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Ionization in heavy-particle collisions: Multichannel treatment with discretization of the electronic continuum

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A theoretical treatment of ionization in atomic collisions is developed for quantum-mechanical and semiclassical relative motions. It is based on a molecular-wave-function expansion containing both discrete and continuum spectrum states. The continuum is discretized by further expansion, which leads to normalizable "electronic state packets." A procedure is described to calculate scattering amplitudes that avoids having to orthogonalize continuum states to all the (usually unknown) discrete ones.

I. INTRODUCTION

Collisions between pairs of atoms can lead to ionization in which an electron is emitted and the heavy (atomic) particles are left in bound or scattering states. As examples, we mention first collisions at thermal kinetic energies between a metastable atom A^* and another atom B, with ionization resulting from electronic energy transfer as in

$$A^*+B \rightarrow A+B^+ +e^- \quad \text{(PI)}$$
$$\rightarrow AB^+ +e^- \quad \text{(AI)},$$

which are known as Penning ionization (PI), and associative ionization (AI). Secondly, in ion-atom collisions at energies in the range of 1 keV/amu, an electron may be emitted from outer electronic shells as a result of transfer of relative kinetic energy into electronic motions. For example, for an ion A^q with charge q, the process is

$$A^q+B \rightarrow A^q+B^+ +e^- .$$

If the emitted electron comes from an inner shell of B, the process is instead

$$A^q+B \rightarrow A^q+(B^*)^+ +e^- ,$$

where $(B^*)^+$ indicates an electronically excited ion.

To describe such collision processes it is necessary to include in expansion basis sets electronic states for the continuum of electron kinetic energies. This leads to infinite sets of coupled scattering equations, which must be treated by special methods to discretize in some way the electronic continuum. Early work on this subject was discussed by Bloch[1] in his review of the many-body theory of nuclear reactions. The mentioned PI and AI processes were studied with a discretization procedure leading to finite sets of coupled differential equations.[2] In the area of heavy-particle collisions, related work has been done on the dissociation of diatomic molecules in atom-diatom collisions,[3] and on scattering of atoms by solid surfaces, where a continuum of states is required to describe the phonon modes of the solid surface.[4] Discretization plays also a prominent role in recent studies of photoionization,[5] where, however, the emphasis is on the evaluation of integrals over densities of states. We instead shall focus on the properties and use of the expansion basis of electronic states.

We develop a formalism general enough to include the processes mentioned at the beginning, but to simplify matters we consider here only collisions where the active electrons have velocities greater than the relative velocities of nuclei. In this case it is appropriate to use molecular electronic states, where the electrons move in orbitals around both nuclei.[6] We postpone to the discussion an analysis of extensions of the theory and of other applications of the present molecular-state approach.

We extend the previous formalism[2] by introducing electron state wave packets, which are square integrable, i.e., L^2 states, whenever certain conditions are satisfied in the ionization process. The continuously infinite set of coupled scattering equations is then transformed by expansion in these L^2 states into a denumerable set. We prove within this approach a number of relations which

can be satisfied by introducing a new basis of L^2 electronic states chosen for computational convenience. Expanding the scattering wave functions in the new basis leads to sets of coupled equations, like the ones arising when only bound electronic states are considered. These equations can be solved with standard computational methods[7] to obtain the asymptotic amplitudes of wave functions. Physical scattering amplitudes result from linear combinations of those asymptotic amplitudes.

We also develop a semiclassical (SC) version of our theory. Some previous SC approaches to ionization have used complex potentials, with the imaginary parts representing electron-emission widths.[8] We instead explicitly allow for coupling of continuum and discrete electron states along a classical trajectory of the heavy particles. This has also been the starting point for calculations of ionization in the weak-coupling limit.[9] Here we develop the SC treatment in terms of electron wave packets, as done for the quantum-mechanical case, to obtain a denumerable set of time-dependent first-order differential equations for transition amplitudes. An SC calculation of cross sections for PI has already been carried out for a special case of the present theory and agrees well with quantum-mechanical results.[10]

In what follows, Sec. II presents the starting scattering equations and boundary conditions for neutral or ionized heavy-particle products, introduces the expansion in electron wave packets, and ends with an example of the expansion procedure for electron emission. Section III contains the semiclassical theory in a simple version, chosen to focus on the special problem of ionization. In the discussion, Sec. IV, we briefly consider the relation of the present approach to other theories and mention several other possible applications.

II. QUANTUM THEORY

A. Expansion in molecular electronic states

We introduce a complete set of electronic states in a space-fixed frame, $\{ |\Phi_n(\vec{R})\rangle, |\Phi_\nu(\vec{R})\rangle \}$ for each internuclear position $\vec{R}$, where the bra and ket notation is used to indicate states over electronic variables. The index n in the bound state Φ_n stands for a collection of quantum numbers

$$n=(n_0^{2S+1}\Lambda_{M_S}LM_L),$$

where (S,M_S) are the electronic spin quantum numbers in a space-fixed frame, Λ is the projection of the orbital electronic angular momentum on the molecular axis, and (L,M_L) are electronic angular momentum quantum numbers in a center-of-mass space-fixed frame. The index ν in the continuum state Φ_ν stands for

$$\nu=(n_+\kappa\lambda\mu\sigma),$$

where n_+ is defined for the diatomic ion as n above, κ is the electron wave number, (λ,μ) its angular momentum and projection quantum numbers, and σ its spin projection quantum number. The states Φ are furthermore normalized so that

$$\langle\Phi_n(\vec{R})\,|\,\Phi_{n'}(\vec{R})\rangle=\delta_{nn'}\,, \tag{1a}$$

$$\langle\Phi_n(\vec{R})\,|\,\Phi_\nu(\vec{R})\rangle=0\,, \tag{1b}$$

$$\langle\Phi_\nu(\vec{R})\,|\,\Phi_{\nu'}(\vec{R})\rangle=\delta(\nu-\nu')\,. \tag{1c}$$

These states may be adiabatic or diabatic[11] with respect to changes in $\vec{R}$, but in all cases their limits for $R\to\infty$ are eigenstates of the electronic Hamiltonians of the atomic fragments, with eigenenergies $E_n<0$ and $E_\nu\geq 0$. The total molecular state $|\Psi^{(+)}(\vec{R})\rangle$ for electronic and nuclear motions may be expanded as

$$|\Psi^{(+)}(\vec{R})\rangle=\sum_n |\Phi_n(\vec{R})\rangle F_n(\vec{R}) + \int d\nu\,|\Phi_\nu(\vec{R})\rangle F_\nu(\vec{R})\,, \tag{2}$$

with amplitudes F satisfying outgoing wave boundary conditions for an incoming wave in state $n=a$ and total energy $E>0$. The integral over ν stands for both an integral over κ and a sum over $\alpha=(n_+\lambda\mu\sigma)$. Furthermore, letting $s=n$ or ν,

$$F_s(\vec{R})\sim\delta_{sa}e^{i[\vec{k}_a\cdot\vec{R}+(\gamma/k_a)\ln(k_aR-\vec{k}_a\cdot\vec{R})]} + f_{sa}(\vec{k}_s,\vec{k}_a)\frac{e^{i[k_sR+\beta_s(R)]}}{R}\,, \tag{3a}$$

if $E_s<E$, and

$$F_s(\vec{R})\sim A_{sa}(\vec{k}_s,\vec{k}_a)e^{-|k_s|R+\beta_s(R)}\,, \tag{3b}$$

if $E_s>E$, where $\gamma=q_Aq_Bm/\hbar^2$ in terms of the net charges q_A and q_B of A and B, and $\beta_s(R)=-(\gamma'/|k_s|)\ln(2|k_s|R)$ with γ' referring to the exit channel. Also,

$$E=\hbar^2k_s^2/(2m)+E_s\,, \tag{4}$$

and $\hbar\vec{k}$ indicates a relative momentum for the atomic nuclei. The f_{sa} factors are scattering amplitudes, while the A_{sa} are asymptotic amplitudes for exponentially decaying states in closed channels.

We introduce the nuclear kinetic energy operator $K=-\hbar^2\nabla_R^2/(2m)$ and electronic Hamiltonian $H_{\rm el}$, and replace Eq. (2) in the Schrödinger equation

$$(K+H_{\rm el}-E)\,|\,\Psi^{(+)}(\vec{\mathbf{R}})\rangle=0 \tag{5}$$

to obtain by projection the continuous infinite set of coupled equations

$$\sum_{n'}[\delta_{nn'}(K-E)+V_{nn'}+C_{nn'}]F_{n'} + \int d\nu(V_{n\nu}+C_{n\nu})F_\nu=0, \tag{6a}$$

$$\int d\nu'[\delta(\nu-\nu')(K-E)+V_{\nu\nu'}+C_{\nu\nu'}]F_{\nu'} + \sum_{n'}(V_{\nu n'}+C_{\nu n'})F_{n'}=0\ , \tag{6b}$$

where

$$V_{ss'}(\vec{\mathbf{R}})=\langle\Phi_s(\vec{\mathbf{R}})\,|\,H_{\rm el}\,|\,\Phi_{s'}(\vec{\mathbf{R}})\rangle\ , \tag{7a}$$

$$C_{ss'}(\vec{\mathbf{R}},\vec{\nabla}_R)=\left[\frac{\hbar^2}{m}\right]\langle\Phi_s(\vec{\mathbf{R}})\,|\,\vec{\nabla}_R\Phi_{s'}(\vec{\mathbf{R}})\rangle\cdot\vec{\nabla}_R - \frac{\hbar^2}{2m}\langle\Phi_s(\vec{\mathbf{R}})\,|\,\nabla_R^2\Phi_{s'}(\vec{\mathbf{R}})\rangle\ . \tag{7b}$$

Solving these equations with the boundary conditions of Eq. (3), we obtain the ionization cross sections per unit solid angle and electron wave vector from

$$\frac{d^2\sigma_{\nu a}}{d\Omega\,d\kappa}=(k_\nu/k_a)\,|f_{\nu a}(\vec{\mathbf{k}}_\nu,\vec{\mathbf{k}}_\alpha)|^2\ , \tag{8}$$

where Ω is the solid angle of $\vec{\mathbf{k}}_\nu$ in a reference frame with z axis along $\vec{\mathbf{k}}_a$, and we have assumed that the emitted electron state has a $\delta(\kappa-\kappa')$ normalization.

B. Electronic state packets

The infinite set of coupled Eqs. (6) are not in a convenient form for solution because the continuous index κ required an integration over ν. A basic aspect of the present approach is that Eqs. (6) may be transformed to a more familiar form whenever the amplitudes F_ν are square integrable functions in the variable κ. This has been observed to be the case for the ionization processes to be discussed later on.

Introducing a complete, normalized set of functions $\{g_i(\kappa)\}$ satisfying

$$\int d\kappa\, g_i(\kappa)^* g_{i'}(\kappa)=\delta_{ii'}\ , \tag{9a}$$

$$\sum_i g_i(\kappa)g_i(\kappa')^*=\delta(\kappa-\kappa')\ , \tag{9b}$$

we let $\nu=(\kappa,\alpha)$ and expand

$$F_{\kappa,\alpha}=\sum_i g_i(\kappa)F_{i,\alpha}\ . \tag{10}$$

Replacing in Eq. (2) and rearranging,

$$|\,\Psi^{(+)}(\vec{\mathbf{R}})\rangle=\sum_n|\,\Phi_n(\vec{\mathbf{R}})\rangle F_n(\vec{\mathbf{R}}) + \sum_I|\,\tilde{\Phi}_I(\vec{\mathbf{R}})\rangle F_I(\vec{\mathbf{R}})\ , \tag{11}$$

where $I=(i,\alpha)$ and

$$|\,\tilde{\Phi}_I(\vec{\mathbf{R}})\rangle=\int d\kappa\, g_i(\kappa)\,|\,\Phi_\nu(\vec{\mathbf{R}})\rangle\ , \tag{12}$$

so that

$$|\,\Phi_\nu(\vec{\mathbf{R}})\rangle=\sum_i g_i(\kappa)^*\,|\,\tilde{\Phi}_I(\vec{\mathbf{R}})\rangle\ . \tag{13}$$

The functions $\tilde{\Phi}_I$ are orthonormal by construction, since

$$\langle\tilde{\Phi}_I\,|\,\tilde{\Phi}_{I'}\rangle=\int d\kappa\, g_i(\kappa)^*\int d\kappa'\, g_{i'}(\kappa')\langle\Phi_\nu\,|\,\Phi_{\nu'}\rangle =\int d\kappa\, g_i(\kappa)^* g_{i'}(\kappa)\delta_{\alpha\alpha'}=\delta_{II'}\ . \tag{14}$$

The $\tilde{\Phi}_I$ are *electronic state packets* in the sense that they are square integrable. Hence Eq. (11) gives an expansion of $\Psi^{(+)}$ in two types of square integrable electronic states. Furthermore, the states Φ_n and $\tilde{\Phi}_I$ are orthogonal, as seen from Eqs. (1b) and (12). In actual calculations one would begin with the $\tilde{\Phi}_I$ states and would require that the Φ_ν in Eq. (13) satisfy Eq. (1b). This can be done as follows. From Eqs. (1b) and (13)

$$\sum_i g_i(\kappa)^*\langle\Phi_n\,|\,\tilde{\Phi}_I\rangle=0\ . \tag{15}$$

For each n and α index, this may be considered a set of linear equations for the unknowns $\langle\Phi_n\,|\,\tilde{\Phi}_I\rangle$. Choosing as many $\kappa=\kappa_{i'}$ values as there are unknowns, Eq. (15) becomes a set of coupled linear equations with coefficients $g_i(\kappa_{i'})$. By properly choosing the $\kappa_{i'}$ values one can assure that $\det[g_i(\kappa_{i'})^*]\neq0$, hence one must necessarily have $\langle\Phi_n\,|\,\tilde{\Phi}_I\rangle=0$.

The preceding development constitutes proof that $\Psi^{(+)}$ can be expanded in a set of square in-

tegrable, orthogonal basis functions, provided the amplitudes F_ν are square integrable functions of κ. In applications, the functions Φ_n would be known from the outset, but the $\tilde{\Phi}_I$ would have to be constructed and orthogonalized to all the Φ_n. This procedure can be simplified by introducing a new basis set. Let us consider a set of orthonormal electronic states $|\, j,\vec{R}\rangle$ which diagonalize the asymptotic form of $H_{\rm el}$, so that

$$V_{jj'}(R) \underset{R\to\infty}{\sim} \delta_{jj'}E_j \ . \tag{16}$$

For $R\to\infty$, some of the E_j values will be negative and others positive. Hence the set $\{|\, j,\vec{R}\rangle\}$ spans the spaces of both bound and continuum electronic states. We expand next

$$|\, \Phi_n(\vec{R})\rangle = \sum_j |\, j,\vec{R}\rangle b_{jn}(\vec{R}) \ , \tag{17a}$$

$$|\, \tilde{\Phi}_I(\vec{R})\rangle = \sum_j |\, j,\vec{R}\rangle b_{jI}(\vec{R}) \ . \tag{17b}$$

Substituting these in Eq. (11) we obtain

$$|\, \Psi^{(+)}(\vec{R})\rangle = \sum_j |\, j,\vec{R}\rangle F_j(\vec{R}) \ , \tag{18}$$

which replaced in the Schrödinger equation may be solved for the F_j with asymptotic conditions

$$F_j \sim A_{ja}\frac{e^{-|k_j|R+\beta_j(R)}}{R}, \quad E_j \geq E \ , \tag{19a}$$

$$F_j \sim \delta_{ja}\, e^{i[\vec{k}_j\cdot\vec{R}+(\gamma/k_j)\ln(k_jR-\vec{k}_j\cdot\vec{R})]} + f_{ja}\frac{e^{i[k_jR+\beta_j(R)]}}{R}, \quad E_j < E \ , \tag{19b}$$

where

$$E = \hbar^2 k_j^2/(2m) + E_j \ . \tag{20}$$

The infinite set of coupled-channel Eqs. (6) become a standard set,

$$\sum_{j'}[\delta_{jj'}(K-E)+V_{jj'}+C_{jj'}]F_{j'}(\vec{R})=0 \tag{21}$$

with matrix elements defined as in Eqs. (7) but for the $\{|\, j,\vec{R}\rangle\}$ basis.

It remains to express the scattering amplitudes $f_{\nu a}(\Omega)$ in terms of the calculated $f_{ja}(\Omega)$. From the Lippman-Schwinger transition operator $\hat{T}$, in the $|\, j,\vec{R}\rangle$ representation, one has

$$f_{ja}(\Omega) = -\frac{m}{2\pi\hbar^2}\langle \vec{k}_j j\,|\,\hat{T}\,|\,\vec{k}_a a\rangle \ , \tag{22}$$

where we use for heavy-particle states the normalization $\langle \vec{k}\,|\,\vec{k}'\rangle = (2\pi)^3\delta(\vec{k}-\vec{k}')$, $|\, j\rangle = \lim |\, j,\vec{R}\rangle$, and $|\, a\rangle = \lim |\, \Phi_a(\vec{R})\rangle$ for $R\to\infty$, and where the orientation of $\vec{k}_j$ is given by Ω. Similarly, in the $\Phi_\nu(\vec{R})$ representation we have

$$f_{\nu a}(\Omega) = -\frac{m}{2\pi\hbar^2}\langle \vec{k}_\nu \nu\,|\,\hat{T}\,|\,\vec{k}_a a\rangle \ , \tag{23}$$

where $|\, \nu\rangle = \lim |\, \Phi_\nu(\vec{R})\rangle$ for $R\to\infty$. We can relate the amplitudes in Eqs. (22) and (23) by restricting ourselves to $\vec{k}_\nu = \vec{k}_j$ and $|\, \nu\rangle = |\, \nu_j\rangle$, the latter meaning that $E_\nu = E_j$, so that the total energy is always E. Using the completeness of the $\{|\, j\rangle\langle j\,|\}$ set in the space of electronic states,

$$\sum_j |\, j\rangle\langle j\,| = 1 \ , \tag{24}$$

we find

$$\left[-\frac{m}{2\pi\hbar^2}\right]^{-1} f_{\nu_j a}(\Omega) = \langle \vec{k}_j\nu_j\,|\,\hat{T}\,|\,\vec{k}_a a\rangle = \sum_{j'}\langle \vec{k}_j\nu_j\,|\,j'\rangle\langle j'\,|\,\hat{T}\,|\,\vec{k}_a a\rangle = \sum_{j'}\langle \nu_j\,|\,j'\rangle\langle \vec{k}_j j'\,|\,\hat{T}\,|\,\vec{k}_a a\rangle \ . \tag{25}$$

Furthermore, $|\, \nu_j\rangle$ and $|\, j'\rangle$ are solutions at $R\to\infty$ of the same electronic Hamiltonian for the atomic fragments, so that $\langle \nu_j\,|\,j'\rangle = 0$ if $E_j \neq E_{j'}$. The result is

$$f_{\nu_j a}(\Omega) = \sum_{j'(E_{j'}=E_j)}\langle \nu_j\,|\,j'\rangle f_{j'a}(\Omega) \ , \tag{26}$$

hence $f_{\nu a}(\Omega)$ may be obtained for each energy E_j as a linear combination of all the $f_{j'a}$ amplitudes for asymptotic states $|\, j'\rangle$ of the same final energy $E_{j'} = E_j$.

Comparing the expansions of Eqs. (11) and (18) we find that the second one is more advantageous because it does not require a knowledge of all bound states $|\, \Phi_n\rangle$, to which the $|\, \tilde{\Phi}_I\rangle$ must be made orthogonal. The set of states $|\, j,\vec{R}\rangle$ must only be large enough to properly represent the $|\, \Phi_n\rangle$ states of interest and to give enough states within the continuum spectrum to allow for interpolation of transition amplitudes.

C. Two examples

The basis $\{g_i(\kappa)\}$ should be chosen so that the electron distribution can be described with the smallest possible number of expansion terms. In one application already carried out[2] the functions $g_i(\kappa)$ were chosen as

$$g_i(\kappa)=a_i(\epsilon)=(\Delta\epsilon)^{-1/2}, \quad i=1 \text{ to } N_d \tag{27}$$

for $\epsilon_i-\Delta\epsilon/2\leq\epsilon\leq\epsilon_i+\Delta\epsilon/2$ and zero otherwise. Here $\epsilon=\hbar^2\kappa^2/(2m_e)$ is the kinetic energy of an electron of mass m_e and ϵ_i is the energy of the ith band of width $\Delta\epsilon$. This simple choice provides a basis which is orthonormal and complete in the limit $\Delta\epsilon\to 0$. Replacing Eq. (27) into Eq. (12) one finds that the state packets $\tilde{\Phi}_I$ have energy spread $\Delta\epsilon$ and tend to Φ_{ν_i} for $\Delta\epsilon\to 0$. In the applications, $\Delta\epsilon$ was decreased and N_d increased to cover the same region of ϵ values, until convergence of scattering amplitude values was achieved.

In a second example, consider a case where it is experimentally known that the energy distribution of the emitted electron decreases exponentially at large κ. We choose

$$g_i(\kappa)=e^{-\kappa/2}L_i(\kappa), \quad i=0,1,2,\ldots, \tag{28}$$

where L_i is the Laguerre polynomial of ith order, so that Eq. (9a) is satisfied. Indicating with $\chi_{\kappa\lambda\mu\sigma}(\vec{r},\zeta)$ the spin orbital of the electron that flies away, where $(\vec{r},\zeta)$ are position and spin electron variables, we define

$$\tilde{\chi}_{i\lambda\mu\sigma}(\vec{r},\zeta)=\int_0^\infty d\kappa\, g_i(\kappa)\chi_{\kappa\lambda\mu\sigma}(\vec{r},\zeta)\,, \tag{29a}$$

$$|I,\vec{R}\rangle=C_I\mathscr{A}\,|\Phi_{n_+}(\vec{R})\tilde{\chi}_{i\lambda\mu\sigma}\rangle\,, \tag{29b}$$

where C_I is a normalization constant and $\mathscr{A}$ is the electron antisymmetrizer. To be more specific, let the electron that flies away be in the free s orbital

$$\chi_{\kappa 00}(\vec{r})=r^{-1}\sin(\kappa r)/(\sqrt{2}\pi) \tag{30}$$

normalized to $\delta(\kappa-\kappa')$. Replacing it and Eq. (27) in Eq. (29a), and temporarily replacing the index i by j, we obtain

$$\tilde{\chi}_{j00}(\vec{r})=\frac{1}{\sqrt{2}\pi}\frac{(-1)^j\,\mathrm{Im}(\frac{1}{2}+ir)^{2j+1}}{r(\frac{1}{4}+r^2)^{j+1}}\,,$$

$$j=0,1,2,\ldots, \tag{31}$$

where Im means the imaginary part of the following complex expression. These packets are square integrable, decreasing as r^{-2} for $r\to\infty$, and have j nodes each. Their form is shown in Fig. 1.

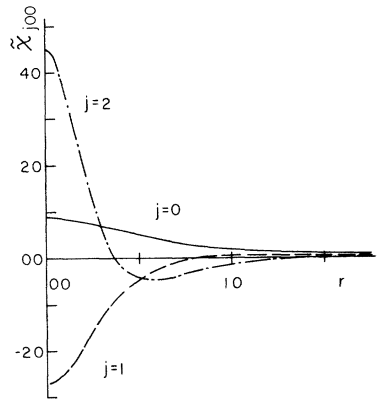

FIG. 1. The first three state packets of Eq. (31) for an electron with zero angular momentum versus the radial electron position, in atomic units.

Next we can orthogonalize the $|I,\vec{R}\rangle$ states of Eq. (29b) to the N-electron bound states $|\Phi_n(\vec{R})\rangle$ to obtain from the first ones the states $|\tilde{\Phi}_I(\vec{R})\rangle$ in Eq. (11). More directly, to avoid orthogonalization, we can introduce a discrete basis of one-electron molecular spin orbitals $\{|\eta_p,\vec{R}\rangle\}$ for each electron $p, 1\leq p\leq N$, and construct N-electron states as follows. Working in a reference frame attached to the diatomic nuclei and indicating with $\{\phi_{a\mu},\ a=1 \text{ to } N_\phi\}$ the collection of known molecular orbitals of bound electrons with quantum numbers μ, we construct the orthogonalized molecular orbital packets

$$\tilde{\chi}'_{j\mu}=\tilde{\chi}_{j\lambda\mu}-\sum_{a=1}^{N_\phi}\phi_{a\mu}\langle\phi_{a\mu}|\tilde{\chi}_{j\lambda\mu}\rangle\,. \tag{32}$$

Then the pth molecular spin orbital $|\eta_p,\vec{R}\rangle$ will be equal to $|\phi_{a\mu}\sigma\rangle$ for $\underline{\eta}=a=1$ to N_ϕ, and equal to $|\tilde{\chi}'_{j\mu}\sigma\rangle$ for $\underline{\eta}=N_\phi+1,\ldots$. We can next construct the N-electron states,

$$|\underline{\eta},\vec{R}\rangle=(N!)^{-1/2}\mathscr{A}\prod_{p=1}^{N}|\eta_p,\vec{R}\rangle\,, \tag{33}$$

to diagonalize in this basis the operator H_{el} at $R\to\infty$. This results in a set of states $|j,\vec{R}\rangle$, each of which is a superposition of configurations obtained by solving an N-electron bound-state problem, to be used in Eq. (18).

III. SEMICLASSICAL THEORY

When wavelengths $2\pi k_j^{-1}$ for relative motion are small and potentials V_{jj} are slowly varying, the

relative motion may be described classically. In the present approach we use the simplest semiclassical treatment, where quantum corrections such as path interference and tunneling are neglected.[12] To further simplify the discussion, assume that $V_{jj'}$ and $C_{jj'}$ in Eq. (21) depend only on the radial variable R. Then the orbital angular momentum is conserved and its quantum numbers (l,m) are fixed. Choosing $m=0$, i.e., orbital motion in the x,z plane, the discrete value l may be transformed into the continuum impact parameter ρ through the relation $\rho=(l+\frac{1}{2})/k_a$, where k_a is the initial wave number. A classical trajectory may be introduced for an average interatomic potential $\bar{V}(R)$ so that R is a function of time t for each (k_a,ρ), and one obtains the angular deflection function $\theta(k_a,\rho)$.[13] The amplitudes F_j in Eq. (18) may be replaced for each $(l,m=0)$ by the correspondence

$$F_{jl0} \Longrightarrow c_j(t,k_a,\rho)\, e^{-i\int_{-\infty}^{t} \mathscr{E}_j(t')\,dt'/\hbar} , \tag{34}$$

where $\mathscr{E}_j=V_{jj}[R(t;k_a,\rho)]$. The coefficients c_j, which denote the time-dependent transition amplitudes, satisfy the normalization condition

$$\sum_j |\, c_j(t;k_a,\rho)\,|^2=1 . \tag{35}$$

Also, provided the initial state $|\, a\,\rangle$ coincides with one of the states $|\, j\,\rangle$, the initial conditions are

$$c_j(t\to-\infty;k_a,\rho)=\delta_{ja} . \tag{36}$$

Further defining $|\, \varphi_j(t)\rangle = |\, j,\vec{R}(t)\rangle$ one obtains the following set of coupled equations for given (k_a,ρ) and initial state a:

$$\frac{\partial c_j}{\partial t}=\sum_{j'} \langle \varphi_j(t)\,|\, -i(H_{\rm el}-\mathscr{E}_j)/\hbar-\partial/\partial t\,|\,\varphi_{j'}(t)\rangle c_{j'}(t) \times e^{i\int_{-\infty}^{t}[\mathscr{E}_j(t')-\mathscr{E}_{j'}(t')]dt'/\hbar} . \tag{37}$$

The matrix elements $\langle\,|\,\partial/\partial t\,|\,\rangle$ may further be transformed into two terms using the relation

$$\frac{\partial}{\partial t}=\dot{R}\frac{\partial}{\partial R}+\frac{\hbar k_a\rho}{mR^2}iL_y , \tag{38}$$

where L_y is the y component of the orbital angular momentum operator. This expression gives rise to radial matrix elements $\langle\,|\,\partial/\partial R\,|\,\rangle$ with the restriction $\Lambda'=\Lambda$ and the rotational matrix elements $\langle\,|\,iL_y\,|\,\rangle$ with $\Lambda'=\Lambda\pm1$. A program for solving Eq. (32) in the case where the trajectories are of the Coulomb type has been developed by Piacentini and Salin.[14]

The transition amplitudes required for calculation of cross sections are not the $c_{ja}(t\to+\infty)$ but instead $c_{\nu a}(t\to+\infty)$ corresponding to the physical transition $a\to\nu$. By analogy with Eq. (26) the latter are given by

$$c_{\nu_j a}(+\infty)=\sum_{j'(E_{j'}=E_j)} \langle \nu_j\,|\,\varphi_{j'}(+\infty)\rangle c_{j'a}(+\infty) . \tag{39}$$

From this, the double differential cross section for emission of an electron with angular momentum quantum numbers (λ,μ) within the wave-number increment $d\kappa$ and with the nuclei scattered into solid angle $d\Omega$, assuming a unique relation between $\Theta=|\,\theta\,|$ and ρ, is[12]

$$\frac{d^2\sigma_{\nu a}}{d\kappa\, d\Omega}=\left[\frac{d\sigma}{d\Omega}\right]_a^{cl} |\, c_{\nu a}(+\infty,k_a,\Theta)\,|^2 , \tag{40}$$

valid provided neither Θ nor k_a are too small. Finally, the integral cross section $d\sigma_{\nu a}/d\kappa$ for ionization within the differential $d\kappa$ follows from

$$\frac{d\sigma_{\nu a}}{d\kappa}=2\pi\int_0^\infty d\rho\,\rho\,|\, c_{\nu a}[+\infty;k_a,\Theta(\rho)]\,|^2 , \tag{41}$$

while the total integral cross section for emission of an electron with $(\lambda\mu\sigma)$ is

$$\sigma_{n_+a}^{(\lambda\mu\sigma)}(k_a)=\int_0^\infty d\kappa \left[\frac{d\sigma_{\nu a}}{d\kappa}\right] . \tag{42}$$

IV. DISCUSSION

We have developed an expansion procedure for the treatment of the electronic continuum states in heavy-particle collisions, in terms of (L^2) electronic state wave packets $\tilde{\Phi}_I$. We found that this expansion is justified whenever the channel wave functions for ionization are square integrable functions of the emitted electron wave number. Also, we have proved that the use of the $\tilde{\Phi}_I$ satisfies the requirement of orthogonality between discrete and continuum spectrum states. However, to impose this orthogonality it was found more convenient to introduce from the outset a new basis $|\, j,\vec{R}\,\rangle$. The final expressions are summarized in Eqs. (19), (20), and (26) for the quantal treatment and Eqs. (36), (37), and (39) for the semiclassical one.

Two theoretical problems must be considered in applications. If the velocity of the active electrons is not appreciably larger than the relative velocity

of the nuclei, then the momentum coupling terms $C_{jj'}$, in Eq. (21) cannot be ignored. Secondly, if the basis set is not large enough, one should include electron-translation factors to satisfy the correct asymptotic conditions.[15]

Total wave functions of the form of Eq. (18) appear in Sturmian and pseudostate methods.[16] To some extent, our procedure justifies the use in these methods of L^2 states for the continuum.

Besides the application of the present theory to the processes mentioned in the Introduction, other problems could be treated, such as photoionization,[5] ionization processes in the presence of strong electromagnetic fields,[17] and neutralization and electron emission in ion-surface collisions.[18] The possibility also exists for studying the role played by the electronic continuum in collisions leading to bound-to-bound state transitions of the diatomic electrons.[16]

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