

Lawrence Berkeley National Laboratory

Recent Work

Title

NONPERTURBATIVE THEORY OF SINGLE/MULTIPHOTON PROCESSES IN ATOMS AND MOLECULES INDUCED BY INTENSE LASER FIELDS

Permalink

<https://escholarship.org/uc/item/9nx148mm>

Author

Lau, Albert M.F.

Publication Date

1975-04-01

LBL-3647
c. 1

RECEIVED
LAWRENCE
BERKELEY LABORATORY

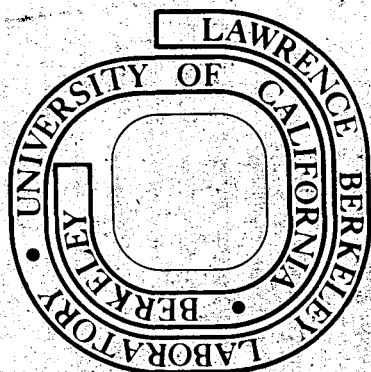
AUG 1 1975

LIBRARY AND
DOCUMENTS SECTION

NONPERTURBATIVE THEORY OF SINGLE/MULTIPHOTON PROCESSES IN ATOMS
AND MOLECULES INDUCED BY INTENSE LASER FIELDS

Albert M. F. Lau
(Ph.D. Thesis)

April 1975



Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

000-4301200

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

CONTENTS

Abstract	1
Part A: Interaction with Single Mode Field	2a
Sec. I. Introduction	3
Sec. II. Time-dependent Equations	5
Sec. III. The Adiabatic Eigenvalue Problem	11
Sec. IV. Transition Probabilities	38
Sec. V. Slow Atomic Collision in an Intense Field	50
Sec. VI. Multiphoton Dissociation of Molecules	53
Sec. VII. Single Atom/Molecule Irradiated by Laser Pulses	56
Acknowledgment	61
Part B: Interaction with Multimode Field	87
Sec. I. Introduction	88
Sec. II. Two- and Multimode Field	88
Sec. III. Stimulated Emission in Molecules by Intensity- dependent Lowering of Potential Barrier	97
Acknowledgment	101

000 430 267

NONPERTURBATIVE THEORY OF SINGLE/MULTIPHOTON PROCESSES
IN ATOMS AND MOLECULES INDUCED BY INTENSE LASER FIELDS*

Albert M. F. Lau

Department of Physics and Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720

April 21, 1975

ABSTRACT

000004301268

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 $\text{Li} + \text{H}(X^1\Sigma^+) \rightarrow \text{Li} + \text{H}(A^1\Sigma^+ \text{ or } B^1\Pi)$ induced by a $\lambda = 0.826 \mu$ field of intensities 10^9 - 10^{12} W/cm^2 and for dissociation (via $B^1\Pi$) cross section of LiH molecule by absorption of 4 photons in a YAG:Nd^{3+} ($\lambda = 1.0648 \mu$) laser field over intensities 10^9 - 8×10^{11} W/cm^2 . The transition probabilities of

Na ($3s \rightarrow 5s$ by absorption of two photon of $\lambda = 0.60233\mu - 0.602396 \mu$) 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.

Part A.

INTERACTION WITH SINGLE-MODE FIELD

(January 29, 1975)

I. INTRODUCTION

To our knowledge, all the previous nonperturbative (or "exact") solutions¹ 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) transition between a pair of atomic levels. With the above restriction removed, Kroll and Watson² 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 atomic³ 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 (≥ 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 multilevel systems, several as well as two levels can be in one- or multiphoton resonant transition with each other. After setting up the Schrodinger 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 Li + H system over a range of field intensity ($10^9 - 10^{12}$ watt/cm²).

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 4-photon dissociation of LiH molecule from the ground state $X^1\Sigma^+$ via the $B^1\Pi$ state. The molecule is in an intense radiation field of wavelength $\lambda = 1.0648\mu$ (YAG:Nd³⁺). The

00004301269

thermal averaged cross section over the range of intensities $10^9 - 8.0 \times 10^{11} \text{ W/cm}^2$ is presented. In the latter case, we consider the 2-photon transition in sodium atom ($3s \rightarrow 5s$) and 8-photon transition in lithium ($2s \rightarrow 5s$) 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

$$i\hbar\dot{\Psi} = (K + H)\Psi, \quad (2.1)$$

where K is the kinetic energy operator for the atoms and $H \equiv h_R + h_p + h'$. Here, h_R is the adiabatic molecular hamiltonian for the colliding atoms at a given internuclear separation R . Besides the electronic terms, h_R 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

$$h_R\phi_\alpha = u_\alpha(R)\phi_\alpha,$$

where ξ denotes the set of atomic electron coordinates, R being considered as a parameter.

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

$$h_p = \sum_{\lambda=1}^m \hbar\omega_\lambda a_\lambda^+ a_\lambda,$$

in the usual notations. Finally the interaction hamiltonian is

$$h' \equiv - \sum_i \left\{ \frac{q_i}{m_i c} \mathbf{p}_i \cdot \mathbf{A}(\mathbf{r}_i) - \frac{q_i^2}{2m_i c^2} \mathbf{A}(\mathbf{r}_i) \cdot \mathbf{A}(\mathbf{r}_i) \right\} \quad (2.2)$$

where i is summed over all the electrons as well as the nuclei. As usual in the Schrödinger picture and in plane wave modes,

$$\mathbf{A}(\mathbf{r}) = \sum_{\lambda}^m c \left(\frac{2m\hbar}{\omega_\lambda V} \right)^{\frac{1}{2}} \left(a_\lambda e^{i\mathbf{k}_\lambda \cdot \mathbf{r}} + a_\lambda^+ e^{-i\mathbf{k}_\lambda \cdot \mathbf{r}} \right) \hat{\mathbf{e}}_{\lambda},$$

where V is the cavity volume. A unitary equivalent interaction hamiltonian well suited for systems of bound charges like atoms and molecules is⁴

$$h' = - \sum_i q_i \mathbf{r}_i \cdot \frac{\mathbf{E}(0)}{m} + \text{higher multiple terms}, \quad (2.3)$$

where

$$\mathbf{E}(\mathbf{r}) \equiv - \frac{1}{c} \frac{\partial}{\partial t} \mathbf{A}(\mathbf{r}).$$

Since only matrix elements of h' between two orthogonal electronic states (ϕ_α 's) will appear in our theory, the leading nonzero matrix elements from the $\mathbf{A} \cdot \mathbf{A}$ term in Eq. (2.2) for intense radiation field

($N \gg 1$) are the dipole terms (for one charge)

$$|A^2| \equiv \frac{q^2}{2m} \left(\frac{2\pi\hbar}{\omega V} \right) |\langle \alpha, N \pm 2 | 2(a^2 - a^{+2})_{ik} \cdot \hat{r}_{ik} | \beta, N \rangle|$$

while those from the $\frac{A \cdot p}{m}$ term are

$$|Ap| \equiv |\langle \alpha, N \pm 1 | \frac{q}{mc} c \left(\frac{2\pi\hbar}{\omega V} \right)^{\frac{1}{2}} (a + a^+)_{p_i} \cdot \hat{e}_i | \beta, N \rangle|$$

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

$$\frac{|A^2|}{|A \cdot p|^2 / \hbar \omega} \sim \alpha \sim \frac{1}{137}$$

which takes account of the fact that $|A^2|$ ($|Ap|$) connects states whose photon numbers differ by 2 (1). The numerical value is obtained with

the assumed typical values for $u_\alpha - u_\beta$ to be $\hbar\omega$ and

$|\langle \alpha | \hat{r} \cdot \hat{e} | \beta \rangle| \sim |\langle \alpha | \hat{r} \cdot \hat{k} | \beta \rangle| \sim a_0$. Thus we may neglect the $\frac{A \cdot A}{m}$ term.

Therefore the dipole⁵ interaction hamiltonian we will use from Eq. (2.2) is

$$h_- \equiv - \sum_i \frac{q_i}{m_i c} p_{i\alpha} \cdot A(0);$$

and that from Eq. (2.3) is

$$h_+ \equiv - \sum_i q_i r_{i\alpha} \cdot E(0)$$

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.⁶ 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 (G_+ 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 ($\approx \alpha c \approx 10^8$ 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 α . 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,

$$i\hbar\dot{\Psi}' = H_c(t)\Psi' \quad (2.4)$$

where $H_c(t)$ is obtained from H by replacing the operator R with the classical orbit $R(t)$.

To solve Eq. (2.4), we let

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

where ρ is any coordinate representation of the photon field.

Substituting this expansion into (2.4) we obtain

$$i\hbar\dot{c}_{\alpha} = u_{\alpha}c_{\alpha} + h_p c_{\alpha} + \sum_{\beta} (\phi_{\alpha}, h' \phi_{\beta}) c_{\beta} - i\hbar \sum_{\beta} c_{\beta} (\phi_{\alpha}, \dot{\phi}_{\beta}). \quad (2.5)$$

The last term on the right corresponds to collisional transition due to nonadiabatic motion of the nuclei. It has been treated elsewhere⁷ and is negligible when the electronic energy levels are not very close together. We assume such are the cases we consider. The secular term $(\phi_{\alpha}, h' \phi_{\alpha})$ 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 ϕ_{α} , and is responsible for radiative transition between molecular nuclei states for the same ϕ_{α} . Therefore, consistent with the classical orbit approximation for

internuclear motion, we neglect the radiative transitions within the same electronic state and drop this term.⁸ Hence

$$i\hbar\dot{c}_{\alpha} = u_{\alpha}c_{\alpha} + h_p c_{\alpha} + \sum_{\beta \neq \alpha} (\phi_{\alpha}, h' \phi_{\beta}) c_{\beta}. \quad (2.6)$$

We restrict ourselves to cases of one mode of radiation with linear polarization \hat{e}_{α} . Let $\Omega(N - \nu)$ be the photon-number state of the radiation field where N is the initial number of photons and ν the number of photons absorbed by the quasimolecule. Since we are interested in intense radiation field, N is very much larger than the maximum ν of interest. Thus we will make the excellent approximation,

$$N - \nu + 1 \approx N - \nu \approx N.$$

Defining the probability amplitude $b_{\nu}(\alpha)$ by

$$c_{\alpha} = \sum_{\nu} i^{\nu} b_{\nu}(\alpha) e^{-\frac{i}{\hbar} \int_0^t (u_{\alpha} + \hbar\omega N) dt} \Omega(N - \nu),$$

and making the change to dimensionless time variable

$$y \equiv \frac{v}{a_0} t$$

where v is any convenient constant speed, a_0 the Bohr radius, we obtain from Eqs. (2.6)

$$i \frac{d}{dy} b_{\nu}(\alpha) = W_{\nu}(\alpha) b_{\nu}(\alpha) + \sum_{\beta} G_{\pm}(\alpha, \beta) (b_{\nu-1}(\beta) \pm b_{\nu+1}(\beta)) \quad (2.7)$$

where

$$W_{\nu}(\alpha) \equiv \frac{a_0}{\hbar\nu} (u_{\alpha} - u_1) - \nu F$$

$$F \equiv \frac{a_0}{\hbar\nu} \hbar\omega$$

$$G_{\pm}(\alpha, \beta) \equiv \frac{a_0}{\hbar\nu} \left(\frac{2\pi I}{c} \right)^{\frac{1}{2}} \left(\phi_{\alpha}, - \sum_i q_i \frac{r_i}{\hbar} \phi_{\beta} \right) \cdot \hat{\epsilon} \begin{pmatrix} 1 \\ \frac{u_{\alpha} - u_{\beta}}{\hbar\omega} \end{pmatrix}$$

corresponding to the dipole⁵ interaction h'_{\pm} , and

$$G_{\pm}(\alpha, \alpha) \equiv 0.$$

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

If h_R is real, a set of the real ϕ_{α} 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

$$b_{\nu}(\alpha) \equiv e^{-i \int^y E(y') dy'} a_{\nu}(\alpha) \quad (3.0)$$

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

$$\frac{da_{\nu}(\alpha)}{dy} = 0.$$

Substituting these expressions into Eqs. (2.7), we obtain

$$E a_{\nu}(\alpha) = W_{\nu}(\alpha) a_{\nu}(\alpha) + \sum_{\beta} G_{\pm}(\alpha, \beta) (a_{\nu-1}(\beta) \pm a_{\nu+1}(\beta)). \quad (3.1)$$

The quantities $W_{\nu}(\alpha)$ correspond to the photon-electronic (ν, α) eigenlevels of the noninteracting hamiltonian $h_c + h_p$. We shall call them the "noninteracting eigenlevels." In absence of interaction, these levels may cross each other (Fig. 1). In such case $G_{\pm}(\alpha, \beta) = 0$ in Eq. (2.7), then

$$b_{\nu}(\alpha) = c_{\nu}(\alpha) e^{-i \int^y W_{\nu}(\alpha) dy'}$$

where $c_{\nu}(\alpha)$ are constant and hence no transition occurs. But with the interaction "on", $G_{\pm}(\alpha, \beta) \neq 0$, the adiabatic eigensolutions of Eq. (3.1) would yield E 's which are in general different from $W_{\nu}(\alpha)$'s. In particular, near where there was a crossing between the $W_{\nu}(\alpha)$'s, due to the now-present interaction between them, the $W_{\nu}(\alpha)$'s "repel each other." As a result, the corresponding E 's form a pseudocrossing (PC). In the adiabatic limit, the quasimolecule follows a particular E (a solid line in Fig. 1), at each PC all throughout the collision and no transition occurs. (This is related to the fact that for each PC at $-y < 0$, there is a corresponding PC at y .) But in the nonadiabatic situation where $dR/dt \neq 0$, transitions can occur at the PC's.

Following I, we shall label the adiabatic eigensolution (E, \underline{a}) by that set of index (ν, α) such that at each y

$$E_{\nu\alpha} \rightarrow W_{\nu}(\alpha), \quad \text{as all } G_{\pm}(\alpha, \beta) \rightarrow 0.$$

Thus the same (E, \underline{a}) switch indices at each PC as indicated in

00004301270

Fig. 1. In the rest of the paper, we shall drop this adiabatic eigenindices on (E, a) whenever no confusion results.

We observe that at any y if a particular $(E_{\lambda_0 \alpha}, a_{\lambda_0 \alpha})$ are found, then $(E_{(\lambda_0 + \lambda) \alpha}, a_{(\lambda_0 + \lambda) \alpha})$ for the same α but any λ can be generated from it by

$$E_{(\lambda_0 + \lambda) \alpha} = E_{\lambda_0 \alpha} - \lambda F$$

and,

$$a_{\nu}^{(\lambda_0 + \lambda) \alpha}(\beta) = a_{\nu - \lambda}^{\lambda_0 \alpha}(\beta), \quad \text{for all } \nu, \beta.$$

This can be shown simply by substitution into Eqs. (3.1). Thus we need only to find the $(\lambda_0 \alpha)$ adiabatic eigensolution for one λ_0 in order to know all other $(\lambda \alpha)$ eigensolutions for the same α .

In principle the sum over β runs over all quasimolecular electronic states of the pseudomolecule. However, if we are interested in the low-lying electron eigenlevels only, we may restrict the sum to an appropriate set of discrete electronic states (see examples below). The higher lying states may be negligible because the coupling with states of interests, $G_{\pm}(\alpha, \beta)$, are relatively much smaller than those of states included in the sum; or because their contributions are of higher orders. Thus restricting ourselves to a finite number $n(\geq 3)$ of discrete electronic states, we now proceed to solve Eqs. (3.1).

It is convenient to convert at this point to matrix notation. Let G_{\pm} be the $n \times n$ matrix $[G_{\pm}(\alpha, \beta)]$. Let D_{\pm} be the $n \times n$ diagonal matrix $[(E - W_{\nu}(\alpha))\delta_{\alpha\beta}]$; and a_{ν} be the $n \times 1$ column matrix. Then Eq. (3.1) can be rewritten as, for all ν

$$D_{\pm \nu} a_{\nu} = G_{\pm}(a_{\nu-1} \pm a_{\nu+1}). \quad (3.2)$$

We shall call the above n equations of a given ν "the ν th set of equations" and specify an individual equation in Eqs. (3.2) by "the (ν, α) equation."

In the above equations, D_{\pm} and G_{\pm} (and therefore a_{ν}) are a function of R (and therefore of y). In a given quasimolecular system, we encounter no, two-level, and/or multilevel PC of the noninteracting electron-photon levels $W_{\nu}(\alpha)$ at different R (see Figs. 1 and 2). The exact procedure we follow depends on the kind of PC. Therefore we shall treat the no-PC, 2-level PC and 3-level PC cases separately below. Any higher-than-3-level PC cases are straightforward extension of the 3-level case.

A. The No-PC Case

Suppose we are interested in finding the adiabatic eigensolution, say $(\nu = 0, \alpha)$, at y . (Recall that from this we can generate all other (ν, α) of the same α .) For not too high an intensity, we expect that the noninteracting eigensolution $(\nu = 0, \alpha)$ will be dominant. Therefore we let

$$a_{\nu}(\beta) = d_{\nu}(\beta) a_0(\alpha), \quad (3.3)$$

for all ν, β . This implies $d_0(\alpha) = 1$. Substituting Eqs. (3.3) into Eqs. (3.2) and factorizing out $a_0(\alpha)$, we obtain

$$D_{\pm \nu} d_{\nu} = G_{\pm}(d_{\nu-1} \pm d_{\nu+1}). \quad (3.4)$$

Barring unusual coincident, D_v^{-1} exist, then

$$d_{mV} = U_{mV}^{\pm} (d_{mV-1} \pm d_{mV+1}) ,$$

where

$$U_{mV}^{\pm} \equiv D_{mV}^{-1} G_{m\pm} .$$

For $v > 0$, we define H_{mV} such that $d_{mV} = U_{mV}^{\pm} H_{mV} d_{mV-1}$. Then Eqs.

(3.4) can be written as

$$U_{mV}^{\pm} H_{mV} c_{mV-1} = U_{mV}^{\pm} [c_{mV-1} \pm U_{mV+1}^{\pm} H_{mV+1} U_{mV}^{\pm} H_{mV} c_{mV-1}] .$$

If the inverse of U_{mV}^{\pm} exist (which is the case if $G_{m\pm}^{-1}$ exists),

then the above equations can be simplified to give

$$H_{mV} c_{mV-1} = [I \mp U_{mV+1}^{\pm} H_{mV+1} U_{mV}^{\pm}]^{-1} c_{mV-1} .$$

Since this is to be satisfied for a general c_{mV-1} , we have

$$H_{mV} = [I \mp U_{mV+1}^{\pm} H_{mV+1} U_{mV}^{\pm}]^{-1} . \quad (3.5)$$

In particular,

$$H_{m1} = [I \mp U_{m2}^{\pm} H_{m2} U_{m1}^{\pm}]^{-1} ,$$

and

$$d_{m1} = U_{m1}^{\pm} H_{m1} d_{m0} \equiv X_{m1} d_{m0} .$$

Since

$$D_{mV}^{-1} \rightarrow 0 \quad \text{as } v \rightarrow \infty ,$$

then $H_{mV} \rightarrow I$ in this limit.

For $v < 0$, let

$$d_{mV} = U_{mV}^{\pm} H'_{mV} d_{mV+1} .$$

Substituting into Eqs. (3.4) and after manipulations similar to those

leading to Eqs. (3.5), we obtain

$$H'_{mV} = \pm [I - U_{mV-1}^{\pm} H'_{mV-1} U_{mV}^{\pm}]^{-1} . \quad (3.6)$$

Again D_{mV}^{-1} (hence U_{mV}^{\pm}) $\rightarrow 0$ as $v \rightarrow -\infty$, therefore $H'_{mV} \rightarrow \pm I$. In particular

$$H'_{m-1} = \pm [I - U_{m-2}^{\pm} H'_{m-2} U_{m-1}^{\pm}]^{-1}$$

and

$$d_{m-1} = U_{m-1}^{\pm} H'_{m-1} d_{m0} \equiv X_{m-1} d_{m0} .$$

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

$$\sum_{\gamma \neq \sigma} \left[(E - W_0(\alpha)) \delta_{\alpha\gamma} - \sum_{\beta} G_{\pm}(\alpha, \beta) (X_2(\beta, \gamma) \pm X_1(\beta, \gamma)) \right] d_0(\gamma) = \sum_{\beta} G_{\pm}(\alpha, \beta) (X_2(\beta, \sigma) \pm X_1(\beta, \sigma)) . \quad (3.7a)$$

If the above equations are represented in matrix form, then

$$P_{m0} d' = b'$$

where

000 > 43.01271

$$\underline{d}'_{\underline{m}0} \equiv (d'_0(1), d'_0(2), \dots, d'_0(\sigma-1), d'_0(\sigma+1), \dots, d'_0(n)),$$

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

$$\underline{d}'_{\underline{m}0} = \underline{P}_{\underline{m}}^{-1} \underline{b}'_{\underline{m}}. \quad (3.7b)$$

Thus in order to find all $\underline{H}_{\underline{m}\nu}$'s and $\underline{H}'_{\underline{m}\nu}$'s (hence the $d_{\nu}(\alpha)$'s), in principle we may start with $\underline{H}_{\underline{m}\infty} = \underline{I}_{\underline{m}}$ and $\underline{H}'_{\underline{m}-\infty} = \pm \underline{I}_{\underline{m}}$ (+ corresponds to \underline{h}'_{\pm} hamiltonian while - corresponds to the \underline{h}_{\pm} hamiltonian). However, in actual numerical calculations, we may choose a cut-off M ($-M \leq \nu \leq M$) such that the error in the matrix elements of \underline{H}_1 and \underline{H}'_{-1} is negligible. An estimate of this error is given roughly by $(G(\alpha, \beta)/FM)^{M/2}$. The actual choice of M depends on the particular system and field intensity of interest. In the examples we have done, a relative error of magnitude less than 10^{-15} can be achieved with M being around 10 even for the highest intensity considered.

Thus starting with $\underline{H}_{\underline{m}M+1} = \underline{I}_{\underline{m}}$, we find successive $\underline{H}_{\underline{m}M}, \underline{H}_{\underline{m}M-1}, \dots, \underline{H}_{\underline{m}2}, \underline{H}_{\underline{m}1}$ according to Eqs. (3.5). Then $\underline{d}'_{\underline{m}1} = \underline{U}_{\underline{m}1}^{\pm} \underline{H}_{\underline{m}1} \underline{d}'_{\underline{m}0}$. Similarly starting with $\underline{H}'_{\underline{m}-M-1} = \pm \underline{I}_{\underline{m}}$, we find $\underline{H}'_{\underline{m}-M}, \underline{H}'_{\underline{m}-M+1}, \dots, \underline{H}'_{\underline{m}-2}, \underline{H}'_{\underline{m}-1}$ according to Eqs. (3.6). Then $\underline{d}'_{\underline{m}-1} = \underline{U}_{\underline{m}-1}^{\pm} \underline{H}'_{\underline{m}-1} \underline{d}'_{\underline{m}0}$. Then we obtain $\underline{d}'_{\underline{m}0}$ as in Eqs. (3.7).

So far we have not used the ($\nu = 0, \alpha = \sigma$) equation

$$E = W_0(\sigma) + \sum_{\beta, \gamma} G_{\pm}(\sigma, \beta) (X_{\underline{m}2}(\beta, \gamma) \pm X_{\underline{m}1}(\beta, \gamma)) d_{\underline{m}0}(\gamma)$$

where $d_0(\sigma) = 1$ has been used. The second term on the right may be considered as the shift of level $W_0(\sigma)$ due to interaction. For low intensity, it agrees in value with that given by perturbation theory. We use this equation for successive iteration to find the adiabatic eigenvalues $E_0(\sigma)$, by starting with a trial E close to $W_0(\sigma)$. The number of iterations depends on the accuracy desired as well as the strength of coupling $G(\alpha, \beta)$. In all calculations we have done, values accurate to four or more significant figures are obtained with roughly 2 (for $I = 1 \times 10^9$ W/cm²) to 5 iterations (for $I \approx 10^{12}$ W/cm²).

The above procedure also yields the coefficients $d_{\nu}(\beta)$ of the adiabatic eigenvector \underline{a}_{ν} , if needed. Normalization would fix the value of $a_0(\sigma)$.

B. Two-level PC

When two noninteracting photon-electronic levels, say (ν_2, σ_2) and (ν_1, σ_1) , are too close to each other (degenerate) at a certain $R(y)$, we must modify the previous procedure in order to find the adiabatic eigensolutions. Suppose $\sigma_2 > \sigma_1$ and $\eta \equiv \nu_2 - \nu_1 > 0$.

At the y of interest, let

$$a_{\nu}(\alpha) = d_{\nu}(\alpha) a_{\nu_1}(\sigma_1) + s_{\nu}(\alpha) a_{\nu_2}(\sigma_2), \quad (3.8)$$

for all ν, α . It follows that

$$\begin{aligned} d_{\nu_1}(\sigma_1) &= 1, & s_{\nu_1}(\sigma_1) &= 0; \\ d_{\nu_2}(\sigma_2) &= 0, & s_{\nu_2}(\sigma_2) &= 1. \end{aligned} \quad (3.9)$$

To find $d_v(\alpha)$'s, which are independent of $a_{v_2}(\sigma_2)$, we substitute $d_v(\alpha)a_{v_1}(\sigma_1)$ in place of $a_v(\alpha)$ in Eqs. (3.2) and obtain

$$D_{\mathbb{M}v} d_v = G_{\mathbb{M}\pm}(d_{\mathbb{M}v-1} \pm d_{\mathbb{M}v+1}), \quad -M \leq v \leq M. \quad (3.10)$$

For $v > v_1$, let $d_{\mathbb{M}v} = U_{\mathbb{M}v}^{\pm} H_{\mathbb{M}v} d_{\mathbb{M}v-1}$, where $U_{\mathbb{M}v}^{\pm} \equiv D_{\mathbb{M}v}^{-1} G_{\mathbb{M}\pm}$. Then after manipulations similar to those from Eqs. (3.4) to Eqs. (3.5), we obtain as before

$$H_{\mathbb{M}v} = \left[I_{\mathbb{M}} \mp U_{\mathbb{M}v+1}^{\pm} H_{\mathbb{M}v+1} U_{\mathbb{M}v}^{\pm} \right]^{-1}, \quad v = M, \dots, v_2 + 1, v_2 - 2, \dots, v_1 + 1. \quad (3.11)$$

Now, however, among the v_2 th set of equations in Eq. (3.2), all the $n - 1$ equations with $\alpha \neq \sigma_2$, and $d_{v_2}(\sigma_2) = 0$ from Eqs. (3.9), can be satisfied to an arbitrary degree of accuracy if we write

$$d_{\mathbb{M}v_2} = \bar{D}_{\mathbb{M}2}^{-1} G_{\mathbb{M}\pm}(d_{\mathbb{M}v_2-1} \pm d_{\mathbb{M}v_2+1}) \quad (3.12a)$$

where

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

and

$$\bar{D}_{v_2}(\sigma_2, \beta) \equiv \ell d_{\sigma_2, \beta}$$

ℓ being an (1) arbitrarily large but (2) finite number. Condition (1) enables $d_{v_2}(\sigma_2) \approx 0$ to be satisfied while condition (2) fulfills the formal requirement that $\bar{D}_{\mathbb{M}}^{-1}$ exists. Then with

$$\bar{U}_{\mathbb{M}v_2}^{\pm} \equiv \bar{D}_{\mathbb{M}2} G_{\mathbb{M}\pm}$$

we obtain as before

$$H_{\mathbb{M}v_2} = \left[I_{\mathbb{M}} \mp U_{\mathbb{M}v_2+1}^{\pm} H_{\mathbb{M}v_2+1} \bar{U}_{\mathbb{M}v_2}^{\pm} \right]^{-1}, \quad (3.12b)$$

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

$$H_{\mathbb{M}v_2-1} = \left[I_{\mathbb{M}} \mp \bar{U}_{\mathbb{M}v_2}^{\pm} H_{\mathbb{M}v_2} U_{\mathbb{M}v_2-1}^{\pm} \right]^{-1}.$$

For $v < v_1$, with $d_{\mathbb{M}v} \equiv U_{\mathbb{M}v}^{\pm} H'_{\mathbb{M}v} d_{\mathbb{M}v+1}$, $H'_{\mathbb{M}v}$ with $v \leq v_1 - 1$ are obtained the same way as in Eqs. (3.6).

With the equations above, various $d_{\mathbb{M}v}$'s can be expressed in terms of $d_{\mathbb{M}v_1}$. For use below, we write

$$d_{\mathbb{M}v_2+1} \equiv X_{\mathbb{M}1} d_{\mathbb{M}v_1},$$

$$d_{\mathbb{M}v_2-1} \equiv X_{\mathbb{M}2} d_{\mathbb{M}v_1},$$

$$d_{\mathbb{M}v_1+1} \equiv X_{\mathbb{M}3} d_{\mathbb{M}v_1},$$

$$d_{\mathbb{M}v_1-1} \equiv X_{\mathbb{M}4} d_{\mathbb{M}v_1}.$$

The explicit forms of $X_{\mathbb{M}i}$'s depend on $\eta (\equiv v_2 - v_1)$. When $\eta \geq 2$,

00004301272

$$X_{M1} = U_{M\nu_2+1}^+ H_{M\nu_2+1} \tilde{U}_{M\nu_2}^+ H_{M\nu_2} \cdots U_{M\nu_1+1}^+ H_{M\nu_1+1} ,$$

$$X_{M2} = U_{M\nu_2-1}^+ H_{M\nu_2-1} \cdots U_{M\nu_1+1}^+ H_{M\nu_1+1} ,$$

$$X_{M3} = U_{M\nu_1+1}^+ H_{M\nu_1+1} ,$$

$$X_{M4} = U_{M\nu_1-1}^+ H_{M\nu_1-1} .$$

When $\eta = 1$,

$$X_{M1} = U_{M\nu_2+1}^+ H_{M\nu_2+1} \tilde{U}_{M\nu_2}^+ H_{M\nu_2} ,$$

$$X_{M2} = I ,$$

$$X_{M3} = \tilde{U}_{M\nu_2}^+ H_{M\nu_2} ,$$

$$X_{M4} = U_{M\nu_1-1}^+ H_{M\nu_1-1} . \quad (3.13)$$

The $d_{M\nu_1}' \equiv (d_{\nu_1}(1), \dots, d_{\nu_1}(\sigma_1 - 1), d_{\nu_1}(\sigma_1 + 1), \dots, d_{\nu_1}(n))$

can be found from the ν_1 th set of Eqs. (3.10) with $\alpha = 1, 2, \dots, \sigma_1 - 1, \sigma_1 + 1, \dots, n$ 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 $s_{\nu}(\alpha) a_{\nu_2}(\sigma_2)$ in place of $a_{\nu}(\alpha)$ into Eqs. (3.2)

$$D_{M\nu} s_{M\nu} = G_{M\pm}(s_{M\nu-1} \pm s_{M\nu+1}) , \quad -M \leq \nu \leq M . \quad (3.14)$$

For $\nu > \nu_2$, we define $s_{M\nu} = U_{M\nu}^+ K_{M\nu} s_{M\nu-1}$ and obtain as before

$$K_{M\nu} = \left[I - U_{M\nu+1}^+ K_{M\nu+1} U_{M\nu}^+ \right]^{-1} .$$

Comparing with Eqs. (3.11), we observe that, $K_{\nu} = H_{\nu}$, for

$\nu_2 < \nu \leq M$, since the cut-off conditions ($H_{M+1} = I$; $K_{M+1} = I$) are the same. For $\nu < \nu_2$, with $s_{M\nu} \equiv U_{M\nu}^+ K'_{M\nu} s_{M\nu+1}$, $K'_{M\nu}$ are found from Eqs. (3.14) to be

$$K'_{M\nu} = \pm \left[I - U_{M\nu-1}^+ K'_{M\nu-1} U_{M\nu}^+ \right]^{-1}$$

$$\nu = -M, -M+1, \dots, \nu_1 - 1, \nu_1 + 2, \dots, \nu_2 - 1 .$$

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

The $K'_{M\nu_1}$ matrix is obtained in a way similar to obtaining $H_{M\nu_2}$ in Eqs. (3.12). Now we use the ν_1 th set of Eqs. (3.14) with $\alpha = 1, 2, \dots, \sigma_1 - 1, \sigma_1 + 1, \dots, n$ and $s_{\nu_1}(\sigma_1) = 0$ to write

$$s_{M\nu_1} = \bar{D}_{M\nu_1}^{-1} G_{M\pm}(s_{M\nu_1-1} \pm s_{M\nu_1-1})$$

where

$$\bar{D}_{M\nu_1}(\alpha, \beta) \equiv D_{M\nu_1}(\alpha, \alpha) \delta_{\alpha, \beta} \quad \text{for } \alpha \neq \sigma_1 ;$$

and

$$\bar{D}_{M\nu_1}(\sigma_1, \beta) \equiv \ell \delta_{\sigma_1, \beta} ,$$

ℓ being an arbitrary large but finite number. Then

$$K'_{\mathbb{M}v_1} = \pm \left[I - U_{\mathbb{M}v_1-1}^{\pm} K'_{\mathbb{M}v_1-1} \tilde{U}_{\mathbb{M}v_1}^{\pm} \right]^{-1},$$

where $\tilde{U}_{\mathbb{M}v_1}^{\pm} \equiv \bar{D}_{\mathbb{M}v_1}^{-1} G_{\mathbb{M}v_1}^{\pm}$. From the $(v_1 - 1)$ th set of equations, we obtain

$$K'_{\mathbb{M}v_1+1} = \pm \left[I - U_{\mathbb{M}v_1}^{\pm} K'_{\mathbb{M}v_1} U_{\mathbb{M}v_1+1}^{\pm} \right]^{-1}.$$

Defining

$$s_{\mathbb{M}v_2+1} \equiv Y_{\mathbb{M}1} s_{\mathbb{M}v_2},$$

$$s_{\mathbb{M}v_2-1} \equiv Y_{\mathbb{M}2} s_{\mathbb{M}v_2},$$

$$s_{\mathbb{M}v_1+1} \equiv Y_{\mathbb{M}3} s_{\mathbb{M}v_2},$$

$$s_{\mathbb{M}v_1-1} \equiv Y_{\mathbb{M}4} s_{\mathbb{M}v_2},$$

for $\eta \geq 2$, we obtain

$$Y_{\mathbb{M}1} = U_{\mathbb{M}v_2+1}^{\pm} K_{\mathbb{M}v_2+1},$$

$$Y_{\mathbb{M}2} = U_{\mathbb{M}v_2-1}^{\pm} K'_{\mathbb{M}v_2-1},$$

$$Y_{\mathbb{M}3} = U_{\mathbb{M}v_1+1}^{\pm} K'_{\mathbb{M}v_1+1} U_{\mathbb{M}v_1+2}^{\pm} K'_{\mathbb{M}v_1+2} \cdots U_{\mathbb{M}v_2-1}^{\pm} K'_{\mathbb{M}v_2-1},$$

$$Y_{\mathbb{M}4} = U_{\mathbb{M}v_1-1}^{\pm} K'_{\mathbb{M}v_1-1} \tilde{U}_{\mathbb{M}v_1}^{\pm} K'_{\mathbb{M}v_1} \cdots U_{\mathbb{M}v_2-1}^{\pm} K'_{\mathbb{M}v_2-1};$$

while for $\eta = 1$, we obtain

$$Y_{\mathbb{M}1} = U_{\mathbb{M}v_2+1}^{\pm} K_{\mathbb{M}v_2+1}$$

$$Y_{\mathbb{M}2} = \tilde{U}_{\mathbb{M}v_1}^{\pm} K'_{\mathbb{M}v_1},$$

$$Y_{\mathbb{M}3} = I,$$

$$Y_{\mathbb{M}4} = U_{\mathbb{M}v_1-1}^{\pm} K'_{\mathbb{M}v_1-1} \tilde{U}_{\mathbb{M}v_1}^{\pm} K'_{\mathbb{M}v_1}. \quad (3.15)$$

All $s_{\mathbb{M}v}$ are thus expressed in terms of $s_{\mathbb{M}v_2}$. The $s'_{\mathbb{M}v_2} \equiv (s_{v_2}(1), \dots, s_{v_2}(\sigma_2 - 1), s_{v_2}(\sigma_2 + 1), \dots, s_{v_2}(n))$ are found from the v_2 th set of equations with $\alpha = 1, 2, \dots, \sigma_2 - 1, \sigma_2 + 1, \dots, n$, and $s_{v_2}(\sigma_2) = 1$ in a way similar to that of $d'_{\mathbb{M}v_1}$ in Eqs. (3.7).

Finally, we use the two remaining equations

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

and

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

to find the adiabatic eigenvalue E . Substitutions of a_{v_1} 's as given in Eqs. (3.8), (3.13), and (3.15) gives

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

00004301273

where

$$W'_{v_1}(\sigma_1) \equiv W_{v_1}(\sigma_1) + \Delta_1,$$

$$\Delta_1 \equiv \sum_{\gamma, \beta} G_{\pm}(\sigma_1, \gamma) (X_4(\gamma, \beta) \pm X_3(\gamma, \beta)) d_{v_1}(\beta);$$

$$W'_{v_2}(\sigma_2) \equiv W_{v_2}(\sigma_2) + \Delta_2,$$

$$\Delta_2 \equiv \sum_{\gamma, \beta} G_{\pm}(\sigma_2, \gamma) (Y_2(\gamma, \beta) \pm Y_1(\gamma, \beta)) s_{v_2}(\beta);$$

$$G_{12} \equiv - \sum_{\gamma, \beta} G_{\pm}(\sigma_1, \gamma) (Y_4(\gamma, \beta) \pm Y_3(\gamma, \beta)) s_{v_2}(\beta);$$

$$G_{21} \equiv - \sum_{\gamma, \beta} G_{\pm}(\sigma_2, \gamma) (X_2(\gamma, \beta) \pm X_1(\gamma, \beta)) d_{v_1}(\beta). \quad (3.16)$$

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

Solutions to the above equations exist for the adiabatic eigenvalues,

$$E_u = \frac{1}{2} \left[(W'_{v_2}(\sigma_2) + W'_{v_1}(\sigma_1)) + ((W'_{v_2}(\sigma_2) - W'_{v_1}(\sigma_1))^2 + 4G_{12}G_{21})^{\frac{1}{2}} \right],$$

$$E_l = \frac{1}{2} \left[(W'_{v_2}(\sigma_2) + W'_{v_1}(\sigma_1)) - ((W'_{v_2}(\sigma_2) - W'_{v_1}(\sigma_1))^2 + 4G_{12}G_{21})^{\frac{1}{2}} \right].$$

(3.17)

Starting with a trial E , e.g., $\frac{1}{2}(W_{v_2}(\sigma_2) + W_{v_1}(\sigma_1))$, we

can use one of these two equations for iteration to find (E_u, a_m^u) and/or (E_l, a_m^l) .

The level separation $E_u - E_l$ is then $((W'_{v_2}(\sigma_2) - W'_{v_1}(\sigma_1))^2 + 4G_{12}G_{21})^{\frac{1}{2}}$ and the degeneracy is removed. The minimum of $E_u - E_l$ 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, σ_1) , (v_2, σ_2) , and (v_3, σ_3) . At each $R(y)$, we express all $a_v(\alpha)$ in terms of the three coefficients of the degenerate noninteracting states, as

$$a_v(\alpha) = d_v(\alpha) a_{v_1}(\sigma_1) + s_v(\alpha) a_{v_2}(\sigma_2) + t_v(\alpha) a_{v_3}(\sigma_3). \quad (3.18)$$

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, σ_1) , (v_2, σ_2) , and (v_3, σ_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 $d_v(\alpha) a_{v_1}(\sigma_1)$ in place of $a_v(\alpha)$ in Eqs. (3.2). Defining $d_{m\nu}^+ = U_{m\nu}^+ H_{m\nu} d_{m\nu-1}^+$ for $\nu > v_1$ and $d_{m\nu}^+ = U_{m\nu}^+ H_{m\nu}^+ d_{m\nu+1}^+$ for $\nu < v_1$, we obtain, with $H_{mM+1} = I$ and $H_{m-M-1}^+ = \pm I$,

$$H_{m\nu} = \left[I \mp U_{m\nu+1}^+ H_{m\nu+1} U_{m\nu}^+ \right]^{-1}, \quad \nu = M, \dots, v_3 + 1, v_3 - 2, \dots, v_2 + 1, v_2 - 2, \dots, v_1 + 1;$$

$$H_{m\nu_3} = \left[I \mp U_{m\nu_3+1}^+ H_{m\nu_3+1} \tilde{U}_{m\nu_3}^+ \right]^{-1},$$

$$H_{m\nu_3-1} = \left[I \mp \tilde{U}_{m\nu_3}^+ H_{m\nu_3} U_{m\nu_3-1}^+ \right]^{-1},$$

$$H_{m\nu_2} = \left[I \mp U_{m\nu_2+1}^+ H_{m\nu_2+1} \tilde{U}_{m\nu_2}^+ \right]^{-1},$$

$$H_{m\nu_2-1} = \left[I \mp \tilde{U}_{m\nu_2}^+ H_{m\nu_2} U_{m\nu_2-1}^+ \right]^{-1},$$

and

$$H_{m\nu}^+ = \pm \left[I - U_{m\nu-1}^+ H_{m\nu-1}^+ U_{m\nu}^+ \right]^{-1}, \quad -M \leq \nu \leq v_1 - 1.$$

Here,

$$\tilde{U}_{m\nu_i}^+ \equiv \bar{D}_{m\nu_i}^{-1} G_{m\nu_i}^+ \quad (3.19)$$

where

$$\bar{D}_{m\nu_i}(\alpha, \beta) \equiv D_{m\nu_i}(\alpha, \alpha) \delta_{\alpha\beta}, \quad \alpha \neq \sigma_i$$

$$\bar{D}_{m\nu_i}(\sigma_i, \beta) \equiv \ell \delta_{\sigma_i \beta}$$

ℓ being an arbitrarily large but finite number. For $i = 2, 3$, the equations $d_{m\nu_3}(\sigma_3) = 0$, $d_{m\nu_2}(\sigma_2) = 0$ and that $\bar{D}_{m\nu_i}^{-1}$ exist, are all satisfied as desired.

We define

$$d_{m\nu_3+1} \equiv X_{m1} d_{m\nu_1},$$

$$d_{m\nu_3-1} \equiv X_{m2} d_{m\nu_1},$$

$$d_{m\nu_2+1} \equiv X_{m3} d_{m\nu_1},$$

$$d_{m\nu_2-1} \equiv X_{m4} d_{m\nu_1},$$

$$d_{m\nu_1+1} \equiv X_{m5} d_{m\nu_1},$$

$$d_{m\nu_1-1} \equiv X_{m6} d_{m\nu_1}.$$

(3.20a)

While other cases may be written down as need arises, we have considered the following two typical cases: with $\eta \equiv v_2 - v_1$, $\kappa \equiv v_3 - v_2$,

for case $\kappa > 2, \eta > 2:$

$$X_{M0} = U_{M\nu_1-1}^{\pm} H_{M\nu_1-1}^{\pm} ,$$

$$X_{M5} = U_{M\nu_1+1}^{\pm} H_{M\nu_1+1}^{\pm} ,$$

$$X_{M4} = U_{M\nu_2-1}^{\pm} H_{M\nu_2-1}^{\pm} U_{M\nu_2-2}^{\pm} H_{M\nu_2-2}^{\pm} \cdots U_{M\nu_1+2}^{\pm} H_{M\nu_2+2}^{\pm} X_5 ,$$

$$X_{M3} = U_{M\nu_2+1}^{\pm} H_{M\nu_2+1}^{\pm} \tilde{U}_{M\nu_2}^{\pm} H_{M\nu_2}^{\pm} X_{M4} ,$$

$$X_{M2} = U_{M\nu_3-1}^{\pm} H_{M\nu_3-1}^{\pm} \cdots U_{M\nu_2+2}^{\pm} H_{M\nu_2+2}^{\pm} X_{M3} ,$$

$$X_{M1} = U_{M\nu_3+1}^{\pm} H_{M\nu_3+1}^{\pm} \tilde{U}_{M\nu_3}^{\pm} H_{M\nu_3}^{\pm} X_{M2} ; \quad (3.20b)$$

while for case $\kappa = 1, \eta = 2:$

$$X_{M0} = U_{M\nu_1-1}^{\pm} H_{M\nu_1-1}^{\pm} ,$$

$$X_{M5} = U_{M\nu_1+1}^{\pm} H_{M\nu_1+1}^{\pm} ,$$

$$X_{M4} = X_{M5} ,$$

$$X_{M3} = \tilde{U}_{M\nu_3}^{\pm} H_{M\nu_3}^{\pm} \tilde{U}_{M\nu_2}^{\pm} H_{M\nu_2}^{\pm} X_{M4} ,$$

$$X_{M2} = \tilde{U}_{M\nu_2}^{\pm} H_{M\nu_2}^{\pm} X_{M4} ,$$

$$X_{M1} = U_{M\nu_3+1}^{\pm} H_{M\nu_3+1}^{\pm} X_{M3} . \quad (3.20c)$$

Then $d_{\nu_1}(1), d_{\nu_1}(2), \dots, d_{\nu_1}(\sigma_1 - 1), d_{\nu_1}(\sigma_1 + 1), \dots, d_{\nu_1}(n)$

are found from the ν_1 th set of equations without the (ν_1, σ_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 $L_{M\nu}$ and $L'_{M\nu}$ by

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

and,

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

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

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

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

$$L'_{M\nu_i} = \pm \left[I - U_{M\nu_i-1}^{\pm} L'_{M\nu_i-1} \tilde{U}_{M\nu_i}^{\pm} \right]^{-1} , \quad i = 1, 2$$

$$L'_{M\nu_i+1} = \pm \left[I - \tilde{U}_{M\nu_i}^{\pm} L'_{M\nu_i} U_{M\nu_i+1}^{\pm} \right]^{-1} , \quad i = 1, 2$$

where $\tilde{U}_{M\nu_i}^{\pm}$ are defined as in Eqs. (3.19) in order to satisfy $t_{\nu_1}(\sigma_1) = 0$ and $t_{\nu_2}(\sigma_2) = 0$. Note that

$$L_{m\nu} = H_{m\nu}, \quad M \geq \nu \geq \nu_3 + 1$$

and

$$L'_{m\nu} = H'_{m\nu}, \quad -M \leq \nu \leq \nu_1 - 1.$$

Defining Z_i ($i = 1, \dots, 6$) by

$$t_{m\nu_3+1} = Z_1 t_{m\nu_3},$$

$$t_{m\nu_3-1} = Z_2 t_{m\nu_3},$$

$$t_{m\nu_2+1} = Z_3 t_{m\nu_3},$$

$$t_{m\nu_2-1} = Z_4 t_{m\nu_3},$$

$$t_{m\nu_1+1} = Z_5 t_{m\nu_3},$$

$$t_{m\nu_1-1} = Z_6 t_{m\nu_3},$$

for case $\kappa \geq 2, \eta \geq 2$, we obtain

$$Z_1 = U_{m\nu_3+1}^+ L_{m\nu_3+1},$$

$$Z_2 = U_{m\nu_3-1}^+ L'_{m\nu_3-1},$$

$$Z_3 = U_{m\nu_2+1}^+ L'_{m\nu_2+1} \tilde{U}_{m\nu_2}^+ L'_{m\nu_2} \cdots U_{m\nu_3-1}^+ L'_{m\nu_3-1},$$

$$Z_4 = U_{m\nu_2-1}^+ L'_{m\nu_2-1} \tilde{U}_{m\nu_2}^+ L'_{m\nu_2} Z_3,$$

$$Z_5 = U_{m\nu_1+1}^+ L'_{m\nu_1+1} \cdots Z_4,$$

$$Z_6 = U_{m\nu_1-1}^+ L'_{m\nu_1-1} \tilde{U}_{m\nu_1}^+ L'_{m\nu_1} Z_5;$$

for case $\kappa = 1; \eta = 2$:

$$Z_1 = U_{m\nu_3+1}^+ L_{m\nu_3+1},$$

$$Z_2 = \tilde{U}_{m\nu_2}^+ L'_{m\nu_2},$$

$$Z_3 = I_m,$$

$$Z_4 = U_{m\nu_2-1}^+ L'_{m\nu_2-1} Z_2,$$

$$Z_5 = Z_4,$$

$$Z_6 = U_{m\nu_1-1}^+ L'_{m\nu_1-1} \tilde{U}_{m\nu_1}^+ L'_{m\nu_1} Z_5. \quad (3.21)$$

Thus all t_{ν} 's are expressed in terms of $t_{m\nu_3}$. But $t_{\nu_3}(\sigma_3) = 1$ while $t_{\nu_3}(1), t_{\nu_3}(2), \dots, t_{\nu_3}(\sigma_3 - 1), t_{\nu_3}(\sigma_3 + 1), \dots, t_{\nu_3}(n)$ can be found by solving the $n - 1$ inhomogeneous equations labelled by $(\nu_3; 1, 2, \dots, \sigma_3 - 1, \sigma_3 + 1, \dots, n)$ as that leading to Eqs. (3.7).

004 4301275

To find $s_\nu(\alpha)$'s, we substitute $s_\nu(\alpha) a_{\nu_2}(\sigma_2)$ in place of $a_\nu(\alpha)$ into Eqs. (3.2). Defining $K_{\mu\nu}$ and $K'_{\mu\nu}$ by

$$s_{\mu\nu} \equiv U_{\mu\nu}^\pm K_{\mu\nu} s_{\mu\nu-1}, \quad \nu > \nu_2$$

and

$$s_{\mu\nu} = U_{\mu\nu}^\pm K'_{\mu\nu} s_{\mu\nu+1}, \quad \nu < \nu_2$$

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

$$K_{\mu\nu} = H_{\mu\nu}, \quad M \geq \nu \geq \nu_2 + 1$$

$$K'_{\mu\nu} = L'_{\mu\nu}, \quad -M \leq \nu \leq \nu_2 - 1.$$

Again defining Y_i , $i = 1, 2, \dots, 6$, by

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

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

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

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

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

$$s_{\mu\nu-1} = Y_{\mu 6} s_{\mu\nu}.$$

For case $\kappa \geq 2$, $\eta \geq 2$, we obtain

$$Y_{\mu 3} = U_{\mu\nu+1}^\pm K_{\mu\nu+1},$$

$$Y_{\mu 2} = U_{\mu\nu-1}^\pm K_{\mu\nu-1} \cdots U_{\mu\nu+1}^\pm K_{\mu\nu+1},$$

$$Y_{\mu 1} = U_{\mu\nu+1}^\pm K_{\mu\nu+1} \tilde{U}_{\mu\nu+1}^\pm K_{\mu\nu+1} Y_{\mu 2},$$

$$Y_{\mu 4} = U_{\mu\nu-1}^\pm K'_{\mu\nu-1},$$

$$Y_{\mu 5} = U_{\mu\nu+1}^\pm K'_{\mu\nu+1} \cdots U_{\mu\nu-1}^\pm K'_{\mu\nu-1},$$

$$Y_{\mu 6} = U_{\mu\nu-1}^\pm K'_{\mu\nu-1} \tilde{U}_{\mu\nu-1}^\pm K'_{\mu\nu-1} Y_{\mu 5};$$

and for case $\kappa = 1$, $\eta = 2$:

$$Y_{\mu 3} = \tilde{U}_{\mu\nu}^\pm K_{\mu\nu},$$

$$Y_{\mu 2} = I_{\mu\nu},$$

$$Y_{\mu 1} = U_{\mu\nu+1}^\pm K_{\mu\nu+1} \tilde{U}_{\mu\nu+1}^\pm K_{\mu\nu+1},$$

$$Y_{\mu 4} = U_{\mu\nu-1}^\pm K'_{\mu\nu-1},$$

$$Y_{\mu 5} = Y_{\mu 4},$$

$$Y_{\mu 6} = U_{\mu\nu-1}^\pm K'_{\mu\nu-1} \tilde{U}_{\mu\nu-1}^\pm K'_{\mu\nu-1} Y_{\mu 5}. \quad (3.22)$$

Again $s_{v_2}(1), s_{v_2}(2), \dots, s_{v_2}(\sigma_2 - 1), s_{v_2}(\sigma_2 + 1), \dots, s_{v_2}(n)$

are found from the $(v_2; 1, 2, \dots, \sigma_2 - 1, \sigma_2 + 1, \dots, n)$ 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 $(v_1, \sigma_1), (v_2, \sigma_2), (v_3, \sigma_3)$ 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

$$W'_{v_1}(\sigma_1) \equiv W_{v_1}(\sigma_1) + \Delta_1$$

$$W'_{v_2}(\sigma_2) \equiv W_{v_2}(\sigma_2) + \Delta_2$$

$$W'_{v_3}(\sigma_3) \equiv W_{v_3}(\sigma_3) + \Delta_3$$

and with the σ th component of a vector a denoted by $\{a\}_\sigma$,

$$\Delta_1 \equiv \left\{ G_{m \pm m_6 \pm m_5} (X_{m_6} \pm X_{m_5}) d_{m v_1} \right\}_{\sigma_1},$$

$$\Delta_2 \equiv \left\{ G_{m \pm m_4 \pm m_3} (Y_{m_4} \pm Y_{m_3}) s_{m v_2} \right\}_{\sigma_2},$$

Equation (3.23) continued next page

Equation (3.23) continued

$$\Delta_3 \equiv \left\{ G_{m \pm m_2 \pm m_1} (Z_{m_2} \pm Z_{m_1}) t_{m v_3} \right\}_{\sigma_3},$$

$$G_{12} \equiv - \left\{ G_{m \pm m_6 \pm m_5} (Y_{m_6} \pm Y_{m_5}) s_{m v_2} \right\}_{\sigma_1},$$

$$G_{13} \equiv - \left\{ G_{m \pm m_6 \pm m_5} (Z_{m_6} \pm Z_{m_5}) t_{m v_3} \right\}_{\sigma_1},$$

$$G_{21} \equiv - \left\{ G_{m \pm m_4 \pm m_3} (X_{m_4} \pm X_{m_3}) d_{m v_1} \right\}_{\sigma_2},$$

$$G_{23} \equiv - \left\{ G_{m \pm m_4 \pm m_3} (Z_{m_4} \pm Z_{m_3}) t_{m v_3} \right\}_{\sigma_2},$$

$$G_{31} \equiv - \left\{ G_{m \pm m_2 \pm m_1} (X_{m_2} \pm X_{m_1}) d_{m v_1} \right\}_{\sigma_3},$$

$$G_{32} \equiv - \left\{ G_{m \pm m_2 \pm m_1} (Y_{m_2} \pm Y_{m_1}) s_{m v_2} \right\}_{\sigma_3}. \quad (3.23)$$

The Δ '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 $G_{ij} \approx G_{ji}$. The characteristic equation is a cubic equation in E whose solution is well known. If we define

000 v 43.01276

$$p \equiv -W'_{v_1}(\sigma_1) - W'_{v_2}(\sigma_2) - W'_{v_3}(\sigma_3)$$

$$q \equiv W'_{v_1}(\sigma_1) W'_{v_2}(\sigma_2) + W'_{v_2}(\sigma_2) W'_{v_3}(\sigma_3) + W'_{v_3}(\sigma_3) W'_{v_1}(\sigma_1) \\ - G_{12}G_{21} - G_{23}G_{32} - G_{31}G_{13}$$

$$r \equiv -W'_{v_1}(\sigma_1) W'_{v_2}(\sigma_2) W'_{v_3}(\sigma_3) + G_{12} G_{21} W'_{v_3}(\sigma_3) \\ + G_{23} G_{32} W'_{v_1}(\sigma_1) + G_{13} G_{31} W'_{v_2}(\sigma_2) + G_{12} G_{23} G_{31} \\ + G_{13} G_{32} G_{21}$$

$$a \equiv \frac{1}{3} (3q - p^2)$$

$$b \equiv \left(\frac{1}{3}\right)^3 (2p^3 - 9pq + 27r)$$

$$\phi \equiv \frac{1}{3} \cos^{-1} \left(-\frac{b}{2} \left(-\frac{a}{3}\right)^{-3/2} \right)$$

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

$$b/2 \left(-\frac{a}{3}\right)^{3/2} \leq 0,$$

is satisfied, the three real roots are given by

$$E_1 \equiv 2 \left(-\frac{a}{3}\right)^{\frac{1}{2}} \cos^2 \phi$$

$$E_2 \equiv 2 \left(-\frac{a}{3}\right)^{\frac{1}{2}} \cos \left(\phi + \frac{2\pi}{3} \right)$$

$$E_3 \equiv 2 \left(-\frac{a}{3}\right)^{\frac{1}{2}} \cos \left(\phi - \frac{2\pi}{3} \right).$$

Any one of these equations can be used for iteration to find the adiabatic eigensolutions $(E_{v_i \sigma_i}, a^{v_i \sigma_i})$, $i = 1, 2, 3$. In the next section, we will consider nonadiabatic transition at the point where $E_2 - E_1$ and $E_3 - E_1$ are minimum as functions of $R(y)$.

IV. TRANSITION PROBABILITIES

In the previous section, we have solved the eigenvalue problem of Eqs. (2.7) in the adiabatic limit. Now we consider radiative transitions caused by the nonadiabatic relative motion of the atoms. Only transitions at the PC's (i.e., between near-resonant levels) need be considered while those between off-resonant levels are negligible.

A. Transition at A 2-Level PC

Suppose we consider the transition at the PC between levels labelled by $1 \equiv (v_1, \sigma_1)$ and $2 \equiv (v_2, \sigma_2)$. Only the probability amplitudes $b_1 \equiv b_{v_1}(\sigma_1)$ and $b_2 \equiv b_{v_2}(\sigma_2)$ will change significantly. Therefore we may approximate all other $b_{v_i}(\alpha)$'s in the (v_1, σ_1) and (v_2, σ_2) equations in Eqs. (2.7) with their adiabatic counterparts given in the last section. We may use those of E^M or of E^k . As will be shown below, the transition probability for formulae depend only on quantities evaluated at the point of closed approach of the PC.

At this point, the difference between E_{μ} and E_k (hence a^{μ} and a^k) is usually small and becomes smaller for lower intensity (see Eqs. (3.17)).⁹

Thus using Eqs. (3.0), (3.8), (3.13), and (3.15) in the Eqs. (2.7) with (v_1, σ_1) and (v_2, σ_2) , we obtain two coupled linear equations in b_i 's,

$$\begin{aligned} i \frac{db_1}{dy} - W_1' b_1 &= G b_2, \\ i \frac{db_2}{dy} - W_2' b_2 &= G b_1, \end{aligned} \quad (4.1)$$

where $G \equiv G_{12} = G_{21}$, $W_i' \equiv W_{v_i}'(\sigma_i)$, ($i = 1, 2$) 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), $b_2 \sim 0$ 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 time¹⁰

$$W_2' - W_1' \equiv -\alpha y \quad (4.2a)$$

with $y = 0$ chosen at the point of crossing of W_2' and W_1' ; and we ignore the small R-variation of G ,

$$\frac{dG}{dy} \approx 0. \quad (4.2b)$$

With these approximations, Eqs. (4.1) can be casted into the Weber's equation with well-known solutions.¹¹ The solution satisfying above boundary conditions is

$$b_2(y) = p^{\frac{1}{2}} e^{-\frac{\pi}{4}p} D_{-n-1}(\mp iz) e^{-i \int^y W_1' dy' + i \frac{\alpha}{4} y^2}, \quad \alpha \geq 0 \quad (4.3)$$

where $n \equiv iG^2/\alpha$, $p \equiv |n|$, $z \equiv y\alpha^{\frac{1}{2}} e^{-i\frac{\pi}{4}}$ and D is the parabolic cylinder function. For large and positive $|\alpha|^{\frac{1}{2}} y$, the transition probability is

$$|b_2|^2 \sim 1 - e^{-2\pi p}, \quad \alpha \geq 0. \quad (4.4)$$

This formula is useful if Eqs. (4.2) remain approximately satisfied into the asymptotic domain of $D_{-n-1}(\mp iz)$, 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 $\exp\left(-\frac{2}{3}\left(\frac{a^3}{b}\right)^{\frac{1}{2}}\right) \ll 1$.

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

00014301277

$$W_2' - W_1' = \begin{cases} a - by & y \leq 0 \\ a + b'y & y > 0 \end{cases}$$

where ($a \geq 0$; $b, b' > 0$) corresponds to case in Fig. 3b and ($a \leq 0$; $b, b' < 0$) corresponds to case in Fig. 3c. In the case (c), $a = 0$ corresponds to the situation when a PC occurs at a classical turning point.

The only drawback in the above approximation is the introduction of discontinuity of slope of $W_2' - W_1'$ at y . However, the advantage is that without further approximation, a transition probability formula can be obtained rigorously and is applicable even when $a = 0$.

We introduce, with $k_1 \equiv \int_0^y W_1'(y') dy'$,

$$b_2(y) = U(y) e^{-ik_1} e^{-i\frac{a}{2}y} \begin{cases} e^{i\frac{b}{4}y^2} \\ e^{-i\frac{b'}{4}y^2} \end{cases}, \text{ for } \begin{cases} y \leq 0 \\ y > 0 \end{cases}$$

into Eq. (4.3) and obtain

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

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

We need to find only the solution $U(y; |a|, |b|, |b'|)$; for the solution $U(y; -|a|, -|b|, -|b'|) = U^*(y, |a|, |b|, |b'|)$ as can be shown easily from the above equations.

Now with definitions

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

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

the above equations are reduced to the Weber's equations

$$\frac{d^2U(z_-)}{dz_-^2} + \left[n_- + \frac{1}{2} - \frac{z_-^2}{4} \right] U(z_-) = 0 \quad y \leq 0$$

$$\frac{d^2U(z_+)}{dz_+^2} + \left[n_+ + \frac{1}{2} - \frac{z_+^2}{4} \right] U(z_+) = 0 \quad y > 0$$

where

$$n_- \equiv ip, \quad n_+ \equiv ip' - 1,$$

$$p \equiv \frac{G^2}{b}, \quad p' \equiv \frac{G^2}{b'}.$$

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

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

A general solution for $y > 0$ 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_2 and of its slope at $y = 0$. We obtain

$$L = N' \left[(D_1/D_5) - (K_1/K_3) \right] / \left[(D_3/D_5) - (K_2/K_3) \right]$$

$$M = N' \left[(D_1/D_3) - (K_1/K_2) \right] / \left[(D_5/D_3) - (K_3/K_2) \right]$$

where

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

$$D_1 \equiv D_{-n_+-1} \left(\frac{a}{b^{\frac{1}{2}}} e^{i\frac{\pi}{4}} \right) ,$$

$$D_2 \equiv D_{-n_+-2} \left(\frac{a}{b^{\frac{1}{2}}} e^{i\frac{\pi}{4}} \right) ,$$

$$D_3 \equiv D_{-n_+-1} \left(\frac{a}{b^{\frac{1}{2}}} e^{-i\frac{3\pi}{4}} \right) ,$$

$$D_4 \equiv D_{-n_+-2} \left(\frac{a}{b^{\frac{1}{2}}} e^{-i\frac{3\pi}{4}} \right) ,$$

$$D_5 \equiv D_{n_+} \left(\frac{a}{b^{\frac{1}{2}}} e^{i\frac{3\pi}{4}} \right) ,$$

$$D_6 \equiv D_{n_+-1} \left(\frac{a}{b^{\frac{1}{2}}} e^{i\frac{3\pi}{4}} \right) ,$$

$$K_1 \equiv \frac{a}{2b^{\frac{1}{2}}} e^{i\frac{\pi}{2}} D_1 + (n_+ + 1) e^{i\frac{\pi}{4}} D_2 ,$$

$$K_2 \equiv \frac{a}{2b^{\frac{1}{2}}} e^{-i\frac{\pi}{2}} D_3 + (n_+ + 1) e^{i\frac{\pi}{4}} D_4 ,$$

$$K_3 \equiv \frac{a}{2b^{\frac{1}{2}}} e^{i\frac{\pi}{2}} D_5 + n_+ e^{i\frac{3\pi}{4}} D_6 .$$

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

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

from which the transition probability is

$$|b_2|^2 = \left| L e^{-\frac{3\pi}{4} p'} + M \frac{(2\pi)^{\frac{1}{2}}}{\Gamma(1 - ip')} e^{-\frac{\pi}{4} p'} \right|^2 . \quad (4.5)$$

In the derivation of the above asymptotic formula, nothing is required of the magnitude of $\frac{a}{b^{\frac{1}{2}}}$ and $\frac{a}{b}$. Usually in applications, we will be interested in $\frac{a}{b^{\frac{1}{2}}}$ and $\frac{a}{b}$ being not large. But from a

00004301278

mathematical viewpoint, let us consider the extreme case $\frac{a}{b^{\frac{1}{2}}} \gg 1$

and $\frac{a}{b^{\frac{1}{2}}} \gg 1$, then L and M can be simplified by asymptotic expansion of the D_i 's. The results are

$$L = N' \frac{(1 + (b/b')^{\frac{1}{2}})^{\frac{1}{2}} \Gamma(ip') e^{\frac{(p+p')\pi}{4}}}{(2\pi)^{\frac{1}{2}} (3 + e^{-\frac{\pi}{2}p'} / \sinh \pi p')}$$

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

and

$$M = N' \frac{(1 + (b/b')^{\frac{1}{2}})^{\frac{1}{2}} e^{\frac{\pi}{4}p + \frac{3\pi}{4}p'}}{2(1 + 3e^{\pi p'} \sinh \pi p')}$$

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

If furthermore p' is large, then

$$|b_2|^2 = \frac{1}{9} \left(1 + \left(\frac{b}{b'}\right)^{\frac{1}{2}}\right)^2 e^{-2\pi p'}$$

while for $p' \ll 1$

$$|b_2|^2 = \frac{\pi |G|^2 \left(1 + \left(\frac{b}{b'}\right)^{\frac{1}{2}}\right)^2}{8 b'}$$

We note that in the case $\frac{a}{b^{\frac{1}{2}}}$ and $\frac{a}{b^{\frac{1}{2}}} \gg 1$, 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 say between $v_1\sigma_1$, $v_2\sigma_2$, and $v_3\sigma_3$, as depicted in Fig. 2. Then the coupled equations similar to Eqs. (4.1), are

$$i \frac{d b_1}{dy} - W'_1 b_1 = G_{12} b_2 + G_{13} b_3$$

$$i \frac{d b_2}{dy} - W'_2 b_2 = G_{21} b_1 + G_{23} b_3 \quad (4.6)$$

$$i \frac{d b_3}{dy} - W'_3 b_3 = G_{31} b_1 + G_{32} b_2$$

where $b_i \equiv b_{v_i}(\sigma_i)$, $W'_i \equiv W'_{v_i}(\sigma_i)$, and the G_{ij} 's are all defined in Eqs. (3.23). The boundary conditions for y negative and of sufficient magnitude are $b_1 \sim \exp\left[-i \int^y W_1(y') dy'\right]$, $b_2 \sim 0$, $b_3 \sim 0$. A formal solution is

$$b_1 = e^{-iK_1(y)} - i e^{-iK_1(y)} \int_0^y dy' (G_{12} b_2 + G_{13} b_3) e^{iK_1(y')}$$

$$b_2 = -i e^{-iK_2(y)} \int_0^y dy' (G_{21} b_1 + G_{23} b_3) e^{iK_2(y')}$$

Equation (4.7) continued

$$b_3 = -i e^{-iK_3(y)} \int_0^y dy' (G_{31} b_1 + G_{32} b_2) e^{iK_3(y')} , \quad (4.7)$$

where $K_1(y) \equiv \int_0^y W_1(y') dy'$. 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

$$b_2^1 = -i e^{-iK_2(y)} \int_{-\infty}^y e^{iK_2(y')} G_{21} b_1^{1(2)} ,$$

$$b_1^{1(2)} = e^{-iK_1(y)} - i e^{-iK_1(y)} \int_{-\infty}^y e^{iK_1(y')} G_{12} b_2^1 ;$$

and the corresponding solutions for level 1 and 3 are

$$b_3^1 = -i e^{-iK_3(y)} \int_{-\infty}^y e^{iK_3(y')} G_{31} b_1^{1(3)} ,$$

$$b_1^{1(3)} = e^{-iK_1(y)} - i e^{-iK_1(y)} \int_{-\infty}^y e^{iK_1(y')} G_{13} b_3^1 .$$

Substitution of these expressions into the right-hand side of Eqs. (4.7)

gives

$$b_2(y) = b_2^1(y) - i e^{-iK_2(y)} \int_{-\infty}^y dy' e^{+iK_2(y')} G_{23} b_3^1(y') ,$$

$$b_3(y) = b_3^1(y) - i e^{-iK_3(y)} \int_{-\infty}^y dy' e^{iK_3(y')} G_{32} b_2^1(y') ,$$

$$b_1(y) = b_1^{1(2)} - i e^{-iK_1(y)} \int_{-\infty}^y dy' e^{iK_1(y')} G_{13} b_3^1(y') ,$$

$$\text{or } = b_1^{1(3)} - i e^{-iK_1(y)} \int_{-\infty}^y dy' e^{iK_1(y')} G_{12} b_2^1(y') .$$

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 $|\alpha_{21}|^{\frac{1}{2}} y$ and $|\alpha_{31}|^{\frac{1}{2}} y \gg 1$ 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 $\alpha_{21} < 0$, $\alpha_{31} < 0$, we obtain with $G_{ij} = G_{ji}$,

$$|b_2|^2 = 2\pi p_{21} + \pi \frac{|G_{23}|^2}{|\alpha_{31}|} + \Gamma_2 , \text{ to lowest order in } \left(|\alpha_{21}|^{\frac{1}{2}} y \right)^{-1}$$

000-4301279

$$|b_3|^2 = 2\pi p_{31} + \pi \frac{|G_{23}|^2}{|\alpha_{21}|} + \Gamma_3, \text{ to lowest order in } \left(|\alpha_{31}|^{\frac{1}{2}} y\right)^{-1}$$

where

$$\Gamma_2 \equiv 2^{3/2} \pi \frac{|G_{12}| |G_{23}|}{q_{21}^{\frac{1}{2}} q_{31}^{\frac{1}{2}}} \cos \left[\frac{\pi}{2} - p_{21} \ln q_{21}^{\frac{1}{2}} y + \frac{1}{2} p_{31} \ln \frac{q_{21}}{q_{31}} + \frac{p_{31}}{2} \right. \\ \left. - 0.577 p_{21} - \frac{1}{2} p_{31} \ln p_{31} \right]$$

$$\Gamma_3 \equiv 2^{3/2} \pi \frac{|G_{13}| |G_{23}|}{q_{31}^{\frac{1}{2}} q_{21}^{\frac{1}{2}}} \cos \left[\frac{\pi}{2} - p_{31} \ln q_{31}^{\frac{1}{2}} y + \frac{1}{2} p_{21} \ln \frac{q_{31}}{q_{21}} + \frac{p_{21}}{2} \right. \\ \left. - 0.577 p_{31} - \frac{1}{2} p_{21} \ln p_{21} \right]$$

where α_{ij} , p_{ij} , n_{ij} are defined as

$$W_i^! - W_j^! \equiv -\alpha_{ij} y,$$

$$n_{ij} \equiv i \frac{G_{ij}^2}{\alpha_{ij}},$$

$$q_{ij} \equiv |\alpha_{ij}|,$$

and

$$p_{ij} \equiv |n_{ij}|.$$

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 Γ_2 and Γ_3 . Therefore

$$|b_2|^2 = 2\pi p_{21} + (\pi |G_{23}|^2 / q_{31}),$$

$$|b_3|^2 = 2\pi p_{31} + (\pi |G_{23}|^2 / q_{21}). \quad (4.8)$$

These last two expressions are expected to be true also for other cases: $(\alpha_{21} > 0, \alpha_{31} \lesseqgtr 0)$, and $(\alpha_{21} > 0, \alpha_{31} < 0)$.

V. SLOW ATOMIC COLLISION IN AN INTENSE FIELD

The orbit of the relative motion of the two colliding atoms enters into our calculations through the $G_{\pm}(\alpha, \beta)$'s and dR/dt in the α 's in the transition formula Eqs. (4.4), (4.5), and (4.8). For the present application, it is convenient to express α_{ij} as

$$\alpha_{ij} = a_0 \frac{d}{dR} \left(\frac{W_i^! - W_j^!}{v} \right) \frac{dR}{dt}. \quad (5.1)$$

Since $W_i^! \propto v^{-1}$, and $G^2 \propto v^{-2}$, therefore p_{ij} is independent of the arbitrary v , as it should.

Recall that $G(\alpha, \beta) \propto (\phi_{\alpha}, \sum_i r_{\alpha i} \phi_{\beta})$ are usually evaluated with respect to the coordinates of the quasi-molecule ($\hat{i}, \hat{j}, \hat{k}$ in Fig. 4) while the linear polarization $\hat{\underline{\underline{\epsilon}}}$ is fixed in direction. Therefore for the geometry in Fig. 4, we need only to know $\hat{i} \cdot \hat{\underline{\underline{\epsilon}}}$ and $\hat{k} \cdot \hat{\underline{\underline{\epsilon}}}$ in order to find $G_{\pm}(\alpha, \beta)$.

For a given orbit, let R_0 denote the distance of closest approach between the two atoms. Let $\theta^-(R)$ and $\theta^+(R)$ denote respectively the value of θ at R before and after passing $(R_0, \theta(R_0))$. Then

$$\theta^+(R) = 2\theta(R_0) - \theta^-(R) .$$

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

$$\theta^-(R) = \theta_i + \int_{R_i}^R -b r^{-2} (1 - u(r)/\epsilon - b^2/r^2)^{-\frac{1}{2}} dr$$

where b is the impact parameter, ϵ 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

$$1 - (u(R_0)/\epsilon) - (b^2/R_0^2) = 0 .$$

In evaluating the radial velocity 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

$$\frac{dR}{dt} = v_\infty [1 - u'_1(R)/\epsilon - (b/R)^2]^{\frac{1}{2}}$$

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

Evaluation of cross section: for a given orbit defined by b and ϵ , 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

$$\sigma_i(\epsilon) = 2\pi \int_0^{b_{\max.}} db b P_{b,\epsilon}(i)$$

where b_{\max} is the maximum b value for which $P_{b,\epsilon}(i) \neq 0$ for a given ϵ .

We obtain $P_{b,\epsilon}(i)$ as follows. Suppose we have included n electronic states in our calculations. Suppose for a given orbit, there are N PC's at $Y_1, Y_2, Y_3, \dots, Y_N$. 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_ℓ , let $T_\ell(i,j)$ (where $i \neq j$) be the transition probability from electronic state j to i and is given by e.g., Eq. (4.4); and $T_\ell(i,i) \equiv 1 - \sum_{k \neq 1} T_\ell(k,i)$ be the probability of remaining in state i . We let $T_\ell(i,j) = T_\ell(j,i)$ for $i \neq j$. Let $Q_\ell(i) \equiv \sum_v |b_v(i)|^2$ be the probability that the quasi-molecule will be in the state i after passing the Y_ℓ - PC. Then

$$Q_{\ell} = T_{\ell} Q_{\ell-1}$$

and $P_{b,\epsilon} \equiv Q_N$ for the given orbit (b,ϵ) .

As example, we have considered the slow collision of Li with H in an intense radiation with $\lambda = 0.826\mu$ in the geometry of Fig. 4 for relative speed $v_\infty = 5 \times 10^5$ cm/sec. Values of $u_\alpha(R)$ and $(\phi_\alpha, \sum_i n_i \phi_\beta)$ for the lowest lying singlet states $X^1\Sigma^+$, $A^1\Sigma^+$, and $B^1\Pi$ are based on the values calculated by Docken and Hinze.¹² These three levels represent a fairly good approximation because according to the less accurate calculation of Bender and Davidson,¹³ the higher levels all lie at least about one-photon ($\hbar\omega \approx 1.5$ 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

000 4301280

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.,

$$\left(\int \chi_n^\alpha \chi_m^\beta dR \right) \left(\psi_\alpha(\bar{R}), \sum_i r_{i\alpha} \psi_\beta(\bar{R}) \right)$$

The $\psi_{\alpha,\beta}$ include nuclear rotational as well as electronic wavefunctions. Our treatment is good when $\int \chi_n^\alpha \chi_m^\beta dR \approx 1$.

A rough estimate of the integral $\int \chi_n^\alpha \chi_m^\beta dR$ can be obtained as follows. Since Coolidge, James, and Present¹⁴ have shown that it is an extremely good approximation in evaluating $\int \chi_n^\alpha \chi_m^\beta dR$ to

replace the repulsive eigenfunction χ^α with $\text{const. } \delta(R - R_c)$ where R_c is the classical turning point. Therefore assuming¹⁵ $\text{const.} \approx 1$, $\chi_m(R_c)$ 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_0 ,

$$\left(\frac{u\omega_0}{\pi\hbar} \right)^{\frac{1}{2}} \exp \left[-\frac{u\omega_0}{2\hbar} (R_c - R_0)^2 \right]$$

For our example below, this quantity is 1.3.

Consider the internuclear axis \hat{k} oriented at an angle ϕ 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

$$f \equiv 2T(1 - T)$$

where T is given if valid, e.g., Eq. (4.4). If $2\pi p$ is small, then $f = 2(2\pi p)$.

When the diatomic molecule irradiated has a permanent dipole moment \underline{d}_α (which is always either parallel or antiparallel to the internuclear axis) in the bound state ϕ_α , it will experience a torque to orient the \underline{d}_α parallel to $\hat{\epsilon}$. Therefore in the thermodynamical equilibrium situation, the thermal-averaged transition probability per oscillation would be

$$\bar{f} = \frac{\int_{-1}^1 d(\cos \phi) f(\phi) e^{-V(\phi)/kT}}{\int_{-1}^1 d(\cos \phi) e^{-V(\phi)/kT}}$$

where $V(\phi) = -\text{sgn}[\underline{d} \cdot \cos \phi \underline{\epsilon}_0]$, sgn being $+$ ($-$) if \underline{d} is parallel (antiparallel) to the given internuclear \hat{k} axis, and $\underline{\epsilon}_0 \equiv \left(\frac{2\pi}{c} I\right)^{\frac{1}{2}}$ 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 $\hat{\underline{\epsilon}}_0$. In such case,

$$\bar{f} = \frac{1}{2} \int_{-1}^1 d(\cos \phi) f(\phi) .$$

The averaged cross section for either process is then

$$\bar{\sigma} = \frac{\nu_0 \hbar \omega}{I} \bar{f}$$

where ν_0 is the vibrational frequency of the molecule in the bound state.

We have evaluated the averaged cross section for L_1H 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.¹⁶ Since the potential curve of Docken and Hinze for excited state $A^1\Sigma^+$ 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 $B^1\Pi$ 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_0 field is used to orient the molecule at an angle to ϕ to the electromagnetic field $\hat{\underline{\epsilon}}_0$ to optimize transition), we presented them for a few typical intensities in Table I. The cross sections for both thermal equilibrium ($T = 300^\circ \text{ K}$) 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,¹⁷ the theory is similar as before except now " h_R " is the hamiltonian for the atomic electrons and is not a function of R . Since ϕ_α are not parametrically dependent on $R(t)$ and have definite parities, therefore the last term and the term

000 4301281

$(\phi_\alpha, h' \phi_\alpha)$ in Eqs. (2.5) vanishes automatically. For the change of variable $y = \frac{vt}{a_0}$, we may choose $v = c$. 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 choice of the laser λ , one may get for example a PC (Fig. 7). Thus the nonadiabatic transition is due to the temporal variation in intensity of pulse, instead of the relative near-adiabatic motion of the colliding atoms in Sec. V.

Now α may be written as

$$\begin{aligned} \alpha &= - \frac{d(W'_{v_2}(\sigma_2) - W'_{v_1}(\sigma_1))}{dI} \frac{dI}{dt} \frac{dt}{dy} \\ &= - \frac{a_0}{v} \frac{d(W'_{v_2}(\sigma_2) - W'_{v_1}(\sigma_1))}{dI} \frac{dI}{dt} \end{aligned} \quad (7.1)$$

Since $W'_{v_2}(\sigma_2) - W'_{v_1}(\sigma_1) \propto \frac{1}{v}$, and $G^2 \propto \frac{1}{v^2}$, therefore the p's in the transition probability formulae are independent of the arbitrary v . The quantity dI/dt is the temporal slope of the pulse at the "critical intensity" I' at which the point of closest approach of the adiabatic eigenlevels occur. Thus through this quantity, the transition probability depends on the irradiating pulse.

The final transition probability per pulse peak, f , is given by

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

which has a maximum value of $\frac{1}{2}$ at $T = \frac{1}{2}$. From Eq. (4.4) and Eq. (7.1), this means that the temporal slope of pulse for optimum transition is

$$\left| \frac{dI}{dt} \right| = + \frac{2\pi}{(-\ln \frac{1}{2})} \delta$$

where

$$\delta \equiv G^2 \left/ \left| \frac{a_0}{v} \frac{d(W'_{v_2}(\sigma_2) - W'_{v_1}(\sigma_1))}{dI} \right| \right. \quad (7.2)$$

where all quantities are evaluated at I' .

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

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

where I' ($< I_0$) is the critical intensity. According to Eq. (7.2), for given δ and I' , there is a pair of optimum values (I'_0, τ') such that $f = \frac{1}{2}$. They are related by

$$\tau' = \frac{(-\ln \frac{1}{2}) I'}{\pi \delta} (\ln I'_0 - \ln I')^{\frac{1}{2}} \quad (7.3)$$

If δ is in atomic units, I' in watt/cm², τ' in sec, then

$$\tau' = 7.516 \times 10^{-23} \frac{(-\ln \frac{1}{2})'}{\pi} I' (\ln I'_0 - \ln I')^{\frac{1}{2}} / \delta .$$

The validity condition for applying the transition formulae, imposes restrictions on the pulse parameters (I'_0, τ) . For gaussian pulses, this validity condition can be expressed as

$$2.41 \times 10^5 \delta I' \tau \left(-\ln \frac{I'}{I'_0} \right)^{3/2} \gg 1 . \quad (7.4)$$

where δ are in atomic units, I', I'_0 in watts/cm² and τ in sec.

As examples, we have considered two atomic transitions: the transition from ground state 3s to 5s state of sodium atom via 2-photon absorption and the transition from the ground 2s state to the 3s state via 8-photon absorption. Since J_z and parity are good quantum numbers with respect to H, only states of the same m_j are coupled together. Therefore we need only to consider $m_j = \frac{1}{2}$ states.

In each case, we have included only 24 states ($m_j = \frac{1}{2}$). 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 $[G_{\pm}(\alpha, \beta)]$ which is a formal requirement in our solution to the adiabatic eigenvalue problem.

The energy levels are based on experimental spectral data.¹⁸ The magnitude of the dipole matrix elements are calculated from the oscillator strengths calculated by Anderson and Zilites¹⁹ and their

signs, from Bates and Damgaard.²⁰ However, we notice that with a different choice of phase of the wavefunctions, namely,

$$\phi'_{n\ell jm} \equiv (-1)^{n-\ell} \phi_{n\ell jm}$$

where $\phi_{n\ell jm}$ stands for the wavefunction used by Bates and Damgaard, then the dipole matrix elements $\langle n\ell s j m_j | \sum \mathbf{r}_i \cdot \hat{\mathbf{e}} | n'\ell's'j'm'_j \rangle$ have regularity (in relation to $n \leq n'$ or $n > n'$) in their sign pattern (Table II). This is useful in deciding a few ambiguous and unimportant elements that may be needed for inclusion in a calculation.

In the sodium case, the relative shifts in the 3s and 5s level can be explained qualitatively as follows: we choose wavelengths such that level separation between the 3s and 5s states are slightly less than 2-photon energy resonance (see Fig. 7). For the same wavelength, the 3p levels "push" the 3s level down much stronger than they "pull" the 5s level down, because $E_{3p} - \hbar\omega$ is more nearly in resonance with 3s than $E_{3p} + \hbar\omega$ with 5s. As the intensity is increased, the gap between level 5s and 3s becomes wider until a PC occurs at I' .

In the lithium case, we choose wavelengths such that the level separation of 2s and 3s states are "slightly larger" than the 8-photon energy. At these wavelengths, the 3p states "push" the 3s level down via first-order coupling while they "push" the 2s level down via ninth-order coupling. Hence 3s and 2s levels are shifted closer towards each other. At high enough intensity they hit the 8-photon resonance.

In both cases, we have considered a range of wavelengths with which the above qualitative pictures are valid. For a given

00004301282

wavelength, the "critical intensity" I' and the corresponding δ in Eq. (7.2) are tabulated in Table III. (See also Figs. 8 and 9.) The pairs of parameters (I'_0, τ') Eq. (7.3) of gaussian pulses are presented in Table IV for transition in sodium ($\lambda = 0.602396\mu$).

We have also calculated the final transition probabilities for a few nonoptimum gaussian pulses. Results for one such pulse ($I'_0 = 6.0 \times 10^8 \text{ W/cm}^2$, $\tau = 1 \text{ nsec}$) are presented in Table V. It is noticed from the Tables IV and V that at $\lambda = 0.602396\mu$ for the sodium case, we almost have the optimum gaussian pulse and the final transition is almost $\frac{1}{2}$. And for fixed I'_0 , f decreases as τ deviates from τ' (Fig. 10), so is the case for deviation from I'_0 for fixed τ' (Fig. 11). These shifts are also true for other λ 's as indicated in the figures.

ACKNOWLEDGMENT

The author is grateful to Professor K. M. Watson for suggesting the problem, his advice and support. He wishes also to thank Professor H. F. Schaefer for discussion on available potential curves and dipole matrix elements and for bringing the work in reference 12 to his attention; to thank Dr. C. K. Rhodes, Professor Y. R. Shen, Dr. R. Carman, and Dr. A. Schmidt for discussions on laser systems.

FOOTNOTES AND REFERENCES

- * This work was supported by the Air Force Office of Scientific Research, U. S. Air Force under Grant No. 74-2716 and by the U. S. Atomic Energy Commission.
1. An excellent brief review and list of references to earlier works are given by S. Swain, J. Phys. A5, 1587 (1972).
 2. N. Kroll and K. M. Watson, Institute for Defense Analyses, paper P-933 (February 1973).
 3. Although for simplicity they are referred to as atoms, one or both of the bound charged systems may be molecules. The collisional orbits would then be along potential surfaces.
 4. E. A. Power and S. Zienau, Phil. Trans. Roy. Soc. London 251, A427 (1959).
 5. When the dipole matrix element is zero, one is then interested in the electric quadrupole and/or magnetic dipole terms. In such case, all subsequent expressions remain the same except now the $G_{\pm}(\alpha, \beta)$ in Eqs. (2.7) are defined differently.
 6. V. N. Genkin and P. M. Mednes, Izv. VUZ. Radiofizika 10, 192 (1967) (Radiophysics and Quantum Electronics 10, 99 (1968)). The disadvantage of the h_{\pm} is mainly due to the factor $(u_{\alpha} - u_{\beta})/k\omega$ in the dipole matrix elements.
 7. See, for example, J. C. Y. Chen and K. M. Watson, Phys. Rev. 174, 152 (1968).
 8. Had we included the nuclear part of the molecular wavefunction in a full quantum treatment, the corresponding term between the same molecular states does not exist because of the selection rule $\Delta J = \pm 1$ of the nuclear rotational wavefunction.

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_{u, a_M^u}) or (E_{l, a_M^l}) usually runs from 0.01% for intensity 10^8 W/cm² to less than 5% for 10^{12} W/cm². 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} - 8×10^{11} W/cm². For such cases, we take the mean of the two values.
10. Detail analyses for the case of 2-level PC were given in reference 2 and C. Zener, Proc. Roy. Soc. London A137, 1696 (1932).
11. See, for example, E. T. Whittaker and G. N. Watson, Modern Analysis (Cambridge University Press, 1973), 4th ed., Chapter 16.
12. K. K. Docken and J. Hinze, J. Chem. Phys. 57, 4928 and 4936 (1972).
13. C. F. Bender and E. R. Davidson, J. Chem. Phys. 49, 4222 (1968).
14. A. S. Coolidge, H. M. James, and R. D. Present, J. Chem. Phys. 4, 193 (1936).
15. Compare, G. Herzberg, Spectra of Diatomic Molecules (Van Nostrand Reinhold Co., New York, 1950), 2nd ed., p. 393.
16. F. H. Crawford and T. Jorgensen, Jr., Phys. Rev. 49, 741 (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.

18. C. E. Moore, Atomic Energy Levels (U. S. National Bureau of Standards, 1971), Vol I.
19. E. M. Anderson and V. A. Zilitis, Opt. Spectrosc. 16, 99 and 211 (1964).
20. D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. London A242, 101 (1949).

00004301283

Table I. Photodissociation probability $f(\phi)$ per oscillation of LiH molecule in ground state by absorption of four ($\lambda = 1.0648\mu$) photons. ϕ is angular orientation of nuclear axis relative to the linear polarization vector of the radiation field.^a

ϕ (rad)	$f(\phi)/2$ at 10^9 W/cm ²	$f(\phi)/2$ at 5×10^9 W/cm ²	$f(\phi)/2$ at 10^{10} W/cm ²	$f(\phi)/2$ at 5×10^{10} W/cm ²	$f(\phi)/2$ at 10^{11} W/cm ²	$f(\phi)/2$ at 5×10^{11} W/cm ²
5.00000E-02	1.37E-21	8.56E-19	1.36E-17	8.54E-15	1.36E-13	8.40E-11
1.00000E-01	5.03E-21	3.14E-18	5.03E-17	3.14E-14	5.01E-13	3.06E-10
2.00000E-01	1.40E-20	8.75E-18	1.40E-16	8.71E-14	1.38E-12	8.34E-10
3.00000E-01	1.51E-20	9.43E-18	1.50E-16	9.35E-14	1.48E-12	8.95E-10
4.00000E-01	5.30E-21	3.31E-18	5.30E-17	3.30E-14	5.27E-13	3.21E-10
5.00000E-01	1.10E-21	6.87E-19	1.08E-17	6.44E-15	1.00E-13	4.90E-11
6.00000E-01	3.47E-20	2.16E-17	3.43E-16	2.09E-13	3.29E-12	1.76E-09
7.00000E-01	1.35E-19	8.42E-17	1.33E-15	8.18E-13	1.28E-11	6.77E-09
8.00000E-01	3.05E-19	1.89E-16	3.00E-15	1.84E-12	2.88E-11	1.48E-08
9.00000E-01	5.07E-19	3.14E-16	4.98E-15	3.05E-12	4.76E-11	2.37E-08
1.00000E+00	6.72E-19	4.16E-16	6.60E-15	4.04E-12	6.28E-11	3.03E-08
1.10000E+00	7.30E-19	4.51E-16	7.17E-15	4.37E-12	6.78E-11	1.44E-08
1.20000E+00	6.47E-19	4.00E-16	6.35E-15	3.87E-12	5.98E-11	1.16E-08
1.30000E+00	4.48E-19	2.76E-16	4.40E-15	2.67E-12	4.13E-11	7.53E-09
1.40000E+00	2.12E-19	1.31E-16	2.08E-15	1.26E-12	1.95E-11	3.39E-09
1.50000E+00	4.00E-20	2.47E-17	3.93E-16	2.38E-13	3.67E-12	6.23E-10
1.60000E+00	6.93E-21	4.27E-18	6.80E-17	4.13E-14	6.35E-13	1.07E-10
1.70000E+00	1.27E-19	7.87E-17	1.25E-15	7.60E-13	1.17E-11	2.01E-09
1.80000E+00	3.48E-19	2.15E-16	3.42E-15	2.08E-12	3.21E-11	5.72E-09
1.90000E+00	5.75E-19	3.55E-16	5.64E-15	3.43E-12	5.31E-11	1.00E-08

a) In all the tables, the number nEm means $n \times 10^m$.

Table I continued on next page.

Table I continued. Photodissociation probability $f(\phi)$ per oscillation of LiH molecule in ground state by absorption of four ($\lambda = 1.0648\mu$) photons. ϕ is angular orientation of nuclear axis relative to the linear polarization vector of the radiation field.^a

ϕ (rad)	$f(\phi)/2$ at 10^9 W/cm ²	$f(\phi)/2$ at 5×10^9 W/cm ²	$f(\phi)/2$ at 10^{10} W/cm ²	$f(\phi)/2$ at 5×10^{10} W/cm ²	$f(\phi)/2$ at 10^{11} W/cm ²	$f(\phi)/2$ at 5×10^{11} W/cm ²
2.00000E+00	7.13E-19	4.41E-16	7.00E-15	4.27E-12	6.61E-11	1.35E-08
2.10000E+00	7.12E-19	4.41E-16	7.00E-15	4.27E-12	6.64E-11	1.50E-08
2.20000E+00	5.85E-19	3.62E-16	5.74E-15	3.51E-12	5.48E-11	2.69E-08
2.30000E+00	3.89E-19	2.41E-16	3.82E-15	2.34E-12	3.66E-11	1.86E-08
2.40000E+00	1.99E-19	1.23E-16	1.96E-15	1.20E-12	1.88E-11	9.83E-09
2.50000E+00	6.75E-20	4.19E-17	6.67E-16	4.07E-13	6.40E-12	3.42E-09
2.60000E+00	8.49E-21	5.27E-18	8.38E-17	5.08E-14	7.98E-13	4.24E-10
2.70000E+00	1.24E-21	7.77E-19	1.24E-17	7.89E-15	1.26E-13	8.14E-11
2.80000E+00	1.18E-20	7.42E-18	1.18E-16	7.36E-14	1.17E-12	7.06E-10
2.90000E+00	1.59E-20	9.97E-18	1.59E-16	9.90E-14	1.57E-12	9.48E-10
3.00000E+00	8.99E-21	5.61E-18	8.98E-17	5.59E-14	8.92E-13	5.41E-10
3.10000E+00	9.56E-22	5.97E-19	9.55E-18	5.96E-15	9.52E-14	5.86E-11
3.12500E+00	1.54E-22	9.66E-20	1.54E-18	9.64E-16	1.54E-14	9.50E-12
3.14159E+00	3.96E-30	2.47E-27	3.96E-26	2.47E-23	3.95E-22	2.43E-19

a) in all the tables the number nEm means $n \times 10^m$.

Table II(a). Dipole matrix elements $\langle n'l'sjm_j | \sum_{i=1}^2 \mathbf{r}_i \cdot \hat{\mathbf{e}} | n'l's'j'm'_j \rangle$ ($m'_j = m_j = \frac{1}{2}$) of 24 states of sodium atom.

$n'l'j'$ nlj	$3p_{\frac{1}{2}}$	$3p_{\frac{3}{2}}$	$4p_{\frac{1}{2}}$	$4p_{\frac{3}{2}}$	$5p_{\frac{1}{2}}$	$5p_{\frac{3}{2}}$
$3s_{\frac{1}{2}}$	-1.455E + 0	-2.057E + 0	-1.310E - 1	-1.852E - 1	-4.803E - 2	-6.792E - 2
$4s_{\frac{1}{2}}$	1.428E + 0	2.019E + 0	-3.301E + 0	-4.669E + 0	-3.891E - 1	-5.502E - 1
$5s_{\frac{1}{2}}$	3.043E - 1	4.304E - 1	3.420E + 0	4.839E + 0	-6.111E + 0	-8.642E + 0
$6s_{\frac{1}{2}}$	1.571E - 1	2.222E - 1	6.459E - 1	9.135E - 1	6.114E + 0	8.647E + 0
$7s_{\frac{1}{2}}$	1.024E - 1	1.448E - 1	3.217E - 1	4.549E - 1	1.084E + 0	1.533E + 0
$8s_{\frac{1}{2}}$	7.452E - 2	1.054E - 1	2.071E - 1	2.929E - 1	5.260E - 1	7.439E - 1
$n'l'j'$ nlj	$3d_{\frac{3}{2}}$	$3d_{\frac{5}{2}}$	$4d_{\frac{3}{2}}$	$4d_{\frac{5}{2}}$	$5d_{\frac{3}{2}}$	$5d_{\frac{5}{2}}$
$3p_{\frac{1}{2}}$	-2.731E + 0	0.0	-8.134E - 1	0.0	-4.123E - 1	0.0
$3p_{\frac{3}{2}}$	-3.863E - 1	-2.838E + 0	-1.150E - 1	-8.453E - 1	-5.831E - 2	-4.285E - 1
$4p_{\frac{1}{2}}$	4.415E + 0	0.0	-4.831E + 0	0.0	-1.517E + 0	0.0

-67-

Table II(a) continued. Dipole matrix elements $\langle n'l'sjm_j | \sum_{i=1}^2 \mathbf{r}_i \cdot \hat{\mathbf{e}} | n'l's'j'm'_j \rangle$ ($m'_j = m_j = \frac{1}{2}$) of 24 states of sodium atom.

$n'l'j'$ nlj	$3d_{\frac{3}{2}}$	$3d_{\frac{5}{2}}$	$4d_{\frac{3}{2}}$	$4d_{\frac{5}{2}}$	$5d_{\frac{3}{2}}$	$5d_{\frac{5}{2}}$
$4p_{\frac{3}{2}}$	6.244E - 1	4.588E + 0	-6.832E - 1	-5.021E + 0	-2.146E - 1	-1.577E + 0
$5p_{\frac{1}{2}}$	7.222E - 2	0.0	9.219E + 0	0.0	-7.600E + 0	0.0
$5p_{\frac{3}{2}}$	1.021E - 2	7.506E - 2	1.309E + 0	9.581E + 0	-1.075E + 0	-7.898E + 0
$n'l'j'$ nlj	$4f_{\frac{7}{2}}$	$4f_{\frac{5}{2}}$	$5f_{\frac{7}{2}}$	$5f_{\frac{5}{2}}$	$6f_{\frac{7}{2}}$	$6f_{\frac{5}{2}}$
$3d_{\frac{3}{2}}$	0.0	4.928E + 0	0.0	1.629E + 0	0.0	8.884E - 1
$3d_{\frac{5}{2}}$	6.346E + 0	2.874E - 1	2.098E + 0	9.504E - 2	1.144E + 0	5.181E - 2
$4d_{\frac{3}{2}}$	0.0	-7.799E + 0	0.0	6.718E + 0	0.0	2.515E + 0
$4d_{\frac{5}{2}}$	-1.004E + 1	-4.548E - 1	8.651E + 0	3.918E - 1	3.238E + 0	1.467E - 1
$5d_{\frac{3}{2}}$	0.0	8.861E - 1	0.0	-1.473E + 1	0.0	8.818E + 0
$5d_{\frac{5}{2}}$	1.141E + 0	5.168E - 2	-1.897E + 1	-8.592E - 1	1.130E + 1	5.143E - 1

-68-

Table II(b). Dipole matrix elements $\langle n'l'sjm_j | \sum_{i=1}^n r_i \hat{\epsilon} | n'l's'j'm'_j \rangle$ (with $m'_j = m_j = \frac{1}{2}$) of 24 states of lithium atom.

$n'l'j'$ nlj	$2p_{\frac{1}{2}}$	$2p_{\frac{3}{2}}$	$3p_{\frac{1}{2}}$	$3p_{\frac{3}{2}}$	$4p_{\frac{1}{2}}$	$4p_{\frac{3}{2}}$
$2s_{\frac{1}{2}}$	-1.359E + 0	-1.922E + 0	8.080E - 2	1.142E - 1	6.938E - 2	9.812E - 2
$3s_{\frac{1}{2}}$	1.012E + 0	1.432E + 0	-3.478E + 0	-4.918E + 0	-2.760E - 2	-3.904E - 2
$4s_{\frac{1}{2}}$	2.611E - 1	3.693E - 1	2.447E + 0	3.460E + 0	-6.395E + 0	-9.045E + 0
$5s_{\frac{1}{2}}$	1.403E - 1	1.984E - 1	6.148E - 1	8.694E - 1	4.482E + 0	6.338E + 0
$6s_{\frac{1}{2}}$	9.307E - 2	1.316E - 1	3.253E - 1	4.600E - 1	1.077E + 0	1.523E + 0
$7s_{\frac{1}{2}}$	6.846E - 2	9.682E - 2	2.150E - 1	3.041E - 1	5.674E - 1	8.025E - 1
$n'l'j'$ nlj	$3d_{\frac{3}{2}}$	$3d_{\frac{5}{2}}$	$4d_{\frac{3}{2}}$	$4d_{\frac{5}{2}}$	$5d_{\frac{3}{2}}$	$5d_{\frac{5}{2}}$
$2p_{\frac{1}{2}}$	2.114E + 0	0.0	7.851E - 1	0.0	4.533E - 1	0.0
$2p_{\frac{3}{2}}$	2.989E - 1	2.196E + 0	1.110E - 1	8.159E - 1	6.410E - 2	4.711E - 1
$3p_{\frac{1}{2}}$	-4.774E + 0	-0.0	3.185E + 0	0.0	1.311E + 0	0.0

Table II(b) continued next page

Table II(b) continued. Dipole matrix elements $\langle n'l'sjm_j | \sum_{i=1}^n r_i \hat{\epsilon} | n'l's'j'm'_j \rangle$ (with $m'_j = m_j = \frac{1}{2}$) of 24 states of lithium atom.

$n'l'j'$ nlj	$3d_{\frac{3}{2}}$	$3d_{\frac{5}{2}}$	$4d_{\frac{3}{2}}$	$4d_{\frac{5}{2}}$	$5d_{\frac{3}{2}}$	$5d_{\frac{5}{2}}$
$3p_{\frac{3}{2}}$	-6.751E - 1	-4.961E + 0	4.505E - 1	3.310E + 0	1.854E - 1	1.362E + 0
$4p_{\frac{1}{2}}$	8.055E - 1	0.0	-9.813E + 0	0.0	4.544E + 0	0.0
$4p_{\frac{3}{2}}$	1.139E - 1	8.371E - 1	-1.387E + 0	-1.019E + 1	6.426E - 1	4.722E + 0
$n'l'j'$ nlj	$4f_{\frac{7}{2}}$	$4f_{\frac{5}{2}}$	$5f_{\frac{7}{2}}$	$5f_{\frac{5}{2}}$	$6f_{\frac{7}{2}}$	$6f_{\frac{5}{2}}$
$3d_{\frac{3}{2}}$	0.0	4.987E + 0	0.0	1.636E + 0	0.0	8.721E - 1
$3d_{\frac{5}{2}}$	6.422E + 0	2.908E - 1	2.106E + 0	9.542E - 2	1.123E + 0	5.086E - 2
$4d_{\frac{3}{2}}$	0.0	-7.781E + 0	0.0	6.826E + 0	0.0	2.539E + 0
$4d_{\frac{5}{2}}$	-1.002E + 1	-4.538E - 1	8.790E + 0	3.981E - 1	3.270E + 0	1.481E - 1
$5d_{\frac{3}{2}}$	0.0	8.304E - 1	0.0	-1.479E + 1	0.0	9.053E + 0
$5d_{\frac{5}{2}}$	1.069E + 0	4.843E - 2	-1.905E + 1	-8.629E - 1	1.165E + 1	5.279E - 1

Table III. Values of critical intensity (I') and pulse-independent factor (δ) in Eq. (7.2) for wavelengths (λ) considered in (a) 2-photon transition in sodium ($3s \rightarrow 5s$); and (b) 8-photon transition in lithium ($2s \rightarrow 3s$).

(a) Na			(b) Li		
$\lambda(\mu)$	$I'(W/cm^2)$	$\delta(a,u)$	$\lambda(\mu)$	$I'(W/cm^2)$	$\delta(a,u)$
6.02396E-01	1.00E+07	1.851E-17	2.94060E+00	1.90E+07	3.414E-49
6.02395E-01	1.74E+07	5.605E-17	2.94075E+00	5.30E+07	1.264E-45
6.02394E-01	2.55E+07	1.204E-16	2.94100E+00	1.10E+08	4.421E-43
6.02393E-01	3.32E+07	2.041E-16	2.94150E+00	2.30E+08	1.658E-40
6.02392E-01	4.00E+07	2.962E-16	2.94200E+00	3.50E+08	4.920E-39
6.02391E-01	4.85E+07	4.355E-16	2.94250E+00	4.70E+08	5.487E-38
6.02390E-01	5.50E+07	5.601E-16	2.94300E+00	6.00E+08	3.656E-37
6.02389E-01	6.50E+07	7.824E-16	2.94350E+00	7.30E+08	1.951E-36
6.02387E-01	8.00E+07	1.185E-15	2.94400E+00	8.65E+08	7.714E-36
6.02385E-01	9.50E+07	1.671E-15	2.94450E+00	1.00E+09	2.560E-35
6.02380E-01	1.35E+08	3.375E-15	2.94500E+00	1.14E+09	7.443E-35
6.02375E-01	1.70E+08	5.354E-15			
6.02370E-01	2.10E+08	8.171E-15			
6.02365E-01	2.50E+08	1.158E-14			
6.02360E-01	2.90E+08	1.558E-14			
6.02355E-01	3.30E+08	2.018E-14			
6.02350E-01	3.75E+08	2.606E-14			
6.02340E-01	4.50E+08	3.754E-14			
6.02330E-01	5.25E+08	5.111E-14			

Table IV. Pair of optimum parameters (I'_0, τ') of gaussian pulses for the 2-photon transition ($3s \rightarrow 5s$) in sodium at $\lambda = 0.602396\mu$. The third column indicates how well the corresponding validity condition Eq. (7.4) is satisfied.

I'_0 (W/cm^2)	τ' (sec)	Validity	I'_0 (W/cm^2)	τ' (sec)	Validity
2.0E + 07	3.728E - 10	4.8E + 00	6.0E + 08	9.061E - 10	1.7E + 02
3.0E + 07	4.693E - 10	1.2E + 01	8.0E + 08	9.374E - 10	1.9E + 02
4.0E + 07	5.272E - 10	1.9E + 01	1.0E + 09	9.610E - 10	2.1E + 02
5.0E + 07	5.681E - 10	2.6E + 01	1.5E + 09	1.002E - 09	2.5E + 02
6.0E + 07	5.994E - 10	3.2E + 01	2.0E + 09	1.030E - 09	2.8E + 02
8.0E + 07	6.457E - 10	4.3E + 01	2.5E + 09	1.052E - 09	3.1E + 02
1.0E + 08	6.795E - 10	5.3E + 01	3.0E + 09	1.069E - 09	3.3E + 02
1.5E + 08	7.369E - 10	7.4E + 01	4.0E + 09	1.096E - 09	3.6E + 02
2.0E + 08	7.751E - 10	9.1E + 01	5.0E + 09	1.116E - 09	3.9E + 02
2.5E + 08	8.034E - 10	1.0E + 02	6.0E + 09	1.132E - 09	4.1E + 02
3.0E + 08	8.258E - 10	1.1E + 02	8.0E + 09	1.157E - 09	4.5E + 02
4.0E + 08	8.601E - 10	1.3E + 02	1.0E + 10	1.176E - 09	4.8E + 02
5.0E + 08	8.857E - 10	1.5E + 02			

000 4301285

Table V. Transition probability per pulse (f) in sodium ($3s \rightarrow 5s$ via 2-photon absorption) at various wavelengths (λ) for the input gaussian pulse ($I_0 = 6 \times 10^8 \text{ W/cm}^2$; $\tau = 1 \text{ nsec.}$) which is nearly optimum for $\lambda = 0.602396\mu$. I' is the critical intensity; T is transition probability at the PC; and the last column is the validity condition Eq. (7.4).

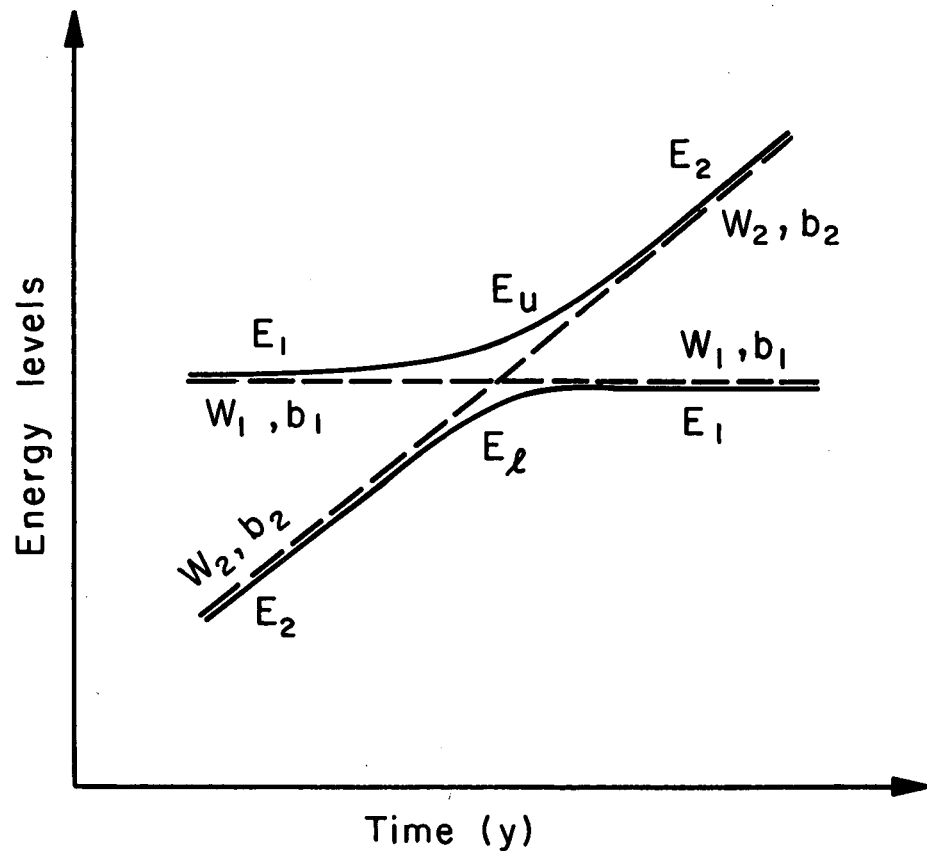
$\lambda(\mu)$	$I'(\text{W/cm}^2)$	T	f	Validity
6.023960E - 01	1.00E + 07	5.346374E - 01	4.976004E - 01	1.8E + 02
6.023950E - 01	1.74E + 07	7.610197E - 01	3.637373E - 01	2.6E + 02
6.023940E - 01	2.55E + 07	8.915052E - 01	1.934473E - 01	3.2E + 02
6.023930E - 01	3.32E + 07	9.512349E - 01	9.277402E - 02	3.7E + 02
6.023920E - 01	4.00E + 07	9.767802E - 01	4.536125E - 02	4.0E + 02
6.023910E - 01	4.85E + 07	9.912079E - 01	1.742953E - 02	4.3E + 02
6.023900E - 01	5.50E + 07	9.959459E - 01	8.075151E - 03	4.6E + 02
6.023890E - 01	6.50E + 07	9.988287E - 01	2.339773E - 03	4.8E + 02
6.023870E - 01	8.00E + 07	9.998375E - 01	3.247668E - 04	5.1E + 02
6.023850E - 01	9.50E + 07	9.999802E - 01	3.942951E - 05	5.3E + 02
6.023800E - 01	1.35E + 08	9.999999E - 01	7.376713E - 08	5.5E + 02
6.023750E - 01	1.70E + 08	9.999999E - 01	1.315072E - 10	5.4E + 02
6.023700E - 01	2.10E + 08	9.999999E - 01	4.263256E - 14	5.1E + 02
6.023650E - 01	2.50E + 08	9.999999E - 01	1.421085E - 14	4.6E + 02
6.023600E - 01	2.90E + 08	9.999999E - 01	1.421085E - 14	4.0E + 02
6.023550E - 01	3.30E + 08	1.000000E + 00	0.	3.4E + 02
6.023500E - 01	3.75E + 08	1.000000E + 00	0.	2.7E + 02
6.023400E - 01	4.50E + 08	1.000000E + 00	0.	1.5E + 02
6.023300E - 01	5.25E + 08	1.000000E + 00	0.	5.7E + 01

FIGURE CAPTIONS

- Fig. 1. A two-level pseudocrossing between levels $1 \equiv (v_1, \sigma_1)$ and $2 \equiv (v_2, \sigma_2)$. --- Noninteracting eigenlevels W_1 , — adiabatic eigenlevels. b_1 is the probability amplitude that the photon-electron system is in state 1.
- 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. $\hat{\epsilon}$ is the linear polarization vector and \hat{k} is the internuclear axis.
- Fig. 5. Cross section of Li and H collision as function of intensity of the radiation field ($\lambda = 0.826\mu$); $v(R = \infty) = 5 \times 10^5 \text{ cm/sec.}$
- Fig. 6. Photodissociation cross section of LiH molecules at thermal equilibrium ($T = 300^\circ \text{ K}$) as a function of field intensity. The dissociative transition is from the ground state of the molecule to $B^1\Pi$ by absorption of four photons ($\lambda = 1.0648\mu$).
- Fig. 7. Illustration of the atomic energy level shifts as a function of the pulse intensity, resulting in a pseudocrossing (PC) between the shifted levels W_2' and W_1' at the critical intensity I' . For the $3s \rightarrow 5s$ 2-photon transition of sodium, $W_2 \equiv W_2(5s)$, $W_1 \equiv W_0(3s)$ in the notations of the text.
- Fig. 8. Critical intensity at which PC occurs vs wavelength for 2-photon transition from $3s$ to $5s$ state of sodium.
- Fig. 9. Critical intensity at which PC occurs vs wavelength for 8-photon transition from $2s$ to $3s$ 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 ($6 \times 10^8 \text{ W/cm}^2$) but different temporal pulse widths.

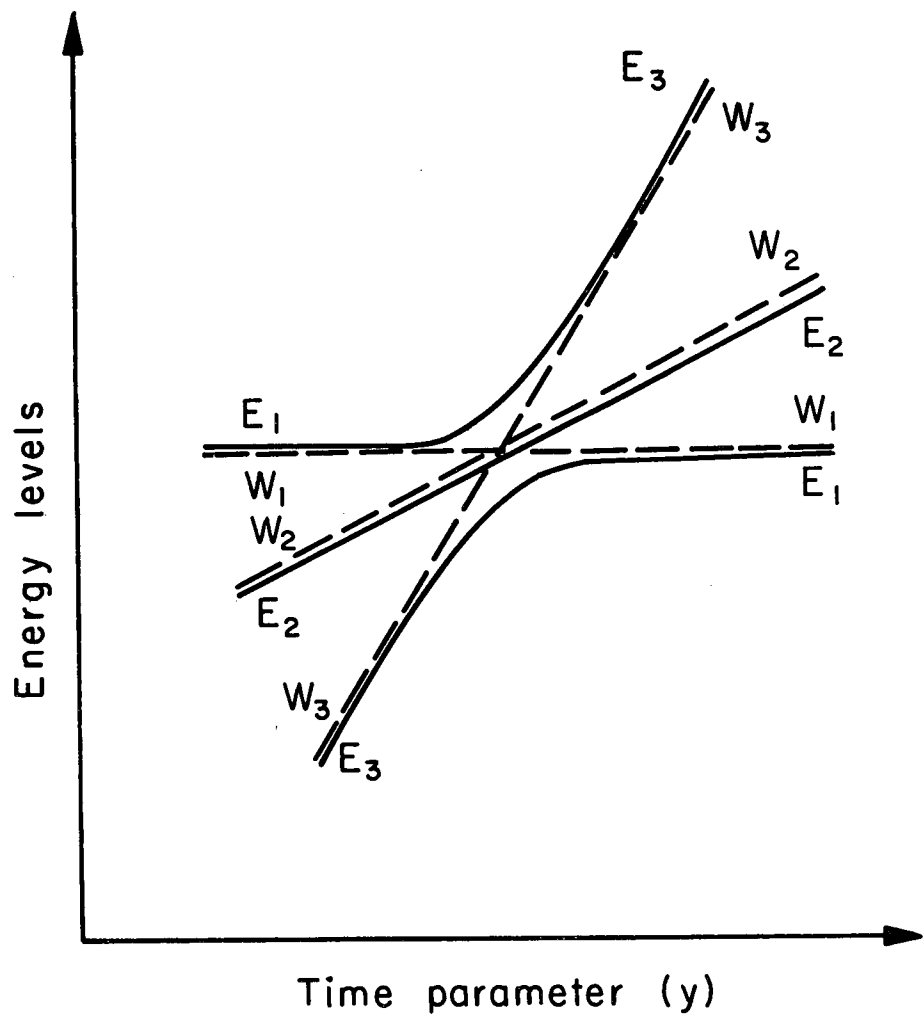
Fig. 11. Transition probability per pulse, f , in the sodium case at several wavelengths for a few input 1-nsec. Gaussian pulses of different peak intensities.



XBL 751-2196

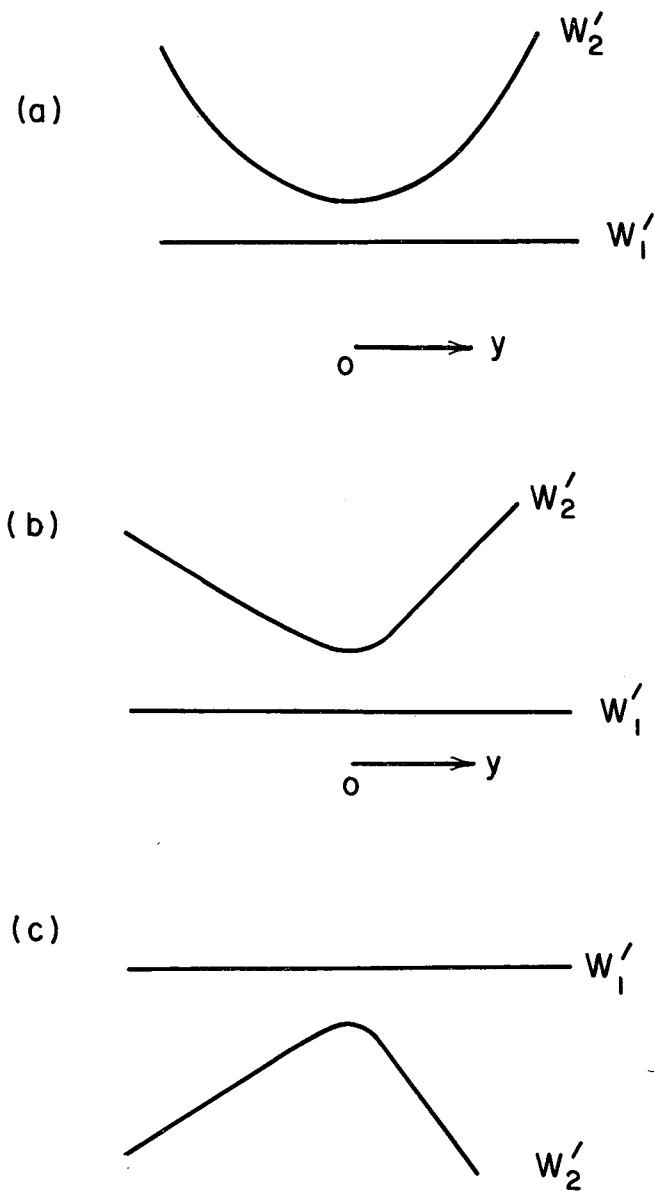
Fig. 1

000-4301286



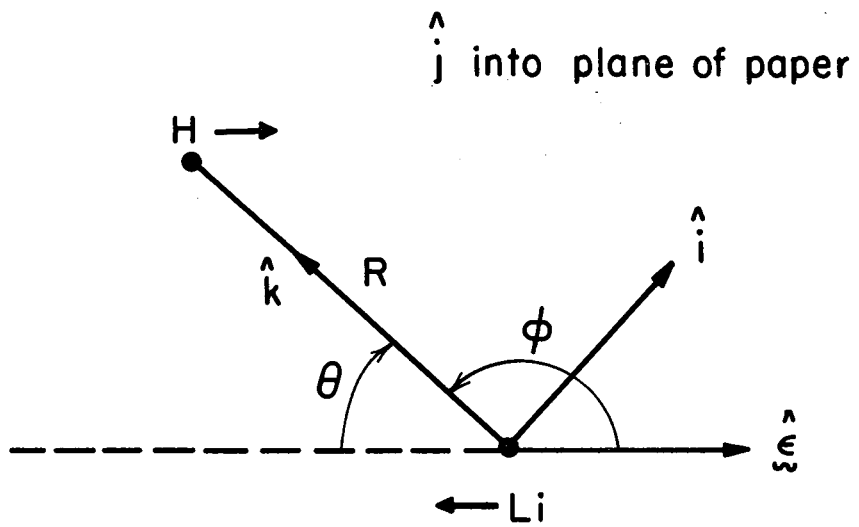
XBL751-2197

Fig. 2



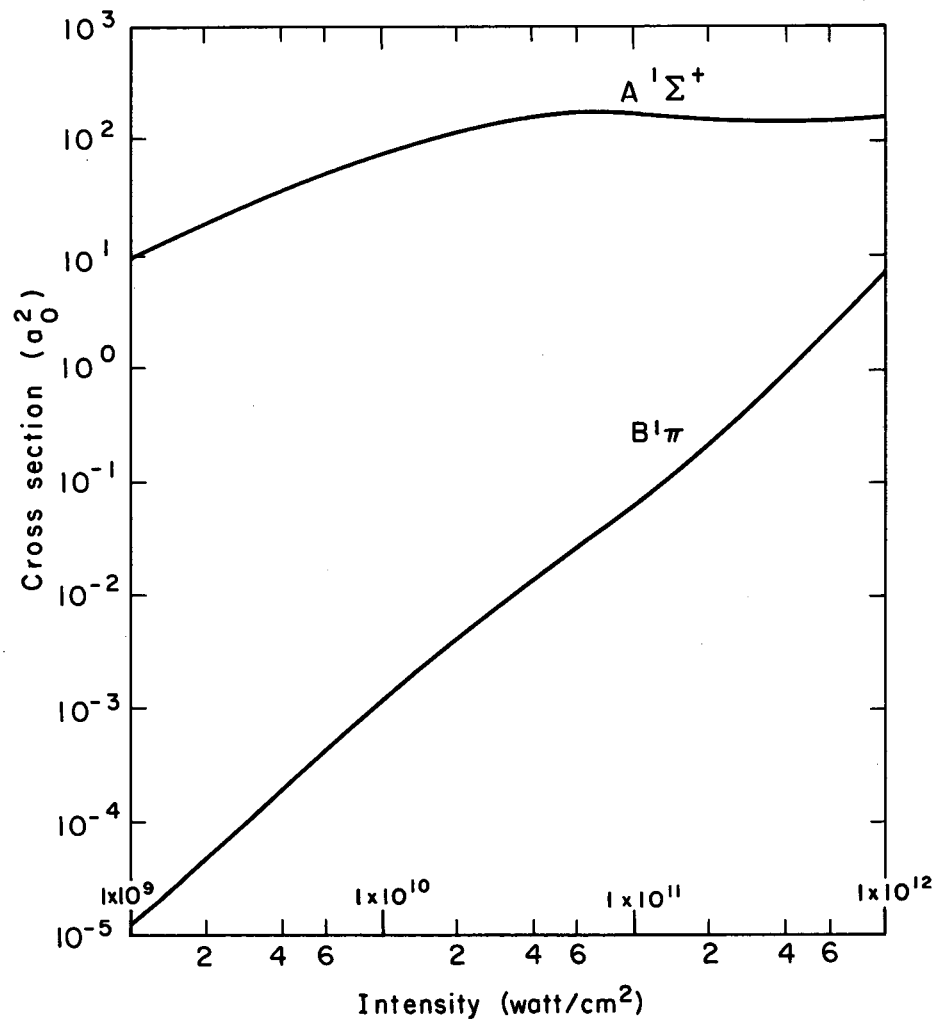
XBL751-2198

Fig. 3



XBL751-2199

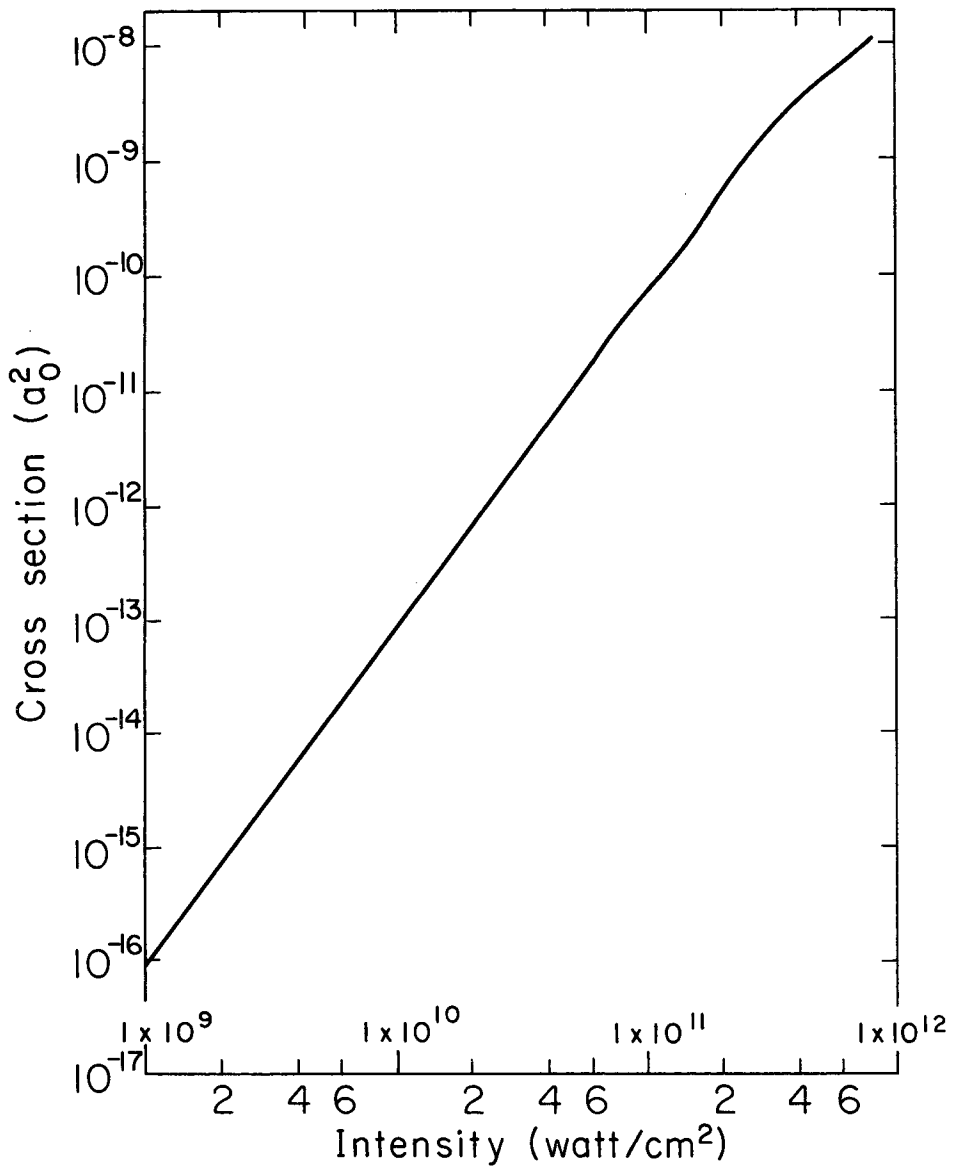
Fig. 4



XBL751-2195

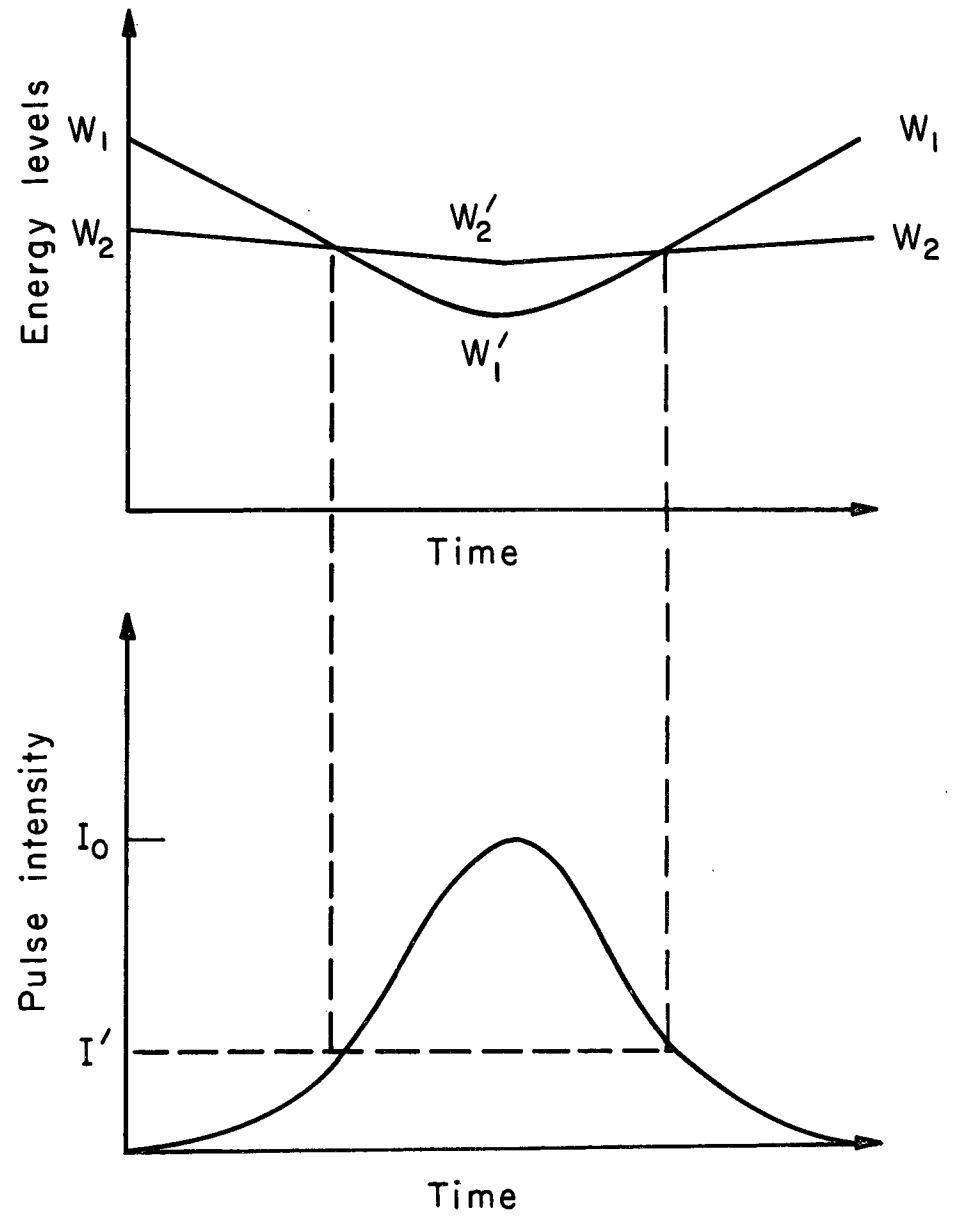
Fig. 5

00004301287



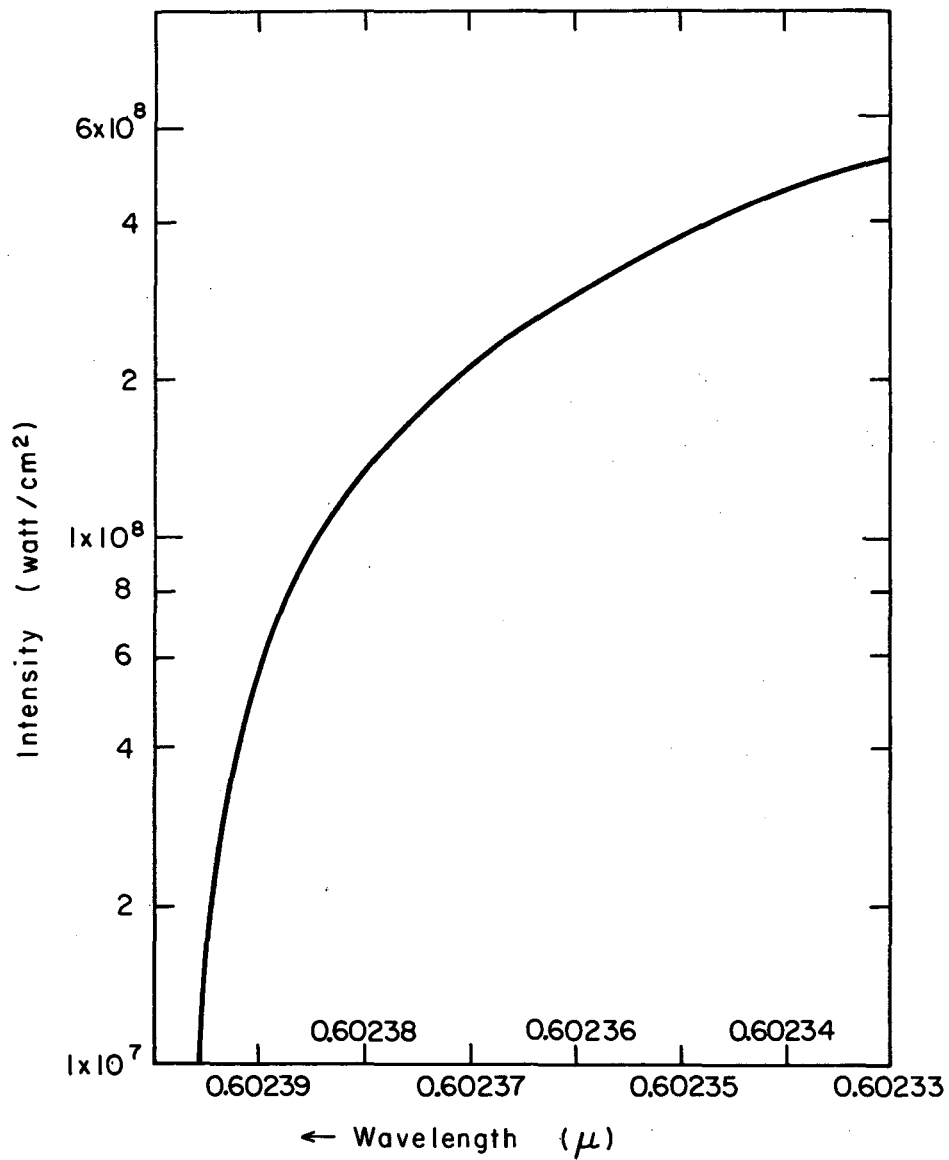
XBL751-2200

Fig. 6



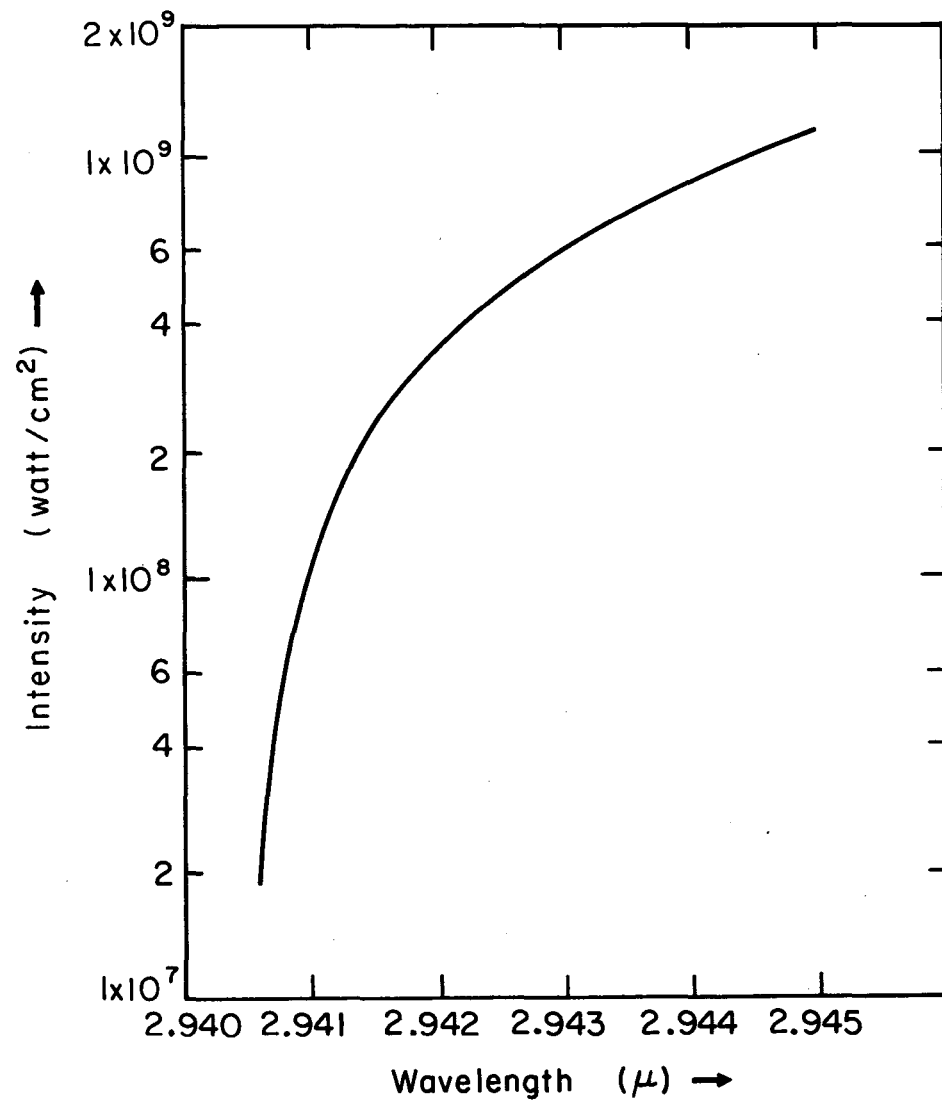
XBL751-2192

Fig. 7



XBL751-2191

Fig. 8



XBL751-2190

Fig. 9

0004301288

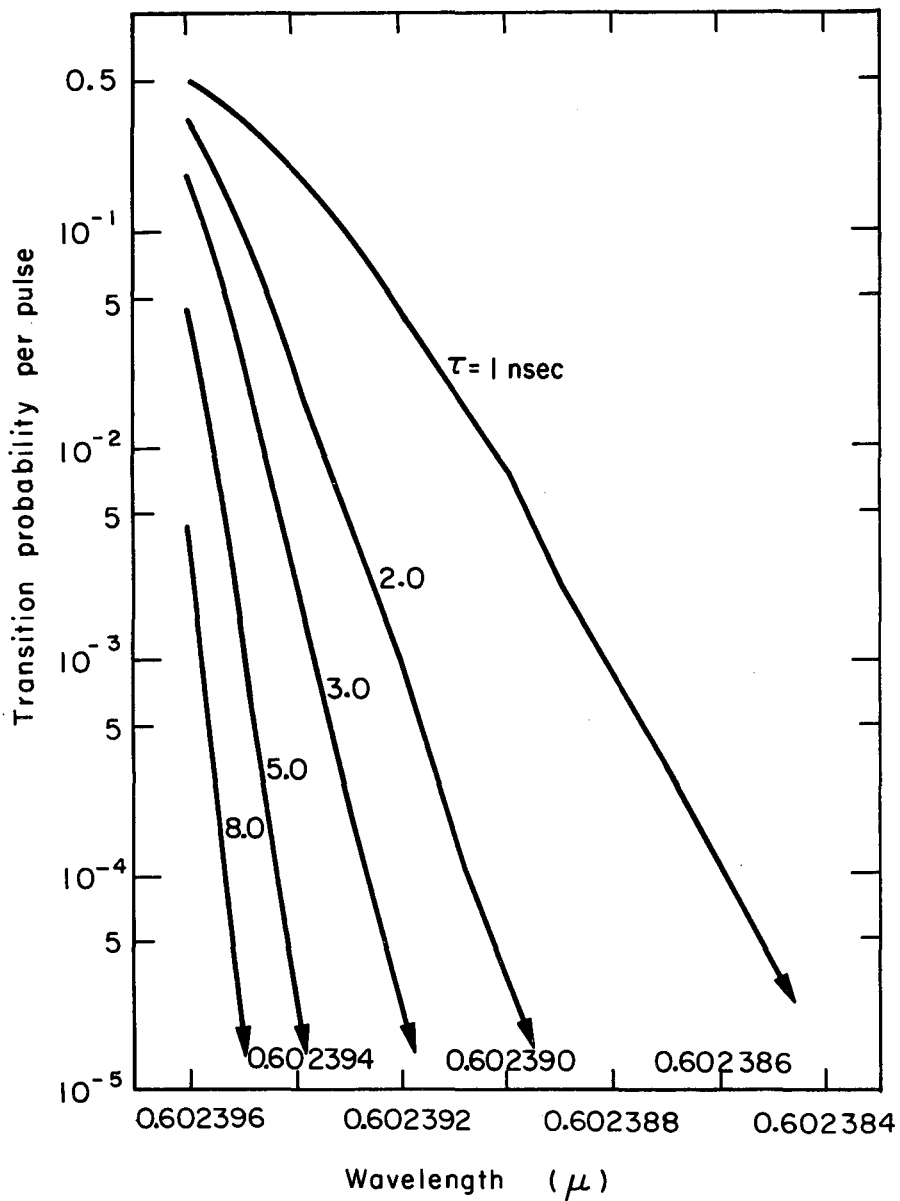


Fig. 10

XBL 751-2193

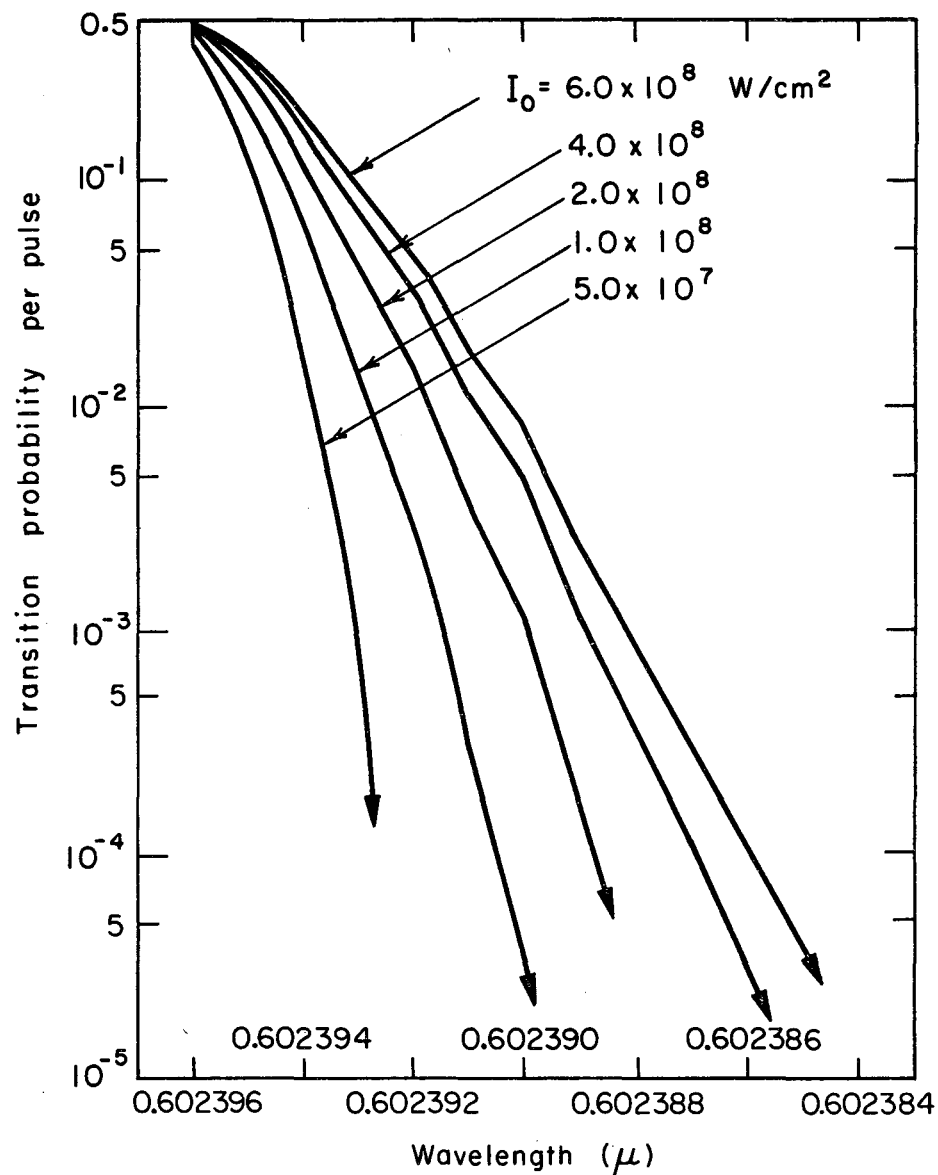


Fig. 11

XBL 751-2194

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 ω , \hat{k} , $\hat{\epsilon}$, respectively the angular frequency, unit propagation vector and the polarization vector. In the electric dipole approximation, modes differing by \hat{k} only is essentially a one-mode problem (i.e., treatment presented earlier is sufficient.) However, for modes differing in \hat{k} in higher multipole approximation and for modes differing by ω and/or $\hat{\epsilon}$, the treatment given below is required.

More often than not, the radiation field of physical processes consists of two or more modes. The second-harmonic generation and stimulated Raman emission are but two common examples from nonlinear optics. Choice of appropriate combination of modes can enhance a desired physical process. The atomic two-photon absorption is enhanced many orders of magnitude by choosing two appropriate frequencies to achieve near-resonance with an intermediate level.¹ Another illustration is provided by the stimulated emission of one mode in molecules by lowering of potential barrier due to another mode. This process is treated in Sec. III, based on the formalism presented in Sec. II. Whereas Part A of this work is applicable to an n discrete-level atomic/molecular system for $n \geq 3$, this part can be applied to cases with $n \geq 2$.

II. THE TWO- AND MULTIMODE FIELD

The Hamiltonian corresponding to $H_c(t)$ in Eq. (A.2.4) for the case of an atom/molecule interacting with a two-mode radiation field is

$$H_c = H_1 + h_2 + h_2' ,$$

000-4301289

where

$$H_1 = h_R + h_1 + h_1' \quad (2.1)$$

Here h_1 denotes the free-field Hamiltonian of the i th ($i = 1, 2$) mode, whereas h_1' 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 ψ' in terms of the complete set of states, $\{\Omega(N_1 - v_1) \Omega(N_2 - v_2) \phi_\beta\}$,

$$\begin{aligned} \psi' = & \sum_{v_1' v_2' \beta} i^{v_1' + v_2'} b_{v_1' v_2'}(\beta) e^{-i \int^t (u_p(t') + \hbar \omega_1 N_1 + \hbar \omega_2 N_2) dt'} \\ & \times \Omega(N_1 - v_1') \Omega(N_2 - v_2') \phi_\beta, \end{aligned}$$

where u_p is a particular electronic energy level chosen 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 $b_{v_1 v_2}(\alpha)$,

$$\begin{aligned} i \frac{d}{dy} b_{v_1 v_2}(\alpha) = & W_{v_1}(\alpha) b_{v_1 v_2}(\alpha) + \sum_{\alpha'} G_{1\pm}(\alpha, \alpha') \\ & \times (b_{v_1-1 v_2}(\alpha') \pm b_{v_1+1 v_2}(\alpha')) - v_2 F_2 b_{v_1 v_2}(\alpha) \\ & + \sum_{\alpha'} G_{2\pm}(\alpha, \alpha') (b_{v_1 v_2-1}(\alpha') \pm b_{v_1 v_2+1}(\alpha')) ; \quad (2.2a) \end{aligned}$$

or in another form more useful to us later

$$\begin{aligned} i \sum_{v_1' \alpha'} \frac{d}{dy} b_{v_1' v_2}(\alpha') \delta_{v_1 v_1'} \delta_{\alpha \alpha'} = & \sum_{v_1' \alpha'} \left[W_{v_1}(\alpha) \delta_{v_1 v_1'} \delta_{\alpha \alpha'} b_{v_1' v_2}(\alpha') \right. \\ & + G_{1\pm}(\alpha, \alpha') (\delta_{v_1 v_1'+1} \pm \delta_{v_1 v_1'-1}) b_{v_1' v_2}(\alpha') \\ & - v_2 F_2 \delta_{v_1 v_1'} \delta_{\alpha \alpha'} b_{v_1' v_2}(\alpha') \\ & \left. + \delta_{v_1 v_1'} G_{2\pm}(\alpha, \alpha') (b_{v_1' v_2-1}(\alpha') \pm b_{v_1' v_2+1}(\alpha')) \right] \quad (2.2b) \end{aligned}$$

The coupling matrices $G_1(\alpha, \alpha')$ and $G_2(\alpha, \alpha')$, defined as in Eq. (A.2.7), differ from each other because of difference in angular frequencies, polarization, intensities of the two modes and/or propagation directions of the modes (when higher-than electric dipole terms are important).

Upon substitution of

$$b_{v_1 v_2}(\alpha) = e^{-i \int^y E(y') dy'} a_{v_1 v_2}(\alpha)$$

$$\frac{d}{dy} a_{v_1 v_2}(\alpha) = 0$$

into above equations, the adiabatic eigenvalue equations are obtained

$$\sum_{v_1 \alpha'} \left(E \delta_{v_1 v_1'} \delta_{\alpha \alpha'} - \langle v_1 \alpha | H_1 | v_1' \alpha' \rangle + v_2 F_2 \delta_{v_1 v_1'} \delta_{\alpha \alpha'} \right) a_{v_1' v_2'}(\alpha')$$

$$= \sum_{v_1 \alpha'} \delta_{v_1 v_1'} G_{2f}(\alpha, \alpha') \left(a_{v_1' v_2-1}(\alpha') \pm a_{v_1' v_2+1}(\alpha') \right), \quad (2.3)$$

Let us label the $(\lambda_1 \lambda_2 \gamma)$ th eigensolution at y as $E_{\lambda_1 \lambda_2 \sigma}$, $\{a_{v_1 v_2}^{\lambda_1 \lambda_2 \sigma}(\alpha)\}$. Then it can be shown from the above equations that

$$E_{\lambda_1 + \lambda_1, \lambda_2 + \lambda_2, \sigma} = E_{\lambda_1 \lambda_2 \sigma} - \lambda_1 F_1 - \lambda_2 F_2,$$

$$a_{v_1 v_2}^{\lambda_1 + \lambda_1, \lambda_2 + \lambda_2, \sigma}(\alpha) = a_{v_1 - \lambda_1, v_2 - \lambda_2}^{\lambda_1 \lambda_2 \sigma}(\alpha).$$

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

If we define $a_{v_2}^{\lambda_1 \lambda_2 \sigma}(v_1 \alpha') \equiv a_{v_1 v_2}^{\lambda_1 \lambda_2 \sigma}(v_1 \alpha')$ as the $(v_1 \alpha')$ th component of the vector $\underline{a}_{v_2}^{\lambda_1 \lambda_2 \sigma}$, then the Eqs. (2.3) can be cast into the matrix form

$$D_{v_2}^{\lambda_1 \lambda_2 \sigma} \underline{a}_{v_2}^{\lambda_1 \lambda_2 \sigma} = G_{\pm}(\underline{a}_{v_2-1}^{\lambda_1 \lambda_2 \sigma} \pm \underline{a}_{v_2+1}^{\lambda_1 \lambda_2 \sigma}),$$

where

$$D_{v_2}^{\lambda_1 \lambda_2 \sigma}(v_1 \alpha, v_1' \alpha') \equiv E \delta_{v_1 v_1'} \delta_{\alpha \alpha'} - \langle v_1 \alpha | H_1 | v_1' \alpha' \rangle + v_2 F_2 \delta_{v_1 v_1'} \delta_{\alpha \alpha'},$$

$$G_{\pm}(v_1 \alpha, v_1' \alpha') = \delta_{v_1 v_1'} G_{2f}(\alpha, \alpha').$$

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 mode 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 PC between say level $(\lambda_1 \lambda_2 \sigma)$ and level $(\mu_1 \mu_2 \tau)$. We let

$$a_{v_2}(v_1 \alpha) \equiv d_{v_2}(v_1 \alpha) a_{\lambda_2}(\lambda_1 \sigma) + s_{v_2}(v_1 \alpha) a_{\mu_2}(\mu_1 \tau).$$

This implies

$$d_{\mu_2}(\mu_1 \tau) = 0, \quad s_{\mu_2}(\mu_1 \tau) = 1,$$

$$d_{\lambda_2}(\lambda_1 \sigma) = 1, \quad s_{\lambda_2}(\lambda_1 \sigma) = 0.$$

With these known values, all other d's and s's are found as in Sec. (A.III). Note, however, $D_{v_2}^{\lambda_1 \lambda_2 \sigma}$ now are not diagonal. Therefore we should not use the artificial ploy in writing for example $\bar{D}_{v_2}^{\lambda_1 \lambda_2 \sigma}$ below Eq. (A.3.12a). Instead $\bar{U}_{v_2}^{\lambda_1 \lambda_2 \sigma}$ can be found by (i) letting its $(\mu_1 \tau)$ th row be all zeroes and (ii) directly inverting the μ_2 th set

0004301290

of equations (without the $(\mu_1\mu_2\tau)$ th equation) to obtain other $n(2M_1 + 1) - 1$ rows.

The two equations $(\lambda_1\lambda_2\sigma)$ and $(\mu_1\mu_2\tau)$ which have not been used to find the d 's and s 's are used to express the adiabatic eigenvalues

$$E_u = \frac{1}{2} \left[\left(W'_{\mu_1\mu_2\tau} + W'_{\lambda_1\lambda_2\sigma} \right) + \left(\left(W'_{\mu_1\mu_2\tau} - W'_{\lambda_1\lambda_2\sigma} \right)^2 + 4G^2 \right)^{\frac{1}{2}} \right],$$

$$E_l = \frac{1}{2} \left[\left(W'_{\mu_1\mu_2\tau} + W'_{\lambda_1\lambda_2\sigma} \right) - \left(\left(W'_{\mu_1\mu_2\tau} - W'_{\lambda_1\lambda_2\sigma} \right)^2 + 4G^2 \right)^{\frac{1}{2}} \right].$$

Here $W'_{\mu_1\mu_2\tau}$ is the shifted $(\mu_1\mu_2\tau)$ -level,

$$W'_{\mu_1\mu_2\tau} \equiv \left(W(\tau) - \mu_1 F_1 - \mu_2 F_2 \right) + \square_{\mu}^{(1)} + \square_{\mu}^{(2)},$$

where $\square_{\mu}^{(1)} \equiv \sum_{\alpha'} G_{1\pm}(\tau, \alpha') \left(s_{\mu_1-1\mu_2\alpha'} \pm s_{\mu_1+1\mu_2\alpha'} \right)$,

$$\square_{\mu}^{(2)} \equiv \sum_{\alpha'} G_{2\pm}(\tau, \alpha') \left(s_{\mu_1\mu_2-1\alpha'} \pm s_{\mu_1\mu_2+1\alpha'} \right),$$

may be considered as the shifting of the $(\mu_1\mu_2\tau)$ -level due to mode 1 and mode 2 respectively. Correspondingly, for the other level,

$$W'_{\lambda_1\lambda_2\sigma} \equiv \left(W(\sigma) - \lambda_1 F_1 - \lambda_2 F_2 \right) + \square_{\lambda}^{(1)} + \square_{\lambda}^{(2)},$$

where $\square_{\lambda}^{(1)} \equiv \sum_{\alpha'} G_{1\pm}(\sigma, \alpha') \left(d_{\lambda_1-1\lambda_2\alpha'} \pm d_{\lambda_1+1\lambda_2\alpha'} \right)$,

$$\square_{\lambda}^{(2)} \equiv \sum_{\alpha'} G_{2\pm}(\sigma, \alpha') \left(d_{\lambda_1\lambda_2-1\alpha'} \pm d_{\lambda_1\lambda_2+1\alpha'} \right).$$

Finally,

$$\begin{aligned} G &\equiv - \sum_{\alpha'} G_{1\pm}(\tau, \alpha') \left(d_{\mu_1-1\mu_2\alpha'} \pm d_{\mu_1+1\mu_2\alpha'} \right) \\ &\quad - \sum_{\alpha'} G_{2\pm}(\tau, \alpha') \left(d_{\mu_1\mu_2-1\alpha'} \pm d_{\mu_1\mu_2+1\alpha'} \right) \\ &= - \sum_{\alpha'} G_{1\pm}(\sigma, \alpha') \left(s_{\lambda_1-1\lambda_2\alpha'} \pm s_{\lambda_1+1\lambda_2\alpha'} \right) \\ &\quad - \sum_{\alpha'} G_{2\pm}(\sigma, \alpha') \left(s_{\lambda_1\lambda_2-1\alpha'} \pm s_{\lambda_1\lambda_2+1\alpha'} \right) \end{aligned}$$

is the effective coupling matrix element between the two shifted levels. The last equality is based on hermiticity.

To calculate the transition probability between these two levels at a PC, we need to consider only the $(\mu_1\mu_2\tau)$ th and the $(\lambda_1\lambda_2\sigma)$ th time-dependent equations from Eqs. (2.2a). These equations are reduced to

$$\begin{aligned} i \frac{d}{dy} b_{\mu_1\mu_2\tau} - W'_{\mu_1\mu_2\tau} b_{\mu_1\mu_2\tau} &= G b_{\lambda_1\lambda_2\sigma}, \\ i \frac{d}{dy} b_{\lambda_1\lambda_2\sigma} - W'_{\lambda_1\lambda_2\sigma} b_{\lambda_1\lambda_2\sigma} &= G b_{\mu_1\mu_2\tau}, \end{aligned} \quad (2.5)$$

which are the same as those of Eqs. (A.4.1). The previous derived formulae for transition probability are directly useful.

An Alternative Approach is particularly advantageous in some circumstances. Here we expand the total wavefunction ψ' in another representation,

$$\psi' = \sum_{\xi'\rho'v_2'} i^{v_2'} b_{v_2'}(\xi'\rho') \Omega(N_2 - v_2') \phi^{\xi'\rho'} e^{-i \int^t (e_p(t') + \hbar\omega_2 N_2) dt'}$$

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 $b_{v_2}(\xi\rho)$'s are

$$i \frac{d}{dy} b_{v_2}(\xi\rho) = E_{\xi\rho, v_2} b_{v_2}(\xi\rho) + \sum_{\xi'\rho'} G_{\pm}(\xi\rho, \xi'\rho') \times (b_{v_2-1}(\xi'\rho') \pm b_{v_2+1}(\xi'\rho')) , \quad (2.7)$$

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

$$E_{\xi\rho, v_2} \equiv \frac{a_0}{\hbar\nu} (e_{\xi\rho} - e_p) - v_2 F_2 ,$$

$$y \equiv \frac{a_0}{\hbar\nu} t ,$$

and

$$G(\xi\rho, \xi'\rho') \propto (\phi^{\xi\rho}, h_2' \phi^{\xi'\rho'}) .$$

The adiabatic eigenvalue equations are

$$E a_{v_2}(\xi\rho) = E_{\xi\rho, v_2} a_{v_2}(\xi\rho) + \sum_{\xi'\rho'} G_{\pm}(\xi\rho, \xi'\rho') \times (a_{v_2-1}(\xi'\rho') \pm a_{v_2+1}(\xi'\rho')) , \quad (2.8)$$

where

$$b_{v_2}(\xi\rho) = e^{-i \int^y E(y') dy'} a_{v_2}(\xi\rho) .$$

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

$$\phi^{\xi\rho} = U \Omega(N_1 - \xi) \phi_{\rho} .$$

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, one may solve Eqs. (2.6) and, for multiphoton transition of the second mode between two levels, treat the weak field

000-4301291

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 $\nu_2 = \mu_2$ to $\nu_2 = \lambda_2 = \mu_2 - 1$ and the H_1 -system from $\mu_1\tau$ to $\lambda_1\sigma$, then from Eqs. (2.7) we consider

$$i \frac{d}{dy} b_{\mu_2}(\mu_1\tau) = E_{\mu_1\tau, \mu_2} b_{\mu_2}(\mu_1\tau) + G_{\pm}(\lambda_1\sigma, \mu_1\tau) b_{\lambda_2}(\lambda_1\sigma) ,$$

$$i \frac{d}{dy} b_{\lambda_2}(\lambda_1\sigma) = E_{\lambda_1\sigma, \lambda_2} b_{\lambda_2}(\lambda_1\sigma) + G_{\pm}(\lambda_1\sigma, \mu_1\tau) b_{\mu_2}(\mu_1\tau) , (2.9)$$

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 2, which has a potential barrier (e.g., due to avoided crossing) at R_b . For $R > R_b$, the dipole transition to the state 1 is forbidden, while for $R < R_b$ it is allowed. However, at thermal velocities, the potential barrier is too high for the classical penetration (or too little quantum mechanical tunnelling) into region $R < R_b$. 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 2

and 3 in the neighborhood of R_b . Once the molecule penetrates into the $R < R_b$ region, it will most likely radiate at the classical turning point R_c at the second frequency.

For diatomic quasimolecule, the initial state 2 is achieved by some sort of pumping. But for polyatomic quasimolecules, the potential surface 2 may represent ground state of one configuration of the molecular complex and no pumping is necessary. Potential surface 1 corresponds to a rearranged configuration. For case depicted in Fig. 1, part of electronic energy upon photoemission is converted to relative kinetic energy of the colliding particles, producing heating of the gas of molecules. Thus the high-intensity laser may be needed only initially to make the process go.

For numerical study, we consider the original potential energy curves $u_i(R)$ (in eV) and dipole matrix elements (in AU)

$$M_{jk} = \langle j | \sum_i r_i | k \rangle$$

for a diatomic colliding system (of reduced mass = 20 × proton mass and relative speed = 10^5 cm/sec).

$$u_1(R) = 1.5 e^{-5(R-3)} ,$$

$$u_2(R) = 2.9 + 0.1(1 - e^{-1.6(R-3.75)})^2 + 0.153 e^{-4.0(R-4.8)^2} ,$$

$$u_3(R) = 4.285 + 1.2 e^{-3(R-3)} ,$$

$$M_{12}(R) = 5 e^{-2.5(R-3)} ,$$

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

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

These analytic representations are meant to be valid only for $R \geq 3.0 a_0$. They are graphed in Fig. 1. The maximum of the bump height of $u_2(R) - u_2(\infty)$ is 0.12 eV at $R = 4.85 a_0$. 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 Λ -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 $\hat{\epsilon}_1$ (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 $\hat{\epsilon}_1$, as depicted in Fig. A.4.

With high-intensity laser field chosen to be the available YAG:Nd³⁺ laser ($\lambda_1 = 1.0648 \mu$), the bump is lowered by about 0.04 eV at $I_1 = 10^{12} \text{ W/cm}^2$. (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 $b_{\text{max}} = 1.97 a_0$) can now penetrate into the $R < R_b$ region. The system has certain probability $P_{I_2}(b)$ 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 $R \approx 3.2 a_0$ ($\hat{\epsilon}_2$ is chosen parallel to $\hat{\epsilon}_1$).

The transition probability formula Eq.(A.4.5) is appropriate and valid for calculating $P_{I_2}(b)$ near R_c . The two methods represented by Eq. (2.5) and Eq. (2.9) in the last section yield results in good agreement with each other.

The cross section (in a_0^2) for stimulated emission into the second mode

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

are calculated for several intensities and are given in Table I. On a log-log plot of σ_{I_2} 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 $\hat{\epsilon}_1$. (See Sec. (A.V)) Thus collisional systems with impact parameter $b = 1.46$ to $1.97 a_0$ 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"

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

are given in Table I. It is not significantly sensitive to I_2 . It is noticed that σ_t is large compared to the corresponding σ_{I_2} . 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 $R = 3.2 a_0$. This trapping will result in a great enhancement of the "observed σ_{I_2} ".

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

00014301292

potential barrier shifts by less than 10%. Thus the selection of the third level (or high intensity laser wavelength) is not severely restrictive.

ACKNOWLEDGMENT

The author wishes to thank Professor K. M. Watson and Dr. C. K. Rhodes for helpful discussions. He is particularly grateful to the latter for proposing the process in Sec. III for study.

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.

REFERENCE

1. P. F. Liao and J. E. Bjorkholm, Phys. Rev. Lett. 34, 1 (1975) and references therein. These experiments are, however, for low intensities.

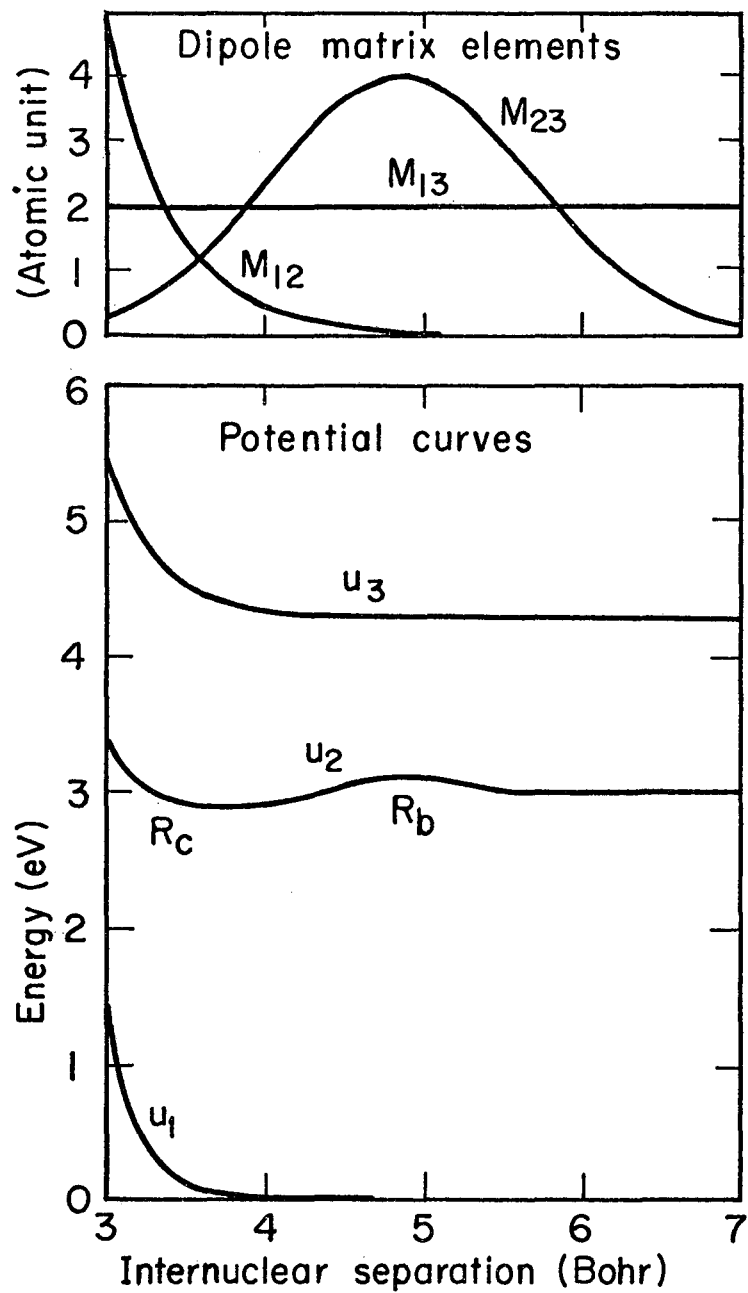
Table I. Cross section of stimulated emission, σ_{I_2} and cross section for trapping, σ_t (see Sec. III of text). I_2 is the intensity of stimulated emission.

$I_2(\text{W/cm}^2)$	$\sigma_{I_2}(\text{a}_0^2)$	$\sigma_t(\text{a}_0^2)$
1×10^7	1.14×10^{-3}	5.5
4×10^7	4.54×10^{-3}	5.5
1×10^8	1.14×10^{-2}	5.5
4×10^8	4.54×10^{-2}	5.5
1×10^9	1.13×10^{-1}	5.5
4×10^9	4.51×10^{-1}	5.5
7×10^9	7.86×10^{-1}	5.5
1×10^{10}	1.12	5.5

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).

00004301293



XBL755-4892

Fig. 1.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720