
4×10^7	4.54×10^{-3}	5.5	1.6×10^{-2}
1×10^8	1.14×10^{-2}	5.5	4.1×10^{-2}
4×10^8	4.54×10^{-2}	5.5	1.6×10^{-1}
1×10^9	1.13×10^{-1}	5.5	4.1×10^{-1}
4×10^9	4.51×10^{-1}	5.5	1.6
7×10^9	7.86×10^{-1}	5.5	2.9
1×10^{10}	1.12	5.5	4.1

VI. TRANSITION DUE TO INTENSITY VARIATION

An intense laser field in experiments is often pulsed. The above theory can be adapted to treat transition in an isolated atom being irradiated by an intense laser pulse.[24] Now the amount of level shift of the atom is a function of intensity of the pulse, which is in turn a function of time. For a particular atomic system with proper choice of the laser λ, one may get two pseudocrossings (PC) per pulse, as shown in Fig. 5. The final transition probability per pulse (assumed symmetric) is given by

$$f = 2T(1-T),$$

where $T = 1 - \exp(-2\pi G^2/|\alpha|)$ is the transition probability[10] at one PC. The relative slope between the two shifted levels W_2' and W_1',

$$\alpha = -\frac{a_0}{v}\frac{d(W_2' - W_1')}{dI}\frac{dI}{dt},$$

is evaluated at the "critical intensity" I' at which the point of closest approach of the adiabatic eigenlevels occurs.

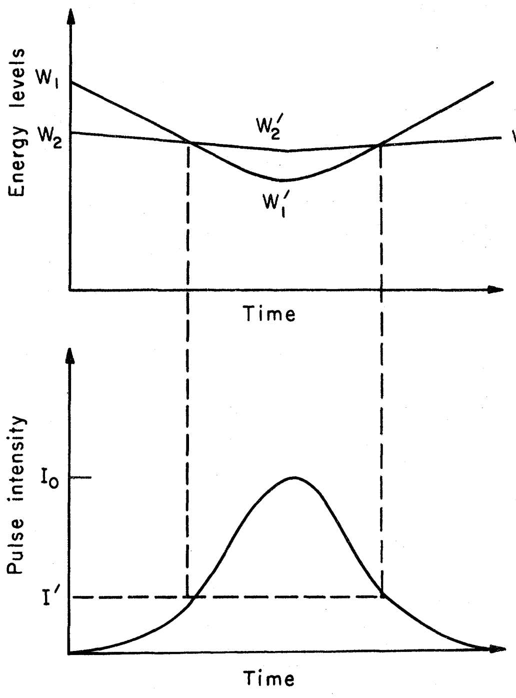

FIG. 5. Unperturbed atomic energy levels W_1 and W_2 are shifted into multiphoton resonances at critical intensity I' of the intense laser pulse.

The analysis below shows that desirable transition probability per pulse can be achieved by choice of pulse shape and pulse parameters. This may have important application in efficient optical pumping and in isotope separation. For example, to attain the maximum value $f=\frac{1}{2}$, the temporal slope of the pulse at I' is given by

$$\left|\frac{dI}{dt}\right| = \frac{2\pi\delta}{\ln 2},$$

where

$$\delta \equiv G^2 \left|\frac{a_0}{v}\frac{d(W_2' - W_1')}{dI}\right|^{-1}. \tag{6.1}$$

For a Gaussian pulse, $I(t) = I_0 e^{-t^2/\tau^2}$,

$$\left|\frac{dI}{dt}\right|_{I'} = \frac{2I'(\ln I_0/I')^{1/2}}{\tau}.$$

This implies that for given δ and I', there is a pair of optimum values (I_0', τ') such that f equals $\frac{1}{2}$. They are related by

$$\tau' = 7.516\times 10^{-23}\ln 2\,\frac{I'(\ln I_0'/I')^{1/2}}{\pi\delta},$$

where δ is in a.u., I' in W/cm^2 and τ' in sec. The validity condition for applying the transition probability formula for T above requires that, for a Gaussian pulse,

$$2.4\times 10^5 \delta I' \tau (\ln I_0/I')^{3/2} \gg 1$$

is to be satisfied.

As examples, we have calculated the quantities δ, I' characterizing the two-photon transition from the ground state $3s$ to $5s$ of the sodium atom and the eight-photon transition from the ground $2s$ state to the $3s$ state of the lithium atom (Table II). From these values, the transition probability for any pulse may be calculated. States of 3-$8s$, 3-$5p$, 3-$5d$, and 4-$6f$ are included in the calculation for sodium, while states of 2-$7s$, 2-$4p$, 3-$5d$, and 4-$6f$ of lithium are used. The energy levels are taken from Moore.[25] The magnitudes of the dipole matrix elements are calculated from the work of Anderson and Zilitiz[26] and their signs from Bates and Damgaard.[27] The range of wavelengths in the sodium case is chosen such that the $3s$ and $5s$ levels are shifted into two-photon resonance because the $3p$ levels repel the $3s$ level more strongly than they pull the $5s$ level. In the lithium case,

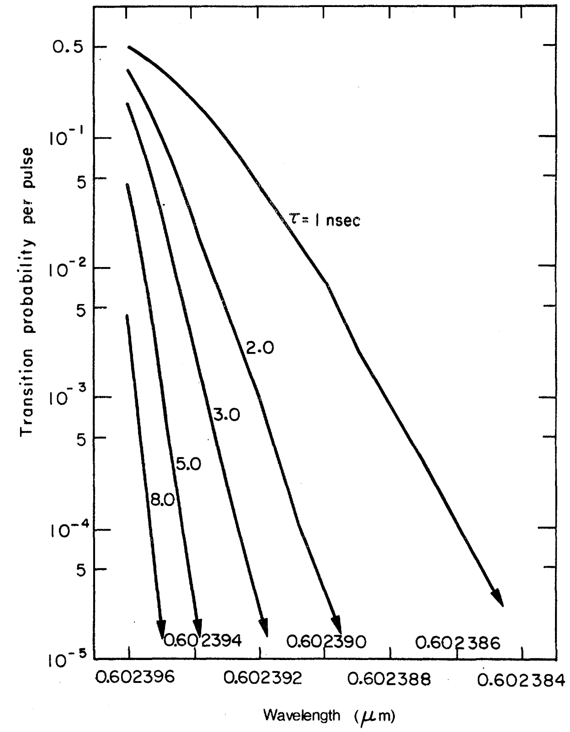

FIG. 6. Transition probability per pulse, f, in Na(3s) $+ 2\hbar\omega \rightarrow$ Na(5s) at several wavelengths for a few Gaussian pulses of the same peak intensity, 6×10^8 W/cm^2.

TABLE II. Values of critical intensity (I') and pulse-independent factor (δ) in Eq. (6.1) for wavelengths (λ) considered in (a) two-photon transition in sodium ($3s\rightarrow 5s$) and (b) eight-photon transition in lithium ($2s\rightarrow 3s$). The notation A (n) means $A\times 10^n$.

	(a) Na			(b) Li	
λ (μ)	I' (W/cm^2)	δ (a.u.)	λ (μ)	I' (W/cm^2)	δ (a.u.)
6.023 96 (−1)	1.00 (+7)	1.851 (−17)	2.940 60 (+0)	1.90 (+7)	3.414 (−49)
6.023 95 (−1)	1.74 (+7)	5.605 (−17)	2.940 75 (+0)	5.30 (+7)	1.264 (−45)
6.023 94 (−1)	2.55 (+7)	1.204 (−16)	2.941 00 (+0)	1.10 (+8)	4.421 (−43)
6.023 92 (−1)	4.00 (+7)	2.962 (−16)	2.941 50 (+0)	2.30 (+8)	1.658 (−40)
6.023 90 (−1)	5.50 (+7)	5.601 (−16)	2.942 00 (+0)	3.50 (+8)	4.920 (−39)
6.023 85 (−1)	9.50 (+7)	1.671 (−15)	2.942 50 (+0)	4.70 (+8)	5.487 (−38)
6.023 80 (−1)	1.35 (+8)	3.375 (−15)	2.943 00 (+0)	6.00 (+8)	3.656 (−37)
6.023 70 (−1)	2.10 (+8)	8.171 (−15)	2.943 50 (+0)	7.30 (+8)	1.951 (−36)
6.023 60 (−1)	2.90 (+8)	1.558 (−14)	2.944 00 (+0)	8.65 (+8)	7.714 (−36)
6.023 50 (−1)	3.75 (+8)	2.606 (−14)	2.944 50 (+0)	1.00 (+9)	2.560 (−35)
6.023 30 (−1)	5.25 (+8)	5.111 (−14)	2.945 00 (+0)	1.14 (+9)	7.443 (−35)

the $3p$ states strongly shift the $3s$ level down into eight-photon resonance with the $2s$ ground state.

It is found that for a sodium atom irradiated by a Gaussian pulse of $\lambda = 0.602396$ μm, $I_0 = 6\times 10^8$ W/cm^2 and $\tau = 1$ nsec, a final transition probability $f = \frac{1}{2}$ is closely attained. Figure 6 shows the sensitivity of f to τ over a range of wavelength. As can be shown from the analytic expressions above, the result is not so sensitive to peak intensities.

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[18] The difference in the final results in this paper due to the use of $\underline{a}^u$ or $\underline{a}^l$ usually runs from 0.01% for intensity 10^8 W/cm^2 to less than 5% for 10^{12} W/cm^2. Alternatively, one may take the mean results.

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