Laser assisted charge transfer reactions in slow ion–atom collisions: Coupled dressed quasimolecularstates approach

TakSan Ho, Shihl Chu, and Cecil Laughlin

Citation: The Journal of Chemical Physics **81**, 788 (1984); doi: 10.1063/1.447712

View online: http://dx.doi.org/10.1063/1.447712

View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/81/2?ver=pdfcov

Published by the AIP Publishing

Laser assisted charge transfer reactions in slow ion–atom collisions: Coupled dressed quasimolecular-states approach

Tak-San Ho, Shih-I Chu,[a] and Cecil Laughlin[b]
Department of Chemistry, University of Kansas, Lawrence, Kansas 66045-2112

(Received 1 March 1984; accepted 6 April 1984)

Semiclassical coupled *dressed-quasimolecular-states* (DQMS) approaches are presented for the *nonperturbative* treatment of charge transfer reactions at low collision velocities and high laser intensities. The DQMS are first obtained via the Floquet theory. The laser assisted collision process can then be treated as the electronic transitions among the DQMS driven by the nuclear motion only. The expansion of the total electronic wave function in a truncated DQMS basis results in a set of coupled *adiabatic* equations. The adiabatic DQMS and their associated quasienergies (depending parametrically upon the internuclear separation R) exhibit regions of avoided crossings, where the electronic transition probabilities are large due to strong radial couplings induced by the nuclear movement. By further transforming the *adiabatic* DQMS into an appropriate *diabatic* DQMS representation, defined via the vanishing of the aforementioned radial couplings, we obtain a new set of coupled *diabatic* equations which offer computational advantage. The method is illustrated by a case study of the laser assisted charge exchange process $He^{++} + H(1s) + \hbar\omega \rightarrow He^{+}(n = 2) + H^{+}$, in a two-state approximation, for the velocity range from 1.5×10^5 to 2×10^7 cm/s and for the laser intensity in the range of 0.4 to 4.0 TW/cm^2. Results of exact coupled diabatic DQMS calculations are presented along with several approximation calculations, using first order perturbation theory, the Magnus approximation, and the average cross section.

I. INTRODUCTION

Charge transfer is an important mechanism in establishing the ionization structure of a plasma containing multiply charged ionic systems. Collisions between multiply charged ions and atomic hydrogen are important in determining the radiation losses and neutral beam heating efficiencies in Tokamak plasmas.[1] Because electron capture by a multiply charged ion on an atom generally results in the production of a highly excited state of the parent multiply charged ion, radiation in the x-ray range is released as the ion electronically relaxes to its ground state. This property is of interest as an x-ray source in the interstellar space[2] and has led to the prediction of the possibility of producing an x-ray laser.[3,4]

Recently Yakovlenko suggested that the nonresonant ion–atom charge transfer, which is normally small at low collision velocities, can be enhanced by the presence of a strong laser field.[5] The observation of a laser-induced charge transfer collision, involving Ca^+ and Sr, has also been reported.[6] More recently, Seely and Elton[7] suggested that photon-induced charge transfer reactions are also useful for the measurement of particle densities in a Tokamak plasma. It is possible to measure the absolute densities of the neutral hydrogen atoms and the alpha particles, with time and space resolution provided by the pumping laser beam.

From a theoretical point of view, most recent work[8–13] concerning $A^+ + B + n\hbar\omega \rightarrow A + B^+$ has been confined to the expansion of the total electronic wave function in terms of field-free quasimolecular $(A–B)^+$ basis, the assumption of the validity of the rotating wave approximation (RWA), and perturbative schemes of one kind or another within the impact parameter formalism. These approaches,[8–13] in general, are difficult to extend to high laser intensity and low collision velocity regions where the laser-induced charge transfer cross sections are the largest.[12,13] As will be exploited later, at very strong laser intensities, a more appropriate physical basis is provided by the *dressed* quasimolecular states, and the assumption of RWA may not be valid. In addition, the perturbative approach tends to break down at low collision velocities and fails to predict the nonlinear behavior of the cross sections as a function of the laser intensity.

In this paper, we advance a nonperturbative coupled *dressed quasimolecular states* (DQMS) approach for the treatment of charge transfer processes at low collision velocities and strong laser intensities. The theory parallels an earlier treatment developed by one of us[14] in the study of multiphoton enhancement of vibrational excitations induced by molecular collisions. Other approaches using the DQMS concept can be found in Refs. 15–18. The essence of the coupled DQMS approach consists of the following elements: As the laser frequency of interest is in the range of quasimolecular electronic energy separations, the laser field oscillates much faster than the motion of the nuclei. It is legitimate to first construct the solutions of the $(A–B)^+$ + field system, namely, the dressed quasimolecular electronic states (also called the quasienergy[14,19] or electronic-field states[15]) with the internuclear separation R fixed.[20] The laser assisted collision process can then be viewed as electronic transitions among the DQMS driven by the nuclear motion only. The DQMS can be determined by invoking either the full quan-

[a] Alfred P. Sloan Foundation Fellow.
[b] Visiting Professor. Permanent address: Department of Mathematics, University of Nottingham, Nottingham, England.

 0021-9606/84/140788-11$02.10

tized treatment[15,16] or the semiclassical Floquet theory,[14,17,19,21] both treatments being equivalent in strong fields.[21(a)] In this paper we adopt the Floquet approach, which has been extensively used recently in the studies of multiphoton excitation[20,22] and dissociation[19,23] of isolated molecules. The DQMS constructed in this way are *adiabatic*, and their associated quasienergies (depending parametrically upon R) exhibit regions of avoided crossings,[19] where the electronic transition probabilities are large due to the strong radial couplings induced by nuclear movement. By further transforming the *adiabatic* DQMS into an appropriate *diabatic* DQMS representation, defined via the vanishing of the radial couplings mentioned above, we obtain a new set of coupled (diabatic) equations which offer computational advantages.

In Sec. II, we present a general treatment of the coupled DQMS approach for slow atomic collisions in the presence of intense laser fields. In Sec. III, the laser-induced charge-transfer process

$$He^{++} + H(1s) + \hbar\omega \rightarrow He^{+}(n=2) + H^{+}$$

is analyzed on the ground of a two-state model. Results of the exact coupled DQMS calculations, as a function of laser intensity and collision velocity, are presented in Sec. IV along with several approximate results, using first-order perturbation theory and the Magnus approximation, etc. This is followed by a conclusion in Sec. V. Atomic units will be used throughout the paper unless otherwise specified.

II. THEORY

We consider the general case of slow ion–atom collisions in the presence of an intense linearly polarized laser field. The frequency of laser field is assumed to be comparable to that of the electronic bound–bound transitions and, therefore, is much larger than the characteristic frequency of the nuclear motion. Within the semiclassical trajectory formalism[24] and the electric dipole approximation, the total electronic wave function evolves according to the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r},t\,|\mathbf{R}(t)) = H(\mathbf{r},t\,|\mathbf{R}(t))\Psi(\mathbf{r},t\,|\mathbf{R}(t)), \tag{1}$$

in which

$$H(\mathbf{r},t\,|\mathbf{R}(t)) = h_{el}(\mathbf{r},\mathbf{R}(t)) - \mathbf{r}\cdot\mathbf{E}_0\cos\omega t, \tag{2}$$

where h_{el} is the field-free adiabatic quasimolecular Hamiltonian and the factor $-\mathbf{r}\cdot\mathbf{E}_0\cos\omega t$ describes the interaction between the active electron, positioned at $\mathbf{r}$, and the applied laser field depicted by the amplitude $\mathbf{E}_0(\theta,\phi)$ and the angular frequency ω. Here $\mathbf{E}_0$ is assumed to be uniform over the region of collision, and θ and ϕ specify the spherical-polar angles of the laser field. The quantity $\mathbf{R}(t)$ is determined by some average potential energy of interaction of the two colliding entities.

Since the nuclei are moving slowly compared to the rates of electronic transitions and of the laser field oscillation, we can construct the dressed-quasimolecular states (DQMS) of electrons in the presence of the laser field at each fixed internuclear separation R. Analogous to the perturbed stationary states (PSS) method,[24] the DQMS may be used to describe the states of electrons in the slow collisions of atoms and molecules. The DQMS wave functions $\phi_{\alpha m}(\mathbf{r},t\,|R)$, with α denoting the field-free quasimolecular states and m an arbitrary integer denoting the photon states, are eigenfunctions of the following eigenvalue equation:

$$\left\{H(\mathbf{r},t\,|R) - i\left(\frac{\partial}{\partial t}\right)_R\right\}\phi_{\alpha m}(\mathbf{r},t\,|R) = \epsilon_{\alpha m}(R)\phi_{\alpha m}(\mathbf{r},t\,|R), \tag{3}$$

where the derivative $(\partial/\partial t)_R$ with respect to time t is evaluated by holding the internuclear separation R fixed. The DQMS eigenenergies $\epsilon_{\alpha m}(R)$ and eigenfunctions $\phi_{\alpha m}(\mathbf{r},t\,|R)$ possess useful periodic properties[14,19,21]:

$$\epsilon_{\alpha,m+n}(R) = \epsilon_{\alpha m}(R) + n\omega \tag{4}$$

and

$$\phi_{\alpha m}(\mathbf{r},t+T\,|R) = \phi_{\alpha m}(\mathbf{r},t\,|R), \tag{5}$$

or, more explicitly

$$\phi_{\alpha,m+n}(\mathbf{r},t\,|R) = e^{in\omega t}\phi_{\alpha m}(\mathbf{r},t\,|R), \tag{6}$$

with

$$T = \frac{2\pi}{\omega}.$$

Equation (3) can be solved by expanding the DQMS wave functions $\phi_{\alpha m}(\mathbf{r},t\,|R)$ in terms of the field-free quasimolecular-states wave functions and the Fourier basis $\{e^{in\omega t}\}$:

$$\phi_{\alpha m}(\mathbf{r},t\,|R) = \sum_{\beta}\sum_{n}\langle\beta n|\epsilon_{\alpha m}\rangle e^{in\omega t}\psi_{\beta}(\mathbf{r}|R) \tag{7}$$

where $\psi_{\beta}(\mathbf{r}|R)$ satisfies the field-free electronic eigenvalue equation

$$h_{el}(\mathbf{r}|R)\psi_{\beta}(\mathbf{r}|R) = E_{\beta}(R)\psi_{\beta}(\mathbf{r}|R) \tag{8}$$

with $E_{\beta}(R)$ being the field-free electronic state energy. Substituting Eq. (7) into Eq. (3) results in a time-independent infinite-dimensional eigenvalue equation for the expansion coefficients $\langle\beta n|\epsilon_{\alpha m}\rangle$,

$$\sum_{\beta}\sum_{n}\langle\alpha m|\hat{H}_F|\beta n\rangle\langle\beta n|\epsilon_{\gamma k}\rangle = \epsilon_{\gamma k}\langle\alpha n|\epsilon_{\gamma k}\rangle, \tag{9}$$

where

$$\langle\alpha m|\hat{H}_F|\beta n\rangle = E_{\alpha}\delta_{\alpha\beta}\delta_{mn} + m\omega\delta_{\alpha\beta}\delta_{mn} - \tfrac{1}{2}\langle\psi_{\alpha}|\mathbf{r}|\psi_{\beta}\rangle \times\mathbf{E}_0(\delta_{m,n+1} + \delta_{m,n-1}). \tag{10}$$

Here the bracket $\langle|\cdots|\rangle$ denotes integration over the electronic coordinates $\mathbf{r}$. We should remark that the number of the field-free quasimolecular states used in the expansion (7) is finite. The electronic Floquet Hamiltonian $\hat{H}_F$ in its matrix representation has the following tridiagonal block form:

$$\begin{bmatrix} \ddots & & & & & & \\ & A+2\omega I & B & & 0 & & \\ & B & A+\omega I & B & & & \\ & & B & A & B & & \\ & & & B & A-\omega I & B & \\ & & 0 & & B & A-2\omega I & \\ & & & & & & \ddots \end{bmatrix},$$

where A is a diagonal matrix with the field-free quasimolecular electronic energies $\{E_{\alpha},E_{\beta},E_{\delta},\cdots\}$ as the diagonal matrix elements, I is the unit matrix, and B is the electric dipole

coupling matrix $\{b_{ij}(R)\}$ defined by

$$b_{ij}(R) = -\tfrac{1}{2}\langle\psi_i|\mathbf{r}|\psi_j\rangle\cdot\mathbf{E}_0(\theta,\phi)\,,$$

where $i,j=\alpha,\beta,\gamma,\ldots$.

The total electronic wave function of Eq. (1) in the presence of the laser field may be expanded in the basis set of the DQMS, namely,

$$\psi(\mathbf{r},t\,|R(t)) = \sum_{\alpha}\sum_{m}\chi_{\alpha m}(I)\phi_{\alpha m}(\mathbf{r},t\,|R) \tag{11}$$

subject to the required scattering boundary conditions. Here we note that the expansion coefficients $\chi_{\alpha m}(R)$ depend upon the time t only via the parameter $R(t)$, the internuclear distance. By inserting Eq. (11) into Eq. (1), and projecting it onto an arbitrary DQMS $\phi_{\beta n}(\mathbf{r},t\,|R)$, we obtain a set of the coupled *adiabatic* equations

$$i\frac{\partial}{\partial t}\chi_{\beta n}(R(t)) = \epsilon_{\beta n}(R)\chi_{\beta n}(R) - i\dot{\mathbf{R}} \times\sum_{\alpha}\sum_{m}\langle\langle\phi_{\beta n}|\nabla_{\mathbf{R}}|\phi_{\alpha m}\rangle\rangle_R\chi_{\alpha m}(R)\,, \tag{12}$$

where

$$\langle\langle\phi_{\beta n}|\nabla_R|\phi_{\alpha m}\rangle\rangle_R \equiv\frac{1}{T}\int_0^T dt\int d\mathbf{r}\,\phi_{\beta n}(\mathbf{r},t\,|R)\nabla_R\phi_{\alpha m}(\mathbf{r},t\,|R) \tag{13}$$

with the parameter R kept fixed when integrating. Furthermore, we have assumed the quantities $(\partial/\partial t)\chi_{\beta n}(R)$, $\chi_{\beta n}(R)$, and $\dot{\mathbf{R}}$ remain almost unchanged for each short time span $T\equiv 2\pi/\omega$, which characterizes the laser field oscillation. By making use of the periodic relations (4) via Eqs. (6) and (7), the coupling matrix element $\langle\langle\phi_{\beta n}|\nabla_R|\phi_{\alpha m}\rangle\rangle_R$ can be written explicitly as follows:

$$\begin{aligned}\langle\langle\phi_{\beta n}|\nabla_R|\phi_{\alpha m}\rangle\rangle_R &= \sum_{\gamma}\sum_{k}\langle\gamma k\,|\epsilon_{\beta n}\rangle\nabla_R\langle\gamma k\,|\epsilon_{\alpha m}\rangle \\ &\quad+\sum_{\gamma}\sum_{\gamma'}\sum_{k}\langle\gamma' k\,|\epsilon_{\beta n}\rangle\langle\gamma k\,|\epsilon_{\alpha m}\rangle\langle\psi_\gamma|\nabla_R|\psi_\gamma\rangle\,.\end{aligned} \tag{14}$$

Equation (12) is to be solved upon the initial conditions

$$\chi_{\alpha m}(R)\to\delta_{\alpha\mu}\delta_{m0}\,,\quad\text{at } t=-\infty \tag{15}$$

which implies that

$$\Psi(\mathbf{r},t\,|R)\to\phi_{\mu 0}(\mathbf{r},t\,|R)\to\psi_\mu(\mathbf{r}|R)\,,\quad\text{at } t=-\infty$$

with the index μ specifying the initial state of the system before entering the laser field. It is interesting to see that

$$\langle\beta n|\epsilon_{\alpha m}\rangle\to\delta_{\alpha\beta}\delta_{mn}\,,\quad\text{as } R\to\infty \tag{16}$$

and, therefore,

$$\Psi(\mathbf{r},t\,|R)\to\sum_{\alpha}\sum_{m=-\infty}^{\infty}(\chi_{\alpha m}e^{im\omega t})\psi_\alpha(\mathbf{r}|R)\,,\quad\text{as } R\to\infty\,. \tag{17}$$

Equations (16) and (17) indicate that the probability to find the system in a field-free quasimolecular state ν after the collision can be defined as

$$P_{\mu\nu}(\rho,\mathbf{v}_0;\mathbf{E}_0,\omega) = \sum_{m=-\infty}^{\infty}|\chi_{\nu m}(t=+\infty)|^2 \tag{18}$$

for each specified impact parameter ρ and initial nuclear impact velocity $\mathbf{V}_0$. The total cross section for the system going from the initial state μ to the final state ν can thus be written as

$$\sigma_{\mu\nu}(\mathbf{v}_0,\mathbf{E}_0,\omega) = 2\pi\int_0^\infty d\rho\,\rho P_{\mu\nu}(\rho,\mathbf{v}_0;\mathbf{E}_0,\omega)\,. \tag{19}$$

It is instructive to examine the coupled adiabatic Eq. (12) in the limit of $|\mathbf{E}_0|$ approaching zero. Noticing that

$$\epsilon_{\alpha m}(R)\to E_\alpha + m\omega$$

and

$$\langle\beta n|\epsilon_{\alpha m}\rangle\to\delta_{\alpha\beta}\delta_{mn}\,,\quad\text{as}|\mathbf{E}_0|\to 0\,, \tag{20}$$

we find that Eq. (12) reduces to

$$i\frac{\partial}{\partial t}\chi_{\beta n}(R) = E_\beta\chi_{\beta n}(R) - i\dot{\mathbf{R}}\sum_{\alpha}\langle\psi_\beta|\nabla_R|\psi_\alpha\rangle\chi_{\alpha n}(R) \tag{21}$$

which are simply the coupled equations for the case of field-free collisions[24] if one sets n equal to zero. Therefore, one can see clearly that the first term on the right-hand side of Eq. (14) is mainly responsible for the transition caused by the interaction between the colliding system and the laser field, while the second term is primarily dominated by the transition caused by the motion of the nuclei. From the discussions so far, we have interpreted the electronic transitions undergoing in the collisions being the transitions between various well-defined DQMS driven only by the motion of the nuclei, instead of being the transitions between different field-free quasimolecular states caused by both the nuclear motion and the applied laser field.

We note that the DQMS defined by Eq. (3) form a set of adiabatic basis which incorporate both the motion of the nuclei and the presence of the laser field. The corresponding adiabatic DQMS energy curves $\epsilon_{\alpha m}(R)$ will have regions of the avoided crossings which, in turn, provoke strong couplings, represented by the matrix elements of the operator ∇_R in Eq. (12), between the adiabatic DQMS. In the regions of the avoided crossings of the adiabatic DQMS energy curves, a more appropriate physical description may be obtained by transforming the existing adiabatic DQMS basis into a set of the diabatic DQMS basis for which the coupling matrix elements of ∇_R are small and transitions are driven by a potential matrix. For convenience, we shall use the notations $\epsilon^a_{\alpha m}$, $\phi^a_{\alpha m}$, and $\chi^a_{\alpha m}$ to denote the quantities defined in the adiabatic DQMS basis. Following closely the definition of the diabatic states introduced by Smith[25(a)] and Heil and Dalgarno,[25(b)] we construct, from the adiabatic DQMS basis $\{\phi^a_{\alpha m}(\mathbf{r},t\,|R)\}$ defined by Eq. (3), the diabatic DQMS basis $\{\phi^d_{\alpha m}\}$ via the transformation

$$\phi^d_{\beta n}(R) = \sum_{\alpha}\sum_{m}\phi^a_{\alpha m}C_{\alpha m,\beta n}(R)\,, \tag{22}$$

where the matrix $[C_{\alpha m,\beta n}(R)]$ satisfies the relation

$$\sum_{\gamma}\sum_{k}[A_{\alpha m,\gamma k}(R)C_{\gamma k,\beta n}(R)] + \nabla_R C_{\alpha m,\beta n}(R) = 0 \tag{23}$$

with $C_{\gamma k,\beta n}(R)\rightarrow\delta_{\gamma\beta}\delta_{kn}$ at large R

and

$$A_{\alpha m,\gamma k}(R)\equiv\langle\langle\phi^a_{\alpha m}|\nabla_R|\phi^a_{\gamma k}\rangle\rangle_R\,. \tag{24}$$

Equations (22) and (23) ensure that

$$\langle\langle\phi^d_{\alpha m}|\nabla_R|\phi^d_{\beta n}\rangle\rangle_R=0 \tag{25}$$

and a set of the coupled *diabatic* equations is thus obtained as follows:

$$i\frac{\partial}{\partial t}\chi^d_{\beta n}(R)=\sum_\alpha\sum_m V_{\beta n,\alpha m}(R)\chi^d_{\alpha m}(R)\,, \tag{26}$$

where the potential matrix [V] is defined by the relation

$$V_{\beta n,\alpha m}=\sum_\gamma\sum_k (C^{-1})_{\beta n,\gamma k}(R)\epsilon^a_{\gamma k}(R)C_{\gamma k,\alpha m}(R)\,. \tag{27}$$

Equation (26) is then solved subject to the initial conditions

$$\chi^d_{\alpha m}(R)=\delta_{\alpha\mu}\delta_{m0}\quad\text{at } t=-\infty \tag{28}$$

with μ indexing the initial state of the colliding system. The transition probability and the total cross section are defined via relations (18) and (19) by simply replacing $\chi^a_{\nu m}(t=+\infty)$ by $\chi^d_{\nu m}(t=+\infty)$ in which ν denotes the final state of the system.

III. TWO-STATE APPROXIMATION

To illustrate the salient features of the general theory outlined in the previous section, we shall confine ourselves now to a two-state approximation defined below. First we assume that only two field-free quasimolecular states, e.g., $\psi_\mu(\mathbf{r}|R)$ and $\psi_\nu(\mathbf{r}|R)$ with one corresponding to the incoming channel and the other an outgoing channel which is coupled most strongly to the incoming channel during the collision, are needed to expand the adiabatic DQMS wave function $\phi_{\alpha m}(\mathbf{r},t|R)$ of Eq. (7). We further assume that only two adiabatic DQMS are needed to expand the total electronic wave function $\Psi(\mathbf{r},t|R)$ of Eq. (11) to describe the dynamics of the collision. A good example, which is to be studied in the following, for the two-state approximation is the single photon laser-assisted charge transfer reaction[12,13]

$$He^{++}+H(1s)+\omega\rightarrow He^+(n=2)+H^+\,, \tag{29}$$

where the system initially is in the $2p\sigma$ state which is connected to the $3d\sigma$ state via a *single* photon absorption. The $2p\sigma$ and $3d\sigma$ states are at resonance with each other at an internuclear distance R_x where large transition dipole moment between the two states is displayed.

Assuming only the $2p\sigma$ and $3d\sigma$ states are involved in the process (29), the two adiabatic DQMS wave functions, to be denoted as $\phi^a_p(\mathbf{r},t|R)$ and $\phi^a_q(\mathbf{r},t|R)$, in the two-state approximation can be written explicitly as

$$\phi^a_p(\mathbf{r},t|R)=\psi_{2p\sigma}\sum_{m=-\infty}^{\infty}\langle 2p\sigma,m|\epsilon^a_p\rangle e^{im\omega t}+\psi_{3d\sigma}\times\sum_{m=-\infty}^{\infty}\langle 3d\sigma,m|\epsilon^a_p\rangle e^{im\omega t} \tag{30}$$

and

$$\phi^a_q(\mathbf{r},t|R)=\psi_{2p\sigma}\sum_{m=-\infty}^{\infty}\langle 2p\sigma,m|\epsilon^a_q\rangle e^{im\omega t}+\psi_{3d\sigma}\times\sum_{m=-\infty}^{\infty}\langle 3d\sigma,m|\epsilon^a_q\rangle e^{im\omega t}\,, \tag{31}$$

where the expansion coefficients can be determined via Eq. (9), and ϵ^a_p and ϵ^a_q are subject to the asymptotic conditions

$$\epsilon^a_p(R=+\infty)=E_{2p\sigma} \tag{32}$$

and

$$\epsilon^a_q(R=+\infty)=E_{3d\sigma}-\omega\,. \tag{33}$$

The sum over m is in general truncated to only a few terms. The coupled adiabatic equations, i.e., Eq. (12), thus reduces to, in the present case,

$$i\frac{d}{dt}\chi^a_p(R)=\epsilon^a_p\chi^a_p(R)-i\dot{\mathbf{R}}\cdot\langle\langle\phi^a_p|\nabla_R|\phi^a_q\rangle\rangle_R\chi^a_q(R) \tag{34}$$

and

$$i\frac{d}{dt}\chi^a_q(R)=\epsilon^a_q\chi^a_q(R)-i\dot{\mathbf{R}}\cdot\langle\langle\phi^a_q|\nabla_R|\phi^a_p\rangle\rangle_R\chi^a_p(R)\,, \tag{35}$$

and are required to fulfill the initial conditions

$$\chi^a_p(t=-\infty)=1 \tag{36}$$

and

$$\chi^a_q(t=-\infty)=0\,. \tag{37}$$

Here we have assumed that (i) $\langle\psi_{2p\sigma}|\nabla_R|\psi_{2p\sigma}\rangle$ and $\langle\psi_{3d\sigma}|\nabla_R|\psi_{3d\sigma}\rangle$ are zero, and (ii) $\langle\psi_{2p\sigma}|\nabla_R|\psi_{3d\sigma}\rangle=-\langle\psi_{3d\sigma}|\nabla_R|\psi_{2p\sigma}\rangle$ and are real. These choices ensure that

$$\langle\langle\phi^a_p|\nabla_R|\phi^a_q\rangle\rangle_R=-\langle\langle\phi^a_q|\nabla_R|\phi^a_p\rangle\rangle_R\,. \tag{38}$$

In the two-state approximation, the coupled diabatic equations, i.e., Eq. (26), can be obtained easily from Eqs. (34) and (35), namely,[25]

$$id\chi^d_p/dt=V_{pp}(R)\chi^d_p(R)+V_{pq}(R)\chi^d_q(R) \tag{39}$$

and

$$id\chi^d_q/dt=V_{qp}(R)\chi^d_p(R)+V_{qq}(R)\chi^d_q(R) \tag{40}$$

in which

$$\chi^d_p(t=-\infty)=1 \tag{41}$$

and

$$\chi^d_q(t=-\infty)=0\,, \tag{42}$$

where

$$V_{pp}(R)=\epsilon^a_p\cos^2\zeta(R)+\epsilon^a_q\sin^2\zeta(R)\,, \tag{43}$$

$$V_{qq}(R)=\epsilon^a_p\sin^2\zeta(R)+\epsilon^a_q\cos^2\zeta(R)\,, \tag{44}$$

and

$$V_{pq}(R)=V_{qp}(R)=\tfrac{1}{2}(\epsilon^a_p-\epsilon^a_q)\sin 2\zeta(R)\,, \tag{45}$$

with

$$\zeta(R)=\int_R^\infty\langle\langle\phi^a_p|\nabla_{R'}|\phi^a_q\rangle\rangle_R\cdot dR' \tag{46}$$

and

$$\langle\langle \phi_p^a|\nabla_R|\phi_q^a\rangle\rangle = \sum_m \{\langle 2p\sigma,m|\epsilon_p^a\rangle \nabla_R \langle 2p\sigma,m|\epsilon_q^a\rangle + \langle 3d\sigma,m|\epsilon_p^a\rangle \nabla_R \langle 3d\sigma,m|\epsilon_q^a\rangle\} + \sum_m \{\langle 2p\sigma,m|\epsilon_p^a\rangle\langle 3d\sigma,m|\epsilon_q^a\rangle - \langle 3d\sigma,m|\epsilon_p^a\rangle \times \langle 2p\sigma,m|\epsilon_q^a\rangle\} \cdot \langle \psi_{2p\sigma}|\nabla_R|\psi_{3d\sigma}\rangle . \quad (47)$$

We remark that the coupling matrix element $\langle \psi_{2p\sigma}|\nabla_R|\psi_{3d\sigma}\rangle$ is purely radial in origin and only depends on the internuclear separation R.[26] Therefore, the coupling matrix element $\langle\langle \phi_p^a|\nabla_R|\phi_q^a\rangle\rangle_R$ is only a function of the internuclear distance R.

Equations (34), (35), (39), and (40) can be readily transformed into their interaction representation, namely,

$$i\frac{d}{dt}\chi_p^a(R) = -i\dot{\mathbf{R}} \cdot \langle\langle \phi_p^a|\nabla_R|\phi_q^a\rangle\rangle_R \times \exp\left\{i\int_0^t (\epsilon_p^a - \epsilon_q^a)dt'\right\} \cdot \chi_q^a(R), \quad (48)$$

$$i\frac{d}{dt}\chi_q^a(R) = +i\dot{\mathbf{R}} \cdot \langle\langle \phi_p^a|\nabla_R|\phi_q^a\rangle\rangle_R \times \exp\left\{-i\int_0^t (\epsilon_p^a - \epsilon_q^a)dt'\right\} \cdot \chi_p^a(R), \quad (49)$$

$$i\frac{d}{dt}\chi_p^d(R) = V_{pq}(R) \cdot \exp\left\{i\int_0^t (V_{pp} - V_{qq})dt'\right\} \cdot \chi_q^d(R), \quad (50)$$

and

$$i\frac{d}{dt}\chi_q^d(R) = V_{pq}(R) \cdot \exp\left\{-i\int_0^t (V_{pp} - V_{qq})dt'\right\} \cdot \chi_p^d(R), \quad (51)$$

subject to the same initial conditions as Eqs. (36), (37), (41), and (42). To solve Eq. (48) via Eq. (51), we shall further, for simplicity, assume that: (i) the effects of $\langle \psi_{2p\sigma}|\mathbf{r}|\psi_{2p\sigma}\rangle$ and $\langle \psi_{3d\sigma}|\mathbf{r}|\psi_{3d\sigma}\rangle$ are ignorable: (ii) the nuclear trajectory will be taken as rectilinear, i.e., $\mathbf{R}(t) = \mathbf{V}_0 t + \boldsymbol{\rho}$ where $\mathbf{V}_0$ is the incident nuclear velocity, $\boldsymbol{\rho}$ the impact parameter, and the origin of the time t is set at the classical turning point of the nuclear motion. Furthermore, for the two-state approximation defined in this section to remain realistic, we have implicitly assumed that the reaction rate for the process (29) is negligibly small in the absence of laser fields. The relative velocity V_0 of the nuclei should satisfy the conditions[24]

$$1/M \ll V_0 \ll 1 \text{ (a.u.)} \quad (52)$$

with M the reduced mass of the nuclei, which is about 1224 a.u. for the $(He\ H)^{++}$ system, in order for the semiclassical treatment of slow collisions to be valid.

IV. RESULTS AND DISCUSSIONS

In the following, we shall examine the structure of the two states, namely, $2p\sigma$ and $3d\sigma$ of the system $(He\ H)^{+2}$, and how they are coupled to each other in (i) the Born–Oppenheimer quasimolecular basis, (ii) the adiabatic DQMS basis, and (iii) the diabatic DQMS basis. Possible approximate procedures for evaluating the charge transfer transition probability from the state $2p\sigma$ to the state $3d\sigma$ and, therefore, the total capture cross section will be introduced as the discussion proceeds. In addition to the conditions aforementioned, we shall specifically study the case where the laser wavelength $\lambda = 3000$ Å, which brings about a resonant situation at $R_x \approx 6.0$ a.u. nearby the maximum transition dipole moment between the states $2p\sigma$ and $3d\sigma$; [see Fig. 1(b)]. In addition, $\mathbf{E}_0(\theta,\phi)$ the laser amplitude is lying in the collisional plane denoted by $\phi = 0°$, and is perpendicular to the impact velocity $\mathbf{V}_0$, which, in turn, defines the $\hat{z}$ direction of the laboratory frame. The choice of this geometry ensures that the DQMS potential energy curves are symmetrical about the classical turning point of the nuclear motion.

A. Potential energy curves and coupling matrix elements

In Fig. 1(a) we show the field-free quasimolecular potential energy curves, solid lines, of the states $2p\sigma$ and $3d\sigma$ of the system $(He\ H)^{++}$, while in Fig. 1(b), their corresponding transition dipole moment $|\langle \psi_{2p\sigma}|\mathbf{r}|\psi_{3d\sigma}\rangle|$, calculated using the method of Ref. 26, is displayed. In the absence of the laser, these two states are nonresonant and not reactive as

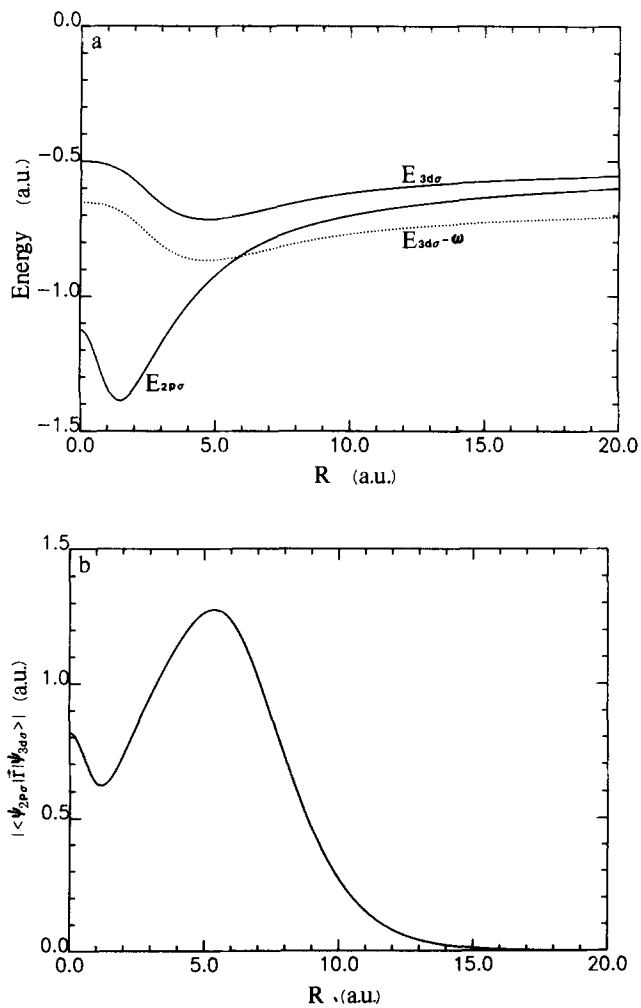

FIG. 1. (a) The field-free quasimolecular electronic energies of the $2p\sigma$ and $3d\sigma$ states of the $(HeH)^{++}$ system (solid curves). By subtraction $\hbar\omega$ from the upper $E_{3d\sigma}$ curve (or equivalently by adding $\hbar\omega$ to the lower $E_{2p\sigma}$ curve), one sees the two curves $E_{3d\sigma} - \hbar\omega$ and $E_{2p\sigma}$ (or $E_{3d\sigma}$ and $E_{2p\sigma} + \hbar\omega$), cross at about $R_x \cong 6.0$ a.u., when $\lambda = 3000$ Å. (b) Electronic transition dipole moment.

the nuclei move very slowly. After turning on the laser of appropriate wavelength, $\lambda = 3000$ Å in this case, the two states will be coupled strongly via the electric dipole interaction nearby the internuclear separation R_x where the energy defect of the two curves is equal to the laser frequency, see the dotted curve in Fig. 1(a). As long as the laser field is weak, the field-free potential energy curves are not significantly distorted, one can always expand the total electronic wavefunction in Eq. (1) in terms of the truncated field-free quasimolecular basis. The transition is thus considered as the transition between the field-free states caused by the nuclear motion and by the laser. Studies based on this picture have been made elsewhere in great detail, and will not be repeated here.

As the laser intensity grows, both adiabatic and diabatic DQMS should provide a more stable basis than the field-free states. In the adiabatic DQMS basis, the two curves which cross each other at $R_x \sim 6.0$ a.u. in Fig. 1(a) will exhibit avoided crossing at the same location, and strong nonadiabatic transition will occur near R_x due to the motion of the nuclei. The curves nearby the avoided crossing region R_x are displayed in Fig. 2(a) for the case that the impact parameter $\rho = 4.7$ a.u., the incident velocity $V_0 = 1\times 10^7$ cm/s, the laser wavelength $\lambda = 3000$ Å, and the laser intensity takes on the values 0.4, 1.0, and 4.0, TW/cm^2, respectively. One sees that the gap between the curves of the avoided crossing grows as the laser intensity increases[19] and, thus, more mixing of the two unperturbed dressed (or Floquet) states. The purely radial coupling strength, i.e., $|dR/dt\,\langle\langle\phi_p^a|d/dR\,|\phi_q^a\rangle\rangle_R|$, of the two adiabatic DQMS is shown in Fig. 2(b). We find that the stronger is the laser field, the lower and the broader the profile of the radial coupling matrix will be. Here we remark that the two DQMS wave functions and their associated energies have converged as far as the Floquet structure calculation is concerned. For the current problem, a 4×4 truncated Floquet Hamiltonian, i.e.,

$$H_F = \begin{bmatrix} E_{3d\sigma}+\omega & b & 0 & 0 \\ b & E_{2p\sigma} & b & 0 \\ 0 & b & E_{3d\sigma}-\omega & b \\ 0 & 0 & b & E_{2p\sigma}-2\omega \end{bmatrix}, \tag{53}$$

will suffice for all cases. At a weaker field case, e.g., $I = 0.4$ TW/cm^2, a 2×2 Floquet Hamiltonian of the inner part of Eq. (53), which is equivalent to a rotating wave approximation, will be sufficient.

Therefore, to a good first-order approximation, the adiabatic DQMS energies may be written as[21(a)]

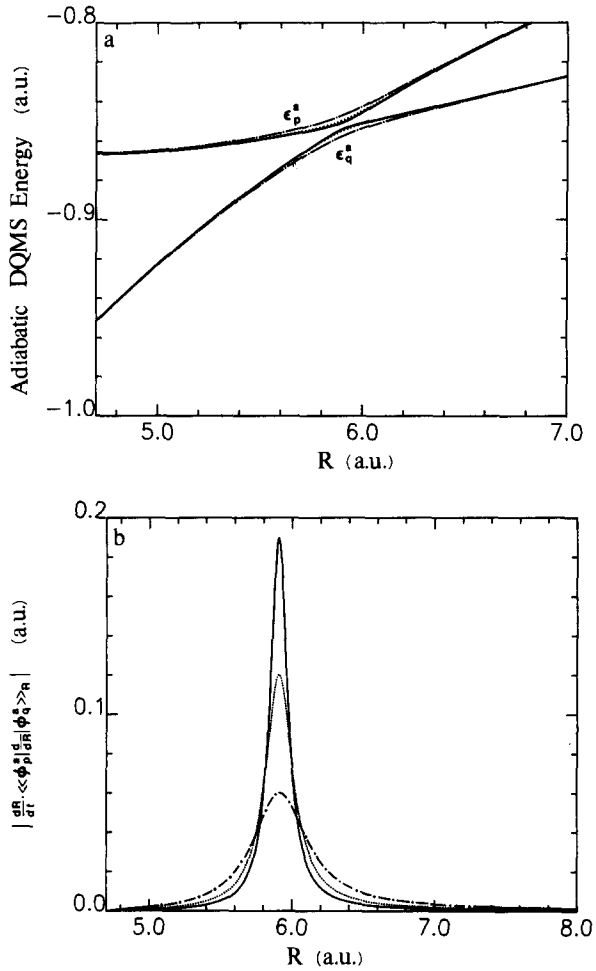

FIG. 2. The adiabatic DQMS energies [Fig. 2(a)] and the corresponding radial coupling matrix elements [Fig. 2(b)] as functions of the internuclear separation R. Cases for the different laser intensities (I) are shown: solid curves, $I = 0.4$ TW/cm^2, dotted curves, $I = 1.0$ TW/cm^2, and dash–dotted curves, $I = 4.0$ TW/cm^2. Note that the avoided crossing pattern nearby R_x is strongly intensity dependent [Fig. 2(a)], and so are the radial coupling matrix elements [Fig. 2(b)].

$$\epsilon_p^a(R) = \tfrac{1}{2}\left\{(E_{2p\sigma}+E_{3d\sigma}-\omega) + \sqrt{\left(E_{2p\sigma}-E_{3d\sigma}+\omega-\frac{b^2}{\omega}\right)^2+|b|^2}\right\} \tag{54}$$

and

$$\epsilon_q^a(R) = \tfrac{1}{2}\left\{(E_{2p\sigma}+E_{3d\sigma}-\omega) - \sqrt{\left(E_{2p\sigma}-E_{3d\sigma}+\omega-\frac{b^2}{\omega}\right)^2+|b|^2}\right\}, \tag{55}$$

and the adiabatic radial coupling matrix element becomes

$$\frac{dR}{dt}\cdot\left\langle\left\langle\phi_p^a\left|\frac{d}{dR}\right|\phi_q^a\right\rangle\right\rangle_R = -\frac{dR}{dt}\left\{|b|\frac{d}{dR}\left(E_{2p\sigma}-E_{3d\sigma}+\omega-\frac{b^2}{\omega}\right) - \left(E_{2p\sigma}-E_{3d\sigma}+\omega-\frac{b^2}{\omega}\right)\frac{d}{dR}|b|\right\}\Big/\left\{\left(E_{2p\sigma}-E_{3d\sigma}+\omega-\frac{b^2}{\omega}\right)^2+4|b|^2\right\}, \tag{56}$$

where

$$b \equiv -\tfrac{1}{2}\langle \psi_{2p\sigma} | \mathbf{r} | \psi_{3d\sigma} \rangle \cdot \mathbf{E}_0(\theta = 90°, \phi = 0°) .$$

Here the factor $|b|^2/\omega$ is responsible for the lowest order correction to the simple rotating wave approximation, and the quantity $|b|$ is not only a function of R, but is also a function of the impact parameter ρ.

In Figs. 3(a) and 3(b), we depict, respectively, the diagonal and off-diagonal matrix elements of the potential matrix $V(R)$ in the diabatic DQMS basis. The diagonal matrix elements cross each other at a certain internuclear distance R_x which is determined by the relation

$$\zeta(R_x) = \int_{R_x}^{\infty} \left\langle \left\langle \phi_p^a \left| \frac{d}{dR} \right| \phi_q^a \right\rangle \right\rangle dR = \pm \frac{\pi}{4} . \tag{57}$$

This can be readily seen from Eqs. (43) and (44). The off-diagonal matrix elements become larger as the laser intensity increases since they are proportional to the difference of the two adiabatic DQMS energies which become more separated from each other at stronger laser fields. One also sees that these off-diagonal matrix element are in general small in magnitude and are a smooth function of the internuclear distance. It is the smallness of these off-diagonal matrix elements of the diabatic potential, i.e., Eq. (45), which enables one to pursue either exact numerical integration of Eqs. (50) and (51), or to adopt some sort of perturbative scheme to evaluate the transition probability of the laser assisted charge transfer reaction (29).

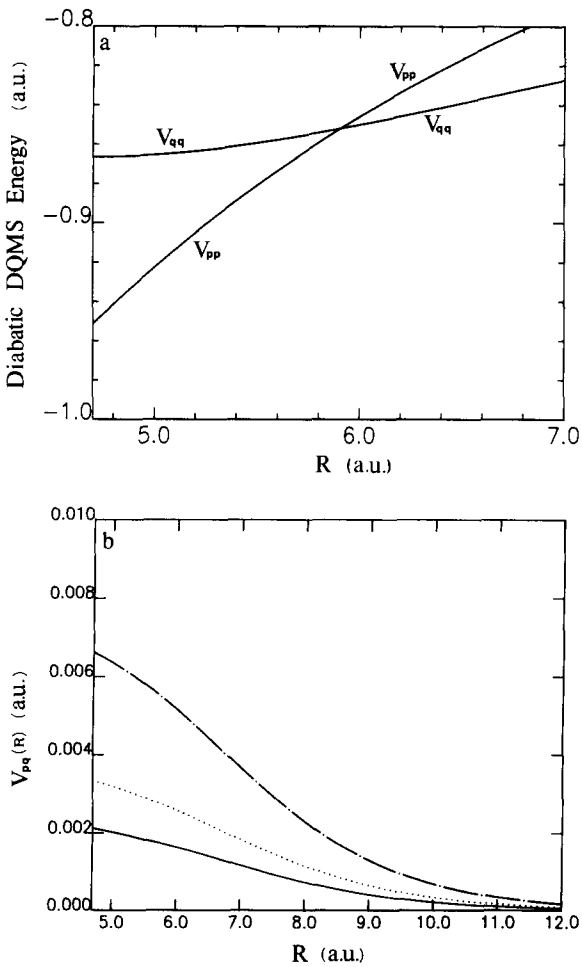

FIG. 3. The diabatic DQMS energies [Fig. 3(a)] and the corresponding off-diagonal potential matrix elements [Fig. 3(b)] as functions of the internuclear separation R, for three different laser intensities. Curve notations are the same as in Fig. 2. Note that the diabatic curves cross at R_x [Fig. 3(a)]. The off-diagonal matrix elements, which are strongly intensity dependent [Fig. 3(b)], in general are small in magnitude and smooth functions of the internuclear separation R [in sharp contrast to the adiabatic radial coupling matrix elements which peak at R_x, cf. Fig. 2(b)].

B. Charge transfer transition probabilities and total cross sections

In this section we shall evaluate the charge transfer transition probabilities and total cross sections based solely upon the diabatic DQMS basis, i.e., solve the diabatic coupled equations (50) and (51) subject to the proper initial conditions. The reason for this choice has been given previously. We shall now first examine some symmetry properties of Eqs. (50) and (51). Since the field is assumed to be perpendicular to the impact velocity, we have

$$V_{pq}(-t) = V_{pq}(t) \tag{58}$$

and

$$\int_0^t (V_{pp} - V_{qq})dt' = -\int_0^{-t} (V_{pp} - V_{qq})dt' . \tag{59}$$

Thus the time evolution operator $\mathbf{U}(t,t_0)$, which obeys the equation

$$i\frac{d}{dt}\mathbf{U}(t,t_0) = \mathbf{V}(t)\mathbf{U}(t,t_0) , \quad \text{with } \mathbf{U}(t_0,t_0) = 1 \tag{60}$$

has the following time-reversal symmetry:

$$\mathbf{U}^*(-t,0) = \mathbf{U}(t,0) . \tag{61}$$

Equation (61) leads to the following equality relations:

$$\mathbf{U}(+\infty,-\infty) = \mathbf{U}(\infty,0)\mathbf{U}^T(\infty,0) \tag{62a}$$

$$= \mathbf{U}^T(0,-\infty)\mathbf{U}(0,-\infty) , \tag{62b}$$

where $\mathbf{U}^T$ denotes the simple transpose. Equations (62) suggest that the integration of Eqs. (50) and (51) needs to be carried out only for the interval $0 < t < +\infty$ or $-\infty < t < 0$. Furthermore, if we write down the unitary matrix $\mathbf{U}(\infty,0)$ explicitly as

$$\mathbf{U}(\infty,0) = \begin{pmatrix} \sqrt{1-p}\,e^{i\eta_1} & -\sqrt{p}\,e^{-i\eta_2} \\ \sqrt{p}\,e^{i\eta_2} & \sqrt{1-p}\,e^{-i\eta_1} \end{pmatrix} , \tag{63}$$

we can express the charge transfer transition probability as[27]

$$P_{2p\sigma-3d\sigma}(\rho,\mathbf{V}_0;\mathbf{E}_0,\omega) = 2(1-p)p \cdot 2\sin^2(\eta_1+\eta_2) , \tag{64}$$

where p may be considered as the probability that the system makes a transition in a single passage through the crossing region. η_1 and η_2 are the phase shifts which are responsible for large oscillations of the transition probability when expressed as a function of the impact parameter ρ. It will be seen that the less oscillatory part, i.e., $2(1-p)p$, of Eq. (64) alone can describe nicely the averaged behavior of the transition probability $P_{2p\sigma-3d\sigma}$, especially when $\rho < R_x$.

Besides exactly solving Eqs. (50) and (51), various approximate schemes can be invoked. Here we shall only present our data in the following four versions: (i) the exact calcu-

lations by integrating numerically Eqs. (50) and (51), incorporating the symmetries just mentioned; (ii) the first order Magnus M 1 calculation, i.e., the time evolution operator $\mathbf{U}(t,t_0)$ is approximated as[28]

$$\mathbf{U}(t,t_0) = \exp\left\{ -i \int_0^t \mathbf{V}(t')dt' \right\}, \tag{65}$$

so the transition probability can be expressed as

$$P^{(M1)}_{2p\sigma-3d\sigma}(\rho,\mathbf{V}_0;\mathbf{E}_0,\omega) = \sin^2 \left| 2 \int_0^\infty dt\, V_{pq}(t) \times \exp\left\{ i \int_0^t (V_{pp} - V_{qq})dt' \right\} \right| \tag{66}$$

for the two-state approximation; (iii) the ordinary first order perturbation (P 1) calculation, i.e., the transition probability can be written as[29]

$$P^{(P1)}_{2p\sigma-3d\sigma}(\rho,\mathbf{V}_0;\mathbf{E}_0,\omega) = 4 \left| \int_0^\infty dt\, V_{pq}(t) \times \exp\left\{ i \int_0^t (V_{pp} - V_{qq})dt' \right\} \right|^2, \tag{67}$$

and finally; (iv) the expression

$$\overline{P}_{2p\sigma-3d\sigma}(\rho,\mathbf{V}_0;\mathbf{E}_0,\omega) = 2p(1-p) \tag{68}$$

from Eq. (64). Here we note that although further approximations can be made on the preceding derivations, e.g., the nonperturbative Landau–Zener model[30] on Eqs. (50) and (51), or the stationary phase approximation (SPA)[31] on Eqs. (66) and (67), it is not our current concern.

In Figs. 4(a), 4(b), and 4(c) we present the scaled laser assisted transition probabilities $\rho P_{2p\sigma-3d\sigma}$ as a function of the impact parameter ρ for the reaction (29). We note that: (i) the incident velocities under study fall in the region where purely a collisional transition between the states $2p\sigma$ and $3d\sigma$ is not probable; and (ii) the calculations are performed using the converged Floquet Hamiltonian equation (53) for all the intensities considered. It is understood that the RWA may suffice at a relatively weak laser field, e.g., below 1 TW/cm^2. From Fig. 4 we can conclude that: (i) the transition probability, in the range of the velocities of our interest, is a fast oscillatory function of the impact parameter ρ; the smaller the impact velocity, the more rapid the oscillations; (ii) the exact, M 1, and P 1 results agree on the way they oscillate as a function of ρ; (iii) the M 1 data are in good agreement with, in magnitude, the exact ones at all of the intensities and the impact velocities we consider; (iv) the magnitude of the P 1 calculations deviate more and more from the exact ones as the intensity gets larger, or as the impact velocity gets smaller; and (v) the $\overline{P}_{2p\sigma-3d\sigma}$ of Eq. (68) does give a satisfactory description of the average behavior of the fast oscillating quantity $P_{2p\sigma-3d\sigma}$ of Eq. (64); the tails of the $\overline{P}_{2p\sigma-3d\sigma}$ which survive beyond the crossing point, i.e., $R_x \approx 6.0$ a.u. for $\lambda = 3000$ Å in this case, may introduce some error, but the error is small as can be seen later.

It is thus instructive to study the quantity $\rho\overline{P}_{2p\sigma-3d\sigma}$ as a function of the impact parameter ρ in more detail. Figures 5(a) and 5(b) depict $\rho \cdot \overline{P}_{2p\sigma-3d\sigma}$ at the laser intensity $I = 1.0$ TW/cm^2 and wavelength $\lambda = 3000$ Å for the impact velocity ranging from 1.55×10^7 to 5×10^5 cm/s. One observes

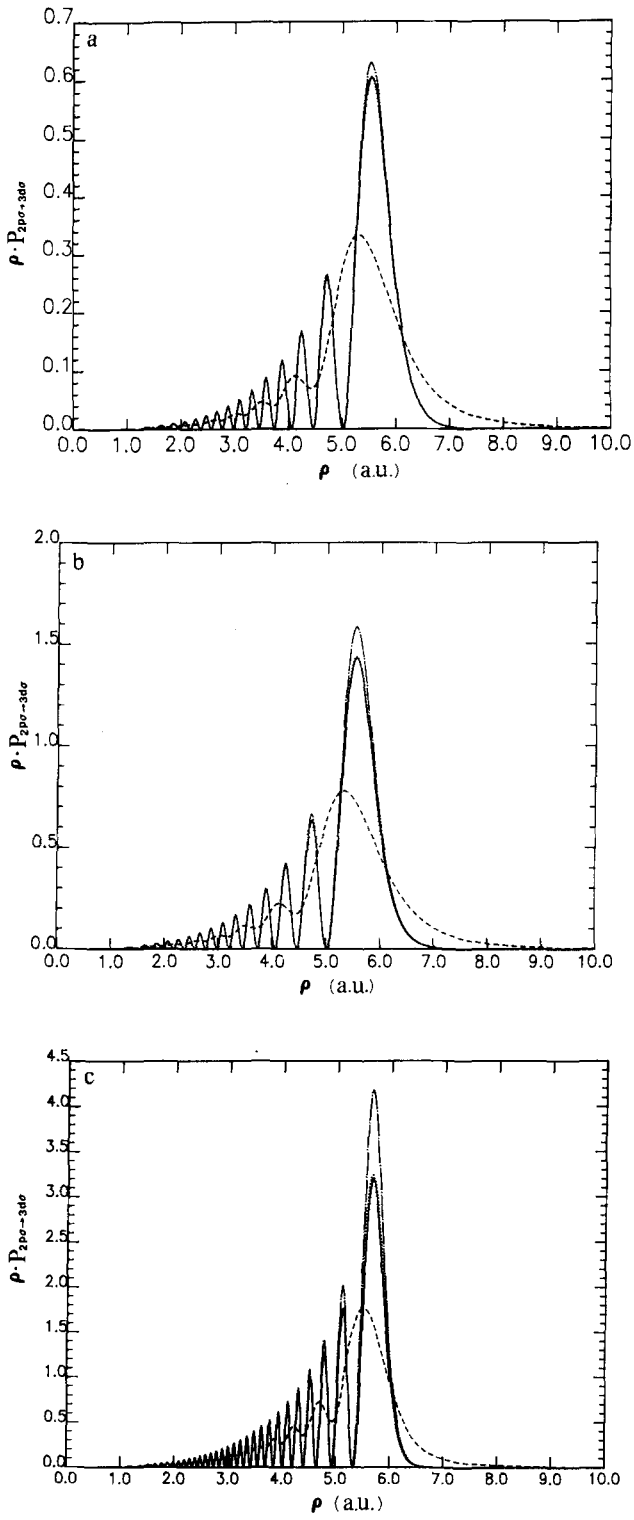

FIG. 4. The scaled charge transfer transition probabilities $\rho \cdot P_{2p\sigma-3d\sigma}$ of the process (29) as functions of the impact parameter ρ at (a) $I = 0.4$ TW/cm^2, $\lambda = 3000$ Å, and $V = 1.0\times10^7$ cm/s; (b) $I = 1.0$ TW/cm^2, $\lambda = 3000$ Å, and $V = 1.0\times10^7$ cm/s; and (c) $I = 1.0$ TW/cm^2, $\lambda = 3000$ Å, and $V = 5\times10^6$ cm/s. Solid curves, the exact results; dotted curves, the M 1 results; long-dash–dotted curves, the P 1 results; and short-dashed curves, the average results.

that at first, as one decreases the impact velocity, the whole profile of $\rho \cdot \overline{P}_{2p\sigma-3d\sigma}$, as a function of the impact parameter ρ, grows higher and the associated maximum peak moves toward $\rho \approx R_x$. As this trend continues, the average

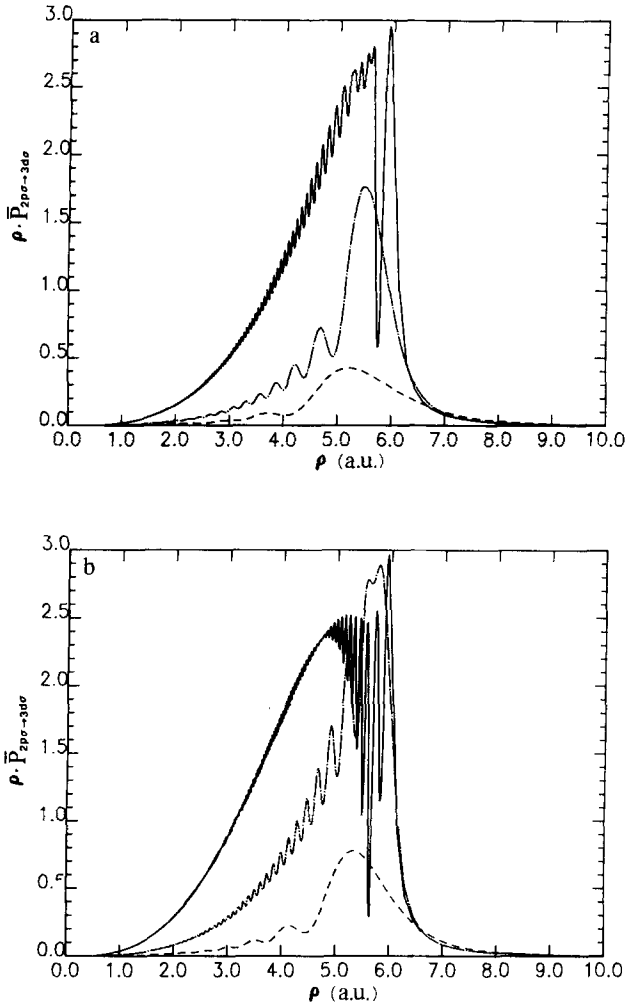

FIG. 5. The scaled average charge transfer transition probabilities $\rho \cdot \bar{P}_{2p\sigma-3d\sigma}$ of the process (29) as functions of the impact parameter ρ at $I = 1.0$ TW/cm^2 and $\lambda = 3000$ Å. In Fig. 5(a), $V = 0.155\times10^8$ cm/s, dashed curve; 0.05×10^8 cm/s, long-dash–dotted curve; and 0.01×10^8 cm/s, solid curve. In Fig. 5(b), $V = 0.10\times10^8$ cm/s, dashed curve; 0.02×10^8 cm/s, long-dash–dotted curve; and 0.005×10^8 cm/s, solid curve.

$\bar{P}_{2p\sigma-3d\sigma}$ can represent the exact $P_{2p\sigma-3d\sigma}$ of Eq. (64) better and better. Then when one further reduces the impact velocity, the profile is shifted backward and becomes lower and broader. Moreover, although the $\bar{P}_{2p\sigma-3d\sigma}$ still oscillates and oscillates more, but considerably less than that of the exact P, at slower impact velocity, the wiggling structure is diminishing except nearby the region around $\rho \simeq R_x$. This behavior of the average $\bar{P}_{2p\sigma-3d\sigma}$ will reduce the amount of the calculations tremendously when one computes the total charge capture cross sections which are to be seen below.

The total charge transfer cross sections of the reaction (29) are illustrated in two ways: (i) as a function of the laser intensity, and (ii) as a function of the impact velocity V_0, while keeping all other parameters fixed. At higher impact velocity, $V_0 = 1.0\times10^7$ cm/s, and the wavelength $\lambda = 3000$ Å (the same for the rest of the presentations), i.e., Fig. 6(a), we find that: (i) the P 1 result is (almost) linearly dependent upon the intensity; (ii) the M 1 results give a rather good agreement with the exact ones, (iii) the average results, i.e., $\bar{\sigma} = 2\pi\int_0^\infty d\rho \cdot \rho\bar{P}$, follow very closely to the exact ones; and finally (iv) the exact total cross section shows a strong nonlinear dependence upon the laser intensity. In Fig. 6(b) we show the same dependence of the cross section on the intensity, but at a smaller impact velocity, i.e., $V_0 = 2\times10^6$ cm/s. At this velocity, we see that the P 1 calculations still remain linearly as a function of the intensity and become very much deviated from all other three predictions.

In Figs. 7(a) and 7(b), we show the dependence of the charge transfer cross sections on the impact velocity at the laser wavelength $\lambda = 3000$ Å and laser intensities of (a) 0.4 TW/cm^2 and (b) 1.0 TW/cm^2. The P 1 results exhibit strong linear dependence on the reciprocal of the impact velocity, while the other three follow closely to each other. At the higher velocity end all four calculations are in good agreement with each other. The deviation of the approximate results, i.e., P 1, M 1, and the average from the exact ones becomes pronounced at the lower velocity end. It is interesting to see that among the three approximate calculations (P 1, M 1, and the average), the average results maintain the best

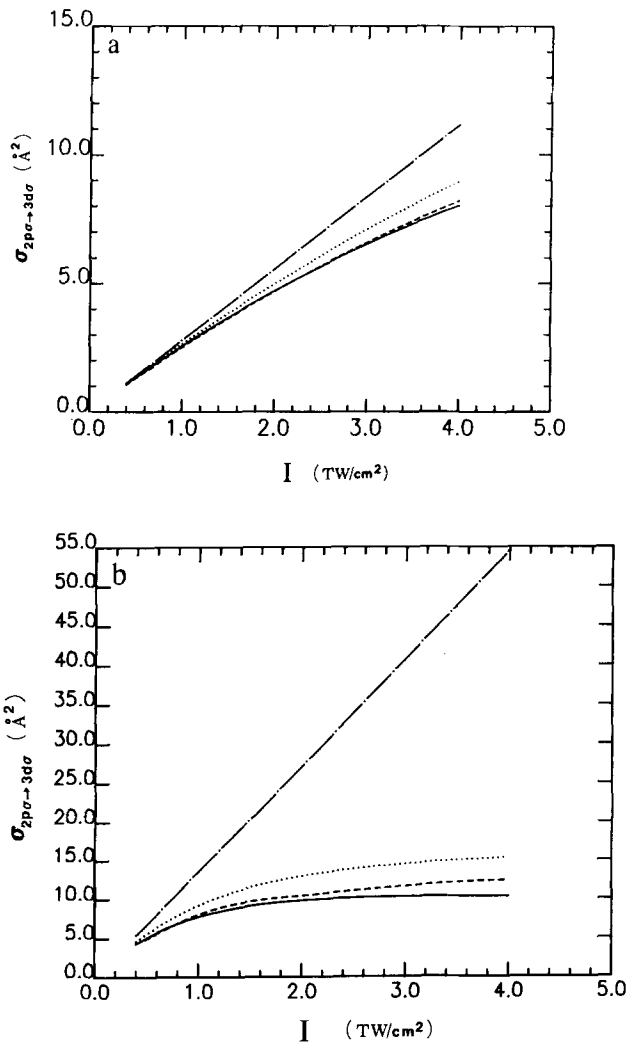

FIG. 6. The total charge transfer cross sections of the process (29) as functions of the laser intensity I, in TW/cm^2, at (a) $\lambda = 3000$ Å, $V = 1.0\times10^7$ cm/s, and (b) $\lambda = 3000$ Å, $V = 2\times10^6$ cm/s. Curve notations are the same as in Fig. 4.

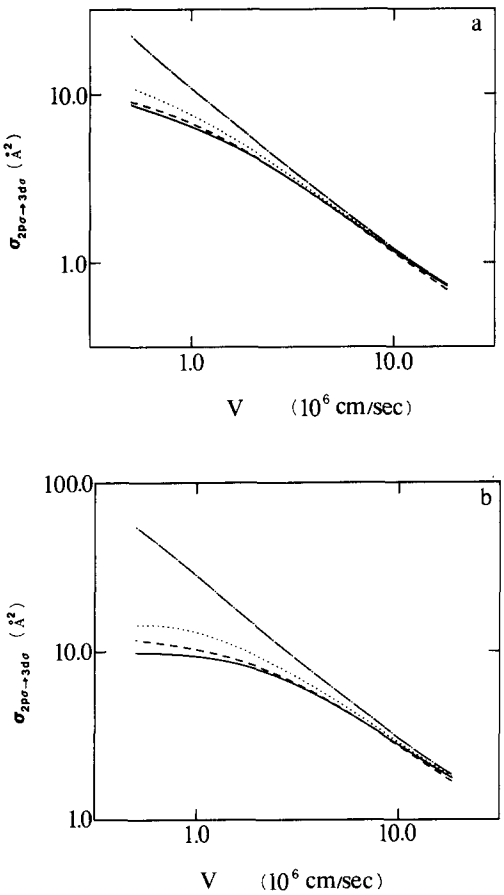

FIG. 7. The total charge transfer cross sections of the process (29) as functions of the impact velocity V, in cm/s, at (a) $I = 0.4\ \mathrm{TW/cm^2}$, $\lambda = 3000$ Å, and (b) $I = 1.0\ \mathrm{TW/cm^2}$, $\lambda = 3000$ Å. For curve notations see the caption of Fig. 4.

resemblance of the exact results except at the higher velocity end where the dependence of the cross section is linear in the reciprocal of the impact velocity and $P1$ and $M1$ serve as better approximations.

V. CONCLUSIONS

We have presented a nonperturbative semiclassical coupled dressed quasimolecular state theory for the general treatment of slow atomic collisions in the presence of an intense laser field. The theory was illustrated by a study of laser-assisted charge transfer processes of the bare heliums slowly impinging on ground-state neutral hydrogen atoms. It is found that the fast oscillating transition probability, as a function of the impact parameter, at slow impact velocity can be adequately described by an average and much less oscillatory quantity. In the diabatic DQMS basis, the first-order Magnus approximation generally gives a good account of the nonlinear dependence of the total capture cross sections, while the ordinary first-order perturbation calculations always show a linear dependence, on both the laser intensity and the reciprocal of the impact velocity. Although for the $(He–H)^{++}$ system of current interest, it has been shown[13] that the two-state model provides a good description of the collisional dynamics, our approach can be readily extended to a multistate basis. The assumption of a rectilinear trajectory for the nuclear motion, though a reasonable approximation for the velocity range under consideration, has to be relaxed for even slower collision processes. More accurate treatment of the nuclear trajectory is currently under consideration. Extension of the current approach to several laser-assisted charge exchange processes is in progress. Finally, we are also currently developing a quantum-mechanical (time-independent) close-coupling approach, in dressed-quasimolecular states, for the exact nonperturbative treatment of laser-assisted charge transfer processes.

ACKNOWLEDGMENTS

This work was initiated while one of us (SIC) was visiting the Center of Astrophysics, Harvard University, in the summer of 1983. He would like to thank Professor Dalgarno for his hospitality. This research was supported in part by the Department of Energy, Division of Chemical Sciences, under contract No. DE-AC02-80ER 10748, by the Alfred P. Sloan Foundation, and by the University of Kansas General Research Fund. Acknowledgment is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

[1]See, for example, R. C. Isler and E. C. Crume, Phys. Rev. Lett. **41**, 1296 (1978).
[2](a) D. W. Rule and K. Omidvar, Astrophys. J. **229**, 1198 (1979); (b) G. Steigman, *ibid.* **199**, 642 (1975).
[3]R. H. Dixon, J. F. Seely, and R. C. Elton, Phys. Rev. Lett. **40**, 122 (1978).
[4](a) A. V. Vinogradov and I. I. Sobelman, Sov. Phys. JETP **36**, 115 (1973); (b) W. H. Louisell, M. O. Scully, and W. B. McKnight, Phys. Rev. A **11**, 989 (1975).
[5]S. I. Yakovlenko, Sov. J. Quantum Electron. **8**, 151 (1978).
[6]W. R. Green, M. D. Wright, J. F. Young, and S. E. Harris, Phys. Rev. Lett. **43**, 120 (1979).
[7]J. F. Seely and R. C. Elton, Naval Research Laboratory, Memorandum Report 4317 (1980).
[8]R. Z. Vitlina, A. V. Chaplik, and M. V. Entin, Sov. Phys. JETP **40**, 829 (1975).
[9]D. A. Copeland and C. L. Tang, J. Chem. Phys. **65**, 3161 (1976); **66**, 5126 (1977).
[10]L. I. Gudzenko and S. I. Yakovlenko, Sov. Phys. Tech. Phys. **20**, 150 (1975).
[11]E. A. Andreev and A. S. Prostnev, Sov. Phys. JETP **49**, 998 (1979).
[12]J. F. Seely, J. Chem. Phys. **75**, 3321 (1981).
[13]L. F. Errea, L. Méndez, and A. Riera, J. Chem. Phys. **79**, 4221 (1983).
[14]S. I. Chu, Chem. Phys. Lett. **70**, 205 (1980).
[15]For a recent review, see, T. F. George, J. Phys. Chem. **86**, 10 (1982), and references therein.
[16](a) N. M. Kroll and K. M. Watson, Phys. Rev. A **13**, 1018 (1976); (b) A. M. F. Lau, *ibid.* **13**, 139 (1976).
[17]M. Mohan, K. F. Milfeld, and R. E. Wyatt, Chem. Phys. Lett. **99**, 411 (1983).
[18]J. Light and A. Szöke, Phys. Rev. A **18**, 1363 (1978).
[19]S. I. Chu, J. Chem. Phys. **75**, 2215 (1981).
[20](a) S. I. Chu, T. S. Ho, and J. V. Tietz, Chem. Phys. Lett. **99**, 422 (1983); (b) T. S. Ho and S. I. Chu, J. Chem. Phys. **79**, 4708 (1983).
In these references, we have introduced a similar idea to study the resonant molecular multiphoton absorption processes in intense infrared laser fields, where the slow moving rotational motion is separated from the much faster pace of the vibrational motion and the laser oscillation.
[21](a) J. H. Shirley, Phys. Rev. B **138**, 979 (1965); (b) D. R. Dion and J. O. Hirschfelder, Adv. Chem. Phys. **35**, 265 (1976).
[22]See, for example (a) J. V. Moloney and F. H. M. Faisal, J. Phys. B **12**, 2829

(1979); (b) S. I. Chu, J. V. Tietz, and K. K. Datta, J. Chem. Phys. **77**, 2968 (1982); (c) S. C. Leasure, K. F. Milfeld, and R. E. Wyatt, J. Chem. Phys. **74**, 6197 (1981); (d) J. V. Tietz and S. I. Chu, Chem. Phys. Lett. **101**, 446 (1983).

[23]See, for example, S. I. Chu, C. Laughlin, and K. K. Datta, Chem. Phys. Lett. **98**, 476 (1983).

[24](a) N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions*, 3rd ed. (McGraw–Hill, New York, 1965); (b) M. S. Child, *Molecular Collision Theory* (Academic, London, 1974); (c) B. H. Bransden, *Atomic Collision Theory*, 2nd ed. (Addison–Wesley, Benjamin, Reading, Mass., 1983).

[25](a) F. T. Smith, Phys. Rev. **179**, 111 (1969); (b) T. G. Heil and A. Dalgarno, J. Phys. B **12**, L557 (1979) and references therein.

[26](a) R. D. Piacentini and A. Salin, J. Phys. B **7**, 1666 (1974); (b) **9**, 563 (1976); (c) **10**, 1515 (1977); (d) T. Winter and N. F. Lane, Phys. Rev. A **17**, 66 (1978).

[27]J. B. Delos and W. R. Thorson, Phys. Rev. A **6**, 728 (1972).

[28](a) W. Magnus, Comm. Pure Appl. Math. **7**, 649 (1954); (b) P. Pechukas and J. C. Light, J. Chem. Phys. **44**, 3897 (1966); (c) U. Wille, Z. Phys. A **308**, 3 (1982).

[29]L. I. Schiff, *Quantum Mechanics* 3rd ed. (McGraw–Hill, New York, 1968), pp. 289–292.

[30](a) L. D. Landau, Phys. Z. Sowjetunion **2**, 46 (1932); (b) C. Zener, Proc. R. Soc. London Ser. A **137**, 696 (1932); (c) E. C. G. Stueckelberg, Helv. Phys. Acta **5**, 369 (1932).

[31]J. Mathews and R. L. Walker, *Mathematical Methods of Physics*, 2nd ed. (Benjamin, New York, 1970), p. 90.