PHYSICAL REVIEW VOLUME 181, NUMBER 1 5 MAY 1969

Impact Ionization in the Proton–H-Atom System: I. Theory

Walter R. Thorson
Department of Chemistry, University of Alberta, Edmonton, Canada

and

Hiram Levy II*
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 20 December 1968)

In a series of papers, of which this is the first, the calculation of the total cross section $\sigma_I(\epsilon)$ for the process $H^+ + H(1s) \rightarrow 2H^+(E') + e^-(\epsilon)$, for initial relative energies $E < 500$ eV, is described and performed. Here E' is the relative energy of the final protons. This paper (I) describes the theory used, and paper II describes the calculation and results for the electronic part of the problem (wave functions and transition matrix elements). Work is being completed on the trajectory integrals which form the last part of the calculation. $\sigma_I(\epsilon)$ is a total cross section with respect to scattering angles, but is differential in the final electron energy. The principle upon which the calculation is based is the approximate separability of electron and heavy-particle dynamics for both initial and final states, due to the mass disparity. The theory is an extension of that developed earlier by Thorson for transitions to discrete states.

A. INTRODUCTION

We describe here the calculation of the total cross section $\sigma_I(\epsilon)$ for the impact ionization process $H^+ + H(1s) \rightarrow 2H^+(E') + e^-(\epsilon)$ for initial relative energies $E < 500$ eV. We have calculated $\sigma_I(\epsilon)$ for the entire significant range of electron energies, with a resolution of better than 1 eV; the approximations made in the theory are such (Sec. C) that differential cross sections with respect to angle cannot be accurately obtained. (For the direct impact mechanism of which this system is the prototype we do not, of course, expect fine structure of the order of our resolution or less.)

At c.m. energies below 500 eV, the collision of two protons is "slow" in the sense that proton speeds are significantly lower than that of an electron with energy of 1 a.u. Under these conditions a suitable adiabatic approximation may provide a reasonable zero-order description of the bound electronic states of the system, bearing in mind that a "molecular" description of the electronic subsystem will be necessary for these low energies (during collision a valence electron will make many circuits around the "molecule"). However, it has long been known[1] that the Born-Oppenheimer or perturbed-stationary-states approximation is not an adequate description, because it ignores a kinematic factor describing electron motion with respect to the collision center, due to motion of the heavy particles to which electrons are asymptotically bound. Inclusion of this factor significantly alters the transition operators for inelastic scattering. An adiabatic formulation including this factor, yet retaining a fully molecular description of electronic states, has been given by Thorson[2] for "tightly-bound" electronic states of the $H^+ + H$ system; a first-order perturbative theory of inelastic scattering to discrete final states was presented and formulas derived for the necessary transition matrix elements. Although this formulation can easily be extended to many-electron heteronuclear diatomic systems, its usefulness is essentially limited to one-electron systems; when two or more electrons are present in a diatomic system, the possibility of competition between different spin and orbital configurations leads to the crossing or pseudo-crossing of adiabatic potential curves. At such crossing points the probability of transition from one state to another may become quite large, and adiabatic separations of the two states become invalid. A careful study of the primitive one-electron case may be justified, nevertheless, on the ground that it provides a background framework, within which the problem of curve-crossing can be placed; it is also a system for which the electronic solutions can be easily and exactly computed.

Impact ionization presents a further problem: the description of the continuum states of an electron in the field of two moving heavy particles. The continuum states are not adiabatic in the sense of a *following* of the nuclear configuration, as occurs in discrete states; indeed, this is specifically excluded by the nature of continuum states. Very little is known about practical solutions to the general three-body problem. However, again by taking advantage of the small electron-proton mass ratio, we have been able to find an approximate solution to the problem, valid for our purposes. This solution is developed in Sec. D.

The sort of description used here for the electronic continuum of the system $H^+ + H$ can be extended in principle to more general systems. However, many-electron systems exhibit a variety of complex mechanisms for impact ionization. Many of these are basically a sort of collisional autoionization: Suppose a discrete state, either arising from the ground manifold, or easily accessible by some strong coupling from it, has a potential curve which extends into the continuum at smaller internuclear distances [if we may consider it to "cross" curves corresponding to other configurations (a so-called "diabatic" potential curve[3])]. In a violent collision the system may penetrate to internuclear distances where autoionization in effect may occur. The collision energy at which such a process can become effective has nothing to do with the adiabatic criteria we have applied to the one-electron system, but is determined by the energy required to bring the diatomic system into the autoionizing region. Since this energy is of the same order of magnitude as the ionization threshold, efficient impact ionization can be and is observed down to energies not far from threshold. Also, because of the nature of the mechanism, such impact ionization cross sections will possess considerable structure, as function of both collision energy E and electron energy ϵ.

This mechanism cannot exist in the proton–H-atom system, however, and although there is strong coupling from the ground manifold in H_2^+ to the $2p\pi_u^\pm$ molecular state,[4] this state is "tightly bound" throughout the low-energy region of interest to us. We may call the mechanism we treat here "direct impact ionization." Since classically only a hard collision between a fast electron and a slow proton would permit much momentum transfer, the name seems especially appropriate. For the direct impact mechanism, ionization is relatively inefficient in the adiabatic region (nonadiabatic interactions are small perturbations) and the cross section does not exhibit much structure as a function of energy. An accurate calculation is of value because no such study has ever been made, even for this prototype system, at low energies. It may also become experimentally feasible to measure low-energy impact ionization in the proton–H-atom system.

In Sec. B the physical ideas behind the calculation are discussed. Section C describes the electronic basis set and the "fast electron" approximation for the continuum; Section D deals with the problem of three-body final states, and indicates how the scattering amplitude can be calculated. Sections E and F describe the initial state, the transition operator, and the trajectory integrals which must be evaluated to find the cross section. In the second paper of the series (II; Ref. 5) the details of computation of electronic wave functions and transition elements are presented. Subsequent work will present the calculation of trajectory integrals and the final cross section.

B. PHYSICAL ASSUMPTIONS

1. Nature of Electronic States

We begin by recalling a point made in Ref. 2: For the colliding system an adiabatic description is reasonable only for "tightly-bound" states. These are states whose static binding energies substantially exceed the kinetic energy

$$\epsilon_c = \tfrac{1}{4}(m/\mu)E ,$$

which a bound electron possesses due to heavy particle motion relative to the collision center (ϵ_c is also the critical binding energy for which the classical electron speed is comparable to that of the protons). It is easy to see why states less tightly bound than ϵ_c interact strongly with the continuum. Because of the strong attraction of the second proton, an electron in any state has a high probability of resonant charge transfer, for static protons. However, if the static binding energy is less than ϵ_c, an electron "jumping" from one moving proton to the other will not remain bound, since it possesses more than the escape momentum with respect to the second proton. As a result, for the dynamical system we must recognize that such loosely bound states mix strongly with the continuum during collision, and indeed are indistinguishable from it. Effectively there is a finite number of discrete states in the dynamical system, plus a continuum.

How does this continuum differ from that of the static H_2^+ system? A qualitative answer is suggested by noting that a gauge transformation to remove the "electron translation factor" from the wave function introduces a fictitious vector potential in the electronic Hamiltonian. The effects of this vector potential are not fully analogous to changes of the scalar potential, but one effect is similar to the screening of the Coulomb field at a distance for which the potential is $\sim \epsilon_c$. A Yukawa-type potential with such a range will possess the appropriate number of bound states. But for the case of the Yukawa potential, the effect of screening on the continuum is important, primarily for those states with positive energies ϵ less than or comparable to ϵ_c. These are states which correspond to an electron moving slowly beyond the screening range, and therefore having dynamical characteristics similar to the corresponding Rydberg levels. For continuum states of higher energy, the change from an unscreened to a screened potential is unimportant to the wave function at reasonable distances, and appears only asymptotically, in the logarithmic term in the phase shift; "fast" electrons are less affected by screening than are slow ones. Though we do not strictly have Yukawa-type screening, the general line of reasoning is also applicable to the dynamical effects of interest to us.

This point is essential to our solution of the impact ionization problem. For the dynamical system we can divide electronic states into three types: (a) Discrete, "tightly-bound" states, which can be described by an adiabatic approximation as in Ref. 2. (b) Continuum states of energy ϵ substantially greater than ϵ_c. Electrons in such states are moving rapidly in comparison to the protons, but their motion is not periodic as in the discrete states. The fact that they are "fast electrons" will be the basis for a discussion of such states below. (c) A band of complicated nonadiabatic states, corresponding asymptotically to static electron energies between $-\epsilon_c$ and $+\epsilon_c$. We have no quantitative description of such states. The impact ionization problem can be treated because for collision energies E below 0.5 keV, ϵ_c is less than 0.2 eV, and the band of states of type (c) is quite narrow. Since the density of continuum states decreases as $\epsilon \to 0$, these states constitute a negligible fraction of the states to which transitions may occur. The only way in which even just ignoring them could cause trouble would be if for some reason the transition matrix elements for direct impact ionization near threshold, or excitation of high Rydberg levels, were abnormally large, but this is not the case. Only if the initial state were highly excited itself would a "ladder" process of excitations through Rydberg levels be important. A classical argument which suggests the same answer is the following: A direct impact excitation corresponds to a single, very impulsive collision between electron and proton, not to a succession of small ones; the probability of such a collision is small owing to the relative speeds of electron and proton, but when such a violent event occurs there are no restrictions on the amount of momentum transferred, related to threshold considerations for the electron; the protons have energy and momentum substantially in excess of threshold. In short, an event in which an electron receives several times the threshold energy and escape momentum is nearly as likely as one in which it receives precisely the threshold requirements, and statistically there are more ways the former can happen.

Accordingly, we ignore the fact that states of type (c) exist, on the justifiable assumption that transitions to them make no significant contribution to the total cross section, and proceed to the discussion of the "fast-electron" states, type (b).

2. The "Fast-Electron" Approximation

For $\epsilon \gg \epsilon_c$, an electron is moving much faster than the protons. If at some point in the collision process an excitation to a continuum state of energy ϵ occurs, the resulting unbound electron will move out "to infinity" essentially instantaneously, on the time scale of the proton motion. In effect, just as in the case of the adiabatic approximation for the bound states, electron dynamics in the interaction region is determined mainly by the field of the protons at rest; the electron "sees the protons as if they were stationary."

But there is an important difference between the discrete, adiabatic, "tightly bound" states, and these "fast electron" continuum states. In the adiabatic approximation, the validity of the scheme requires that discrete levels be separated by $\Delta\epsilon$'s such that the periodic motion associated classically with a given level can be clearly resolved from that of neighboring levels $(\Delta\epsilon\Delta t \gg \hbar)$, in the period of interaction; to achieve this, electrons must carry out many cycles of their periodic motion as the nuclei move slowly. This feature builds in an "adiabatic following" of the nuclei by the electronic states; as nuclear configuration $\vec{R}' \to \vec{R}$, we expect the discrete state $\phi_n(\vec{r};\vec{R}')$ to map into $\phi_n(\vec{r};\vec{R})$. But in the case of a "fast electron" in the continuum the classical motion is aperiodic. The extent to which an electron's dynamical behavior in the interaction region is influenced by nuclear motion is determined primarily by the time it takes the electron to reach "infinity", i.e., a distance so far away that subsequent motion of the protons cannot perturb the electron further. A simple classical estimate shows that for $\epsilon \gg \epsilon_c$ this time is so short that we can say the electron "moves out to infinity" in a way determined by the static proton configuration $\vec{R}'$ at the time of excitation, and the contribution to the amplitude for ϵ at much later times which such excitation makes does not depend on subsequent proton configurations $\vec{R}$. This fact will have important consequences for the form of the three-body Green's function (Sec. D).

There is one exception to the idea that the "fast electron" solutions depend only on the static configuration of the protons: The protons are at rest in a rotating frame. As a result, regardless of the speed of an electron, there are long-range Coriolis forces which will affect it, even at "infinity"; and these must be taken into account in determining the asymptotic characteristics of the continuum states, and, from these as boundary conditions, the continuum eigenfunctions themselves. The approximate solution to this problem appears in Sec. C.

In a fully quantum-mechanical treatment of the theory, a corollary to the "fast electron" approximation for continuum states will be that in the final states the protons are not screened or coupled to the electron system, but propagate with only the Coulomb repulsion, for energy $E'[\approx E + \epsilon(1s) - \epsilon]$ and rotational angular momentum N. However, we have chosen to treat the heavy-particle motion classically in this paper.

3. Classical versus Quantum Trajectory Integrals

In Ref. 2 the theory for the proton–H-atom system is developed in completely quantum-mechanical terms, although the semiclassical approximation for the heavy-particle wave functions is certainly valid. The coupling of nuclear rotation and electronic orbital angular momentum is treated explicitly in a representation diagonal in the total angular momentum.

An analogous treatment can easily be made for the problem of impact ionization, in principle. Such a stationary-state formulation requires the knowledge of the three-body Green's function for the continuum, which (as we show in Sec. D) can be constructed from suitable electronic and associated heavy-particle wave functions. The asymptotic amplitude for impact ionization at energy ϵ involves an integral of suitable electronic transition matrix elements associated with each proton configuration, with the semiclassical initial- and final-state heavy-particle wave functions. Such "trajectory integrals", as we call them in analogy with the classical treatment, control the efficiency of energy and momentum transfer to the electron system. The transfer leads to change in the de Broglie wavelength of the protons; the difference wavelength may be as short as $0.05a_0$ or as long as the interaction region, depending on the amount of momentum transfer, and this oscillating efficiency factor modulates the electronic transition matrix elements severely. Indeed, for low-energy E it is this factor, rather than the decrease in the electronic transition elements, which cuts off the cross section for increasing ϵ at fixed E.

Many of the same physical features are retained in a classical treatment of the heavy-particle motion. Mittleman[6] has given a discussion of the proton–H-atom system, and argues for the validity of such an "impact-parameter" treatment of the general scattering problem (not necessarily assuming straight-line trajectories). If it be supposed that the internuclear vector $\vec{R}$ is a known function of time (given initial conditions on the internal states, the impact parameter, etc.), the problem becomes that of solving the time-dependent Schrödinger equation for the electron. In this formulation the transition amplitudes contain trajectory integrals, integrals over time along a (specified) classical trajectory for each set of initial conditions. These integrals also contain an oscillatory efficiency factor, which arises in this case from the time integral of the energy difference of the initial and final states. In the limit that the energy transfer $\epsilon - \epsilon(1s)$ is a small fraction of the collision energy E, this factor is identical to the oscillatory factor in the quantum trajectory integral, and they are always closely related. The two trajectory integrals differ mainly in their treatment of the probability distribution (the second term in WKB expansion, in the quantum case). In principle the quantum-mechanical, stationary-state method gives a full account not only of the action transfer to the electron system but also of the *reaction* of the protons; the classical, time-dependent approach accounts only for action on the electronic system by a specified nonconservative Hamiltonian, and takes no account of the detailed reaction of the heavy particles. But both methods take essentially identical account of the crucial transfer-efficiency factor, implying that in some sense it is associated with the interface between the subsystems. It appears that such an oscillatory factor appears when action in any form is transferred from one system to another (cf. Sec. F, where such a factor arises from angular momentum transfer, as well as from energy transfer).

For reasons of computational simplicity we have elected to perform the impact ionization calculation using the classical, time-dependent formulation, and the theory is mainly so presented in this paper. At a few points where it is instructive, we have indicated the corresponding quantum-mechanical formulation, (as for example in Sec. D where the solution of the three-body final-state Green's function problem is given).

There is ambiguity in the classical approach: the prescription of the "specified" classical trajectories. In Mittleman's paper[6] it appears that this may be determined by a probability-weighted average over the effective potentials for the various internal states; i.e., if the probability to be in the ground electronic state is dominant, one should use the elastic scattering potential for that state to calculate the classical trajectory. This is an appealing and reasonably consistent approach for a nondegenerate ground state, at least in the limit of small inelastic transition probabilities. Recently Chen and Watson[7] have used the eikonal approximation (essentially a three-dimensional WKB approximation) to calculate semiclassical wave functions for the heavy particles, and attempt the reduction of the resulting three-dimensional integrals for elastic and inelastic transitions by the use of stationary phase approximations for integrals over the surfaces normal to a specifiable family of curves. The method is rigorously justifiable for elastic scattering because of the asymptotic character of the important contributions in that case. If the stationary phase approximation for the surface integrals were equally justifiable for the more complex case of inelastic scattering, the calculation would then reduce to a "trajectory integral" once again; but the "trajectory" is neither the classical trajectory for initial or final states, nor an average of them, but a curve which can be constructed from these.[7] It should be stressed, however, that there is no continuous chain of reasoning connecting this essentially quantum-mechanical formulation to any classical formulation; one cannot simply interpret the prescription of the Chen-Watson curves of integration as a specification of $\vec{R}(t)$ in a classical sense. Accordingly, we have specified $\vec{R}(t)$ along the general lines indicated by Mittleman.[6]

4. Strong-Coupled Initial State

As is well known,[1,4] collision of a proton with a ground-state hydrogen atom involves a number of internal states. The 1*s* atomic state is a superposition of *g* and *u* molecular states, and using the formulation of Ref. 2 it can be shown that there is rigorously no interaction between states of different centrosymmetric parity, for the exact Hamiltonian. In the case of H_2^+, the σ_u molecular state maps into the $2p\sigma_u$ state of the He^+ united atom; as a result, at small R its increasing degeneracy with the $2p\pi_u$ level leads to strong Coriolis coupling between them, and substantial probability for exciting the 2*p* level of the H atom upon collision. The original solution of this problem by Bates and Williams[4] was modified and improved slightly by F. J. Smith[4]; in this laboratory we are also completing a slightly different study of the same process.[8] Our calculation differs from the one outlined in principle by F. J. Smith[4] in several respects. As electronic basis functions we have used the functions X_u introduced in Ref. 2, obtained by diagonalizing the electronic Hamiltonian, including Coriolis couplings, in the $2p\sigma_u - 2p\pi_u^{\pm}$ manifold. At $R \to \infty$ our electronic basis functions X_μ correlate with the σ_u or π_u molecular states, and we shall use that notation to distinguish them although it is only approximate at finite R.

Resulting from our strong-coupling solutions will be amplitudes $a_\mu(t)$ associated with the internal states $X_\mu(1s\sigma_g$, "σ_u", "π_u") as functions of time along specified classical trajectories. For the σ_g state, a_{σ_g} is of course constant, and the trajectory assumed is that determined for given energy E and impact parameter by the potential surface for the $1s\sigma_g$ state; we call it $\vec{R}_g(t)$. For the strong-coupled *u* solutions, $\vec{R}_u(t)$ is determined by the elastic potential for the lower, asymptotically "σ_u"-like state, even though some probability for excitation of the "π_u"-like state exists.

Our final prescription of classical trajectory then differs from that implicit in a nondegenerate ground manifold only by the choice of the distinct trajectories for *g* and *u* states. Since the mechanism for direct impact ionization preserves parity on excitation, the two problems can be treated entirely separately.

Bates and Holt[9] have presented arguments to the effect that the error involved in determining the strong-coupling solutions via such classical procedures is not great. Since we are interested in the strong-coupled system only as the initial state, it seems appropriate to make the approximation for computational advantages it gives.

C. IONIZED STATES AND THE FAST ELECTRON APPROXIMATION

The notation of Ref. 2 is used, with some changes and corrections, but we shall adapt the definitions of electronic states given there to a classical description of the proton motion; a major change is a shift to a classical description of nuclear rotation. Let $\vec{R} = \vec{R}_B{}^0 - \vec{R}_A{}^0$ be the interproton coordinate (the reverse definition in Ref. 2 is an error); its orientation in a space fixed reference (SFR) frame is prescribed by Euler angles Θ, ψ. The quantity $\vec{r}$ is the electron coordinate with respect to the center of mass of the nuclei (CMN). In the SFR frame $\vec{r}$ has Cartesian components (x', y', z'), polar coordinates (r, θ', φ'), while in the MR (molecular reference) frame these are (x, y, z) and (r, θ, φ) (note change from Ref. 2); the polar axis is along $\vec{R}$. The kinetic energy in the center-of-mass system is

$$T = P_R{}^2/2\mu + p_r{}^2/2m \, , \tag{1}$$

and the potential energy is

$$U = e^2(R^{-1} - r_A{}^{-1} - r_B{}^{-1}) \, . \tag{2}$$

The Hamiltonian is clearly centrosymmetric with respect to $\vec{r}$ (and $\vec{R}$); electronic solutions are rigorously of *g* or *u* parity. A state initially arising from a proton and a 1*s* H atom consists of equal amounts of states of each parity, but aside from phase relations imposed by the initial conditions the problem can be solved independently for each parity. For the calculation of total cross section even the phase is irrelevant. Since the elastic scattering potential associated with the $1s\sigma_g$ state is quite different from that for the lowest *u* state, we shall assume two distinct classical trajectories $\vec{R}_g(t), \vec{R}_u(t)$ exist for each energy E and impact parameter b. We may now proceed to a description of electronic states of given parity.

The Born-Oppenheimer (BO) Hamiltonian $H_e(\vec{r};\vec{R})$ is

$$H_e(\vec{r};\vec{R}) = p_r{}^2/2m + U(\vec{r};\vec{R}) \, ; \tag{3}$$

in the MR frame H_e depends parametrically on R, but not on Θ, ψ. The eigenfunctions $\{\phi(n\Gamma\Lambda; \vec{r}; R)\}$ of H_e are well known[10]; the discrete states satisfy

$$H_e \phi(n\Gamma\Lambda) = \epsilon(n\Gamma\Lambda; R)\phi(n\Gamma\Lambda) \, , \tag{4a}$$

where $(n\Gamma)$ specifies principal quantum number and other asymptotic symmetry, and $\Lambda\hbar$ is the component of orbital angular momentum on $\vec{R}$:

$$L_z\,\phi(n\Gamma\Lambda) = \Lambda\hbar\,\phi(n\Gamma\Lambda)\,. \qquad \text{(4b)}$$

$\{\phi(n\Gamma\Lambda)\}$ is an orthonormal discrete set for each R. We shall also be concerned eventually with the continuum eigenfunctions $\phi(\epsilon\mu\Lambda;\vec{r};R)$ which satisfy

$$H_e(\vec{r};R)\phi(\epsilon\mu\Lambda;\vec{r};R) = \epsilon\phi(\epsilon\mu\Lambda;\vec{r};R)\,, \qquad \text{(5a)}$$

$$L_z\,\phi(\epsilon\mu\Lambda) = \Lambda\hbar\phi(\epsilon\mu\Lambda)\,, \qquad \text{(5b)}$$

and are normalized with respect to energy, for each R,

$$\int_{\text{all }\vec{r}} d^3r\,\phi^*(\epsilon'\mu'\Lambda';\vec{r};R)\phi(\epsilon\mu\Lambda;\vec{r};R) = \delta_{\Lambda'\Lambda}\delta_{\mu'\mu}\delta(\epsilon'-\epsilon); \qquad \text{(5c)}$$

μ is an index associated with the variable separation possible in prolate spheroidal coordinates.

In the MR frame additional terms must be included in the electronic Hamiltonian, representing Coriolis couplings and the angular kinetic energy of the electron due to rotation of the frame. The latter plays no role in the problem (except formally) and we shall ignore it. Classically a collision is confined to a plane, and we take $\psi = 0$. For $t \to -\infty$, $\Theta \to 0$ and $R \to \infty$. The collision energy is $E = \mu V_0^2/2$, the impact parameter is b, the angular momentum is $\mu V_0 b$, and the angular velocity, $\dot{\Theta} = bV_0/R^2$. The (time-dependent) electronic Hamiltonian we shall employ is therefore

$$H_{\text{MR}} = H_e(\vec{r};R) - \dot{\Theta}\hat{L}_y\;, \qquad \text{(6)}$$

where $\hat{L}_y$ is the electronic orbital angular momentum perpendicular to the collision plane.

1. Discrete States

As in Ref. 2, instead of the BO states $\phi(n\Gamma\Lambda)$ it is useful to employ a set of states $\{X_i\}$, obtained from the BO states by a unitary transformation which renders an important part of H_B diagonal. The asymptotic Coriolis interaction between components in orbitally degenerate atomic manifolds plays no part in the problem and is ignored. (See Ref. 11.) However, the Coriolis interaction also mixes BO levels strongly at small R values if they belong to an orbitally degenerate level of the *united atom*. For H_2^+ this is the case with the $1s\sigma_u$ state from the ground components and $2p\pi_u^\pm$ excited states: These belong to the $2p$ level of the united atom. For the ground manifold we therefore define $X_{1g} \equiv \phi(1s\sigma_g)$, and a set of functions $\{X_{iu}, i = 1, 2, 3\}$ as the eigenfunctions of H_{MR} in the space spanned by the $1s\sigma_u$ and $2p\pi_u^\pm$ states. We need not specify the functions $\{X_i\}$ for higher discrete components; those specified are orthogonal to all other BO states including continuum components.

2. Electron Translation Factor

Dynamical description of the electron is not complete without a factor representing radial translation of an electron bound to moving protons. In Ref. 2 we used the form

$$\exp[\pm(im/2\hbar)V_R(R)r]\;,$$

where $V_R(R)$ is the radial speed of the protons, and the sign indicates outgoing or incoming motions. Generalizations of this form have been considered by K. Smith and by S. B. Schneiderman.[12] A definite improvement is introduced by the choice[5,13]

$$f(\vec{r}) = (r_A^{\,2} - r_B^{\,2})/(r_A^{\,2} + r_B^{\,2})\;.$$

This weights the velocity by the ratio of the difference between the attraction forces of the protons divided by their sum. As $r \to \infty$ for fixed R, the velocity realistically then tends to zero.

In Ref. 2 $V_R(R)$ depends on the electronic state and introduces some small nonorthogonality; but in our classical treatment $\dot{R}$ and the translation factor are the same for all components. The discrete adiabatic basis functions we employ are thus given by

$$\Phi_i(\vec{r};\vec{R}(t)) = X_i(\vec{r};\vec{R}(t)) \times \exp\left[+\frac{im}{2\hbar}\dot{R}\left(\frac{r_A^{\,2}-r_B^{\,2}}{r_A^{\,2}+r_B^{\,2}}\right)z\right]; \qquad \text{(7)}$$

these form an orthonormal set for given E, b, and R.

3. Continuum Components

In the fast electron approximation, a continuum electron is assumed to move so rapidly relative to the protons that its probability amplitude is distributed over a region of space arbitrarily large compared to the interaction region near the protons. The energy, density of states, etc. for the electron then do not depend at all upon the proton configuration, but are those of a free particle.[14] In the interaction region the static configuration of the protons, not their motion, is the major influence on the wave function. In principle, we want to obtain the continuum eigenfunctions of H_{MR} [Eq. (6)]. The Coriolis interaction due to rotation of the MR frame is important even outside the interaction region, and must be included. Asymptotically it guarantees that continuum states are characterized by free-particle properties in the SFR, rather than MR, frame.

It is not computationally practical to obtain the true continuum eigenstates of H_{MR}, since as many as twenty coupled equations could be involved for each energy. Instead reasonably good approximate solutions are obtained as follows. Let all electron configuration space be divided into two regions, divided by a spherical (or ellipsoidal) boundary at r_c. Assume that in the internal or interaction region near the protons, the BO Hamiltonian, especially the bipolar terms, is the dominant part of H_{MR} and that the Coriolis interaction is negligible; in the outer or asymptotic region, on the other hand, the nonspherical terms in the BO Hamiltonian are assumed negligible in comparison to the Coriolis interaction. In the internal region the BO continuum states $\phi(\epsilon\mu\Lambda)$ form a complete set of continuum components; in the external region solutions are characterized by energy (in a Coulombic spherically symmetric field), and the orbital angular momentum L and its component M_L. A solution of the problem with correct asymptotic characteristics ϵ, L, M_L is obtained by choosing a linear combination of BO components which match the wave function and its derivative at r_c with the external wave function having the desired boundary conditions. Finally, the choice of r_c must be made. A study of the relative magnitudes of bipolar terms in the potential and the Coriolis interaction suggests that r_c is 10–20 a_0 or more. It is in keeping with the spirit of the fast electron approximation to take $r_c \to \infty$; the continuum wave functions are then linear combinations of BO continuum components, the expansion coefficients being functions of R and the Euler angles Θ, ψ. (See Ref. 15.)

In detail: Using the well-known prolate spheroidal coordinates (ξ, η, φ), the BO problem for H_2^+ is separable[10] and continuum solutions are of the form

$$\phi(\epsilon\mu\Lambda;\vec{r},R)=F(\epsilon\mu\Lambda;\xi;R)h(\mu\Lambda;y;\eta) \times(2\pi)^{-\frac{1}{2}}\underline{e}^{i\Lambda\varphi}, \tag{8}$$

where $y=\epsilon R^2/4$. The quantity $h(\mu\Lambda;y;\eta)$ can be expanded in Legendre functions and satisfies the orthogonality relation

$$\int_{-1}^{+} h(\mu'\Lambda;y;\eta)h(\mu\Lambda;y;\eta)d\eta=\delta_{\mu'\mu}\ ; \tag{9}$$

$F(\epsilon\mu\Lambda;\xi;R)$ is the regular solution to the ξ equation, obtained by numerical integration. Here we need only know the explicit form of ϕ in the asymptotic limit R fixed, $r\to\infty$; in that case $\eta \to \cos\theta$, $\xi \to 2r/R$, and

$$\lim_{\substack{r\to\infty\\ R\text{ fixed}}} \phi(\epsilon\mu\Lambda;\vec{r};R) =2(hv)^{-1/2}\,r^{-1}\sin[kr+2k^{-1}\ln r+\delta(\epsilon\mu\Lambda;R)] \times\sum_{L=|\Lambda|}^{\infty} B(\mu\Lambda;L;y)Y_{L\Lambda}(\theta,\varphi), \tag{10}$$

where $\epsilon=\hbar^2k^2/2m=mv^2/2$.

Solutions to the problem are linear combinations of the set $\{\phi(\epsilon\mu\Lambda;\vec{r};R)\}$ for fixed R, ϵ which correspond to certain asymptotic boundary conditions. The boundary condition we shall impose is that the outgoing parts of the continuum solutions be characterized by definite ϵ, L, and M_L, where M_L is the component of $\hat{L}$ on the SFR axis z'. Because of the bipolar field, the incoming parts will not be so characterized. To transform to such a basis, we take advantage of the orthogonality of the matrix $\vec{\mathrm{B}}$ in Eq. (10), and the unitary transformation

$$Y_{L\Lambda}(\theta,\varphi)=\sum\nolimits_{M_L} Y_{LM_L}(\theta',\varphi') \times[d_{\Lambda M_L}{}^{(L)}(\Theta)e^{-iM_L\psi}]\ ; \tag{11}$$

$$d_{\Lambda M_L}{}^{(L)}(\Theta)=d_{M_L\Lambda}{}^{(L)}(-\Theta)$$

is defined by Edmonds.[16] Define

$$X^{+}(\epsilon LM_L;\vec{r};R,\Theta) \equiv\sum\nolimits_{\mu}\sum\nolimits_{\Lambda}\{B(\mu\Lambda;L;y)d_{\Lambda M_L}{}^{(L)}(\Theta) \times\exp[-i\delta(\epsilon\mu\Lambda;R)]\}\,\phi(\epsilon\mu\Lambda;\vec{r};R). \tag{12}$$

Asymptotically X^+ has the form (recall that $\psi=0$):

$$\lim_{\substack{r\to\infty\\ R\text{ fixed}}} X^{+}(\epsilon LM_L;\vec{r};R,\Theta)=-i\,(hv)^{-1/2}r^{-1} \times\exp[+i(kr+2k^{-1}\ln r)]\,Y_{LM_L}(\theta',\varphi') +i(hv)^{-1/2}r^{-1}\exp[-i(kr+2k^{-1}\ln r)] \times\sum_{\mu\Lambda}\ \sum_{L'M'_L}\ \{B(\mu\Lambda;L;y)B(\mu\Lambda;L';y)$$

$$\times \exp[-2i\delta(\epsilon\mu\Lambda;R)]d_{\Lambda M_L}{}^{(L)}(\Theta) \times d_{\Lambda M_L'}{}^{(L')}(\Theta)\} Y_{L'M_L'}(\theta',\varphi') . \qquad (13)$$

Although the incoming wave does not have an unique angular momentum, its energy is asymptotically ϵ. In Sec. D it will be shown that the asymptotic properties of the incoming wave are irrelevant since it can make no contribution to the scattering amplitude. The error involved in using linear combinations of BO components to approximate solutions of H_{MR} is essentially a loss of resolution, since the Coriolis interaction, if included, would mix components from BO energies ϵ' in a band about ϵ of width approximately the magnitude of the Coriolis interaction. In the most severe cases (small R, high E, large impact parameter b), this interaction may amount to about 1 eV; usually it is much smaller.

The set of fast electron continuum components is defined by

$$\Phi^+(\epsilon LM_L;\vec{r};R,\Theta) \equiv X^+(\epsilon LM_L;\vec{r};R,\Theta) \times \exp\left[+\frac{im}{2\hbar}\dot{R}\left(\frac{r_A{}^2-r_B{}^2}{r_{A^2}+r_B{}^2}\right)z\right]. \qquad (14)$$

The reason for including the electron translation factor in the continuum components is that they are then rigorously orthogonal to the discrete components Φ_i defined by Eq. (7). In the limit $r \to \infty, R$ fixed, this factor tends to a constant and therefore does not shift the energy ϵ. More discussion of this point is given in Paper II.[5]

A set of discrete adiabatic electronic states, and a set of fast electron continuum states orthogonal to them, have been defined. These make a formally complete set describing electron states, although for a narrow band of states with $|\epsilon| \lesssim \epsilon_c$ (states of type "c": cf. Sec. B.1) the approximation is of no physical value; the success of the theory rests upon the validity of the assumption that transitions to such states are of negligible probability. The only remaining problem is to show how correct three-body final states describing ionization can be generated using such a set, and obtain the formula for the cross section.

D. THREE-BODY FINAL STATES

In this section it is shown that correct final states representing ionization can be generated using the basis set defined in Sec. C. Since the actual problem is complicated by many details not relevant to this question, it is clearer to examine a simple model problem which retains only the essentials.

1. Model Problem: Nonadiabatic Ionization of a Spherically Symmetric System

This derivation resembles Mott and Massey's treatment of ionization of an atom by a time-dependent perturbation.[17] Consider an electronic system with a spherically symmetric Hamiltonian, $H(\vec{r};t)$ which varies (slowly) with time in a specified way; for large positive and negative t, $H(\vec{r},t)$ tends to $H_0(\vec{r})$, and

$$\int d^3r \int_{-\infty}^{\infty} dt\, |H(\vec{r};t) - H_0(\vec{r})|$$

is bounded. Suppose also that in the limit $r \to \infty$, $H_0(\vec{r})$ [and $H(\vec{r};t)$] is Coulombic, with constant effective charge $+2e$. At each t there exists a set of discrete adiabatic states Φ_n (angular momentum eigenfunctions) which are solutions of the equation

$$H(\vec{r};t)\Phi_n(\vec{r};t) = \epsilon_n(t)\Phi_n(\vec{r};t) , \qquad (15)$$

and also a set of continuum components with energy $\epsilon > 0$,

$$H(\vec{r};t)\Phi_\epsilon(\vec{r};t) = \epsilon\Phi_\epsilon(\vec{r};t) ; \qquad (16)$$

note that ϵ does *not* depend on time, though Φ_ϵ may do so in the interaction region. $\{\Phi_n\}$ are orthonormal and $\{\Phi_\epsilon\}$ is so normalized that

$$\int d^3r\, \Phi^*_{\epsilon'}(\vec{r};t)\Phi_\epsilon(\vec{r};t) = \delta(\epsilon' - \epsilon) . \qquad (17)$$

In the asymptotic limit $r \to \infty$ (for s waves)

$$\Phi_\epsilon(\vec{r};t) \sim (\pi\hbar v)^{-1/2} r^{-1} \times \sin[kr + 2k^{-1}\ln r + \delta_\epsilon(t)] , \qquad (18)$$

with $\epsilon = mv^2/2$. As boundary condition we assume the system is in the state Φ_0 at $t \to -\infty$, and Φ_0 is an s state.

H varies with time at a finite rate in the interaction region, and as a result transitions from Φ_0 to other discrete states and the continuum can occur. The same sorts of physical questions arise about the description of fundamentally nonadiabatic levels near $\epsilon \approx 0$, the fast-electron states, the likelihood of exciting states near $\epsilon \approx 0$, etc., as occur in the actual impact ionization problem; we assume the same conditions and assumptions to hold here. We can write the solution Ψ to the time-dependent Schrödinger equation

$$\Psi = \Psi_0 + \Psi_1{}^D + \Psi_1{}^C , \qquad (19)$$

where we take

$$\Psi_0 = a_0(t)\Phi_0(\vec{r};t) \exp[-(i/\hbar)\int_0^t \epsilon_0(t')dt'] ; \qquad (20)$$

$a_0(-\infty)=1$, and indeed $a_0(t)\approx 1$ for all t because we assume the total transition rate is small. The definition of $t=0$ is arbitrary except that it occurs during the finite period τ when $H(\vec{r};t)$ differs from $H_0(\vec{r})$. Ψ_1^D and Ψ_1^C are given by

$$\Psi_1^D=\sum_{n\neq 0} a_n(t)\Phi_n(\vec{r};t) \times \exp[-(i/\hbar)\int_0^t \epsilon_n(t')dt'] , \qquad (21a)$$

$$\Psi_1^C=\int_0^\infty d\epsilon\, e^{-i\epsilon t/\hbar} \times \int_{-\infty}^t dt' \mathring{a}_\epsilon(t')\Phi_\epsilon(\vec{r};t') . \qquad (21b)$$

$a_n(-\infty)=0$, and by definition we see that $\Psi_1^C=0$ as $t\to-\infty$. The reason for writing the contribution to the continuum at ϵ at time t as an integral over earlier contributions is that though $\Phi_\epsilon(\vec{r};t')$ changes with t', its contribution at subsequent time t to ionization does not follow the Hamiltonian adiabatically from t' to t, but appears asymptotically, with characteristics specified by H at the time t' of excitation: the fast electron approximation. With this assumption we will derive familiar expressions for $\mathring{a}_n(t)$ and the formal $\mathring{a}_\epsilon(t)$ (the latter is not a time derivative).

Since all components in Ψ_1 are small, Ψ_0 is the source of excitations. This source term is

$$\left[H(\vec{r};t)-i\hbar\frac{\partial}{\partial t}\right]\Psi_0 \approx -i\hbar\frac{\partial\Psi_0}{\partial t}\exp[-(i/\hbar)\int_0^t \epsilon_0(t')dt'] . \qquad (22)$$

The terms arising from Ψ_1^D are

$$\left[i\hbar\frac{\partial}{\partial t}-H(\vec{r};t)\right]\Psi_1^D = +i\hbar\sum_{n\neq 0}\left[\mathring{a}_n(t)\Phi_n(\vec{r};t)+a_n(t)\frac{\partial}{\partial t}\Phi_n(\vec{r};t)\right] \times \exp[-(i/\hbar)\int_0^t \epsilon_n(t')dt'] . \qquad (23)$$

For truly adiabatic discrete states (those separated from neighboring levels by $\Delta\epsilon \gg |\partial H/\partial t|$), $(\partial\Phi_n/\partial t)$ can be shown to be small enough that the second term in the sum on the right-hand side of Eq. (23) is negligible. This is not true for the Rydberg levels but for these we have assumed in advance that transitions from Φ_0 into them are negligible. Finally the terms arising from Ψ_1^C are

$$\left[i\hbar\frac{\partial}{\partial t}-H(\vec{r};t)\right]\Psi_1^C = \int_0^\infty d\epsilon[i\hbar\mathring{a}_\epsilon(t)]\Phi_\epsilon(\vec{r};t)e^{-i\epsilon t/\hbar} + \int_0^\infty d\epsilon\, e^{-i\epsilon t/\hbar} \times \int_{-\infty}^t dt'\mathring{a}_\epsilon(t')[(\epsilon-H(\vec{r};t))\Phi_\epsilon(\vec{r};t')] . \qquad (24)$$

Note first that terms in $(\partial\Phi_\epsilon/\partial t)$ automatically do not arise because of the definition of Ψ_1^C; secondly, $H(\vec{r};t)\Phi_\epsilon(\vec{r};t')$ is equal to $\epsilon\Phi_\epsilon(\vec{r};t')$ for all $(\vec{r},t)$, except when $\vec{r}$ is in the interaction region. Therefore, as long as we do not choose (r,t) so that $\Psi_1^C(r;t)$ has amplitude in the interaction region, we may neglect the last term in Eq. (24). Collecting all terms in the Schrödinger equation and selecting the component at ϵ', we obtain

$$\mathring{a}_{\epsilon'}(t)=T_{\epsilon'0}(t) \times \exp\{(i/\hbar)\int_0^t[\epsilon'-\epsilon_0(t')]dt'\} , \qquad (25)$$

where

$$T_{\epsilon'0}(t)\equiv-\int d^3r\,\Phi^*_{\epsilon'}(\vec{r};t)\frac{\partial}{\partial t}\Phi_0(\vec{r};t) . \qquad (26)$$

Substitution of Eq. (25) in Eq. (21b) permits the calculation of Ψ_1^C in the asymptotic limit $t\to\infty$. From this point we follow the procedure of Mott and Massey.[17] An ionized electron should move to large r as $t\to\infty$, hence we can use Eq. (11). Ψ_1^C is the sum of outgoing and incoming asymptotic parts $\Psi_1^{C\pm}$:

$$\Psi_1^{C\pm}(\vec{r};t)\sim[\mp i/r(4\pi\hbar)^{\frac{1}{2}}\int_0^\infty d\epsilon\, v^{-\frac{1}{2}} \times \exp[-i\epsilon t/\hbar\pm i(kr+2k^{-1}\ln r)]\,C^\pm(\epsilon) , \qquad (27)$$

where

$$C^\pm(\epsilon)=\int_{-\infty}^\infty dt'\,T_{\epsilon 0}(t')\exp\{\pm i\delta_\epsilon(t') + (i/\hbar)\int_0^{t'}[\epsilon-\epsilon_0(t'')]dt''\} . \qquad (28)$$

Since $|T_{\epsilon 0}(t')|\to 0$ as $t'\to\pm\infty$, $C^\pm(\epsilon)$ is a constant and it is permissible to use it in Eq. (28) as $t\to\infty$. We shall assume $C^\pm(\epsilon)$ is a slowly-varying function of ϵ in comparison with the exponential in Eq. (28). Finally we convert the integral over ϵ to an integral over v, and use the stationary phase approximation to evaluate it. Ψ_1^{C-} has no stationary phase point, hence it vanishes. For Ψ_1^{C+} the point of stationary phase occurs at $v'(\epsilon',k')$ such that $r=v't$. This is just the velocity which would classically bring an electron to r at time t if it left the origin at $t=0$. Evaluation of the integral gives

$$\Psi_1^{C}(\mathrm{r};t) = -(\epsilon'/2\pi)^{\frac{1}{2}}C^{+}(\epsilon')r^{-\frac{3}{2}} \times \exp[+i(k'r+2k'^{-1}\ln r-\epsilon' t/\hbar+\pi/4)]. \tag{29}$$

The probability of finding an electron between r and $r+dr$ at time t is $4\pi r^2|\Psi_1^{C}(\vec{\mathrm{r}};t)|^2dr$; since r and ϵ' are related at t, this gives also the probability $P(\epsilon')d\epsilon'$ that an electron with energy ϵ' to $\epsilon'+d\epsilon'$ is ionized:

$$P(\epsilon')d\epsilon' = |C^{+}(\epsilon')|^2d\epsilon'. \tag{30}$$

The application to a collision system is clear; $P(\epsilon')$ is the ionization probability for a collision of specified energy E and impact parameter b; the ionization cross section is

$$\sigma_I(\epsilon') = \int_0^{\infty} 2\pi bP(\epsilon')db. \tag{31}$$

2. Construction of Approximate Three-Body Green's Function

The above treatment can be modified to give a stationary-state, quantum mechanical account of the collision process, with the result that an approximation for the adiabatic Green's function including correct three-body final states is obtained. Again we disregard complicated details and outline only the schematic procedure, for the case of a system which has spherical symmetry for the electron. The total Hamiltonian is

$$H_{\mathrm{Total}} = H_e(\vec{\mathrm{r}};R)+T_R+e^2/R, \tag{32}$$

where

$$T_R = -\frac{\hbar^2}{2\mu}R^{-2}\frac{\partial}{\partial R}\;R^2\frac{\partial}{\partial R}\;+\frac{\vec{\mathrm{N}}^2}{2\mu R^2}, \tag{33}$$

and $\vec{\mathrm{N}}$ is the rotational angular momentum operator. Let $\Phi_{nLM}(\vec{\mathrm{r}};R), \Phi_{\epsilon LM}(\vec{\mathrm{r}};R)$ be the discrete adiabatic states and continuum components which are the eigenfunctions of $H_e(\vec{\mathrm{r}};R)$ for given R; except that they parametrically depend on R rather than on t, they are just like the electronic eigenfunctions of Eqs. (15)–(18); L, M refer to electron orbital angular momentum. The set of states $\{\Phi\}$ is complete:

$$\sum_{LM}\Big\{\sum_n \Phi_{nLM}(\vec{\mathrm{r}};R)\Phi^{*}_{nLM}(\vec{\mathrm{r}}';R) + \int_0^{\infty} d\epsilon\;\Phi_{\epsilon LM}(\vec{\mathrm{r}};R)\Phi^{*}_{\epsilon LM}(\vec{\mathrm{r}}';R)\Big\} = \delta(\vec{\mathrm{r}}'-\vec{\mathrm{r}}). \tag{34}$$

An approximate solution to the Schrödinger equation

$$H_{\mathrm{Total}}\Psi = E_{\mathrm{Total}}\Psi$$

is $\Psi_0+\Psi_1$, where $E_{\mathrm{Total}} \equiv E+\epsilon_{100}(\infty)$,

$$\Psi_0 \equiv \Phi_{100}(\vec{\mathrm{r}};R)\chi_{100}(R,\Theta,\psi), \tag{35a}$$

and χ_{100} meets the asymptotic boundary conditions

$$\chi_{100} \sim \exp[i\vec{\mathrm{K}}_0\cdot\vec{\mathrm{R}}] + R^{-1}\exp[+iK_0R]\,f_0(\Theta,\psi), \tag{35b}$$

and is a solution to the equation

$$[T_R+e^2/R+\epsilon_{100}(R)-E_{\mathrm{Total}}]\chi_{100} = 0. \tag{35c}$$

Transitions to other states occur because $\Phi_{100}(\vec{\mathrm{r}};R)$ varies with R. If we designate the source terms due to this variation by the name $H'\Psi_0$, then Ψ_1 can be found as the solution to the equation

$$(H_{\mathrm{Total}}-E_{\mathrm{Total}})\Psi_1 = -H'\Psi_0, \tag{36}$$

satisfying the proper boundary conditions (outgoing waves only). If we can construct the Green's function $G^{+}_{E_T}(\vec{\mathrm{r}},\vec{\mathrm{R}};\vec{\mathrm{r}}',\vec{\mathrm{R}}')$,

$$[H_{\mathrm{Total}}(\vec{\mathrm{r}},\vec{\mathrm{R}})-E_T]\,G^{+}_{E_T} = \delta(\vec{\mathrm{r}}-\vec{\mathrm{r}}')\delta(\vec{\mathrm{R}}-\vec{\mathrm{R}}') \tag{37}$$

and having appropriate boundary conditions as $R\to\infty$, then

$$\Psi_1(\vec{\mathrm{r}};\vec{\mathrm{R}}) = -\int d^3r'd^3R' \times[G^{+}_{E_T}(\vec{\mathrm{r}},\vec{\mathrm{R}};\vec{\mathrm{r}}',\vec{\mathrm{R}}')H'\Psi_0]. \tag{38}$$

We can now exhibit an approximation to $G^{+}_{E_T}$ valid for calculating the ionization cross section. It is useful to define some heavy-particle Green's functions $G_{nL}^{N+}(R;R')$ and $G_\epsilon^{N+}(R;R')$, which satisfy the equations

$$[H^N(R)-E_T+\epsilon_{nL}(R)]\,G_{nL}^{N+}(R;R') = \delta(R-R'), \tag{39a}$$

$$[H^N(R)-E_T+\epsilon]\,G_\epsilon^{N+}(R;R') = \delta(R-R'), \tag{39b}$$

where

$$H^N(R) = -\frac{\hbar^2}{2\mu R^2}\left[\frac{d}{dR}\left(R^2\frac{d}{dR}\right)-N(N+1)\right]+\frac{e^2}{R}; \tag{39c}$$

these are constructed in the usual way from the regular and asymptotically outgoing solutions of the corresponding homogeneous equations. The Green's function $G^{+}_{E_T}$ is then given by

$$\begin{aligned} G^{+}_{E_T}(\vec{r},\vec{R};\vec{r}',\vec{R}') &= \sum_{NM_N}\sum_{LM}\{Y_{NM_N}(\Theta,\psi)Y^{*}_{NM_N}(\Theta',\psi')\} \\ &\quad\times[\textstyle\sum_n\{\Phi_{nLM}(\vec{r};R)\Phi^{*}_{nLM}(\vec{r}';R')\} \\ &\quad\times G_{nL}^{N+}(R,R')+\int_0^{\infty}d\epsilon\{\Phi_{\epsilon LM}(\vec{r};R') \\ &\quad\times\Phi^{*}_{\epsilon LM}(\vec{r}';R')\}G_E^{N+}(R,R')] \,. \end{aligned} \tag{40}$$

Note that the response at $(\vec{r},\vec{R})$ to a continuum component in the source at $(\vec{r},\vec{R}')$ is not $\Phi_{\epsilon LM}\times(\vec{r};R)$, but $\Phi_{\epsilon LM}(\mathrm{r};R')$, just as in the time-dependent formalism of Sec. D. 1 above. The proof that $G^{+}_{E_T}$ as defined by Eq. (40) satisfies Eq. (37) proceeds as follows:

(a) Derivatives of the discrete components $\Phi_{nLM}(\vec{r};R)$ with respect to R are small and can be neglected for the tightly bound adiabatic states, while for the Rydberg levels we again ignore the problem on the assumption that $H'\Psi_0$ has negligible components on these states.

(b) For the continuum no such derivatives occur, and $\Phi_{\epsilon LM}(\vec{r};R')$ satisfies

$$H_e(\vec{r};R)\Phi_{\epsilon LM}(\vec{r};R')=\epsilon\Phi_{\epsilon LM}(\vec{r};R') \tag{41}$$

rigorously for $R'\rightarrow R$, while for $R'\neq R$ it holds everywhere in $\vec{r}$ space except the neighborhood of the protons. It is important that the latter condition be met in the asymptotic limit, where we wish to examine $\Psi_1(\vec{r};\vec{R})$. Note that this clearly restricts the validity of our approximation to those electrons for which we can be confident that $r\gg R$ in the asymptotic limit; this Green's function cannot describe the complex intermediate situation which occurs for a slow electron, or for the finite interim period during which an ionized electron "moves out to infinity." In the other crucial region, $\vec{R}\rightarrow\vec{R}'$, the limiting approximation to the singularity in Eq. (27) is accurate; the only regions where false signals are produced are those for which $R-R'$ is finite and $\vec{r}$ remains near the protons. Obviously we cannot use $G^{+}_{E_T}$, then, to consider secondary events, such as recapture, deceleration, etc., processes which are improbable in the fast electron approximation. This defect with respect to reverse processes is also manifest in the asymmetry of $G^{+}_{E_T}(\vec{r},\vec{R};\vec{r}',\vec{R}')$ with respect to primed and unprimed coordinates.

If $G^{+}_{E_T}$ is used to find the asymptotic form for Ψ_1 via Eq. (38), a procedure analogous to that of the preceding subsection (D. 1) shows that the asymptotically outgoing properties of the heavy particle force the appearance of outgoing electron waves only, via energy conservation, at r values classically correlated with R and the known velocity ratio; a formula analogous to Eq. (30) is obtained.

Conclusions of this section can be directly extended to the actual proton–H-atom system. In the remaining sections we obtain the resulting formulas.

E. THE INCIDENT CHANNEL AND TRANSITION OPERATORS

For a specified collision energy E and impact parameter b, the probability of ionizing an electron with energy ϵ is expressible as the sum of probabilities $P_I(E,b,s;\epsilon)$ for each of the separate parities g,u. $P_I(E,b,s;\epsilon)$ is obtained from the solution Ψ^S to a time-dependent Schrödinger equation controlled by the appropriate trajectory, $\vec{R}_S(E,b;t)$. The Ψ^S is written

$$\Psi^S(\vec{r};t)=\Psi_0^{\,S}(\vec{r};t)+\Psi_1^{\,S}(\vec{r};t)\,, \tag{42}$$

where $\Psi_0^{\,S}(\vec{r},t)$ is the incident channel or initial state solution, to be defined, and $\Psi_1^{\,S}$ is generated from it in a perturbative fashion.

1. Incident Channel Solutions

For convenience assume the electron bound to proton A before collision, though this is irrelevant to final results, and affects only the relative phase of g and u solutions.

(a) *Gerade State*

For this case $\Psi_0^{\,g}(\vec{r};t)$ is completely specified by a single BO component:

$$\begin{aligned} \Psi_0^{\,g}(\vec{r};t)&\equiv a_{1g}\Phi_{1g}(\vec{r};\vec{R}(t)) \\ &\quad\times\exp[-(i/\hbar)\int_0^t\epsilon_{1g}(\vec{R}(t'))dt']\,, \end{aligned} \tag{43}$$

where Φ_{1g} is defined by Eq. (7) and

$$X_{1g}\equiv\phi(1s\sigma_g;\vec{r};R(t))\,;$$

$a_{1g}=1/\sqrt{2}$, and $\vec{R}_g(t)$ is the trajectory (for E,b) determined for elastic scattering on the potential surface $\epsilon_{1g}(R)$.

(b) *Ungerade State*

$\Psi_0^{\,u}$ is more complicated because strong-coupled inelastic scattering occurs. Three BO states $(1s\sigma_u, 2p\pi_u^{\pm})$ are involved but the operator $\hat{L}_y$ in H_{MR} [Eq. (6)] couples only $1s\sigma_u$ and the "$2p\pi_u^{\,x}$" state, which has a node in the yz plane:

$$\phi(2p\pi_u{}^x) \equiv (i/\sqrt{2})[\phi(2p\pi_u^+) - \phi(2p\pi_u^-)] . \qquad (44)$$

The other π_u component is not involved. Thus only two components Φ_{1u}, Φ_{2u} occur, defined by Eq. (7), with X_{1u}, X_{2u} the eigenfunctions of H_{MR} within the two-dimensional space $(1s\sigma_u, 2p\pi_u{}^x)$. The transformation from the BO states to X_{iu} is characterized by an angle $\zeta(E,b,R)$, $0 \leqslant \zeta \leqslant \pi/4$:

$$X_{1u}(\vec{r};R) = \cos\zeta\, \phi(1s\sigma_u) + \sin\zeta\, \phi(2p\pi_u{}^x) , \qquad (45a)$$

$$X_{2u}(\vec{r};R) = -\sin\zeta\, \phi(1s\sigma_u) + \cos\zeta\, \phi(2p\pi_u{}^x); \qquad (45b)$$

$\zeta \to 0$ at $R \to \infty$.

The eigenvalues $\epsilon_{1u}(R), \epsilon_{2u}(R)$ are associated with these states. $\Psi_0{}^u(\vec{r};t)$ can now be defined:

$$\begin{aligned} \Psi_0{}^u(\vec{r};t) \equiv {} & a_{1u}(t)\Phi_{1u}(\vec{r};t) \\ & \times \exp[-(i/\hbar)\textstyle\int_0^t \epsilon_{1u}(R(t'))dt'] \\ & + a_{2u}(t)\Phi_{2u}(\vec{r};t) \\ & \times \exp[-(i/\hbar)\textstyle\int_0^t \epsilon_{2u}(R(t'))dt'] , \qquad (46) \end{aligned}$$

where $a_{1u}(-\infty) = -1/\sqrt{2}$, $a_{2u}(-\infty) = 0$. Because $\zeta(E,b,R)$ varies along the trajectory $\vec{R}_u(t)$, the states Φ_{1u} and Φ_{2u} are coupled, and the coefficients a_{iu} change with time. In the X representation, however, the coupling is substantially reduced in strength, in comparison with the BO representation employed in Ref. 4. The solutions for $a_{iu}(t)$ in the X representation are calculated in Ref. 8, and are assumed known here. Because the coupling to Φ_{2u} is not usually strong, we can prescribe the effective classical trajectory $\vec{R}_u(t)$ for given E, b as that determined by the potential surface $\epsilon_{1u}(R)$.

2. Transition Operators

Transitions out of the incident channel arise from nonzero source terms given by

$$\left[H_{\mathrm{MR}}(\vec{r};t) - i\hbar\frac{\partial}{\partial t}\right]\Psi_0{}^s \equiv -H'\Psi_0{}^s . \qquad (47)$$

Three important terms occur:

(a) Terms due to intrinsic R dependence, hence t dependence, in the BO components $\phi(1s\sigma_g)$, $\phi(1s\sigma_u)$, $\phi(2p\pi_u{}^x)$ (solution of the strong-coupling problem accounts for the time-variation of ζ and the coefficients $a_{iu}(t)$. With respect to BO components these terms are diagonal in Λ.

(b) Terms arising from action of the electron Hamiltonian on products of BO components and the electron translation factor,

$$\exp[(im/2\hbar)\dot{R}z\{(r_A{}^2 - r_B{}^2)/(r_A{}^2 + r_B{}^2)\}] ;$$

these are also diagonal in Λ and are grouped with the type (a) terms.

(c) Terms arising from matrix elements of the Coriolis interaction between BO states in the incident channel and excited components. These link states Λ', Λ if $\Lambda' = \Lambda \pm 1$.

The detailed derivation and calculation of these terms is presented in Paper II.[5] Terms of types (a) and (b) are proportional to $\dot{R}(t)$; we can symbolically write them in terms of the BO matrix elements of an operator H_R', given by

$$\begin{aligned} H_R' \equiv \Bigg\{ & \frac{\partial}{\partial R} + \frac{1}{2}\left[\vec{\nabla}_r\left(z\frac{r_A{}^2 - r_B{}^2}{r_A{}^2 + r_B{}^2}\right)\right]\cdot\vec{\nabla}_r \\ & + \frac{1}{4}\left[\vec{\nabla}_r{}^2\left(z\frac{r_A{}^2 - r_B{}^2}{r_A{}^2 + r_B{}^2}\right)\right]\Bigg\} . \qquad (48) \end{aligned}$$

Terms of type (c) are proportional to $\dot{\Theta}(t)$ and require knowledge of the BO matrix elements of $L_\pm$.

In Sec. F the formulas for the cross section are given, in terms of BO matrix elements of H_R' and $L_\pm$.

F. TRAJECTORY INTEGRALS AND CROSS SECTION

In direct analogy to Sec. D.1, the continuum part of $\Psi_1{}^s$ is defined

$$\Psi_1{}^{s,c} \equiv \int_0^\infty d\epsilon\, e^{-i\epsilon t/\hbar} \sum_{L,M} \int_{-\infty}^t dt'\dot{a}(\epsilon LM;t')\Phi^+[\epsilon LM;\vec{r};R_s(t'),\Theta_s(t')] , \qquad (49)$$

where $\Phi^+(\epsilon LM)$ is defined by Eqs. (14), (12). Substitution in the time-dependent Schrödinger equation, after some tedious calculation, yields explicit expressions for $\dot{a}(\epsilon LM;t)$: (a) g parity (even L):

$$\dot{a}(\epsilon LM;t) = (1/\sqrt{2})\, e^{i\Delta_g(t)} \{\dot{R}_g T^g(\sigma\to\sigma;LM) + \dot{\Theta}_g T^g(\sigma\to\pi;LM)\} , \qquad (50)$$

where $\Delta_g(t) \equiv 1/\hbar \int_0^t [\epsilon - \epsilon_{1g}(t')]\, dt' , \qquad (51)$

and

$$T^{g}(\sigma\to\sigma;LM)=-\sum_{\mu}B(\mu 0;L;y)\exp[-i\delta(\epsilon\mu 0;R)]\,d_{0M}^{(L)}(\Theta)\langle\epsilon\mu 0|H_R'|1s\sigma_g\rangle\ ; \tag{52a}$$

$$T^{g}(\sigma\to\pi;LM)=\sum_{\mu}B(\mu 1;L;y)\exp[-i\delta(\epsilon\mu 1;R)]\,\{\tfrac{1}{2}[d_{1M}^{(L)}(\Theta)+(-1)^{M}d_{1\overline{M}}^{(L)}(\Theta)]\}\langle\epsilon\mu 1|L_{+}/\hbar|1s\sigma_g\rangle\ . \tag{52b}$$

(b) u parity (odd L) (the expression is complicated by strong coupling in the ground state):

$$\begin{aligned}\dot{a}(\epsilon LM;t)=&\{a_{1u}(t)\,e^{i\Delta_{1u}(t)}\cos\zeta-a_{2u}(t)\,e^{i\Delta_{2u}(t)}\sin\zeta\}\\&\times[\dot{R}_u\,T^{u}(\sigma\to\sigma;LM)+\dot{\Theta}_u\,T^{u}(\sigma\to\pi;LM)]\\&+\{a_{1u}(t)\,e^{i\Delta_{1u}(t)}\sin\zeta+a_{2u}(t)\,e^{i\Delta_{2u}(t)}\cos\zeta\}\\&\times[\dot{R}_u\,T^{u}(\pi\to\pi;LM)+\dot{\Theta}_u\,T^{u}(\pi\to\sigma;LM)+\dot{\Theta}_u\,T^{u}(\pi\to\delta;LM)]\ ,\end{aligned} \tag{53}$$

where $\Delta_{iu}(t)\equiv 1/\hbar\int_0^t dt'[\epsilon-\epsilon_{iu}(R_u(t'))]$, (54)

and

$$T^{u}(\sigma\to\sigma;LM)=-\sum_{\mu}B(\mu 0;L;y)\exp[-i\delta(\epsilon\mu 0;R)]\,d_{0M}^{(L)}(\Theta)\langle\epsilon\mu 0|H_R'|1s\sigma_u\rangle\ ; \tag{55a}$$

$$T^{u}(\sigma\to\pi;LM)=\sum_{\mu}B(\mu 1;L;y)\exp[-i\delta(\epsilon\mu 1;R)]\,\{\tfrac{1}{2}[d_{1M}^{(L)}(\Theta)+(-1)^{M}d_{1\overline{M}}^{(L)}(\Theta)]\}\langle\epsilon\mu 1|(L_{+}/\hbar)|1s\sigma_u\rangle\ ; \tag{55b}$$

$$T^{u}(\pi\to\pi;LM)=i\sqrt{2}\sum_{\mu}B(\mu 1;L;y)\exp[-i\delta(\epsilon\mu 1;R)]\,\{\tfrac{1}{2}[d_{1M}^{(L)}(\Theta)+(-1)^{M}d_{1\overline{M}}^{(L)}(\Theta)]\}\langle\epsilon\mu 1|H_R'|2p\pi_u^{+}\rangle\ ; \tag{55c}$$

$$T^{u}(\pi\to\sigma;LM)=(i/\sqrt{2})\sum_{\mu}B(\mu 0;L;y)\exp[-i\delta(\epsilon\mu 0;R)]\,d_{0M}^{(L)}(\Theta)\langle\epsilon\mu 0|L_{-}/\hbar|2p\pi_u^{+}\rangle\ ; \tag{55d}$$

$$\begin{aligned}T^{u}(\pi\to\delta;LM)=&-(i/\sqrt{2})\sum_{\mu}B(\mu 2;L;y)\exp[-i\delta(\epsilon\mu 2;R)]\,\{\tfrac{1}{2}[d_{2M}^{(L)}(\Theta)+(-1)^{M}d_{2\overline{M}}^{(L)}(\Theta)]\}\\&\times\langle\epsilon\mu 2|L_{+}/\hbar|2p\pi_u^{+}\rangle\ .\end{aligned} \tag{55e}$$

In the above we have used the fact that $B(\mu\Lambda;L;y)$ and $\delta(\epsilon\mu\Lambda;R)$ do not depend on the sign of Λ; also that

$$d_{\overline{\Lambda}M}^{(L)}(\Theta)=(-1)^{\Lambda-M}\,d_{\Lambda\overline{M}}^{(L)}(\Theta)\ . \tag{56}$$

Explicit or implicit time dependence occurs in every factor in these equations (e.g., $y=\epsilon R^2/4$); $R_s(t),\Theta_s(t)$ are specified, if E,b are given. Note also that

$$\dot{a}(\epsilon L\overline{M};t)=(-1)^{M}\dot{a}(\epsilon LM;t)\ , \tag{57}$$

which guarantees the necessary symmetry with respect to the plane of collision.

Proceeding just as in Sec. D. 1, we substitute the expressions for $\dot{a}(\epsilon LM;t)$ in Eq. (49), and evaluate $\Psi_1^{s,c}(\vec{r};t)$ in the asymptotic limit $t\to\infty$, using the asymptotic form for $X^{+}[\epsilon LM;\vec{r};\vec{R}(t')]$ given by Eq. (13). Since $\Phi^{+}[\epsilon LM;\vec{r};\vec{R}(t')]$ is to be evaluated in the asymptotic limit for r, but for t' finite, the plane wave factor does not contribute:

$$\lim_{\substack{r\to\infty\\ R(t')\,\text{finite}}}\exp[(im/2\hbar)\dot{R}(t')\{z(r_A{}^2-r_B{}^2)/(r_A{}^2+r_B{}^2)\}]=1\ . \tag{58}$$

The expression for $\Psi_1^{s,c}(\vec{r};t)$ can then be evaluated by doing the integral over ϵ by stationary phase; only the outgoing portion contributes and the result is

$$\Psi_1^{s,c}(\vec{r};t) = -(2\epsilon')^{\frac{1}{2}} r^{-\frac{3}{2}} \exp[+i(k'r + 2k'^{-1}\ln r - \epsilon' t/\hbar + \pi/4)] \sum_{L,M} C^+(\epsilon' LM) Y_{LM}(\theta', \varphi'), \tag{59}$$

where ϵ' is just such that $v't = r$, and

$$C^+(\epsilon' LM) = \int_{-\infty}^{\infty} dt' \dot{a}(\epsilon' LM; t'). \tag{60}$$

Integrating $|\Psi_1{}^{s,c}|^2 r^2 dr$ over all scattering angles for the electron and summing over partial waves, we find the total probability of ionization at ϵ to $\epsilon + d\epsilon$, per collision of specified E, b is

$$P_I(E, b; \epsilon) d\epsilon = \sum_{LM} |C^+(\epsilon, LM)|^2 d\epsilon, \tag{61}$$

and the impact ionization cross section is therefore

$$\sigma_I(\epsilon) = 2\pi \int_0^\infty P_I(E, b; \epsilon) b\, db. \tag{62}$$

The trajectory integrals [Eq. (60)] exhibit some interesting features. Generally speaking the BO matrix elements of H_R' and $L_\pm$, the expansion coefficients $B(\mu\Lambda; L; y)$ and phase shifts $\delta(\epsilon\mu\Lambda; R)$ are slowly-varying functions of R_s and hence also of time; the same is true of the initial-state strong-coupling parameters $a_{iu}(t)$ and ζ. On the other hand the factors $\exp[i\Delta(t)]$ may oscillate rapidly: This feature is familiar in any study of inelastic scattering. The factors $d_{\Lambda M}{}^{(L)}(\Theta)$ provide a novel element: This process differs from many common types of excitation in that it is possible to excite angular momentum states with L values significantly larger than usual (up to ten or twelve quanta). It is interesting to note that the transfer of this angular momentum to the electron is hampered for increasing L by the oscillations in $d_{\Lambda M}{}^{(L)}(\Theta)$. This result suggests that when action in any form is transferred from one subsystem to another during interaction, such an oscillatory "transfer efficiency" factor must appear (in our treatment of the system this "angular" action is independent of the energy transfer).

The factor $e^{i\Delta(t)}$ will exert a dominant influence on the cross section when $\epsilon - \epsilon(1s)$ becomes a significant fraction of the collision energy E. For example, for $E = 100$ eV, at $\epsilon = 10$ eV, Δ will execute 5 to 10 cycles during a collision, while at $\epsilon = 50$ eV, it will execute 30–50 cycles. It is this feature, rather than the ϵ dependence of the BO matrix elements, which will reduce the cross section as ϵ increases at fixed E.

Finally, it may be pointed out that the possibility of transferring substantial amounts of energy to an ionized electron provides the severest possible test of a classical trajectory theory. In the approximation to the quantum trajectory integral, the analog to the factor $e^{i\Delta(t)}$ in Eqs. (50), (53), is a factor

$$\exp[\pm i/\hbar \int_{R_0}^{R} \{p_i(R') - p_f(R')\} dR'], \tag{63}$$

where p_i, p_f are the classical initial and final radial momenta. If we recall that $(p_i^2 - p_f^2)/2\mu = \epsilon_f - \epsilon_i$, and approximate $(p_i + p_f)/2\mu$ by the velocity $\dot{R}$ in the initial state, then (63) is the same factor as $e^{i\Delta(t)}$. However, such an approximation is increasingly serious as the energy transfer $\epsilon_f - \epsilon_i$ increases. The classical cross section will as a result be too large as the energy transferred increases relative to fixed E.

In the second paper of this series (II) we present the details of the electronic calculations, and in subsequent work the trajectory integrals and cross section are calculated.

ACKNOWLEDGMENT

We thank the National Science Foundation (USA) for support of this research in the period June, 1966 through June 1968, through Grant No. GP-5099X at the Massachusetts Institute of Technology.

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[*] Present address: Smithsonian Astrophysical Observatory, 60 Garden Street, Cambridge, Mass. 02138.

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equation requires still further adjustments to the kinematic factor, due to logarithmic phase shifts of the Coulomb field. In our formulation of the problem no such adjustments are needed.

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PHYSICAL REVIEW VOLUME 181, NUMBER 1 5 MAY 1969

Impact Ionization in the Proton-H-Atom System. II. Electronic States and Transition Elements

Hiram Levy II*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

and

Walter R. Thorson

Department of Chemistry, The University of Alberta, Edmonton, Canada

(Received 20 December 1968)

Paper I of this series describes the calculation of the direct impact ionization cross section $\sigma_I(\epsilon)$ for low-energy proton–hydrogen-atom collisions, where an adiabatic description is essentially correct for the initial channel. To calculate this cross section it is necessary to compute Born-Oppenheimer continuum wave functions and evaluate the matrix elements of the transition operators connecting them to the ground-state components. Such electronic calculations and matrix elements are presented in this paper. The transition matrix elements are quite sensitive to the form chosen for the "electron translation factor." Present calculations have removed most of the large error appearing in perturbed stationary states (pss) theory due to neglect of this factor. The computed transition elements presented in this paper should lead to values for $\sigma_I(\epsilon)$ accurate to perhaps 30%; estimated remaining error is due to spurious long-range effects which can be removed by improvement of the translation factor. Further computation making such improvements is in progress.

A. INTRODUCTION

In Paper I[1] it was shown that the total cross section for the impact ionization process

$$\mathrm{H}^+ + \mathrm{H}(1s) \rightarrow 2\mathrm{H}^+(E') + e^-(\epsilon), \qquad (1)$$

for initial relative energy $E \leq 500\,\mathrm{eV}$, can be calculated if the Born-Oppenheimer (BO) states for the incident (ground manifold) channel and the continuum at energy ϵ are known, and the matrix elements of certain transition operators connect-