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A quantum nonperturbative theory is given for the problem of a general n discrete-level atomic/molecular system interacting with a strong single-mode/multimode radiation field. The atomic/molecular energy-level structures are modified due to interaction with the laser field. These energy level shifts are derived in the rigorous solution to the adiabatic eigenvalue problem of the charge-field system, involving a simple iterative procedure. The task of solution is simplified by recurrence relations between matrices connecting probability amplitudes of successive photon numbers. New formulae for calculating probability of single/multiphoton transitions (i) between three resonant shifted levels and (ii) between some cases of two near-resonant shifted levels are derived. This general formalism can be applied to calculate transition probabilities of various atomic/molecular photo processes of interest. Numerical values are obtained for the inelastic cross section of the slow-collisional process \( \text{Li} + \text{H}(X^1\Sigma_g^+) \rightarrow \text{Li} + \text{H}(\Lambda^2\Sigma_g^+) \) induced by a \( \lambda = 0.826 \mu \) field of intensities \( 10^9-10^{12} \text{ W/cm}^2 \) and for dissociation (via \( B^1\Sigma_u^+ \)) cross section of \( \text{LiH} \) molecule by absorption of 4 photons in a YAG:Nd \( (\lambda = 1.0648 \mu) \) laser field over intensities \( 10^9-8 \times 10^{11} \text{ W/cm}^2 \). The transition probabilities of Na (3s \rightarrow 5s) by absorption of two photon of \( \lambda = 0.60233 \mu - 0.60239 \mu \) and of Li (2s \rightarrow 3s) by absorption of eight photons of \( \lambda = 2.9406 \mu - 2.945 \mu \) irradiated by a strong pulse are calculated. These transition probabilities per pulse can be optimized to be \( \frac{1}{2} \) by varying parameters of a (say) Gaussian pulse. Finally a parametric study is carried out for the process where a molecular system is interacting with two intense radiation fields of different wavelengths. Owing to potential barrier shift due to the much more intense field, the molecular system penetrates into an otherwise-inaccessible region in the potential level where it is allowed to radiate to a lower level by emitting photons at a second wavelength.
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I. INTRODUCTION

To our knowledge, all the previous nonperturbative (or "exact") solutions of the quantum mechanical problem describing discrete-level atomic systems interacting with the electromagnetic field of finite number of modes are restricted to cases where all antiresonant terms are neglected a priori (rotating wave approximation) and where only single-photon transitions between a pair of levels are considered. As such they are inapplicable to multiphoton (of the same mode) transitions between a pair of atomic levels. With the above restriction removed, Kroll and Watson have studied the problem of multiphoton transitions between a 2-level atomic/molecular system interacting with a single-mode high-intensity field. In this part of the work, we investigate the problem further by considering single/multiphoton processes in any n-level atomic/molecular system interacting with a single-mode intense field, where \( n \geq 3 \).

Since our present work is similar in spirit to that of Kroll and Watson (thereafter referred to as I), it serves as introduction here to briefly describe their work. They consider the problem mainly in the context of slow atomic collision in an intense radiation field. Because of the near-adiabatic motion, the atoms effectively form a molecule—a quasimolecule. In their work, the relative motion of the atoms is approximated by classical orbits along quasimolecular potential curves. The adiabatic eigenvalue problem for the field-charge system is then solved rigorously by a simple iterative procedure. Level shifts due to radiative interaction arise naturally. Multiphotonic transition between two resonant/near-resonant levels at certain internuclear separation can be calculated by formulae similar to the Landau-Zener formula.
Our present work differs from theirs in treating the more general \( n (\geq 3) \)-level atomic/molecular system (interacting with a single-mode field). We derive new formulae for calculating transition probability between three resonant levels and between two near-resonant levels of certain nature. We give a detailed analysis of transition between shifted levels due to power variation, though the idea and a rough estimate have been given in I. We also apply the analysis to a different process—the multiphoton dissociation of molecules.

With multi-level systems, several as well as two levels can be in single- or multiphoton resonant transition with each other. After setting up the Schrödinger equation appropriate to our problem (Sec. II), we detail the solution of the adiabatic eigenvalue problem for these cases (Sec. III) and derive some new transition formulae (Sec. IV). The dependency on orbit of the photon-electronic coupling is considered in Sec. V, where we also present the results of calculations on the collisional cross section of the \( \text{Li}^+ \text{H} \) system over a range of field intensity \( (10^9 - 10^{12} \text{ watt/cm}^2) \).

The general formalism is not limited to treating collisional processes of atoms/molecules. For example, with slight modification, we can apply it to one- or multiphoton dissociation of molecules, where the internuclear vibrational motion take the place of the collisional motion (Sec. VI) and to transition between shifted levels of an atom irradiated by a strong laser pulse, whose temporal variation of intensity gives rise to nonadiabatic transition (Sec. VII). For the former case, we apply it to the \( 2 \)-photon dissociation of \( \text{LiH} \) molecule from the ground state \( X^1\Sigma_g^+ \) via the \( B^1\Pi \) state. The molecule is in an intense radiation field of wavelength \( \lambda = 1.064 \mu \text{m} \) (YAG:Nd \(^{3+}\)). The
thermal averaged cross section over the range of intensities $10^9 - 3.0 \times 10^{11}$ W/cm² is presented. In the latter case, we consider the 2-photon transition in sodium atom (3s → 5s) and 3-photon transition in lithium (2s → 5s) over a range of wavelengths. The transition probability may be considered to have pulse-independent and pulse-dependent factors. For a given pulse-independent factor, one may optimize the pulse such that maximum transition probability of 1/2 is achieved. We have done such analysis for Gaussian pulses, with numerical results presented for the above-mentioned atomic transitions.

II. THE TIME-DEPENDENT EQUATIONS

For concreteness, let us discuss the general theory in the context of slow atomic collision in an intense laser field first. The Schrödinger equation for a system of atoms interacting with a radiation field is

$$i\hbar \dot{\psi} = \left( K + H_R \right) \psi, \quad (\text{II})$$

where $K$ is the kinetic energy operator for the atoms and

$K = h_{\text{a}} + h_p + h'$. Here, $h_{\text{a}}$ is the adiabatic molecular hamiltonian for the colliding atoms at a given internuclear separation $R$. Besides the electronic terms, $h_{\text{a}}$ includes in particular the Coulomb repulsion between the nuclei and their Coulomb interaction with the atomic electrons. The molecular electronic state $\phi_\alpha(\xi; R)$ and "potential curve" $u_\alpha(R)$ are given by the eigenvalue problem

$$h_{\text{a}} \phi_\alpha = u_\alpha(R) \phi_\alpha.$$
where \( \mathcal{E} \) denotes the set of atomic electron coordinates, \( i \) being considered as a parameter.

The Hamiltonian \( h_p \) for the free radiation field with \( m \) number of modes excited is

\[
h_p = \sum_{\lambda=1}^{m} \hbar \omega_{\lambda} a_{\lambda}^\dagger a_{\lambda},
\]

in the usual notations. Finally the interaction Hamiltonian is

\[
h' = -\sum_i \left\{ \frac{\alpha_1}{m_1^2} \left( \frac{\hbar}{\varepsilon_{\mathcal{E}}} \right)^2 A_i^2 (\mathcal{E}_1) - \frac{\alpha_1^2}{m_1^2 \varepsilon_{\mathcal{E}}} A_i (\mathcal{E}_1) A_i^\dagger (\mathcal{E}_1) \right\}
\]

where \( i \) is summed over all the electrons as well as the nucleus. As usual in the Hartree-Fock picture and in plane wave modes,

\[
A_i (\mathcal{E}) = \sum_{k} \left( \frac{\varepsilon_{\mathcal{E}}}{\varepsilon_{\mathcal{E}}} \right)^{1/2} \left( \frac{\beta + \epsilon_{\mathcal{E}}}{\varepsilon_{\mathcal{E}}} \right)^{1/2} e^{i \mathbf{k} \cdot \mathbf{r}_i} \psi_i (\mathcal{E}),
\]

where \( \psi_i \) is theevity volume. A unitary equivalent interaction Hamiltonian well suited for systems of bound charges like atoms and molecules is

\[
h' = -\sum_i A_i A_i^\dagger - \text{higher multipole terms},
\]

where

\[
A_i (\mathcal{E}) = -\frac{1}{2} \frac{\partial^2}{\partial \mathcal{E}^2} A_i (\mathcal{E}).
\]

Since only matrix elements of \( h' \) between two orthogonal electronic states \( | \mathcal{E} \rangle \) will appear in our theory, the leading nonzero matrix elements from the \( A_i A_i^\dagger \) term in Eq. (8.3) for intense radiation field
\((N >> 1)\) are the dipole terms (for one charge)

\[ |A^2| = \frac{\alpha^2}{2m} \left(\frac{2\pi}{\omega^2}\right)|\langle \alpha, N \pm 2 | 2(a^2 - a'^2)|k \cdot r|\beta, N\rangle| \]

while those from the \(A \cdot \beta\) term are

\[ |A_p| = |\langle \alpha, N \pm 1 | \frac{q}{mc} c \left(\frac{2\pi}{\omega^2}\right)^\frac{1}{2} (a + a^\dagger) p \cdot \hat{r}|\beta, N\rangle| \]

A conservative estimate of the relative magnitude of the two kinds of dipole matrix elements can be obtained by considering the ratio

\[ \frac{|A^2|}{|A \cdot \beta|^2 / i \omega} \sim \alpha \sim \frac{1}{137} \]

which takes account of the fact that \(|A^2| (|A_p|)\) connects states whose photon numbers differ by 2 (1). The numerical value is obtained with the assumed typical values for \(\omega_\alpha - \omega_\beta\) to be \(i \omega\) and

\[ |\langle \alpha | \hat{r} \cdot \hat{e} | \beta \rangle| \sim |\langle \alpha | \hat{r} \cdot \hat{k} | \beta \rangle| \sim \alpha_0. \]

Thus we may neglect the \(A \cdot A\) term.

Therefore the dipole interaction Hamiltonian we will use from Eq. (2.2) is

\[ \mathbf{h}' = - \sum_i \frac{q_i}{m_i c} \mathbf{p}_i \cdot \mathbf{A}(0); \]
and that from Eq. (2.3) is

$$h_+ = -\sum_i q_i r_i \cdot E(0).$$

Depending on the problem there are different merits of these two forms of the dipole interaction Hamiltonian. In particular, for treatment of systems in which higher levels are neglected, as we will do, the form $h_+$ makes it a better approximation. We therefore would prefer $h_+$. However, for solving the adiabatic eigenvalue problem below, $h_+$ may for some systems (e.g., the alkaline atoms) give rise to a singular coupling matrix ($Q_+$ below) while it is formally required for algebraic convenience to be nonsingular. Then we would use $h_-'$ instead.

For the slow collision of atoms in an intense radiation field, the physical situation we have in mind is as follows. The atoms are in collision with each other in the region of intense radiation field (e.g., in an open laser cavity). The relative motion of the atoms is much less than that typical of atomic electrons ($\approx \alpha c = 10^8$ cm/sec). They form therefore in the adiabatic approximation a "quasimolecule." In the presence of the radiation field, all $u_\alpha(R)$'s will be shifted relative to each other. The atoms collide together initially along the shifted electronic energy level $u_\alpha'(R)$ corresponding to the molecular electronic state $\alpha$. At some $R$'s there will be multiphotonic resonant transition between the shifted electronic energy levels. And as they separate after the collision, the atoms have certain probability being in an excited state. We will assume either the intensity profile of the intense radiation is uniform over the collisional region and smooth and gradual in its spatial
boundary, so that we do not have to consider transition due to intensity variation as the atoms enter or leave the region of intense radiation field.

We shall treat the near-adiabatic motion of the atomic nuclei classically. It has been shown in I how one may make the transformation from quantum picture to the corresponding approximate classical orbits. Instead of Eq. (2.1), one may then consider,

$$i\hbar \dot{\Psi'} = \mathcal{H}_c(t)\Psi'$$

where $\mathcal{H}_c(t)$ is obtained from $\mathcal{H}$ by replacing the operator $\mathcal{R}$ with the classical orbit $\mathcal{R}(t)$.

To solve Eq. (2.4), we let

$$\Psi' = \sum_\beta c_\beta(\rho,t) \phi_\beta(\rho|R(t)),$$

where $\rho$ is any coordinate representation of the photon field.

Substituting this expansion into (2.4) we obtain

$$i\hbar \dot{c}_\alpha = a_\alpha c_\alpha + b_\alpha c_\beta + \sum_j (\phi_\alpha h \phi_\beta | \phi_\beta) = i\hbar \sum_j \phi_\alpha (\rho_j, \rho_k).$$

The last term on the right corresponds to nonadiabatic transition to nonadiabatic motion of the nuclei. It has been treated elsewhere and is negligible when the electronic energy levels are not very close together. We assume such are the case, we consider. The secular term $(\phi_\alpha h \phi_\beta)$ in the third term on the right is in general nonzero for unlike atoms. It is related to the permanent dipole moment of the molecule in the electronic state $\phi_\alpha$, and is responsible for radiative transition between molecular nuclei states for the same $\phi_\alpha$. Therefore, consistent with the classical orbit approximation for
intennuclear motion, we neglect the radiative transitions within the same electronic state and drop this term. Hence

\[ \text{im} \hat{\epsilon} = u_0 \hat{a}^\dagger + h_p \hat{a} + \sum_{\theta \neq 1} (\epsilon_\theta \hbar^2 \hat{c}_\theta) \hat{c}_\theta . \] (1.6)

We restrict ourselves to cases of one mode of radiation with linear polarization \( \hat{\epsilon} \). Let \( \mathcal{N}(N - \nu) \) be the photon-number state of the radiation field where \( N \) is the initial number of photons and \( \nu \) the number of photons absorbed by the radiating atom. Since we are interested in intense radiation fields, \( N \) is very much larger than the maximum \( \nu \) of interest. Therefore, we will make the excellent approximation

\[ N \to \nu + 1 \approx N - \nu + 1 . \]

Defining the probability amplitude by

\[ i_{\nu} = \sum_{\nu} \mathcal{N}(N - \nu) \hat{c}^\dagger \hat{c} \hat{\epsilon} \]

and making the change of variable \( x \rightarrow -x \)

\[ x = \frac{\nu}{N} , \]

one obtains the expression for the variance

\[ \sigma^2 = \nu \approx \left( N - \nu - 1 \right) \]

in the limit of intense fields. We have written the expression for the

\[ \frac{1}{\sqrt{\nu}} b_{\nu} (\omega) \equiv \sqrt{\nu} \sum \alpha_{\nu} \left( \cdots , \cdots , \cdots \right) \]

where
corresponding to the dipole interaction $h_d^\gamma$, and
\[ G_{\alpha}(\alpha, \beta) = \frac{a_0}{\hbar \nu} \left( \frac{2\pi c}{\epsilon} \right)^{\frac{1}{2}} \left( \phi_{\alpha'} - \sum_i q_i \phi_i^{\beta} \right) \left( \begin{array}{c} \psi \\ \frac{u_\alpha - u_\beta}{\hbar \omega} \end{array} \right) \]

Here $I \equiv c \frac{\hbar \omega}{V}$ is the power flux or field intensity.

If $h_R$ is real, a set of the real $\phi_{\alpha}$ can be chosen. Then the matrix $G_+(G_-)$ is real and symmetric (antisymmetric).

III. THE ADIABATIC EIGENVALUE PROBLEM

Since we will make use of the adiabatic eigenstates of the whole system in the calculation of transition probabilities, we consider in this section the solution of the eigenvalue problem of Eqs. (2.7) in the adiabatic limit. Let
\[ \psi_{\alpha}(\alpha) = e^{i \int^y E(y')dy'} a_{\alpha}(\alpha) \quad (\alpha) \]

where $(E(y), \alpha)$ is the "adiabatic eigensolution" to be found. In the adiabatic limit,
\[ \frac{da_{\alpha}(\alpha)}{dy} = 0 \]
Substituting these expressions into Eqs. (2.7), we obtain

\[ E_n(a) = W(y) \varphi_a(y) \sum_b \phi_y(a, b) (a_{n+1}(\beta) + a_{n-1}(\beta)). \]

The quantities \( W(y) \) correspond to the photon-electronic \((\nu, \pi)\) eigenlevels of the non-interacting Hamiltonian \( H_0 + H_p \). We shall call them the "non-interacting eigenlevels." In absence of interaction, these levels may cross each other (Fig. 1). In such case \( G_p(a, b) \neq 0 \) in Eq. (2.7), then

\[ b_y(a') = \int_Y W(y) \varphi_a' \]

where \( \varphi'_a \) are constant and hence no transition occurs. But with the interaction "on", \( G_p(a, b) \neq 0 \), the adiabatic eigensolutions of Eq. (2.1) would yield \( E's \) which are in general different from \( W(y) \). In particular, near where there was a crossing between the \( W(y) \)'s, we have the non-pertinent interaction between them, the \( W(y) \)'s "repel each other." As a result, the corresponding \( E's \) form a pronouncements (2) \( \frac{dR}{dy} \neq 0. \) In the adiabatic limit, the quasi-molecule follows a particular \( E \) (a solid line in Fig. 1), at each \( E \) throughout the collision and a transition occurs (This is related to the same \( E \) at every \( E \) at \( E \) that there is a corresponding \( \frac{dR}{dy} \neq 0 \). Transitions can occur at the \( E \)'s.

Following 1, we shall label the adiabatic eigensolution \((E_y)\) by that set of index \((a, n)\) such that at each \( y \)

\[ \psi_y = \varphi_a(y), \quad \text{for all } n \quad (3.1) \]

Thus the same \((E_y)\) switch indices at each \( E \) as indicated in...
In the rest of the paper, we shall drop this adiabatic eigenindices on \((E, \mathbf{a})\) whenever no confusion results.

We observe that at any \(y\) if a particular \((E, \mathbf{a})\) are found, then \(\left(\mathbf{E}(\lambda + \lambda)\mathbf{a}, \mathbf{a}^\dagger\right)\) for the same \(\lambda\) but any \(\alpha\) can be generated from it by

\[
\mathbf{E}(\lambda + \lambda)\mathbf{a} = \mathbf{E}(\lambda)\mathbf{a} + \lambda \mathbf{a}
\]

and,

\[
(\lambda + \lambda)\mathbf{a} = \lambda \mathbf{a}
\]

This can be shown simply by expanding the \(\mathbf{E}(\lambda + \lambda)\mathbf{a}\) and only to find the \((\lambda, \mathbf{a})\) adiabatic electron eigenvalues. In order to know all other \((\lambda, \mathbf{a})\) eigenvalues for the same \(\lambda\).

In principle the sum over \(\mathbf{a}\) generates all the discrete electronic states of the problem. However, it is limited in the low-lying electron eigenvalues only. We need to find an appropriate set of discrete electronic states. The higher lying states may be negligible because the discrete electronic states of interest, \((\lambda, \mathbf{a})\), are relatively far from other possible states included in the sum. As a rule, one finds that only the lowest higher orders. Thus restricting ourselves in this manner to a set of discrete electronic states, we now present the following:

It is convenient to convert at this point a matrix definition. Let \(\mathbf{E}_{\alpha}\) be the \(n \times n\) matrix \(\left[\mathbf{E}(\alpha, \mathbf{a})\right]\). Let \(\mathbf{W}_{\alpha}\) be the lower diagonal matrix \(\left((\mathbf{E} - \mathbf{W}(\alpha))^{\frac{1}{2}}\right)\); and let \(\mathbf{\Lambda}_{\alpha}\) be the a lower identity matrix. Then Eq. (3.1) can be rewritten as, for all \(\alpha\).
We shall now the above equation. We shall solve the equation and justify our solution. Let us look at the steps of solving this equation.

In the above equation, let us substitute a certain value for the variable. This will help us understand the solution better. By substituting the value, we can simplify the equation and solve for the unknown variable.

The equation can be solved by various methods. The most common method is to isolate the variable on one side of the equation. This can be done by adding or subtracting terms from both sides of the equation.

Once the variable is isolated, the equation can be solved by dividing both sides by the coefficient of the variable. This will give us the value of the variable.

We can also use other methods such as graphing or using a computer algebra system to solve the equation. These methods can be more helpful in certain situations.

In conclusion, the above equation can be solved by various methods. By substituting a value for the variable and simplifying the equation, we can solve for the unknown variable. This can be done by isolating the variable on one side of the equation and dividing both sides by the coefficient of the variable.
Barring unusual coincident, $D_v^{-1}$ exist, then

$$d_v = U_v^+(d_v - d_v+1)$$

where

$$U_v^+ \equiv D_v^{-1} G_v.$$ 

For $v > 0$, we define $H_v$ such that $d_v = U_v^+ H_v d_v-1$. Then Eqs. (3.4) can be written as

$$U_v^+ H_v G_v = U_v^+[d_v-1 + U_v^+ U_v^{-1} U_v^+ H_v G_v]$$

If the inverse of $U_v^+$ exist (which is the case if $G_v^{-1}$ exists), then the above equations can be simplified to give

$$H_v G_v = [I + U_v^+ H_v G_v]^{-1}.$$ 

Since this is to be satisfied for a general $G_{v-1}$, we have

$$H_v = [I + U_v^+ H_v G_v]^{-1}.$$ 

(3.5)

In particular,

$$H_v = [I + U_v^+ H_v G_v]^{-1}.$$ 

and

$$d_v = U_v^+ H_v d_v \geq 0 = H_v d_v.$$ 

Since

$$D_v^{-1} \to 0 \quad \text{as} \quad v \to \infty,$$

then $H_v \to 1$ in this limit.
For \( v < 0 \), let

\[
\Delta_v = \Delta_v \quad \Delta_v^{-1}.
\]

Substituting into Eqs. (3.4) and after manipulations similar to those leading to Eqs. (3.4), we obtain

\[
H'_v = \left[ I - \Delta_v^{-1} \right] \left[ I - \Delta_v^{-1} \right]^{-1}.
\]  \hspace{1cm} (3.4)

Again \( H'_v \) (hence \( \Delta_v \)) \( \to \) as \( v \to -\infty \), therefore \( H'_v \to 0 \). In particular

\[
H'_{-1} = \left[ I - \Delta_{-1}^{-1} \right] \left[ I - \Delta_{-1}^{-1} \right]^{-1}.
\]

and

\[
\Delta_{-1}^{-1} \Delta_{-1} \Delta_{-1} \Delta_{-1} = \Delta_{-1} \Delta_{-1}.
\]

Since \( d_0(0) = 1 \), we obtain the following set of \( (n-1) \) inhomogeneous equations from Eqs. (3.4) with \( v = 0 \), and \( \alpha = 1, 2, \ldots \),

\[ \alpha = 1, \alpha + 1, \ldots, n, \]

\[
\sum_{\gamma \neq 0} \left[ (E - W_0(w)) \right]_{\alpha \gamma} \sum_{\beta \in \Sigma} G_\alpha(x, \beta) \left( X_\beta(\beta, \gamma) \right) X_\gamma(\beta, \gamma) \right] d_0(\gamma)
\]

\[ = \sum_{\beta \in \Sigma} G_\alpha(x, \beta) \left( X_\beta(\beta, 0) \right) \right] X_\gamma(\beta, 0) \right) \right. \]

\[ \right. \]  \hspace{1cm} (3.7a)

If the above equations are represented in matrix form, then

\[
\tilde{A} \tilde{x} = \tilde{b},
\]

where
\[ d'_0 = \left( d_0(1), d_0(2), \ldots, d_0(\sigma - 1), d_0(\sigma + 1), \ldots, d_0(n) \right), \]

and \( P \) is the \((n - 1) \times (n - 1)\) coefficient matrix while \( b' \) is the \((n - 1) \times 1\) known right-hand side. Barring unusual coincidence, \( P^{-1} \) exists and the solution is

\[ d'_0 = P^{-1} b'. \tag{3.8} \]

Thus in order to find all \( H'_{\nu} \)'s and \( H'_m \)'s (hence also \( d_0(\alpha) \)'s), in principle we may start with \( H_1 = 1 \) and \( H'_1 = 1 \) (+ corresponds to \( H'_{\nu} \) hamiltonian while - corresponds to the \( H'_m \) hamiltonian). However, in actual numerical calculations, we may impose a cut-off \( M(-M < \nu < M) \) such that the error in the matrix elements of \( H_1 \) and \( H'_1 \) is negligible. An estimate of this error is given roughly by \((\delta(\alpha, \omega)/|\mu|)^{M/2}\). The actual choice of \( M \) depends on a particular system and field intensity of interest. In the examples we have done, a relative error of magnitude less than \( 10^{-3} \) can be achieved with \( M \) being around 10 even for the 

Thus starting with \( \mu_{m+1} = 1 \), we find successively \( \mu_2 \), \( \mu_3 \), \( \mu_4 \), \( \mu_5 \), \( \mu_6 \), \( \mu_7 \), \( \mu_8 \), \( \mu_9 \), \( \mu_{10} \) according to Eqs. (3.4). Then \( \omega_1 = \mu_1/\mu_2 \). Similarly starting with \( \mu'_m = 1 \), we find \( \mu'_2 \), \( \mu'_3 \), \( \mu'_4 \), \( \mu'_5 \), \( \mu'_6 \), \( \mu'_7 \), \( \mu'_8 \), \( \mu'_9 \) according to Eqs. (3.6). Then \( d_{-1} = \omega^{-1}_{-1} \mu'_{-1} \). Then we obtain \( y' \) from Eqs. (3.7).

So far we have not used the \((\nu = 2, n + 1)\) equation

\[ E = W_0(\sigma) + \sum_{\beta, \gamma} \delta_{\beta}(\sigma, \beta)(x(\beta, \gamma) + x(\bar{\beta}, \gamma)) \]

\[ \alpha(\nu) \]
when \( J(r) \) has been used. The normal mode is then identified as the shift of level \( \phi_j(r) \) in interaction with the intensity, it agrees in value with that given by our solution method.

We use this equation for some iterative solution of the eigenvalue \( \lambda_j \), by starting with \( \lambda_j = 0 \). The number of iterations depends on the accuracy needed as well as the strength of coupling \( \lambda_j \). In all calculations we have \( \lambda_j \approx 1 \) for more significant values the required number of iterations is increased.

The above procedure is similar to that of solving the vibrational equation if it is not valid for small values of \( \lambda_j \).

In [1] Smith...
To find $d_v(a)$'s, which are independent of $a_v(\sigma_1)$, we substitute $d_v(a)a_v(\sigma_1)$ in place of $a_v(\alpha)$ in Eqs. (3.2) and obtain

$$\frac{D_v d_v}{d_v} = G_v(d_v^{-1} + d_v^{-1}) , \quad -M \leq v \leq M . \quad (3.10)$$

For $v > v_1$, let $d_v = U_v H_v d_{v-1}$, where $U_v = D_v^{-1} \bar{Q}_v$. Then after manipulations similar to those from Eqs. (3.4) to Eqs. (3.5), we obtain as before

$$H_v = \left[ I + U_v H_v d_{v+1} U_v^{-1} \right]^{-1} , \quad v = v_1, \ldots, v_2 - 1, v_2 - 2, \ldots, v_1 + 1 \quad (3.11)$$

Now, however, among the $v_2$th set of equations in Eq. (3.11), all the $n - 1$ equations with $a \neq \sigma_2$, and $d_{v_2}(\sigma_2) = 0$ from Eqs. (3.9), can be satisfied to an arbitrary degree of accuracy if we write

$$d_{v_2} = \tilde{D}_{v_2}^{-1} G_{v_2}(d_{v_2-1} + d_{v_2+1}) \quad (3.11a)$$

where

$$\tilde{D}_{v_2} (\alpha, \beta) \equiv D_{v_2} (\alpha, \alpha) \delta_{\alpha, \beta} , \quad \alpha \neq \sigma_2 ;$$

and

$$\tilde{D}_{v_2} (\sigma_2, \beta) \equiv \lambda d_{v_2} \delta_{\sigma_2, \beta}$$

$\lambda$ being an (1) arbitrarily large but (2) finite number. Condition (1) enables $d_{v_2}(\sigma_2) \equiv 0$ to be satisfied while condition (2) fulfills the formal requirement that $\tilde{D}_v^{-1}$ exists. Then with
\[ U_{v_2} = \tilde{U}_{v_2} G \]

we obtain as before

\[ H_{v_2} = \left( A^{\tilde{V}_2} \tilde{V}_2 \tilde{V}_2 + 1 \right)^{-1} \]  

(3.12b)

and from the \((v_2 - 1)\)th set,

\[ H_{v_2-1} = \left( A^{\tilde{V}_2} \tilde{V}_2 \tilde{V}_2 + 1 \right)^{-1} \]

For \( v < v_2 \), with \( \tilde{d}_v \), \( \tilde{d}_{v_2} \), \( \tilde{d}_{v+1} \), \( \tilde{d}_v \), with \( v \leq v_2 - 1 \) are obtained the same way as in Eqs. (3.6).

With the equations above, various \( \tilde{d}_v \)'s can be expressed in terms of \( \tilde{d}_{v_2} \). For use below, we write

\[ \tilde{d}_{v+1} = X_1 \tilde{d}_v \]

\[ \tilde{d}_{v-1} = X_2 \tilde{d}_{v+1} \]

\[ \tilde{d}_{v+1} = X_3 \tilde{d}_{v} \]

\[ \tilde{d}_{v-1} = X_4 \tilde{d}_{v+1} \]

The explicit forms of \( X_i \)'s depend on \( n (\tilde{v}_2 - \tilde{v}_2) \). When \( \tilde{v} = 1 \),
When \( n = 1 \),

\[
\begin{align*}
X_1 &= \frac{U_1}{U_2} + 1, \\
X_2 &= X_2, \\
X_3 &= X_3, \\
X_4 &= \frac{U_1}{U_2} - 1.
\end{align*}
\]

(3.13)

The \( \tilde{d}_{\nu}^{1} \) can be found from the \( \nu \)th set of Eqs. (3.10) with \( \alpha = 1, 2, \ldots, \sigma_{\nu} - 1, \sigma_{\nu} + 1, \ldots, n \) and \( d_{\nu_1}(\sigma_1) = 1 \), in a way similar to that of Eqs. (3.7). To find the \( s_\nu(\alpha)'s \), which are independent of \( a_\nu(\sigma_1) \), we substitute \( s_\nu(\alpha) a_\nu(\sigma_2) \) in place of \( a_\nu(\alpha) \) into Eqs. (3.2)

\[
D_{\nu \lambda} s_\nu = s_{\nu_2}(s_{\nu_1} \pm s_{\nu+1}), \quad -M \leq \nu \leq M.
\]  

(3.14)
For \( v > v_2 \), we define \( s_v = U^+_{m\nu} K_{\nu \nu} s_{\nu+1} \) and obtain as before

\[
K_{\nu \nu} = \left[ I + U^+_{m\nu} K_{\nu \nu+1} U^+_{m\nu} \right]^{-1}.
\]

Comparing with Eqs. (3.11), we observe that, \( K_{\nu} = K_{\nu} \), for \( v_2 < v < M \), since the cut-off conditions \( (H_{M-1} = \frac{\pi}{\alpha}; K_{M-1} = \frac{\pi}{\alpha}) \) are the same. For \( v < v_2 \), with \( s_v = U^+_{m\nu} K'_{\nu \nu} s_{\nu+1} \), \( K'_{\nu} \) are found from Eqs. (3.14) to be

\[
K'_{\nu \nu} = \left[ I - U^+_{m\nu} K'_{\nu \nu+1} U^+_{m\nu} \right]^{-1}
\]

where \( \nu = -M, -M+1, \ldots, \nu_1 - 1, \nu_1 + 2, \ldots, \nu_2 - 1 \).

Again since their cut-off conditions \( (H'_{M-1} = \frac{\pi}{\alpha}; K'_{M-1} = \frac{\pi}{\alpha}) \) are the same, \( K'_{\nu} = K'_{\nu} \) for \( M \leq \nu \leq \nu_1 - 1 \).

The \( K'_{\nu \nu} \) matrix is obtained in a way similar to obtaining \( K_{\nu \nu} \) in Eqs. (3.12). Now we use the \( \nu \)th set of Eqs. (3.14) with \( \alpha = 1, 2, \ldots, c_1 - 1, c_1 + 1, \ldots, n \) and \( s_{\nu_{1}}(c_1) = 0 \) to write

\[
s_{\nu_{1}} = \sum_{\nu_{1}} c_{\nu_{1}} (s_{\nu_{1}-1} + \tilde{s}_{\nu_{1}-1} - \tilde{s}_{\nu_{1}})
\]

where

\[
\tilde{s}_{\nu_{1}}(\alpha, \beta) \equiv \tilde{s}_{\nu_{1}}(\alpha, \beta) \xi_{\alpha, \beta} \quad \text{for} \quad \alpha \neq c_1;
\]

and

\[
\tilde{s}_{\nu_{1}}(c_1, \beta) \equiv \xi_{c_1, \beta};
\]

\( \xi \) being an arbitrary large but finite number. Then
where \( \tilde{U} = \tilde{G}^{-1} \). From the \((v_1 - 1)\)th set of equations, we obtain

\[
\begin{align*}
K'_{\bar{m}v_1} &= \pm \left[ I - \tilde{U} \tilde{K}'_{\bar{m}v_1-1} \tilde{K}'_{\bar{m}v_1-1} \right]^{-1}, \\
K'_{\bar{m}v_1+1} &= \pm \left[ I - \tilde{U} \tilde{K}'_{\bar{m}v_1} \tilde{U} \tilde{K}'_{\bar{m}v_1+1} \right]^{-1}.
\end{align*}
\]

Defining

\[
\begin{align*}
\bar{m}v_2' &= \frac{1}{2} \tilde{V}_1 \bar{m}v_2, \\
\bar{m}v_2 &= \frac{1}{2} \tilde{V}_2 \bar{m}v_2, \\
\bar{m}v_1' &= \frac{1}{2} \tilde{V}_3 \bar{m}v_2, \\
\bar{m}v_1 &= \frac{1}{2} \tilde{V}_4 \bar{m}v_2,
\end{align*}
\]

for \( n \geq 2 \), we obtain

\[
\begin{align*}
\bar{m}v_1' &= \frac{1}{2} \tilde{V}_1 \bar{m}v_2 + \frac{1}{2} \tilde{K}'_{\bar{m}v_2} + 1, \\
\bar{m}v_2' &= \frac{1}{2} \tilde{V}_2 \bar{m}v_1 + \frac{1}{2} \tilde{K}'_{\bar{m}v_2} - 1, \\
\bar{m}v_3' &= \frac{1}{2} \tilde{V}_3 \bar{m}v_1 + \frac{1}{2} \tilde{K}'_{\bar{m}v_2} + 2 + \tilde{U} \tilde{K}'_{\bar{m}v_2} + 2' \cdots \tilde{U} \tilde{K}'_{\bar{m}v_2} - 1, \\
\bar{m}v_4' &= \frac{1}{2} \tilde{V}_4 \bar{m}v_1 + \frac{1}{2} \tilde{K}'_{\bar{m}v_2} - 1 + \tilde{U} \tilde{K}'_{\bar{m}v_2} - 1 \tilde{U} \tilde{K}'_{\bar{m}v_2} - 1.
\end{align*}
\]
while for $\eta = 1$, we obtain

$$Y_1 = \frac{U^\pm}{\nu_2 + 1} K_{\nu_2 + 1}$$

$$Y_2 = \frac{U^\pm}{\nu_1 + 1} K'_{\nu_1}$$

$$Y_3 = \frac{1}{\nu_1}$$

$$Y_4 = \frac{U^\pm}{\nu_1 - 1} K'_{\nu_1 - 1} \frac{U^\pm}{\nu_1} K'_{\nu_1}$$

(3.15)

All $s_v$ are thus expressed in terms of $s_{v_2}$. The

$s'_{v_2} \equiv (s_{v_2}(1), \ldots, s_{v_2}(\sigma_2 - 1), s_{v_2}(\sigma_2 + 1), \ldots, s_{v_2}(n))$ are found from

the $v_2$th set of equations with $\alpha = 1, 2, \ldots, \sigma_2 - 1, \sigma_2 + 1, \ldots, n$, and

$s_{v_2}(\sigma_2) = 1$ in a way similar to that of $s'_v$ in Eqs. (3.7).

Finally, we use the two remaining equations

$$\left( E - W_{v_1}(\sigma_1) \right) a_{v_1}(\sigma_1) = \sum_\beta c_{\pm}(\sigma_1, \beta) \left( a_{v_1 - 1}(\beta) \pm a_{v_1 + 1}(\beta) \right)$$

and

$$\left( E - W_{v_2}(\sigma_2) \right) a_{v_2}(\sigma_2) = \sum_\beta c_{\pm}(\sigma_2, \beta) \left( a_{v_2 - 1}(\beta) \pm a_{v_2 + 1}(\beta) \right)$$

to find the adiabatic eigenvalue $E$. Substitutions of $a_v's$ as

given in Eqs. (3.8), (3.15), and (3.15) gives

$$\begin{pmatrix} E - W_{v_1}(\sigma_1) & G_{12} \\ G_{21} & E - W_{v_2}(\sigma_2) \end{pmatrix} \begin{pmatrix} a_{v_1}(\sigma_1) \\ a_{v_2}(\sigma_2) \end{pmatrix} = 0$$
where

\[ W'_{v_1}(\sigma_1) = W_{v_1}(\sigma_1) + \Delta_1, \]
\[ \Delta_1 = \sum_{\gamma, \beta} G_{\gamma}(\sigma_1, \gamma)(X_4(\gamma, \beta) \pm X_3(\gamma, \beta)) s_{v_1}(\beta); \]
\[ W'_{v_2}(\sigma_2) = W_{v_2}(\sigma_2) + \Delta_2, \]
\[ \Delta_2 = \sum_{\gamma, \beta} G_{\gamma}(\sigma_2, \gamma)(Y_2(\gamma, \beta) \pm Y_1(\gamma, \beta)) s_{v_2}(\beta); \]
\[ G_{12} = -\sum_{\gamma, \beta} G_{\gamma}(\sigma_1, \gamma)(Y_4(\gamma, \beta) \pm Y_3(\gamma, \beta)) s_{v_2}(\beta); \]
\[ G_{21} = -\sum_{\gamma, \beta} G_{\gamma}(\sigma_2, \gamma)(X_2(\gamma, \beta) \pm X_1(\gamma, \beta)) s_{v_1}(\beta). \quad (3.1b) \]

If the above calculations are valid, we expect our hamiltonian to remain hermitian, \( G_{12} = G_{21} \). The quantity \( \Delta_i \) \((i = 1, 2)\) may be viewed as shift of the level \( W_{v_1}(\sigma_1) \) due to interaction with other levels. We shall call \( W'_{v_1}(\sigma_1) \) the "shifted \((v_1, \sigma_1)\) level."

Solutions to the above equations exist for the adiabatic eigenvalues,

\[ E_u = \frac{1}{2} \left[ \left( W'_{v_2}(\sigma_2) + W'_{v_1}(\sigma_1) \right) + \left( (W'_{v_2}(\sigma_2) - W'_{v_1}(\sigma_1))^2 + 4G_{12}G_{21} \right)^{\frac{1}{2}} \right], \]
\[ E_d = \frac{1}{2} \left[ \left( W'_{v_2}(\sigma_2) + W'_{v_1}(\sigma_1) \right) - \left( (W'_{v_2}(\sigma_2) - W'_{v_1}(\sigma_1))^2 + 4G_{12}G_{21} \right)^{\frac{1}{2}} \right]. \quad (3.17) \]
Starting with a trial $E$, e.g., $\frac{3}{2}(W_{v_2}(\sigma_2) + W_{v_1}(\sigma_1))$, we can use one of these two equations for iteration to find $(E, r_i)$ and/or $(E, s_i)$.

The level separation $E_u - E_f$ is then $(\langle W_{v_2}^\prime(\sigma_2) - W_{v_1}^\prime(\sigma_1)\rangle^2 + 4G_{12}G_{21})^{1/2}$ and the degeneracy is removed. The minimum of $E_u - E_f$ as a function of $R(y)$ is the "point of closest approach" around which we calculate the transitional probability in Sec. IV.

C. The 3-Level PC

As more electronic states are included, the occurrence of 3-level PC becomes more likely. This section also serves to show how the method in the previous sections may be extended to cases of multilevel PC. However, we will be brief wherever similarities with case of 2-level PC occur.

Suppose we have a 3-level PC occurring among levels $(v_1, \sigma_1)$, $(v_2, \sigma_2)$, and $(v_3, \sigma_3)$. At each $R(y)$, we express all $a_v(\alpha)$ in terms of the three coefficients of the degenerate non-interacting states, as

\[ a_v(\alpha) = d_v(\alpha) a_{v_1}(\sigma_1) + s_v(\alpha) a_{v_2}(\sigma_2) + t_v(\alpha) a_{v_3}(\sigma_3). \]

(7.19)

This implies immediately

\[ d_{v_1}(\sigma_1) = 1, \quad s_{v_1}(\sigma_1) = 0, \quad t_{v_1}(\sigma_1) = 0; \]

\[ d_{v_2}(\sigma_2) = 0, \quad s_{v_2}(\sigma_2) = 1, \quad t_{v_2}(\sigma_2) = 0; \]

\[ d_{v_3}(\sigma_3) = 0, \quad s_{v_3}(\sigma_3) = 0, \quad t_{v_3}(\sigma_3) = 1. \]
The three particular equations \((v_1, \sigma_1), (v_2, \sigma_2),\) and \((v_3, \sigma_3)\) in Eqs. (3.2) are not used to find the unknown coefficients \(d's, s's,\) and \(t's.\)

To find the \(d(v(\alpha))'s,\) which are independent of \(a_{v_2}(\sigma_2)\) and \(a_{v_3}(\sigma_3)\), we substitute \(d(v(\alpha)) a_{v_1}(c_1)\) in place of \(a_{v}(\alpha)\) in Eqs. (3.2). Defining

\[ d_{\nu} = U_{\nu,\nu}^* H_{\nu,\nu}^* d_{\nu-1} \]

for \(\nu > v_1\) and

\[ d_{\nu} = U_{\nu,\nu}^* H_{\nu,\nu}^* d_{\nu+1} \]

for \(\nu < v_1\), we obtain, with \(H_{M+1} = I\) and \(H_{M-1} = \pm I\),

\[ H_{\nu,\nu} = \left[ I_{n,\nu} + U_{\nu,\nu}^* H_{\nu,\nu}^* \right]^{-1}, \quad \nu = M, \ldots, v_3 + 1, v_3 - 2, \ldots, \]

\[ v_2 + 1, v_2 - 2, \ldots, v_1 + 1; \]

\[ H_{\nu,\nu}^{-1} = \left[ I_{n,\nu} - U_{\nu,\nu}^* H_{\nu,\nu}^{-1} \right]^{-1}, \]

\[ H_{\nu,\nu}^{-1} = \left[ I_{n,\nu} - U_{\nu,\nu}^* H_{\nu,\nu}^{-1} \right]^{-1}, \]

\[ H_{\nu,\nu}^{-1} = \left[ I_{n,\nu} - U_{\nu,\nu}^* H_{\nu,\nu}^{-1} \right]^{-1}, \]

and

\[ H_{\nu}^* = \pm \left[ I_{n,\nu} - U_{\nu,\nu}^* H_{\nu,\nu}^{-1} \right]^{-1}, \quad -M \leq \nu \leq v_1 - 1. \]

Here,

\[ U_{\nu,\nu}^* \equiv \frac{B^{-1} G}{\nu} \]  

(3.19)
where 

\[ \tilde{D}_{v_1} (\alpha, \beta) \equiv D_{v_1} (\alpha, \alpha) \delta_{\alpha \beta}, \quad \alpha \neq \sigma_i \]

\[ \tilde{D}_{v_1} (\sigma_i, \beta) \equiv \lambda \delta_{\sigma_i \beta} \]

\( \lambda \) being an arbitrarily large but finite number. For \( i = 2,3 \), the equations \( d_{v_2} (\sigma_i) = 0 \), \( d_{v_3} (\sigma_i) = 0 \) and that \( \tilde{D}^{-1}_{v_1} \) exist, are all satisfied as desired.

We define

\[ \frac{d}{d_{v_2} + 1} \equiv X_1 \frac{d}{d_{v_1}} , \]

\[ \frac{d}{d_{v_3} - 1} \equiv X_2 \frac{d}{d_{v_1}} , \]

\[ \frac{d}{d_{v_2} + 1} \equiv X_3 \frac{d}{d_{v_1}} , \]

\[ \frac{d}{d_{v_2} - 1} \equiv X_4 \frac{d}{d_{v_1}} , \]

\[ \frac{d}{d_{v_1} + 1} \equiv X_5 \frac{d}{d_{v_1}} , \]

\[ \frac{d}{d_{v_1} - 1} \equiv X_6 \frac{d}{d_{v_1}} . \quad (3.20a) \]

While other cases may be written down as need arises, we have considered the following two typical cases: with \( n \equiv v_2 - v_1 \), \( k \equiv v_3 - v_2 \),
for case $K > 2$, $n > 2$:

\[ X_6 = U^+ \nabla_1^{-1} H' \nabla_1^{-1} \, , \]

\[ X_5 = U^+ \nabla_1 + 1 H \nabla_1 + 1 \, , \]

\[ X_4 = U^+ \nabla_2^{-1} H \nabla_2^{-1} U^+ \nabla_2^{-2} H \nabla_2^{-2} \cdots U^+ \nabla_1 + 2 H \nabla_2^{-2} = X_5 \, , \]

\[ X_3 = U^+ \nabla_2 + 1 H \nabla_2 + 1 U^+ \nabla_2 H X_4 \, , \]

\[ X_2 = U^+ \nabla_3^{-1} H \nabla_3^{-1} \cdots U^+ \nabla_2 + 2 H \nabla_2 + 2 X_3 \, , \]

\[ X_1 = U^+ \nabla_3 + 1 H \nabla_3 + 1 U^+ \nabla_3 H X_2 \, ; \quad (3.20b) \]

while for case $K = 1$, $n = 2$:

\[ X_6 = U^+ \nabla_1^{-1} H' \nabla_1^{-1} \, , \]

\[ X_5 = U^+ \nabla_1 + 1 H \nabla_1 + 1 \, , \]

\[ X_4 = X_5 \, , \]

\[ X_3 = \nabla_3 \nabla_3 \nabla_2^{-1} \nabla_2^{-1} U^+ \nabla_3 H \nabla_2 X_4 \, , \]

\[ X_2 = \nabla_2 H X_4 \, , \]

\[ X_1 = U^+ \nabla_3 + 1 \nabla_3 + 1 X_3 \, . \quad (3.20c) \]
Then $d_{\nu_1}(1), d_{\nu_1}(2), \ldots, d_{\nu_1}(\sigma_1 - 1), d_{\nu_1}(\sigma_1 + 1), \ldots, d_{\nu_1}(n)$
are found from the $\nu_1$th set of equations without the $(\nu_1, \sigma_1)$
equation, but with $d_{\nu_1}(\sigma_1) = 1$, in a way similar to that of Eqs.
(3.7).

To find $t_{\nu}(\alpha)$'s, we substitute $t_{\nu}(\alpha) a_{\nu_3}(\sigma_3)$ in place of $a_{\nu}(\alpha)$ in Eqs. (3.2). Defining $L_{\nu}$ and $L'_{\nu}$ by

$$t_{\nu} = U_{\nu}^{\pm} L_{\nu} t_{\nu-1}^{-1}, \quad \nu > \nu_3$$

and,

$$t_{\nu} = U_{\nu}^{\pm} L'_{\nu} t_{\nu+1}^{-1}, \quad \nu < \nu_3$$

and starting with $L_{\nu=M+1} = I$ and $L'_{\nu=M-1} = \pm I$, we calculate all other $L$'s and $L'$'s by the following equations

$$L_{\nu} = \left[ I + \frac{U_{\nu}^{\pm}}{\text{det} L_{\nu} + 1} L_{\nu}^{-1} U_{\nu}^{\pm} \right]^{-1}, \quad M > \nu \geq \nu_3 + 1$$

$$L'_{\nu} = \pm \left[ I - \frac{U_{\nu}^{\pm}}{\text{det} L'_{\nu} - 1} L'_{\nu}^{-1} U_{\nu}^{\pm} \right]^{-1}, \quad \nu = M, M + 1, \nu_1 - 1, \nu_2 + 2, \ldots, \nu_2 - 1, \nu_2 + 2, \ldots, \nu_3 - 1$$

$$L'_{\nu|1} = \pm \left[ I - \frac{U_{\nu|1}^{\pm}}{\text{det} L'_{\nu|1} - 1} L'_{\nu|1}^{-1} U_{\nu|1}^{\pm} \right]^{-1}, \quad i = 1, 2$$

$$L'_{\nu|1+1} = \pm \left[ I - \frac{U_{\nu|1}^{\pm}}{\text{det} L'_{\nu|1+1} - 1} L'_{\nu|1+1}^{-1} U_{\nu|1}^{\pm} \right]^{-1}, \quad i = 1, 2$$

where $\tilde{U}_{\nu|1}^{\pm}$ are defined as in Eqs. (3.19) in order to satisfy

$t_{\nu_1}(\sigma_1) = 0$ and $t_{\nu_2}(\sigma_2) = C$. Note that
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\[
L_{uv} = H_{uv}, \quad M \geq u \geq v_3 + 1
\]

and

\[
L'_{uv} = H'_{uv}, \quad -M \leq u \leq v_1 - 1.
\]

Defining \( Z_{m1} (i = 1,\ldots,6) \) by

\[
t_{v_3+1} = Z_{m1} t_{v_3},
\]

\[
t_{v_3-1} = Z_{m2} t_{v_3},
\]

\[
t_{v_2+1} = Z_{m3} t_{v_3},
\]

\[
t_{v_2-1} = Z_{m4} t_{v_3},
\]

\[
t_{v_1+1} = Z_{m5} t_{v_3},
\]

\[
t_{v_1-1} = Z_{m6} t_{v_3},
\]

for case \( k \geq 2, \ n \geq 2, \) we obtain

\[
Z_1 = U_{v_3+1} t_{v_3+1},
\]

\[
Z_2 = U_{v_3-1} t_{v_3-1},
\]

\[
Z_3 = U_{v_2+1} t_{v_2+1} U_{v_2} t_{v_2} \cdots U'_{v_2-1} t_{v_2-1} U'_{v_2-1},
\]
Thus all $t_v$'s are expressed in terms of $t_{v_3}$. But

$t_{v_3}(o_3) = 1$ while $t_{v_3}(1), t_{v_3}(2), \ldots, t_{v_3}(o_3 - 1), t_{v_3}(o_3 + 1), \ldots, t_{v_3}(n)$ can be found by solving the $n - 1$ inhomogeneous equations labelled by $(v_3; 1, 2, \ldots, o_3 - 1, o_3 + 1, \ldots, n)$ as that leading to Eqs. (3.7).
To find $s_{\nu}(a)$'s, we substitute $s_{\nu}(a) w_{2}^{(a-1)}$ in place of $\eta_{\nu}(a)$ into Eqs. (3.2). Defining $K_{\nu}$ and $K'_{\nu}$ by

$$s_{\nu} = U^{\nu} K_{\nu} s_{\nu-1}, \quad \nu > \nu_{2}$$

and

$$s_{\nu} = U^{\nu} K'_{\nu} s_{\nu+1}, \quad \nu < \nu_{2},$$

we obtain with $K_{M+1} = I_{\nu}$ and $K_{M-1} = I_{\nu}$,

$$K_{\nu} = H_{\nu}, \quad M \geq \nu \geq \nu_{2} + 1$$

$$K'_{\nu} = L_{\nu}, \quad -M \leq \nu \leq \nu_{2} - 1.$$ Again defining $Y_{\nu}, i = 1, 2, \ldots, 6$, by

$$s_{\nu+1} = Y_{1} s_{\nu}$$

$$s_{\nu-1} = Y_{2} s_{\nu}$$

$$s_{\nu+1} = Y_{3} s_{\nu}$$

$$s_{\nu-1} = Y_{4} s_{\nu}$$

$$s_{\nu+1} = Y_{5} s_{\nu}$$

$$s_{\nu-1} = Y_{6} s_{\nu}.$$ For case $k \geq 2, \eta \geq 2$, we obtain
\[ Y_3 = U_{m+1}^{t} K_{m+1}^{1} \, \]
\[ Y_2 = U_{m+1}^{t} K_{m+1}^{1-1} \cdots U_{m-1}^{t} K_{m-1}^{1} \, \]
\[ Y_1 = U_{m+1}^{t} K_{m+1}^{1} U_{m+1}^{t} K_{m+1}^{1} \cdots Y_2 \, \]
\[ Y_0 = U_{m+1}^{t} K_{m+1}^{1} \, \]
\[ Y_{m-1} = U_{m+1}^{t} K_{m+1}^{1} \cdots U_{m-1}^{t} \, \]
\[ Y_{m-2} = U_{m+1}^{t} K_{m+1}^{1} \cdots U_{m-1}^{t} \, \]
\[ Y_{m-3} = U_{m+1}^{t} K_{m+1}^{1} \cdots U_{m-1}^{t} \, \]
\[ Y_{m-4} = U_{m+1}^{t} K_{m+1}^{1} \cdots U_{m-1}^{t} \, \]
and for case \( \kappa = 1, \eta = 2: \)
\[ Y_3 = U_{m+1}^{t} K_{m+1}^{2} \, \]
\[ Y_2 = U_{m+1}^{t} K_{m+1}^{2} \, \]
\[ Y_1 = U_{m+1}^{t} K_{m+1}^{2} \cdots U_{m-1}^{t} \, \]
\[ Y_0 = U_{m+1}^{t} K_{m+1}^{2} \, \]
\[ Y_{m-1} = U_{m+1}^{t} K_{m+1}^{2} \cdots U_{m-1}^{t} \, \]
\[ Y_{m-2} = U_{m+1}^{t} K_{m+1}^{2} \cdots U_{m-1}^{t} \, \]
\[ Y_{m-3} = U_{m+1}^{t} K_{m+1}^{2} \cdots U_{m-1}^{t} \, \]
\[ Y_{m-4} = U_{m+1}^{t} K_{m+1}^{2} \cdots U_{m-1}^{t} \, \]
\[ Y_{m-5} = U_{m+1}^{t} K_{m+1}^{2} \cdots U_{m-1}^{t} \, \] (3.12)
Again \( s_{v_2}(1), s_{v_2}(2), \ldots, s_{v_2}(\sigma_2 - 1), s_{v_2}(\sigma_2 + 1), \ldots, s_{v_2}(n) \) are found from the \((\nu_2; 1,2,\ldots,\sigma_2 - 1,\sigma_2 + 1,\ldots,n)\) equations and \( s_{v_2}(\sigma_2) = 1 \) in the by-now familiar way.

Finally substitutions of Eqs. (3.18), (3.20), (3.21), and (3.22) into the three equations \((\nu_1,\sigma_1), (\nu_2,\sigma_2), (\nu_3,\sigma_3)\) of Eqs. (3.2) give

\[
\begin{bmatrix}
    E - W'_{v_1}(\sigma_1) & G_{12} & G_{13} \\
    G_{21} & E - W'_{v_2}(\sigma_2) & G_{23} \\
    G_{31} & G_{32} & E - W'_{v_3}(\sigma_3)
\end{bmatrix}
\begin{bmatrix}
    a_{v_1}(\sigma_1) \\
    a_{v_2}(\sigma_2) \\
    a_{v_3}(\sigma_3)
\end{bmatrix} = 0
\]

where

\[
W'_{v_1}(\sigma_1) \equiv W_{v_1}(\sigma_1) \cdot \Delta_1
\]

\[
W'_{v_2}(\sigma_2) \equiv W_{v_2}(\sigma_2) \cdot \Delta_2
\]

\[
W'_{v_3}(\sigma_3) \equiv W_{v_2}(\sigma_2) \cdot \Delta_3
\]

and with the \(\sigma\)th component of a vector \(\mathbf{a}\) denoted by \(a_\sigma\),

\[
\Delta_1 \equiv \left\{ G_1(\mathbf{x}_6 \cdot \mathbf{y}_5) s_{v_1} \right\}_{\sigma_1}
\]

\[
\Delta_2 \equiv \left\{ G_2(\mathbf{y}_6 \cdot \mathbf{y}_3) s_{v_2} \right\}_{\sigma_2}
\]

Equation (3.23) continued next page
The $\Delta$'s are shifts of the noninteracting levels due to their interaction with other states. The $G_{ij}$'s are coupling between the shifted photon-electronic states and by hermiticity we expect $G_{ij} = G_{ji}$. The characteristic equation is a cubic equation in $E$ whose solution is well known. If we define
\[ p = -W_{\nu_1}^t(\sigma_1) - W_{\nu_2}^t(\sigma_2) - W_{\nu_3}^t(\sigma_3) \]

\[ q = W_{\nu_1}^t(\sigma_1) W_{\nu_2}^t(\sigma_2) - W_{\nu_3}^t(\sigma_2) W_{\nu_4}^t(\sigma_3) - W_{\nu_1}^t(\sigma_3) W_{\nu_2}^t(\sigma_4) \]

\[ -g_{11}g_{21} - g_{13}g_{32} - g_{23}g_{12} \]

\[ r = -W_{\nu_1}^t(\sigma_1) W_{\nu_2}^t(\sigma_2) W_{\nu_3}^t(\sigma_3) - g_{42} W_{\nu_1}^t(\sigma_1) - g_{41} W_{\nu_2}^t(\sigma_2) - g_{12} W_{\nu_3}^t(\sigma_3) \]

\[ + g_{11} g_{21} W_{\nu_4}^t(\sigma_4) + g_{13} g_{32} W_{\nu_4}^t(\sigma_4) + g_{23} g_{12} W_{\nu_4}^t(\sigma_4) \]

\[ a = \frac{1}{\nu} (3q - p^2) \]

\[ b = \left( \frac{1}{\nu} \right)^3 (\omega_3^3 - \nu \omega_1 \omega_2 \omega_4) \]

\[ \lambda = \frac{1}{\nu} - \nu^{-1} \left( -\frac{\nu}{\pi} \left( \frac{3}{\nu} \right)^{\frac{1}{4}} \right) \]

and if the condition for existence of three real roots of the cubic equation, namely

\[ \frac{1}{\nu} \left( \frac{3}{\nu} \right)^{\frac{1}{4}} \]

is satisfied, the three real roots are given by
\[ E_1 = \left(-\frac{n}{j}\right)^{\frac{1}{3}} \cos \phi \]
\[ E_2 = \left(-\frac{n}{j}\right)^{\frac{1}{3}} \cos \left(\phi + \frac{2\pi}{3}\right) \]
\[ E_3 = \left(-\frac{n}{j}\right)^{\frac{1}{3}} \cos \left(\phi - \frac{2\pi}{3}\right). \]

Any one of these equations can be used for iteration to find the adiabatic eigensolutions \( E_{n+1}, V_{n+1} \), \( n = 1, 2, \ldots \). In the next section, we will consider a nonadiabatic transition at the point where \( E_n - E_{n+1} \) and \( E_{n+1} - E_1 \) are minimum as functions of \( H(y) \).

IV. TRANSITION PROBABILITIES

In the previous section, we have solved the eigenvalue problem of Eq. (2.8) in the adiabatic limit. Now we consider radiative transitions caused by the nonadiabatic relative motion of the electron and the nuclei. The transition rate from the \( 1S \) (i.e., electron at perihelion level) to the \( 1S \) (i.e., electron at nearest level) is considered while the energy between different levels are negligible.

A. Transition at \( y = 0 \)

Suppose we consider the transition in the \( 1S \) between levels 1 and 2. Let the initial \( \psi(1S, 2) \) and \( \psi(2S, 1) \) into the probability amplitudes \( a_{1S, 2} \) and \( a_{2S, 1} \) will change significantly. Therefore, we may approximate all \( \psi \) to be in the \( (1S, 2) \) \( \text{and} (2S, 1) \) equations in Eq. (2.7) with their adiabatic components given in the last section. We note that those of \( \phi^a \) or \( \phi^b \) in the above transitions will not change significantly at the point of level crossing.
At this point, the difference between $E_u$ and $E_l$ (hence $a^u$ and $a^l$) is usually small and becomes smaller for lower intensity (see Eqs. (3.17)).

Thus using Eqs. (3.0), (3.8), (3.13), and (3.15) we obtain the Eqs. (2.7) with $(\nu_1, \sigma_1)$ and $(\nu_2, \sigma_2)$, we obtain two coupled linear equations in $b_1$'s,

\[
\begin{align*}
   i \frac{db_1}{dy} - W'_1 b_1 &= G b_2, \\
   i \frac{db_2}{dy} - W'_2 b_2 &= G b_1,
\end{align*}
\]

where $G \equiv G_{12} = G_{21}$, $W'_i \equiv W'_i(\sigma_i)$, $(i = 1, 2)$ are given in Eqs. (3.16).

Equations (4.1) are to be solved with the boundary conditions that well before the PC is traversed ($y$ negative and "sufficiently large" in magnitude), $b_2 = 0$ and $|b_1| \sim 1$. Then the value $|b_2|^2$ for positive and sufficiently large $y$ will give us the probability that photon-electron system has made a transition from the state with $W'_1$ to the state with $W'_2$.

Around the small region of PC, we may approximate $W'_2 - W'_1$ as a linear function of time

\[
W'_2 - W'_1 = -\alpha y
\]

with $y = 0$ chosen at the point of crossing of $W'_2$ and $W'_1$; and we ignore the small $R$-variation of $G$. 
\[ \frac{dG}{dy} \approx 0 \]  \hspace{1cm} (4.2b)

With these approximations, Eqs. (4.1) can be casted into the Weber's equation with well-known solutions. The solution satisfying above boundary conditions is

\[ b_2(y) = p^{\frac{1}{2}} e^{-\frac{\pi}{4} p} D_{-n-1}(\pi iz) e^{-i \int_1^y W_1 dy' + \frac{\alpha y^2}{2}} , \quad \alpha \geq 0 \]  \hspace{1cm} (4.3)

where \( n \equiv \frac{1}{\alpha}, \quad p \equiv |n|, \quad z = \frac{\alpha}{1+y} e^{-\frac{\pi}{4}} \) and \( D \) is the parabolic cylinder function. For large and positive \( |\alpha|^\frac{1}{2} y \), the transition probability is

\[ |b_2|^2 \approx 1 - e^{-2\pi p} , \quad \alpha \geq 0 \]  \hspace{1cm} (4.4)

This formula is useful if Eqs. (4.2) remain approximately satisfied into the asymptotic domain of \( D_{-n-1}(\pi iz) \), i.e., \( |\alpha|^\frac{1}{2} y \) large.

When the two levels \( W'_1, W'_2 \) do not cross each other, but are in close approach as depicted in Figs. 4a, b, and c, the formula derived above does not apply. The transition formula applicable to the case in Fig. 4a described by

\[ W'_2 - W'_1 = a + by^2 \]

has been presented in I. Their formula is valid if \( \exp \left( -\frac{2}{\gamma} (\frac{a}{b})^2 \right) \ll 1 \).

Now we present the formula applicable to cases in Fig. 3b and c where \( W'_2 - W'_1 \) are characterized by two well-defined slopes \( b(y \leq 0) \) and \( b'(y > 0) \). We make the approximation
\[
W' - W_i \begin{cases} 
   a - ty & y \leq 0 \\
   a + ty & y > 0 
\end{cases}
\]

where \( a \geq 0, b > 0 \) correspond to case in Fig. 10, and \( a > 0, b > 0 \) correspond to case in Fig. 9. In the case \( a < 0, \)
\( b > 0 \), corresponds to the situation where a line curve at a constant
turning point.

The only drawback in the above approximation is the introduction
discontinuity of slope of \( W' - W_i \) at \( y \). However, the
advantage is that one is further guaranteed a transition probability
formula for the relatively linear case in earlier papers.

We introduce with \( y_y = \int_0^y \frac{1}{\sqrt{2\pi}} e^{-x^2/2} dx \)

\[
y_y' = -a + b \begin{cases} 
   \frac{1}{\sqrt{2\pi}} e^{-x^2/2} & y \leq 0 \\
   \frac{1}{\sqrt{2\pi}} e^{-x^2/2} & y > 0 
\end{cases}
\]

We introduce

\[
\frac{dy_y}{dy} \left[ x - \frac{1}{\sqrt{2\pi}} \frac{d}{dx} \left( e^{-x^2/2} \right) \right] = 0.
\]

\[
\frac{dy_y}{dy} \left[ x - \frac{1}{\sqrt{2\pi}} \frac{d}{dx} \left( e^{-x^2/2} \right) \right] = 0.
\]
We need to find only the solution \( U(y; |a|, |b|, |b'|) \), for the
relation \( U(y; -|a|, -|b|, -|b'|) = \frac{U(y; |a|, |b|, |b'|)}{a} \) as can be shown
easily from the above equations.

Now with definitions

\[
    y = \left( y - \frac{a}{b} \right) b e^{-b y} = y - \frac{a}{b} e^{-b y}
\]

\[
    y = \left( y + \frac{a}{b} \right) b e^{+b y} = y + \frac{a}{b} e^{+b y}
\]

above equations are related to the Kelvin's equation.

\[
    \frac{\partial^2}{\partial z^2} - \left( z + \frac{\pi}{2} \right) \frac{\partial}{\partial z} + \frac{\pi^2}{4} \frac{1}{z^2} = 0
\]

\[
    \frac{\partial^2}{\partial z^2} - \left( z - \frac{\pi}{2} \right) \frac{\partial}{\partial z} + \frac{\pi^2}{4} \frac{1}{z^2} = 0
\]
A general solution for \( y > \) 2 is

\[
U(z_+) = L D_{-n_+ -1}(-iz_+) + M D_{n_+}(-z_+)
\]

where \( L \) and \( M \) are coefficients to be determined by demanding continuity of \( b_\psi \) and of its slope at \( y = 0 \). We obtain

\[
L = N' \left( \frac{D_2/D_3}{(D_3/D_5) - (K_3/K_5)} \right) \left[ \frac{(D_3/D_5) - (K_3/K_5)}{(D_2/D_3) - (K_2/K_3)} \right]
\]

\[
M = N' \left( \frac{D_1/D_3}{(D_2/D_3) - (K_1/K_3)} \right) \left[ \frac{(D_1/D_3) - (K_1/K_3)}{(D_2/D_3) - (K_2/K_3)} \right]
\]

where

\[
N' = \frac{|G|}{b^2} e^{-\frac{\pi}{4} p},
\]

\[
D_1 = D_{-n_1 -1} \left( \frac{a}{b} e^{\frac{i\pi}{4}} \right),
\]

\[
D_2 = D_{-n_2 -1} \left( \frac{a}{b} e^{\frac{i\pi}{4}} \right),
\]

\[
D_3 = D_{-n_3 -1} \left( \frac{a}{b} e^{-\frac{i\pi}{4}} \right),
\]

\[
D_4 = D_{-n_4 -1} \left( \frac{a}{b} e^{-\frac{i\pi}{4}} \right),
\]

\[
D_5 = D_{n_5} \left( \frac{a}{b} e^{\frac{3\pi}{4}} \right),
\]

\[
D_6 = D_{n_6} \left( \frac{a}{b} e^{-\frac{3\pi}{4}} \right).
\]
\[ D_b = D_{n+1} \left( \frac{a}{b^2} e^{\frac{i\pi}{4}} \right), \]

\[ \alpha_1 = \frac{a}{2b^2} e^{\frac{i\pi}{4}} D_1 + (n_1 + 1) e^{\frac{i\pi}{4}} D_2, \]

\[ K_2 = \frac{a}{2b^2} e^{-\frac{i\pi}{4}} D_2 + (n_1 + 1) e^{\frac{i\pi}{4}} D_4, \]

\[ K_3 = \frac{a}{2b^2} e^{\frac{i\pi}{4}} D_3 + n_1 e^{\frac{i\pi}{4}} D_6. \]

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

\[ b_2(y) \approx \left( L e^{\frac{-3\pi}{4} p'} + M \frac{(2\pi)^i}{\Gamma(1 - ip')} e^{\frac{-\pi}{4} p'} \right) \]

\[ \times \exp \left[ -i \int_0^y W' dy' + i \frac{a}{2} y - i \frac{a^2}{4b} - i \frac{p'}{2} \ln \left( b'y^2 + \frac{a^2}{b} \right) \right] \]

from which the transition probability is

\[ |b_2|^2 = \left| L e^{\frac{-3\pi}{4} p'} + M \frac{(2\pi)^i}{\Gamma(1 - ip')} e^{\frac{-\pi}{4} p'} \right|^2. \]

In the derivation of the above asymptotic formula, nothing is required of the magnitude of \(\frac{a}{b^{\frac{1}{2}}}\) and \(\frac{a}{b^{\frac{1}{2}}}\). Usually in applications, we will be interested in \(\frac{a}{b^{\frac{1}{2}}}\) and \(\frac{a}{b^{\frac{1}{2}}}\) being not large. But from a
mathematical viewpoint, let us consider the extreme case \( \frac{a}{b^2} \gg 1 \) and \( \frac{a}{b^2} \gg 1 \), then \( L \) and \( M \) can be simplified by asymptotic expansion of the \( D_i \)'s. The results are

\[
L = N \left( \frac{1 + \left( \frac{b}{b'} \right)^2}{\Gamma(i\pi) e^{\frac{i\pi}{b'}}} \right)^{\frac{1}{4}} \frac{(p+p')^\pi}{(2\pi)^{\frac{1}{2}} (3 + e^{\pi p}/\sinh \pi p')}
\]

\[
\times \exp \left[ -i \frac{a^2}{4} \left( \frac{1}{b} + \frac{1}{b'} \right) - \frac{p \ln \frac{a}{b} - i p' \ln \frac{a}{b'}}{b^2} \right]
\]

and

\[
M = N \left( \frac{1 + \left( \frac{b}{b'} \right)^2}{\Gamma(i\pi) e^{\frac{i\pi}{b'}}} \right)^{\frac{1}{4}} \frac{p^\pi e^{\frac{3\pi p}{4}}}{2(1 + 3e^{\pi p}/\sinh \pi p')}
\]

\[
\times \exp \left[ i \left( \frac{\pi}{2} + \frac{a^2}{4b} + \frac{a^2}{2b'} + p \ln \frac{a}{b^2} + p' \ln \frac{a}{b'} \right) \right]
\]

If furthermore \( p' \) is large, then

\[
|b_2|^2 = \left( \frac{1}{b} \left( 1 + \left( \frac{b}{b'} \right)^2 \right) \right)^2 e^{-2\pi p'}
\]

while for \( p' \ll 1 \)

\[
|b_2|^2 = \frac{\pi |c|^2 \left( 1 + \left( \frac{b}{b'} \right)^2 \right)^2}{2 \pi b'}
\]

We note that in the case \( \frac{a}{b^2} \) and \( \frac{a}{b^2} \gg 1 \), the transition probability above does not diminish with larger \( a \). This is probably related to the sole drawback of our approximation mentioned above.
Therefore for large $a$, we should not apply eq. (4.5) but revert to the formula given in I.

**B. Transitions at a 3-Level PC**

When multilevel systems are considered, we may encounter a 3-level PC way between $v^4_j$, $v^2_j$, and $v^0_j$, as depicted in Fig. 2. Then the coupled equations similar to Eqs. (4.1), are

\[
\begin{align*}
\frac{d}{dy} b_1 &= W_1 b_1 + G_{12} b_2 + G_{13} b_3 \\
\frac{d}{dy} b_2 &= W_2 b_2 + G_{21} b_1 + G_{23} b_3 \\
\frac{d}{dy} b_3 &= W_3 b_3 + G_{31} b_1 + G_{32} b_2
\end{align*}
\]

where $b_1 = b_1 v^4_j$, $W_j = W_j v^4_j$, and the $G_{ij}$s are all written in Eqs. (2.10). The boundary conditions for $y \rightarrow -\infty$ positive and of sufficient magnitude are $b_j \rightarrow -i e^{i \int_0^y W_j v^4_j dy} b_j \rightarrow b_j \rightarrow 0$. A formal solution is

\[
\begin{align*}
b_1 &= -\frac{1}{i \pi_1(y)} - i e^{-i \pi_1(y)} \int_0^y (G_{12} b_2 + G_{13} b_3) e^{i \pi_1(y) dy} \\
b_2 &= -i e^{i \pi_2(y)} \int_0^y (G_{21} b_1 + G_{23} b_3) e^{i \pi_2(y) dy} \\
b_3 &= \frac{1}{i \pi_3(y)} \int_0^y (G_{31} b_1 + G_{32} b_2) e^{i \pi_3(y) dy}
\end{align*}
\]

Easily (7) continued next page.
Equation (4.7) continued

\[ b_3 = -i e^{-i K_2(y)} \int_0^y dy' (G_{31} b_1 + G_{32} b_2) e^{i K_2(y')} \]  

where \( K_1(y) = \int_0^y W_1(y') dy' \). Confining ourselves to cases where the \( G \)'s are small, we obtain the solutions by an iteration procedure starting with the solutions for the 2-level PC transition.

The solutions to Eqs. (4.1) for levels 1 and 2 can be written formally as

\[ b_2^1 = -i e^{-i K_2(y)} \int_{-\infty}^y e^{i K_2(y')} G_{21} b_1^1(2) \]

\[ b_1^1(2) = e^{-i K_1(y)} - i e^{-i K_1(y)} \int_{-\infty}^y e^{i K_1(y')} G_{12} b_2^1 \]

and the corresponding solutions for level 1 and 3 are

\[ b_3^1 = -i e^{-i K_3(y)} \int_{-\infty}^y e^{i K_3(y')} G_{31} b_1^1(3) \]

\[ b_1^1(3) = e^{-i K_1(y)} - i e^{-i K_1(y)} \int_{-\infty}^y e^{i K_1(y')} G_{13} b_3^1 \]

Substitution of these expressions into the right-hand side of Eqs. (4.7) gives
Further iteration would only add terms of second or higher order in \( G \)'s. The second terms on the right of the first two equations represent the contribution to the respective level due to presence of the third level.

With the explicit expressions of \( b_2^1 \) (and \( b_3^1 \)) given in Eq. (4.3), we can find \( b_2(y) \) and \( b_3(y) \) in the region \(|\alpha_{31}|^4 y\) and \(|\alpha_{31}|^4 y \gg 1\) by evaluating the integrals with the method of steepest descent.

As before we assume the \( y \)-dependence of \( G \)'s is negligible in the region of transition. For the case \( \alpha_{21} < 0, \alpha_{21} < 0 \), we obtain with \( G_{ij} = G_{ji} \),

\[
|b_2|^2 = 2\pi p_{21} + \pi \frac{|G_{22}|^2}{|\alpha_{31}|^4} \times y \quad \text{to lowest order in } (|\alpha_{31}|^4 y)^{-1}
\]
\[ |b_3|^2 = 2\pi p_{31} + \frac{|G_{23}|^2}{|\alpha_{21}|} \Gamma_2, \text{ to lowest order in } \left( |\alpha_{31}|^{\frac{1}{2}} y \right)^{-1}. \]

where

\[
\Gamma_2 = 2^{3/2} \pi \frac{|G_{12}| |G_{23}|}{q_{21} q_{31}} \cos \left[ \frac{\pi}{2} - p_{21} \ln q_{21} \frac{1}{y} + \frac{1}{2} p_{31} \ln q_{31} \frac{q_{21}}{q_{31}} + \frac{p_{31}}{2} \right]
\]

\[
- 0.577 p_{21} - \frac{1}{2} p_{31} \ln p_{31}
\]

\[
\Gamma_3 = 2^{3/2} \pi \frac{|G_{13}| |G_{23}|}{q_{31} q_{21}} \cos \left[ \frac{\pi}{2} - p_{31} \ln q_{31} \frac{1}{y} + \frac{1}{2} p_{21} \ln q_{21} \frac{p_{21}}{q_{21}} + \frac{p_{31}}{2} \right]
\]

\[
- 0.577 p_{31} - \frac{1}{2} p_{21} \ln p_{21}
\]

where \( n_{ij}, p_{ij}, n_{ij} \) are defined as

\[
W_i - W_j = -\alpha_{ij} y,
\]

\[
n_{ij} = \frac{\alpha_{ij}^2}{\alpha_{ij}},
\]

\[
q_{ij} = |\alpha_{ij}|,
\]

and

\[
p_{ij} = |n_{ij}|
\]

For sufficiently small \( G \)'s (hence \( p \)'s) and large but finite \(|\alpha|^{\frac{1}{2}} y, \frac{\pi}{2}\) is much greater than the rest of the terms in the cosine arguments in \( \Gamma_2 \) and \( \Gamma_3 \). Therefore
\[ |b_2|^2 = \sigma r_{21}^* + \left(\pi r_{21}^* / \lambda_{21}^* \right), \]
\[ |b_1|^2 = \sigma r_{12}^* + \left(\pi r_{12}^* / \lambda_{12}^* \right). \]

These last two expressions are expected to be true also for other cases: \( (\alpha_2 > 0, \alpha_2 > \delta) \), and \( (\alpha_2 > 0, \alpha_2 < \delta) \).

V. CLOW ATOMIC COLLISION IN AN INTENSE FIELD

The orbit of the relative motion of the two colliding atoms enters into our calculations through the \( Q_j(a,\delta) \) and \( d\delta / dt \) in the \( \alpha_i \)'s in the transition formula Eq. (4.1'). For the present application, it is convenient to express \( a_{ij} \) as

\[ a_{ij} = \alpha_j \frac{d}{d\phi} \left( \frac{\lambda_j - \lambda_i}{\phi} \right) \frac{d\phi}{dt}. \]

Since \( \lambda_j = \alpha_j \), and \( \lambda_i = \alpha_i \), therefore \( q_{ij} \) is independent of the arbitrary \( \phi \), as it should.

Recall that \( \sigma(a,\delta) \) \( = (1, \sum \delta_i \phi_i) \) are usually evaluated with respect to the coordinates of the quasi-molecule \( (\phi_1, \phi_2) \) in Fig. 4) while the linear polarization \( \mathbf{\hat{g}} \) is fixed in direction.

Therefore for the geometry in Fig. 4, we need only to know \( \mathbf{\hat{g}} \) and \( \mathbf{\hat{k}} \cdot \mathbf{\hat{g}} \) in order to find \( C_j(a,\delta) \).

For a given orbit, let \( R_0 \) denote the distance of closest approach between the two atoms. Let \( \phi^{-}(R) \) and \( \phi^{+}(R) \) denote respectively the value of \( \phi \) at \( R \) before and after passing \( (R_0, \phi^{+}(R)) \). Then
\[ \theta^+(R) = 2\theta(R_0) - \theta^-(R). \]

The angles \( \theta^-(R) \) are found by the formula

\[
\theta^-(R) = -1 + \int_{R_1}^{R} \frac{b}{r^2} \left(1 - \frac{u(r)}{\epsilon} - \frac{b^2}{r^2}\right)^{\frac{1}{2}} \, dr
\]

where \( b \) is the impact parameter, \( \epsilon \) is the total energy and \( u(r) \) the adiabatic potential energy of the molecule in the given (say ground) electronic state. And \( R_0 \) is given by

\[
1 - \left(\frac{u(R_0)}{\epsilon}\right) - \left(\frac{b^2}{R_0^2}\right) = 0.
\]

In evaluating the radial velocity \( \frac{dR}{dt} \) at the point of closest approach, which is needed in the transition probability formula, the shifted potential energy is used. For the ground electronic state, this is given by

\[
\frac{dR}{dt} = v_\infty \left[1 - \frac{u'(R)}{\epsilon} - \frac{(b/R)^2}{2}\right]^{\frac{1}{2}}
\]

where \( u'(R) = u_1(R) - u_1(\infty) + v_{NW} v_1(1)/a_0 + v_{NW} \) is the shifted potential energy.

**Evaluation of cross section:** for a given orbit defined by \( b \) and \( \epsilon \), there is, after the collision, probability \( P_{b,\epsilon}(1) \) that the quasi-molecule is in the state \( i \). The cross section for transition to state \( i \) is then given by

\[
\sigma_i(\epsilon) = 2\pi \int_0^{b_{\text{max.}}} \, db \, b \, P_{b,\epsilon}(1)
\]
where $b_{\text{max}}$ is the maximum $b$ value for which $P_{b,e}(i) \neq 0$ for a given $e$.

We obtain $P_{b,e}(i)$ as follows. Suppose we have included $n$ electronic states in our calculations. Suppose for a given orbit, there are $N$ PC's at $Y_1, Y_2, Y_3, \ldots, Y_N$. Before collision the quasi-molecule is in the state 1, therefore the probability in electronic state 1, $Q_0(1)$, is 1, and those in any other states are zero i.e., $Q_0(i) = 0$ for $i \neq 1$. At $Y_{\nu}$, let $\tau_\nu(i,j)$ (where $i \neq j$) be the transition probability from electronic state $j$ to $i$ and is given by e.g., Eq. (4.4); and $T_{\nu}(i,i) = 1 - \sum_{k \neq 1} T_{\nu}(k,i)$ be the probability of remaining in state $i$. We let $T_{\nu}(i,j) = T_{\nu}(j,i)$ for $i \neq j$. Let $Q_{\nu}(i) = \sum_j |b_{\nu}(i)|^2$ be the probability that the quasi-molecule will be in the state $i$ after passing the $Y_{\nu}$-PC. Then

$$S_{\nu} = \sum_{i=1}^n Q_{\nu}(i)$$

and $P_{b,e} = Q_N$ for the given orbit $(b,e)$.

As example, we have considered the slow collision of Li with H in an intense radiation with $\lambda = 1.826 \mu$ in the geometry of Fig. 4 for relative speed $v_\infty = 5 \times 10^5$ cm/sec. Values of $u_\alpha(R)$ and $(\Phi_\alpha, \sum_i \alpha \Phi_i)$ for the lowest lying singlet states $X^1\Sigma^+$, $A^1\Pi$, and $B^1\Pi$ are based on the values calculated by Docken and Hinze. These three levels represent a fairly good approximation because according to the less accurate calculation of Bender and Davidson, the higher levels all lie at least about one-photon ($h\omega \approx 1.5$ eV) energy above the $B^1\Pi$ level, thus neglecting them would mean neglecting higher order processes. We assume the incoming atoms are initially in the electronic singlet ground state $X^1\Sigma^+$. There are 1-, 2-photon resonant
transition to \( A^1 \Sigma^+ \) near internuclear separations 9.4 \( a_0 \) and 5.9 \( a_0 \) and 3.7 \( a_0 \) respectively; while 2-, 3-photon resonant transitions to \( B^1 \Pi \) occur at 5.1 \( a_0 \) and 3.1 \( a_0 \) respectively. The resulting cross sections for transition to these two states are presented in Fig. 5. We observe that for weak enough coupling (low intensity), the collisional cross section is proportional to \( I \) and \( I^2 \) for transition to \( A^1 \Sigma^+ \) and \( B^1 \Pi \) respectively, as expected from perturbation theory. But for strong coupling, the deviation from perturbation theory is considerable.

VI. MULTIPHOTON DISSOCIATION OF MOLECULES

The formalism can also be applied to obtain multiphoton dissociation cross section of a diatomic molecule. The previous collisional motion is replaced by the relative oscillation of the two atomic nuclei. In line with our classical approximation to the nuclear motion, we shall replace the quantum oscillator with the classical oscillator. A quantum mechanical treatment with the Franck-Condon assumption would attach a multiplicative factor to the dipole matrix elements that we use in our formalism; i.e.,

\[
\left( \int x_n^\alpha x_m^\beta dR \right) \left( \psi_\alpha^*(\vec{R}), \sum_i r_i \psi_\beta(\vec{R}) \right)
\]

The \( \psi_\alpha, \beta \) include nuclear rotational as well as electronic wavefunctions. Our treatment is good when \( \int x_n^\alpha x_m^\beta dR \approx 1 \).

A rough estimate of the integral \( \int x_n^\alpha x_m^\beta dR \) can be obtained as follows. Since Coolidge, James, and Present \(^{14}\) have shown that it is an extremely good approximation in evaluating \( \int x_n^\alpha x_m^\beta dR \) to
replace the repulsive eigenfunction $\chi$ with $\text{const.}\delta(R - R_c)$ where $R_c$ is the classical turning point. Therefore assuming $\text{const.} = 1$, $\chi_m(R_c)$ will give us a fair indication of how good this approximation is. If the lower state is the "vibrationless" ($n = 0$) state with equilibrium separation $R_o$,

$$\left(\frac{\omega_o}{\pi a}\right)^1 \exp\left[\frac{-\omega_o}{2a}(R_c - R_o)^2\right].$$

For our example below, this quantity is 1.3.

Consider the internuclear axis $\hat{k}$ oriented at an angle $\phi$ relative to the linear polarization vector. (Fig. 4.) We assume that the rotational motion is negligible in the sense that during one oscillation of the nuclei, $\Delta \phi$ is negligible. We have only two PC's per oscillation to consider; and if transitions to other levels are negligible, the final transition probability to the upper repulsive state per oscillation would be

$$' \equiv 2T(1 - T)$$

where $T$ is given, if valid, e.g., Eq. (4.4). If $2\pi \omega_p$ is small, then $' = 2(2\pi)$. When the diatomic molecule irradiated has a permanent dipole moment $\mathbf{d}^{\alpha}$ (which is always either parallel or antiparallel to the internuclear axis) in the bound state $\phi^{\alpha}$, it will experience a torque to orient the $\mathbf{d}$ parallel to $\mathbf{e}$. Therefore in the thermodynamical equilibrium situation, the thermal-averaged transition probability per oscillation would be
\[ \bar{r} = \frac{\int_{-1}^{1} d(\cos \phi) f(\phi) e^{-V(\phi)/kT}}{\int_{-1}^{1} d(\cos \phi) e^{-V(\phi)/kT}} \]

where \( V(\phi) = -\text{sgn}\left| d \right| \cos \phi \varepsilon_o \), \( \text{sgn} \) being \( + (-) \) if \( d \) is parallel (antiparallel) to the given internuclear \( \hat{\mathbf{k}} \) axis, and \( \varepsilon_o = \left( \frac{2\pi}{c} \right)^\frac{1}{2} \) corresponding to the average classical E-field amplitude seen by the molecules.

For diatomic molecules of like atoms (zero permanent dipole moment in any state), or when the gas of diatomic molecules is initially irradiated, we may have random orientation of molecules with respect to \( \hat{\mathbf{e}} \). In such case,

\[ \bar{r} = \frac{1}{2} \int_{-1}^{1} d(\cos \phi) f(\phi) \]

The averaged cross section for either process is then

\[ \bar{\sigma} = \frac{\nu_0 \pi \omega}{I} \bar{r} \]

where \( \nu_0 \) is the vibrational frequency of the molecule in the bound state.

We have evaluated the averaged cross section for \( L_\text{II} \) from the ground vibrational state in \( X^1\Sigma^+ \) electronic state, photodissociating via 4-photon (\( \lambda = 1.0648 \mu \)) transition to \( B^1\Pi \) state. Since now we require greater accuracy of the potential curve of \( X^1\Sigma^+ \) around the equilibrium separation and yet such values of Docken and Hinze's
calculations differ from experiment by about 37 cm⁻¹, we therefore use instead the best available empirical-fitted analytic expression for this ground electronic state taken from Crawford and Jorgensen. Since the potential curve of Docken and Hinze for excited state $A^1Σ^+$ seems to agree well in this domain of $R$ with the RKR curve, we adopted Docken and Hinze's results for this state as well as those for $B^1Π$ and the dipole moments.

We have evaluated the various quantities for a range of intensities. Since $f(\phi)$ may be needed directly for some other physical situation (e.g., a dc $E_o$ field is used to orient the molecule at an angle to $\phi$ to the electromagnetic field $E$ to optimize transition), we presented them for a few typical intensities in Table I. The cross sections for both thermal equilibrium ($T = 300°$ K) and random orientations are calculated. For the same intensity, the former is smaller than the latter, as expected; but they differ by less than 1 in 1000 parts even for highest intensity calculated and therefore only the former is graphed in Fig. 6. For low intensity, we see that the cross section is proportional to $I^{3}$, in agreement with perturbation theory.

VII. SINGLE ATOM/MOLECULE IRRADIATED BY LASER PULSES

For an atom being irradiated by a practically monochromatic pulse, the theory is similar as before except now $\mu_R^2$ is the Hamiltonian for the atomic electrons and is not a function of $R$. Since $\mu_R^2$ are not parametrically dependent on $R(t)$ and have definite positions, therefore the last term and the term
\((\phi, \hbar, \phi')\) in Eqs. (2.5) vanishes automatically. For the change of variable \(y = \frac{vL}{h_o}\), we may choose \(v = 1\). Again, the actual level shifts and transition probabilities are independent of this choice.

With these slight modifications, the formalism can be applied to the calculation of the transition between levels of an atom irradiated by an intense laser pulse. The photon-electronic levels are shifted due to interaction with other levels. The amount of shift is a function of intensity of the pulse, which is in turn a function of time. For a particular atomic system with proper definition of the laser 1, one may set for example \(v = 1\). Then the nonadiabatic transition is due to the temporal variation in intensity of pulse, instead of the relative non-adiabatic motion of the colliding atoms in Sec. V.

Now \(\alpha\) may be written as

\[
\alpha = - \frac{\frac{1}{2} \left( W_{ij}(\gamma_1) - W_{ij}(\gamma_2) \right)}{H} \left( \frac{H}{H + \frac{1}{2}} \right) \cdot
\]

\[
- \frac{1}{2} \left( W_{ij}(\gamma_1) - W_{ij}(\gamma_2) \right) \cdot \left( \frac{H}{H + \frac{1}{2}} \right)
\]

Since \(W_{ij}(\gamma_1) - W_{ij}(\gamma_2) = \frac{1}{2}\), and \(H = \frac{1}{2}\), we find that in the transition probability formulae are independent of the arbitrary \(v\). The quantity \(\frac{1}{2}\) is the temporal slope of the pulse at the "critical intensity" \(I_c\) at which the adiabatic approach of the adiabatic eigenlevels occur. Thus \(\alpha\) is the quantity, the transition probability equation the mixing time.
The final transition probability for phase $\phi_k$ is given by

$$f = \frac{1}{r} (1 - r)$$

which has a maximum value $\frac{1}{r}$ at $\frac{1}{2}$. From Eq. (7.11) and Eq. (7.12), it can be shown that the overall phase of phase for in-phase transition is

$$\left( \begin{array}{c} A \\ B \end{array} \right) \cdot \left( \begin{array}{c} \frac{1}{r} \\ \frac{1}{2} \end{array} \right)$$

where

$$\int \frac{(a \cdot r - 3 \cdot b \cdot c)}{3 \cdot a}$$

where all variables are real. The final equation is

$$\int \frac{(a \cdot r - 3 \cdot b \cdot c)}{3 \cdot a}$$
\[ \tau' = 7.516 \times 10^{-23} \left( \frac{- \ln \frac{2}{\beta}}{\beta^2} \right) \tau \ln \frac{\lambda}{\lambda_0} - \ln \frac{\lambda}{\lambda_0} \] 

The validity condition for applying the transition formulae imposes restrictions on the pulse parameters \((\lambda, \tau')\). For gaussian pulses, this validity condition can be expressed as

\[ 2.41 \times 10^5 \, 4 \, I' \, \tau \left( - \ln \frac{\lambda}{\lambda_0} \right)^{3/2} \gg 1 \quad (7.a) \]

where \( \beta \) are in atomic units, \( I' \) and \( I_0 \) in wats/cm\(^2\) and \( \tau \) in sec.

As examples, we have considered two atomic transitions: the transition from ground state \(3s\) to \(3s\) state of sodium atom via 2-photon absorption and the transition from the ground \(3s\) state to the \(3s\) state via 3-photon absorption. Since \( I' \) and parity are no quantum numbers with respect to \( \hat{H} \), only states of the same \( m \) are coupled together. Therefore we need only to consider \( m_{3s} \). The \( m_{3s} \) states.

In each case, we have included only 74 states \((m_{3s} = \pm \frac{3}{2})\). These states are (i) the states between which transitions are calculated; (ii) the states whose oscillation strengths with the states in (i) are among the first three to four leading order of magnitudes; (iii) states whose energy levels are between those of states in (i) and (ii); and finally (iv) states whose inclusion assures the non-singularity of matrix \([G_2(\alpha, \beta)]\) which is a formal requirement in our solution to the adiabatic eigenvalue problem.

The energy levels are based on experimental spectral data.\(^{12}\)

The magnitude of the dipole matrix elements are calculated from the oscillator strengths calculated by Anderson and Hillier\(^{18}\) and their
signs from Bates and Wemple. However, we notice that with a different choice of phase of the wavefunctions, namely,

\[ \psi_a \psi_b \]

where \( \psi_a \) and \( \psi_b \) are the wavefunctions used by Bates and Wemple, then the dipole matrix elements \( \langle \psi_a | \sum | \psi_b \rangle \) have regularity (in relation to \( n_g \) in \( n_g \alpha \)) in their sign pattern (Table III). This is useful in deciding a few unknown or unimportant elements that may be needed for inclusion in a calculation.

In the lithium case, the relative shifts in the \( n_g \) and \( n_e \) level can be explained qualitatively as follows: we choose wavelengths such that level separation between the \( n_e \) and \( n_g \) states are slightly less than \( -\alpha \hbar n_g \) in energy per atom (see Fig. 7). For the same wavelength, the \( n_g \) level "pushes" the \( n_e \) level down much stronger than they "pull" the \( n_e \) level up. Because \( n_g - n_e \) is relatively in resonance with \( n_e (\Delta n_g = \pm 1) \). As the intensity is increased, the gap between level \( n_e \) and \( n_g \) becomes wider until a \( \hbar \) occurs at \( n_e \).

In the lithium case, we choose wavelengths such that the level separation of \( n_e \) and \( n_g \) states are "slightly larger" than the dipole energy. At these wavelengths, the \( n_e \) states "pull" the \( n_g \) level down via first-order coupling while they "push" the \( n_e \) level down via ninth-order coupling. Hence the \( n_g \) and \( n_e \) levels are shifted closer towards each other. At higher intensity they hit the dipole resonance.
wavelength, the "critical intensity" $I^*$ and the corresponding $\tau^*$ in Eq. (7.2) are tabulated in Table III. (See also Figs. 1 and 2.) The pairs of parameters $(I^*_0, \tau^*)$ in Eq. (7.3) of gaussian pulses are presented in Table IV for transition in sodium $(\lambda = 589.0 \text{ nm})$.

We have also calculated the final transition probability for a few nonoptimum gaussian pulses. Results for the case $I_0 = 6.0 \times 10^8 \text{ W/cm}^2$, $\tau' \leq 1 \text{ micro}$ are presented in Table II. It is noticed from the tables IV and V that in the case of sodium, we almost have the optimum gaussian pulse with the transition is almost $\frac{1}{2}$. And for fixed $I^*_0$, $\tau$ somewhat deviates from $\tau'$ (Fig. 1), as in the case for deviating $\tau'$ for fixed $\tau^*$ (Fig. 11). The figures are not shown for the $\tau'$ as indicated in the figures.

ACKNOWLEDGMENT

The author is grateful to Professor P. M. W. Milne for discussing the problem, his advice and support. We wish to thank Professor H. P. Schaefer for helpful guidance and providing the dipole matrix elements and for bringing the work to our notice. We also wish to thank Dr. R. K. Mont, Dr. R. Carman, and Dr. A. Schmitt for discussions on this paper.
9. We have made explicit checks on this approximation for the numerical examples in this paper. The difference in the final results due to the use of \((E, a^2)\) or \((E^2, a^2)\) usually runs from 0.01% for intensity \(10^6\) W/cm\(^2\) to less than 5% for \(10^{12}\) W/cm\(^2\). An exception is the photodissociation of LiH in Sec. VI, where the difference in the cross section is a few to 30% in the range of intensities \(10^{11.8} \times 10^{12}\) W/cm\(^2\). For such cases, we take the mean of the two values.


16. F. H. Crawford and T. Jorgensen, Jr., Phys. Rev. 49, 742 (1936). This semi-empirical expression is based on Dunham's method and is near the nuclear equilibrium separation, much better than the corresponding semi-empirical Morse and Hulbert-Hirschfelder potential curves.

17. The idea of transition due to power variation is suggested in reference 2, where only rough estimate is made.


Table I. Photodissociation probability \( f(\phi) \) per oscillation of LiH molecule in ground state by absorption of four \( (\lambda = 1.064\mu) \) photons. \( \phi \) is angular orientation of nuclear axis relative to the linear polarization vector of the radiation field.

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Table II(a). Dipole matrix elements \( \langle n'l's'j|m_j \sum r_m \hat{r}_m |n's'j'm_j \rangle \) \((m_j = m_j = \frac{1}{2})\) of 24 states of sodium atom.

<table>
<thead>
<tr>
<th>(n'l's'j')</th>
<th>(3p_{\frac{3}{2}}^1)</th>
<th>(3p_{\frac{3}{2}}^3)</th>
<th>(4p_{\frac{1}{2}}^1)</th>
<th>(4p_{\frac{3}{2}}^2)</th>
<th>(5p_{\frac{1}{2}}^3)</th>
<th>(5p_{\frac{3}{2}}^3)</th>
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<tbody>
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<td>3s_{\frac{1}{2}}</td>
<td>-1.455E + 0</td>
<td>-2.057E + 0</td>
<td>-1.310E - 1</td>
<td>-1.852E - 1</td>
<td>-4.803E - 2</td>
<td>-6.792E - 2</td>
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<tr>
<td>4s_{\frac{1}{2}}</td>
<td>1.428E + 0</td>
<td>2.019E + 0</td>
<td>-3.301E + 0</td>
<td>-4.669E + 0</td>
<td>-3.891E - 1</td>
<td>-5.502E - 1</td>
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<tr>
<td>5s_{\frac{1}{2}}</td>
<td>3.043E - 1</td>
<td>4.304E - 1</td>
<td>3.420E + 0</td>
<td>4.839E + 0</td>
<td>-6.111E + 0</td>
<td>-8.642E + 0</td>
</tr>
<tr>
<td>6s_{\frac{1}{2}}</td>
<td>1.571E - 1</td>
<td>2.222E - 1</td>
<td>6.459E - 1</td>
<td>9.135E - 1</td>
<td>6.114E + 0</td>
<td>8.647E + 0</td>
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<tr>
<td>7s_{\frac{1}{2}}</td>
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<td>1.443E - 1</td>
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<td>4.549E - 1</td>
<td>1.084E + 0</td>
<td>1.533E + 0</td>
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<td>2.071E - 1</td>
<td>2.929E - 1</td>
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<td>7.439E - 1</td>
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<td>-5.331E - 3</td>
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Table III. Values of critical intensity ($I'$) and pulse-independent factor ($\delta$) in Eq. (7.2) for wavelengths ($\lambda$) considered in
(a) 2-photon transition in sodium ($3s \rightarrow 5s$); and (b) 8-photon transition in lithium ($2s \rightarrow 3s$).

<table>
<thead>
<tr>
<th>(a) Na</th>
<th>(b) Li</th>
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</thead>
<tbody>
<tr>
<td>$\lambda (\mu)$</td>
<td>$I'(W/cm^2)$</td>
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<tr>
<td>6.02396E-01</td>
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<td>6.02395E-01</td>
<td>1.74E+07</td>
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<td>6.02394E-01</td>
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<td>6.02389E-01</td>
<td>6.50E+07</td>
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<td>6.02388E-01</td>
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<td>6.02387E-01</td>
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<td>6.02330E-01</td>
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</table>
Table IV. Pair of optimum parameters \( \left( I'_0, \tau' \right) \) of Gaussian pulses for the 2-photon transition \((3s \rightarrow 5s)\) in sodium at \( \lambda = 5.60239 \mu \text{m} \).

The third column indicates how well the corresponding validity condition Eq. (7.4) is satisfied.

<table>
<thead>
<tr>
<th>( I'_0 ) (W/cm(^2))</th>
<th>( \tau' ) (sec)</th>
<th>Validity</th>
<th>( I'_0 ) (W/cm(^2))</th>
<th>( \tau' ) (sec)</th>
<th>Validity</th>
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<tr>
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<td>4.0E + 07</td>
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<td>9.610E - 10</td>
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Table V. Transition probability per pulse ($f$) in sodium ($\lambda = \lambda_0$ via 2-photon absorption) at various wavelengths ($\lambda$) for the input gaussian pulse ($I_o = 6 \times 10^8$ W/cm²; $\tau = 1$ nsec.) which is nearly optimum for $\lambda = 0.602396$ Å. $I'$ is the critical intensity; $T$ is transition probability at the PC; and the last column is the validity condition Eq. (7.4).

<table>
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<tr>
<th>$\lambda (\mu)$</th>
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<th>$T$</th>
<th>$f$</th>
<th>Validity</th>
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</table>
Fig. 1. A two-level pseudocrossing between levels 1 \((\nu_1, \sigma_1)\) and 2 \((\nu_2, \sigma_2)\). --- Noninteracting eigenlevels \(W_1\), --- adiabatic eigenlevels. 

Fig. 2. A three-level pseudocrossing. Labels are defined similar to those in Fig. 1.

Fig. 3. Three cases of two-level close approach.

Fig. 4. Geometry for collision of two atoms in an intense radiation field. \(\mathbf{\hat{e}}\) is the linear polarization vector and \(\mathbf{\hat{x}}\) is the internuclear axis.

Fig. 5. Cross section of \(\text{Li} + \text{H}\) collision as function of intensity of the radiation field \((\nu = \nu_0, v_f, v_i)\): 

\[ y(P + w) \approx 5 \times 10^3 \text{ cm}^{-1}. \]

Fig. 6. Photodissociation cross section of \(\text{LiH}\) molecules at thermal equilibrium \((T = 298\, \text{K})\) as a function of field intensity.

The dissociative transition is from the ground state of the molecule to \(2^1\Sigma^+\) by absorption of four photons \((\nu = 1, 2, 3, 4)\).

Fig. 7. Illustration of the transition dipole shift as a function of the probe intensity, resulting in a pseudocrossing (PC) between the shifted levels \(W_1\) and \(W_2\) of the critical intensity \(P_c\). For the \(-\rightarrow\) 1-photon transition of sodium, \(W_1 = W_2(1\, \text{eV})\), \(W_2 = W_2(1\, \text{eV})\) in the notation of the text.

Fig. 8. Critical intensity at which \(\text{Li}\) appears to be excited for 1-photon transition from \(3^1\Sigma^-\) to \(3^2\Sigma^-\) state of sodium.

Fig. 9. Critical intensity at which \(\text{Li}\) appears to be excited for 8-photon transition from \(3^1\Sigma^-\) to \(3^2\Sigma^-\) states of lithium.
Fig. 10. Transition probability per pulse, \( f \), in the sodium case at several wavelengths for a few input Gaussian pulses of same peak intensity \( (6 \times 10^3 \text{ W/cm}^2) \) but different temporal pulse widths.

Fig. 11. Transition probability per pulse, \( f \), in the sodium case at several wavelengths for a few input 1 nsec. Gaussian pulses of different peak intensities.
Fig. 1

Energy levels vs. Time (y)

- $E_1$, $W_1, b_1$
- $E_2$, $W_2, b_2$
- $E_U$
- $E_U$ (Upper energy level)
- $E_1$ (Lower energy level)
$j$ into plane of paper

Fig. 4
Fig. 5
Fig. 8
Fig. 9

Intensity (watt/cm²)

2 x 10⁻⁹
1 x 10⁻⁹
2
3
4
5
6
7
8
9

Wavelength (μ) →

2.940 2.941 2.942 2.943 2.944 2.945

XBL751-2190
Transition probability per pulse

Wavelength (\(\mu\))

\[ \tau = 1 \text{nsec} \]

\[ 2.0 \]

\[ 3.0 \]

\[ 5.0 \]

\[ 8.0 \]

\[ 0.602394 \]

\[ 0.602390 \]

\[ 0.602388 \]

\[ 0.602384 \]

Fig. 12
Part B.

INTERACTION WITH MULTIMODE FIELD

(April 21, 1975)

Notations

Many notations are used in a way to suggest the same meanings as in Part A and therefore will not be explained. By "Eq. (A.3.2)" we mean Eq. (3.2) in Part A. By "Eq. (3.2)" we mean Eq. (3.2) in this part of the dissertation.
I. INTRODUCTION

A mode of radiation field is characterized by \( \omega, \mathbf{v}, \mathbf{p} \), respectively the angular frequency, unit propagation vector and the polarization vector. In the electric dipole approximation, mode differing by \( \mathbf{v} \) only is essentially a one-mode problem (i.e., treatment presented earlier is sufficient). However, for modes differing in \( \mathbf{p} \) in higher multipole approximations and \( \mathbf{v} \) not differing in \( \mathbf{p} \), the treatment given below is required. More often than not, the radiation field of physics

is made consisting of two parts: \( \mathbf{B} \) and \( \mathbf{E} \). The treatment of electromagnetic and classically linear, nonlinear, and quantum examples of a nonlinear system may require a combination of \( \mathbf{B} \) and \( \mathbf{E} \) treatments. However, appropriate evaluation of \( \mathbf{B} \) may enhance a solution possible in both. The treatment given herein is concerned more with \( \mathbf{E} \) and \( \mathbf{B} \) as approximations to achieve near-resonance with an intermediate level. Another illustration is provided of two treatment concepts of \( \mathbf{B} \) and \( \mathbf{E} \) made in \( \text{Ref. 1} \) working for special boundary conditions, \( \text{Ref. 1} \). This paper is treated in Sec. IIIA based on the formulation presented in Sec. I. Whereas Sec. I of this work is applicable to an \( n \)-dimensional classical nonlinear system from which this paper can be applied to work with an \( n \).

III. THE TM- AND TM-MULTIPLE FORM

The treatment corresponding to Sec. I in Eq. (13) is for the case of a \( n \)-dimensional interacting with a twism by radiation in Sec. II.
\[ H_1 = h_R + h_1 + h_1^\dagger \]  \hspace{1cm} (2.1)

Here \( h_1 \) denotes the free-field Hamiltonian of the \( i \)th (1 \( \rightarrow \) \( j \)) mode, whereas \( h_1^\dagger \) denotes the interaction Hamiltonian of that mode with the charges. As before, \( h_R \) is the atomic or adiabatic molecular Hamiltonian.

We expand the total wavefunction \( \psi' \) in terms of the complete set of states, \( \{ \Omega(N_1 - \nu_1') N(N_2 - \nu_2') \} \).

\[ \psi' = \sum_{\nu_1' \nu_2'} \nu_1^{\dagger} \nu_2^{\dagger} b_{\nu_1' \nu_2'}(s) e^{-i \int_0^t (\nu_{1'}(s)/\nu_{1'} + \nu_{2'}(s)/\nu_{2'}) dt} \times \Omega(N_1 - \nu_1') \Omega(N_2 - \nu_2') \hspace{1cm} (2.2) \]

where \( \nu_p \) is a particular electronic energy level, \nu for convenience of calculation later and other notations are similar to those in Sec. (A.II). The time-dependent Schrödinger equation gives the following set of equations for the probability amplitudes \( b_{\nu_1' \nu_2'}(t) \).

\[ i \frac{d}{dt} b_{\nu_1' \nu_2'}(\alpha) = W_{\nu_1'}(\alpha) b_{\nu_1' \nu_2'}(\alpha) + \sum_{\alpha'} G_{\nu_1' \nu_2'}(\alpha' \alpha) \]

\[ \times \left( b_{\nu_1' - 1 \nu_2'}(\alpha') + b_{\nu_1' + 1 \nu_2'}(\alpha') \right) - \nu_{1'} b_{\nu_1' \nu_2'}(\alpha) \]

\[ + \sum_{\alpha''} G_{\nu_1' \nu_2'}(\alpha, \alpha'' \alpha') \left( b_{\nu_1' \nu_2' - 1}(\alpha') + b_{\nu_1' \nu_2' + 1}(\alpha') \right) \hspace{1cm} (2.3.a) \]
\[ \sum_{i,j} \frac{d}{d} v_{ij}(u^i) e_{ij}(u^i u^j) = \sum_{i,j} \left[ w_{ij}(u^i u^j) + \left( v_{ij}(u^i) + e_{ij}(u^i u^j) \right) \right] \]

The coupling constant \( \lambda \) is not included in the \( e_{ij}(u^i u^j) \) term. (Note: this is different from that in the \( \lambda^F \) term, which is only included in the \( e_{ij}(u^i u^j) \) term.)

\[ \lambda^F = \int \frac{d^4 k}{(2\pi)^4} \epsilon(k) \]

\[ \frac{1}{N} v_{ij}(u^i) \]

Integrating equations, the antisymmetry of \( v_{ij}(u^i) \) is not valid.
\[
\sum_{\nu_1' \alpha'} \left( E \delta_{\nu_1 \nu_1'} \delta_{\alpha \alpha'} - \langle \nu_1' \alpha' | H | \nu_1 \alpha' \rangle + \nu_2 \nu_2' \delta_{\nu_1 \nu_1'} \delta_{\alpha \alpha'} \right) a_{\nu_1' \nu_2}(\alpha') \]

\[
= \sum_{\nu_1' \alpha'} \delta_{\nu_1 \nu_1'} G_{\nu_1' \nu_2}(\alpha', \alpha') \left( a_{\nu_1' \nu_2-1}(\alpha') \pm a_{\nu_1' \nu_2+1}(\alpha') \right). \tag{2.3}
\]

Let us label the \((\lambda_1, \lambda_2, \gamma)\)th eigensolution at \(y\) as \(E_{\lambda_1 \lambda_2 \sigma} \{a_{\nu_1' \nu_2}(\alpha)\}\). Then it can be shown from the above equations that

\[
E_{\lambda_1^1 + \lambda_1, \lambda_2^1 + \lambda_2, \sigma} = E_{\lambda_1^1 \lambda_2^1 \sigma} - \lambda_1^1 F_1 - \lambda_2^1 F_2,
\]

\[
a_{\nu_1' \nu_2}(\alpha) = a_{\nu_1' \nu_2-1}(\alpha) \sigma. \tag{2.3}
\]

These equations have the same significance as those following Eqs. (A.3.1).

If we define \(a_{\nu_2}(\nu_1' \alpha') \equiv a_{\nu_1' \nu_2}(\alpha)\) as the \((\nu_1' \alpha')\)th component of the vector \(a_{\nu_2}(\alpha)\), then the Eqs. (2.3) can be cast into the matrix form

\[
D_{\nu_2} a_{\nu_2} = G_{\nu_2}(\nu_1' \nu_2-1 \pm a_{\nu_2+1}).
\]

where

\[
D_{\nu_2}(\nu_1 \alpha, \nu_1' \alpha') = E \delta_{\nu_1 \nu_1'} \delta_{\alpha \alpha'} \cdot \langle \nu_1 \alpha | H | \nu_1' \alpha' \rangle + \nu_2 \nu_2' \delta_{\nu_1 \nu_1'} \delta_{\alpha \alpha'}.
\]

\[
G_{\nu_2}(\nu_1 \alpha, \nu_1' \alpha') = \delta_{\nu_1 \nu_1'} G_{\nu_1' \nu_2} \alpha, \alpha').
\]
This is formally the same as Eqs. (A.3.2). Thus the method of solution of the adiabatic eigenvalue problem is formally similar to that of Sec. (A.III). In case of transitions where photon numbers of only one mode changes, that mode should be assigned the role of node \( v_2 \) here. It is necessary to consider \( v_1 \) and \( v_2 \) only in the range \(-M_1 \leq v_1 \leq M_1\) and \(-M_2 \leq v_2 \leq M_2\). The best way to determine the smallest values needed for a desired accuracy is to run tests on the actual system under study. For the numerical study in Sec. III, \( M_1 = M_2 = 2\) is sufficient for an accuracy of four or more significant figures.

**Two-level Pseudocrossing.** With the above-mentioned similarity with Sec. (A.III) in mind, we shall briefly describe the most useful case: the two-level FC between say level \((\lambda, \lambda, \sigma)\) and level \((\mu, \mu, \tau)\). We let

\[
\mathcal{v}_2 (v_2, \mu, \tau) = \mathcal{v}_2 (v_2, \mu, \tau) \mathcal{u}_2 (\lambda, \sigma) + \mathcal{v}_2 (v_2, \mu, \tau) \mathcal{u}_2 (\mu, \tau) .
\]

This implies

\[
d_{\mu_2} (\mu, \tau) = 1 , \quad s_{\mu_2} (\mu, \tau) = 1 ,
\]

\[
d_{\lambda_2} (\lambda, \sigma) = 1 , \quad s_{\lambda_2} (\lambda, \sigma) = 0 .
\]

With these known values, all other \( d 's \) and \( s 's \) are found as in Sec. (A.III). Note, however, \( \mathcal{v}_2 \) now are not diagonal. Therefore we should not use the artificial play in writing, for example \( \mathcal{v}_2 \) below Eq. (A.1.1.6). Instead \( \mathcal{v}_2 \) can be found by (i) letting its \((\mu, \mu, \tau)\)th row be all zeros and (ii) directly inverting the \( \mathcal{v}_2 \) with set
of equations (without the $(u_1 u_2 \tau)$th equation) to obtain other
$n(2M_1 + 1) - 1$ rows.

The two equations $(\lambda_1 \lambda_2 \sigma)$ and $(u_1 u_2 \tau)$ which have not been
used to find the $d$'s and $s$'s are used to express the 
relevant eigenvalues

$$E_u = \frac{1}{2} \left[ (W'_{u_1 u_2 \tau} + W'_{\lambda_1 \lambda_2 \sigma}) + \left( (W'_{u_1 u_2 \tau} - W'_{\lambda_1 \lambda_2 \sigma})^2 + 4\Omega^2 \right)^{1/2} \right],$$

$$E_\lambda = \frac{1}{2} \left[ (W'_{u_1 u_2 \tau} + W'_{\lambda_1 \lambda_2 \sigma}) - \left( (W'_{u_1 u_2 \tau} - W'_{\lambda_1 \lambda_2 \sigma})^2 + 4\Omega^2 \right)^{1/2} \right].$$

Here $W'_{u_1 u_2 \tau}$ is the shifted $(u_1 u_2 \tau)$-level,

$$W'_{u_1 u_2 \tau} = (W(\tau) - u_1 F_1 - u_2 F_2) \cdot \Box_{(1)}^{(1)} + \Box_{(1)}^{(2)} \cdot$$

where

$$\Box_{(1)}^{(1)} = \sum_{a'} G_{12}(\tau, a') \left( s_{u_1 u_2 - a'} \cdot s_{1} \cdot \ldots \cdot s_{L} \right),$$

$$\Box_{(1)}^{(2)} = \sum_{a'} G_{22}(\tau, a') \left( s_{u_1 u_2 - a'} \cdot s_{1} \cdot \ldots \cdot s_{L} \right),$$

may be considered as the shifting of mode 1 and mode 2 respectively. Correspondingly, for the two levels,

$$W'_{\lambda_1 \lambda_2 \sigma} = W(\sigma) - \lambda_1 F_1 - \lambda_2 F_2 + \Box_{\lambda}^{(1)} - \Box_{\lambda}^{(2)} \cdot$$

where

$$\Box_{\lambda}^{(1)} = \sum_{a'} G_{12}(\sigma, a') \left( s_{\lambda_1 - a'} \cdot s_{1} \cdot \ldots \cdot s_{L} \right),$$

$$\Box_{\lambda}^{(2)} = \sum_{a'} G_{22}(\sigma, a') \left( s_{\lambda_2 - a'} \cdot s_{1} \cdot \ldots \cdot s_{L} \right).$$
Finally,

\[ z = - \sum_{\alpha'} G_{1,1}(t, \alpha') \left( \prod_{\beta=2}^{m} \left( 1 - z_{\beta, \alpha'} \right) \right) \]

\[ - \sum_{\alpha'} G_{2,1}(t, \alpha') \left( \prod_{\beta=2}^{m} \left( 1 - z_{\beta, \alpha'} \right) \right) \]

\[ = - \sum_{\alpha'} G_{2,1}(t, \alpha') \left( \prod_{\beta=2}^{m} \left( 1 - z_{\beta, \alpha'} \right) \right) \]

\[ - \sum_{t} C_{t-1} \left( \prod_{\beta=2}^{m} \left( 1 - z_{\beta, \alpha'} \right) \right) \]

In the effective transport matrix model, the two equalities are:

\[ z = \sum_{\alpha'} G_{1,1}(t, \alpha') \left( \prod_{\beta=2}^{m} \left( 1 - z_{\beta, \alpha'} \right) \right) \]

\[ = \sum_{\alpha'} G_{2,1}(t, \alpha') \left( \prod_{\beta=2}^{m} \left( 1 - z_{\beta, \alpha'} \right) \right) \]

\[ = \sum_{t} C_{t-1} \left( \prod_{\beta=2}^{m} \left( 1 - z_{\beta, \alpha'} \right) \right) \]
An Alternative Approach is particularly advantageous in some circumstances. Here we expand the total wavefunction $\psi'$ in another representation,

$$\psi' = \sum_{\xi' \rho' \nu'_2} \psi'_{\nu'_2} b_{\nu'_2}(\xi' \rho') \phi(\xi' \rho') e^{i \int_{t'}^{t} (e_p(t') + i \omega_2 N_2) \, dt'}$$

where, with $H_1$ defined in Eq. (2.1),

$$H_1 \phi_{\xi \rho} = e_{\xi \rho} \phi_{\xi \rho}, \quad (2.6)$$

and $e_p$ is a particular $e_{\xi \rho}$ chosen for convenience of calculation.

The time-dependent equations for $b_{\nu'_2}(\xi \rho)$'s are

$$1 \frac{d}{d\tau} b_{\nu'_2}(\xi \rho) = E_{\xi \rho, \nu'_2} b_{\nu'_2}(\xi \rho) + \sum_{\xi' \rho'} G_{\eta}(\xi \rho, \xi' \rho')$$

$$\times \left( b_{\nu'_{2-1}}(\xi' \rho') \pm b_{\nu'_{2+1}}(\xi' \rho') \right), \quad (2.7)$$

where (compare with Eqs. (A.2.7))

$$E_{\xi \rho, \nu'_2} = \frac{a_0}{\hbar \nu} (e_{\xi \rho} - e_p) - \nu'_2 F_2,$$

$$\tau = \frac{a_0}{\hbar \nu} t,$$

and

$$G(\xi \rho, \xi' \rho') \propto \phi_{\xi \rho}^\ast h_{\xi' \rho'} \phi_{\xi' \rho'}.$$
where

\[ b_{\nu_2}(\xi_p) = e^{-i \int_{y_0}^{y} E(y') dy'} a_{\nu_2}(\xi_p) \].

This approach may be interpreted as follows: the first-mode field interacts with the charge system, produces a modified energy level structure which then interacts with the second-mode field.

The above approach entails the solutions of two single-mode adiabatic eigenvalue problems, Eqs. (2.6) and Eqs. (2.8). Formally it is related to the previous approach by the unitary transformation \( U \) connecting the two representations

\[ \phi_{\xi_p} = U \Omega(\xi_1 - \xi) \xi_p \].

By this transformation, Eqs. (2.2b) of the previous approach can be recovered from Eqs. (2.7) directly.

If both modes are of the same high intensity, the previous approach has the advantage over this approach in calculating only those eigenvalues needed and requiring less computer memory. However, this approach has the advantage of inverting in general smaller matrices.

When the second mode has low intensity such that level shifts due to it are negligible, we may write Eqs. (2.6) and, for multiphoton transition of the second mode between \( \nu \) levels, from the weak field
as perturbation. However, for single photon transition of the second mode, we can do better than perturbation method. Suppose we need to consider single-photon transition of second mode from \( \nu_2 = \lambda_2 = \mu_2 - 1 \) and the \( \nu_1 \)-system from \( \nu_1 \tau \) to \( \nu_1 \sigma \), then from Eqs. (2.7) we consider

\[
\frac{1}{i} \frac{d}{d\nu} b_2(\nu_1 \tau) = E_{\nu_1 \nu_2} b_2(\nu_1 \tau) + G_2(\lambda_1 \sigma, \nu_1 \tau) b_2(\nu_1 \tau),
\]

\[
\frac{1}{i} \frac{d}{d\nu} b_1(\lambda_1 c) = E_{\lambda_1 \sigma, \lambda_2} b_2(\lambda_1 c) + G_2(\lambda_1 \sigma, \nu_1 \tau) b_2(\nu_1 \tau),
\]

which is in the form of Eqs. (A.4.1) with already known solutions.

The Multimode Field. It should be clear on how one would extend the above two methods to the multimode case.

**III. STIMULATED EMISSION IN MOLECULE BY INTENSITY-DEPENDENT LOWERING OF POTENTIAL BARRIER**

We consider here the process in which atoms collide at thermal velocity with each other, forming a quasimolecule with potential curves and dipole matrix elements illustrated in Fig. 1. Initially the quasimolecule is in state \( \sigma \), which has a potential barrier (due to avoided crossing) at \( E_c \). For \( R > R_c \), the dipole transition to the state \( \sigma \) is forbidden, while for \( R < R_c \), it is allowed. However, at thermal velocities, the potential barrier is too high for the classical penetration (or too little quantum mechanical tunnelling) into region \( R < R_c \). Therefore one way to make the desired process go is to lower the potential barrier by a sufficiently intense laser field at a photon energy smaller than the energy gap between level \( \sigma \) and \( \tau \).
These analytic representations are meant to be valid only for $R \geq 3.0 \, \AA$. They are graphed in Fig. 1. The maximum of the bump height of $u_2(R) - u_2(\infty)$ is 0.12 eV at $R = 4.85 \, \AA$. The relative kinetic energy at large $R$ for the colliding diatomic is 0.104 eV, about 0.02 eV too low to overcome (classically) the potential barrier.

We assume electronic state 2 and 3 to have the same $\Lambda$-quantum number while that of state 1 differs from theirs by 1. Then only those collisions whose plane of collision has a nonzero projection of $\hat{\varepsilon}_1$ (the linear polarization of the intense laser field $\equiv$ label 1) will have nonvanishing coupling between state 2 and 3. In our numerical example, we consider only those collisions whose collisional planes contain the $\hat{\varepsilon}_1$, as depicted in Fig. A.4.

With high-intensity laser field chosen to be the available YAG:Nd$^{3+}$ laser ($\lambda_1 = 1.0648 \, \mu$), the bump is lowered by about 0.04 eV at $I_1 = 10^{12} \, W/cm^2$. (The amount of shift is roughly proportional to $I_1$ for this single-photon process.) The colliding atoms for certain range of impact parameter ($b = 0$ to $b_{\max} = 1.97 \, \AA$) can now penetrate into the $R < R_b$ region. The system has certain probability $P_1^{(b)}$ to radiate near the classical turning point by stimulated emission into the second mode $\lambda_2 \approx 0.486 \, \mu$, corresponding to the energy difference between the shifted levels 2 and 1 at $R \approx 3.2 \, \AA$ ($\hat{\varepsilon}_2$ is chosen parallel to $\hat{\varepsilon}_1$).

The transition probability formula Eq.(A.4.5) is appropriate and valid for calculating $P_1^{(b)}$ near $R_c$. The two methods represented by Eq. (A.5) and Eq. (2.9) in the last section yield results in good agreement with each other.

The cross section (in $\AA^2$) for stimulated emission into the second mode
are calculated for several intensities and are given in Table I. 
On a log-log plot of $\sigma_{I_2}^T$ vs $I_2$, these eight points form a straight line of slope 1.

An interesting effect occurs which is related to the fact that the coupling between the second and third level depends on the angle between the internuclear axis of the colliding atoms and the space-fixed linear polarization $\hat{\mathbf{e}}_1$. (See Sec. (A.V)) Thus collisional systems with impact parameter $b = 1.46$ to $1.97 \, \text{a}_0$ can get into the region $R < R_b$ but cannot get out (i.e., bound) because the change of the above-mentioned angle on the outgoing trip. Values for cross section for such "trapping"

$$
\sigma_t = 2\pi \int_{1.46}^{1.97} db \, b \left(1 - P_{I_2}(b)\right)
$$

are given in Table I. It is not significantly sensitive to $I_2$. It is noticed that $\sigma_t$ is large compared to the corresponding $\sigma_{I_2}^T$. The trapped colliding system will become a "vibrating" molecule (that keeps on rotating, and translating as a whole). It is expected to radiate predominantly near $R = 3.2 \, \text{a}_0$. This trapping will result in a great enhancement of the "observed $\sigma_{I_2}^T$".

We have assumed that transition to the third level near $R_b$ is negligible, because the shifted levels 2 and 3 at $R_b$ is off-resonant by 0.06 eV. We should mention that raising the third level in our numerical example by 0.4 eV higher changes the amount of
potential barrier shifts by less than 10%. Thus the selection of the third level (or high intensity laser wavelength) is not severely restrictive.

ACKNOWLEDGMENT

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It has been a privilege indeed to work in the Lawrence Berkeley Laboratory. Thanks to Professor J. D. Jackson and Professor K. M. Watson for making this possible. Consultations with Dr. L. Meissner and program consultants of the Mathematics and Computing Group and the secretarial help of Mrs. C. Graham and Miss G. Perry of the Theoretical Group are also gratefully acknowledged.

Finally but not the least is to thank my family, especially SKY, for their love and care.
1. P. F. Liao and J. E. Bjorkholm, Phys. Rev. Lett. 34, 1 (1975) and references therein. These features are, however, for low intensities.
Table I. Cross section of stimulated emission, $\sigma_{I_2}$ and cross section for trapping, $\sigma_t$ (see Sec. III of text). $I_2$ is the intensity of stimulated emission.

<table>
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<th>$I_2$ (W/cm$^2$)</th>
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<th>$\sigma_t$ ($a_o^2$)</th>
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</table>
FIGURE CAPTION

Fig. 1. Potential curves and dipole matrix elements of quasimolecule for parametric study of interaction with two-mode radiation field (Sec. III of text).
Dipole matrix elements

Potential curves

Energy (eV)

Internuclear separation (Bohr)