Electron-Energy and Angular-Distribution Theory for Low-Energy Ion-Atom Collisions

S. Yu. Ovchinnikov* and J. H. Macek

Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996-1501 and Oak Ridge National Laboratory, P.O. Box 2009, Oak Ridge, Tennessee 37831

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We present the first *ab initio* calculations of electron-energy and angular distributions of saddle-point and S-promotion electrons for ionization in proton-hydrogen atom collisions. The calculations are based on outgoing wave Sturmian expansions in the frequency domain. They go beyond the usual Born-Oppenheimer separation of electron and nuclei motion and display the "$v/2$" peaks and the continuum capture cusps, missing in previous theories.

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Measurements of the electron-energy and angular distributions of emitted electrons are widely used probes of atomic dynamics. These probes are mainly used for high-energy ion-atom collisions where two features [1], namely, the binary encounter peak at electron velocities equal to twice the projectile velocity and the continuum capture cusp at electron velocities equal to the projectile velocity, dominate in the spectrum. Analogous experimental studies of low-energy collisions have been initiated [2]. The main difference between electron spectra at low- and high-energy is a small contribution or absence of the binary encounter peak in the low-energy spectra. Standard low-energy theories employing perturbed stationary states [3] usually cannot calculate energy and angular distributions of electrons and especially cannot get the continuum capture cusp that should be present in the spectra. Previous calculations of total cross sections have identified two ionization mechanisms [4,5] in low-energy collisions, called T promotion and S promotion, but have not been able to compute the corresponding electron distributions on an *ab initio* basis.

The electrons promoted to the continuum via a T promotion are called "saddle-point" electrons. This reflects the fact that the electrons are picked up in the saddle region of the potential energy and promoted to the continuum as the two charges recede from each other. The electrons locate in space at the saddle point between the nuclei. For equal charges, their velocities $\mathbf{k}$ are distributed around one-half of the velocity of the incoming particles. Recent calculations [6,7] obtain such distributions for saddle-point electrons, but employ an adjustable parameter $R_{\rm ion}$, where adiabatic and diabatic wave functions are matched. One objective of the present calculations is to eliminate this arbitrary parameter.

The S-promotion electrons are associated with classical, periodic, unstable trajectories, which represent electron motion along the axis joining the charges [8]. The kinetic energy of electrons on these trajectories increases when the charges approach each other. The increase of kinetic energy leads to ionization even when the relative velocity is insufficient to ionize electrons in a single binary collision. A simple analog of this mechanism is the acceleration of elastic balls bouncing between two walls that slowly approach each other. Present "hidden crossing" theory [4,5] cannot compute the complete distribution of these electrons. We will show that the S mechanism is responsible for the continuum capture cusp, missing in previous theories.

This Letter provides the first *ab initio* calculations for proton-hydrogen atom collisions that correlate specific features of electron-energy and angular distributions with the S and T mechanisms. Only calculations at impact parameters $b = 0$ are reported here since such calculations are well adapted to identifying the specific features of both ionization mechanisms. Nevertheless, the reported approach, which goes beyond the usual Born-Oppenheimer separation of electron and nuclei motions, can be used for other collision systems and for impact parameters $b \neq 0$.

The standard formula for the differential ionization amplitude [9]

$$T_{\mathbf{k},i} = \langle \psi_{\mathbf{k}}^{\rm out}(t)|\psi_i^{\rm in}(t)\rangle = \langle \psi_{\mathbf{k}}^{\rm out}(0)|\psi_i^{\rm in}(0)\rangle = \langle \tilde{\psi}_{\mathbf{k}}^{\ \rm in}(0)|\psi_i^{\rm in}(0)\rangle \quad (1)$$

is employed, but the new representation of the initial and final states vectors is used. In Eq. (1) $\psi^{\rm in}(t,\mathbf{r})$ and $\psi^{\rm out}(t,\mathbf{r})$ are solutions of the time-dependent Schrödinger equation

$$\left[i\frac{\partial}{\partial t} - H(R(t),\mathbf{r}) \right]\psi(t,\mathbf{r}) = 0, \quad (2)$$

with initial conditions given at $t \to -\infty$ and $t \to \infty$, respectively, and $\tilde{\psi}^{\rm in}(t,\mathbf{r}) = \psi^{\rm in}(-t,-\mathbf{r})^*$. The last equality in Eq. (1) allows us to define the initial conditions for both initial and final states at $t \to -\infty$ and consider only the first part of the collision $-\infty < t \leq 0$. The initial condition is associated with an electron that is in a bound atomic state $\phi_a(\mathbf{r}_a)$ with an eigenenergy E_a. In the center-of-mass reference frame we have

$$\psi_i^{\rm in}(t,\mathbf{r}) \xrightarrow{t\to-\infty} \phi_a(\mathbf{r}_a)e^{-iE_at}e^{i\mathbf{v}\cdot\mathbf{r}_a/2 - iv^2t/8}, \quad (3)$$

where $\mathbf{r}_a = |\mathbf{r} - \mathbf{R}/2|$, R is the internuclear distance, and v is the incident velocity. The incoming part of the

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final ionization state with an electron of a wave vector $\mathbf{k}$ is represented explicitly

$$\psi_{\mathbf{k}}^{\text{in}}(t,\mathbf{r}) = (2\pi)^{-3/2}\exp(i\mathbf{r}\cdot\mathbf{k} - ik^2t/2) + \psi_{\mathbf{k}}^{\text{scat}}(t,\mathbf{r}), \tag{4}$$

with the initial condition $\psi_{\mathbf{k}}^{\text{scat}}(t,\mathbf{r}) \longrightarrow 0$ as $t \longrightarrow -\infty$. Since only incoming waves are needed in Eq. (1) the superscript "in" is omitted.

Introducing new scaled coordinate variables $\mathbf{q} = \mathbf{r}/R(t)$ and a new time variable $d\tau = dt/R^2(t)$, where $R(t) = -vt$. For $t \le 0$ and $b = 0$ we obtain the time-dependent Schrödinger equation in a $\{\tau,\mathbf{q}\}$ space [10]:

$$\left[i\frac{\partial}{\partial\tau} - H_0(\mathbf{q}) - R(\tau)V(\mathbf{q})\right]\varphi(\tau,\mathbf{q}) = 0, \tag{5}$$

where

$$V(\mathbf{q}) = \left(-\frac{1}{|\mathbf{q}-\hat{\mathbf{R}}/2|} - \frac{1}{|\mathbf{q}+\hat{\mathbf{R}}/2|}\right),$$

$$H_0(\mathbf{q}) = -\frac{1}{2}\nabla_{\mathbf{q}}^2, \tag{6}$$

and $R(\tau) = 1/v\tau$. It is important to note that the Hamiltonian in Eq. (6) depends on τ only through the factor $R(\tau)$ multiplying the potential $V(\mathbf{q})$. The wave functions $\psi(t,\mathbf{r})$ and $\varphi(\tau,\mathbf{q})$ are connected by the transformation [10]

$$\varphi(\tau,\mathbf{q}) = R^{3/2}(\tau)\exp\left[-i\frac{1}{2}\frac{dR(\tau)/d\tau}{R(\tau)}q^2\right] \times \psi[-R(\tau)/v, R(\tau)\mathbf{q}]. \tag{7}$$

According to Eq. (7), the incoming plane-wave part of the final ionization state $\psi_{\mathbf{k}}(t,\mathbf{r})$ is transformed to a Gaussian wave packet, and the wave function that corresponds to the final ionization state is given by

$$\varphi_{\mathbf{k}}(\tau,\mathbf{q}) = (2\pi v\tau)^{-3/2}\exp\left[\frac{i}{2\tau}\left(\mathbf{q}+\frac{\mathbf{k}}{v}\right)^2\right] + \varphi_{\mathbf{k}}^{\text{scat}}(\tau,\mathbf{q}), \tag{8}$$

with the initial condition $\varphi_{\mathbf{k}}^{\text{scat}}(\tau,\mathbf{q}) \longrightarrow 0$ as $\tau \longrightarrow 0$. In this representation the wave functions $\varphi_i(\tau,\mathbf{q})$ and $\varphi_{\mathbf{k}}(\tau,\mathbf{q})$ are Galilean invariant. In standard theories $\psi(\tau,\mathbf{q})$ is expanded in fixed-nucleus basis states, i.e., eigenstates of $H_0 + RV$. These states cannot represent the ionization spectrum correctly and the continuum capture cusp is always absent in such calculations.

To incorporate dynamic variations of $R(\tau)$ we write the wave function as the Fourier transform (Solov'ev [11] used the Laplace transformation in $\{t,\mathbf{r}\}$ space),

$$\varphi(\tau,\mathbf{q}) = (-2\pi vi)^{-1/2}\int_{-\infty}^{\infty} d\omega\,\exp(-i\omega\tau)\chi(\omega,\mathbf{q}), \tag{9}$$

and consider the Schrödinger equation in a $\{\omega,\mathbf{q}\}$ space,

$$\left\{i\frac{\partial}{\partial\omega}[H_0(\mathbf{q}) - \omega] - \frac{1}{v}V(\mathbf{q})\right\}\chi(\omega,\mathbf{q}) = 0. \tag{10}$$

In the $\{\omega,\mathbf{q}\}$ space, the wave function $\chi_{\mathbf{k}}(\omega,\mathbf{q})$ that corresponds to the final continuum state becomes

$$\chi_{\mathbf{k}}(\omega,\mathbf{q}) = (2\pi)^{-3/2}\frac{\exp(i\sqrt{2\omega}\,|\mathbf{q}+\mathbf{k}/v|)}{v|\mathbf{q}+\mathbf{k}/v|} + \chi_{\mathbf{k}}^{\text{scat}}(\omega,\mathbf{q}). \tag{11}$$

When $\tau \longrightarrow \infty$, corresponding to $t \longrightarrow 0$, the integration over ω in Eq. (9) and the transformation (7) give us that $\psi_i(0,\mathbf{r}) = vC_i(v^2r^2/2,\hat{\mathbf{r}})$ and $\psi_{\mathbf{k}}^{\text{scat}}(0,\mathbf{r}) = vC_{\mathbf{k}}(v^2r^2/2,\hat{\mathbf{r}})$, where $C_i(\omega,\hat{\mathbf{q}})$ and $C_{\mathbf{k}}(\omega,\hat{\mathbf{q}})$ are determined by the asymptotic behavior of the wave functions at large q, as follows:

$$\chi_i(\omega,\mathbf{q}) = C_i(\omega,\hat{\mathbf{q}})q^{-1}e^{i\sqrt{2\omega}\,q}$$

$$\text{and}\quad \chi_{\mathbf{k}}^{\text{scat}}(\omega,\mathbf{q}) = C_{\mathbf{k}}(\omega,\hat{\mathbf{q}})q^{-1}e^{i\sqrt{2\omega}\,q}. \tag{12}$$

Then the transition amplitude to the continuum in Eq. (1) is given by

$$T_{\mathbf{k},i} = \frac{1}{v}\int_0^{\infty} d\omega\sqrt{2\omega}\int d\hat{\mathbf{r}}\; C_i(\omega,\hat{\mathbf{r}}) \times [C_{\mathbf{k}}(\omega,\hat{\mathbf{r}}) - C_{\mathbf{k}}^*(\omega,-\hat{\mathbf{r}})]. \tag{13}$$

Note that $T_{\mathbf{k},i}$ in Eq. (13) is determined by the solution of the Schrödinger equation [Eq. (10)] at $\omega \ge 0$; however, as we will see, we should know the solution at $\omega < 0$ to satisfy the initial conditions (3) and (4).

To calculate $C_i(\omega,\hat{\mathbf{q}})$ and $C_{\mathbf{k}}(\omega,\hat{\mathbf{q}})$ we expand the wave function $\chi_i(\omega,\mathbf{q})$ that corresponds to the initial bound state and the wave function $\chi_{\mathbf{k}}^{\text{scat}}(\omega,\mathbf{q})$ that corresponds to the scattering part of the final ionization state in terms of a discrete set of orthonormal Sturmian basis functions,

$$\chi_i(\omega,\mathbf{q}) = \sum_n S_n(\omega;\mathbf{q})B_n^i(\omega)$$

$$\text{and}\quad \chi_{\mathbf{k}}^{\text{scat}}(\omega,\mathbf{q}) = \sum_n S_n(\omega;\mathbf{q})B_n^{\mathbf{k}}(\omega). \tag{14}$$

The positive energy Sturmian functions $S_n(\omega;\mathbf{q}) = \langle\mathbf{q}|S_n(\omega)\rangle$ are defined by $[H_0(\mathbf{q}) + \rho_n(\omega)V(\mathbf{q})] \times S_n(\omega;\mathbf{q}) = \omega S_n(\omega;\mathbf{q})$ with outgoing wave boundary conditions $\partial[\ln S_n(\omega)]/\partial q \longrightarrow i\sqrt{2\omega}$, as $q \longrightarrow \infty$ [12]. In Eq. (14) $\rho_n(\omega)$ are the Sturmian eigenvalues and $S_n(\omega;\mathbf{q})$ are Sturmian eigenfunctions, normalized according to $\langle S_n(\omega)| - V|S_{n'}(\omega)\rangle = \delta_{nn'}$, where $\langle a|b\rangle = \int a(\mathbf{q}) \times b(\mathbf{q})d^3q$. Note that we do not complex conjugate $a(\mathbf{q})$. For ω real and negative the functions $S_n(\omega;\mathbf{q})$ form a complete set. When $\omega > 0$ the set is complete in the space of outgoing waves needed for Sturmian expansions of scattered waves $\chi_{\mathbf{k}}^{\text{scat}}(\omega,\mathbf{q})$ and $\chi_i(\omega,\mathbf{q})$. Our calculations reveal two different subsets of Sturmians related to S and T promotions. The Sturmians associated with the S promotion are defined only for $\omega > 0$ and $\rho_n^S(0) \ne 0$. In contrast the T-promotion Sturmians exist for all ω and $\rho_n^T(0) = 0$. The coupling matrix elements $M_{n'n}(\omega) = \langle S_n(\omega)| - V|\partial S_{n'}(\omega)/\partial\omega\rangle$ between n and $n' = n + 1$ have pole singularities at $\omega = 0$ that are natural for Sturmian representations. All other coupling matrix elements are regular and small.

Introducing $A_n^i(\omega) = B_n^i(\omega)\rho_n(\omega)$ and $A_n^{\mathbf{k}}(\omega) = B_n^{\mathbf{k}}(\omega)\rho_n(\omega)$ we obtain a set of coupled equations

$$v\frac{\partial A_n^i(\omega)}{\partial \omega} - i\frac{A_n^i(\omega)}{\rho_n(\omega)} + v\sum_{n'\neq n} M_{n'n}(\omega)A_{n'}^i(\omega) = 0, \tag{15}$$

$$v\frac{\partial A_n^{\mathbf{k}}(\omega)}{\partial \omega} - i\frac{A_n^{\mathbf{k}}(\omega)}{\rho_n(\omega)} + v\sum_{n'\neq n} M_{n'n}(\omega)A_{n'}^{\mathbf{k}}(\omega) = i\frac{1}{\sqrt{2\pi}\,v}\frac{S_n(\omega;\mathbf{k}/v)}{\rho_n(\omega)}, \tag{16}$$

with initial conditions $A_n^i(\omega) \longrightarrow -i\exp(-\sqrt{\omega/E_a}/v)\delta_{in}$ and $A_n^{\mathbf{k}}(\omega) \longrightarrow 0$, as $\omega \rightarrow -\infty$. We first truncate the coupled equations (15) and (16) at $N \approx 10$ and solve them to find the coefficients $A_n(\omega)$ and $A_n^{\mathbf{k}}(\omega)$. Solution of these equations gives the values of $A_n(\omega)$ and $A_n^{\mathbf{k}}(\omega)$ for the T Sturmians at $\omega = 0$. The coefficients $A_n(\omega)$ and $A_n^{\mathbf{k}}(\omega)$ for the S Sturmians equal zero at $\omega = 0$. The values at $\omega = 0$ are used as starting values to solved Eqs. (15) and (16) for $\omega > 0$. Then we construct $C_i(\omega, \hat{\mathbf{q}})$ and $C_{\mathbf{k}}(\omega, \hat{\mathbf{q}})$ using Padé summation [13]. The sequence of Padé approximants converges fairly rapidly. For $v = 0.4$, one Sturmian gives accurate results (within 10%).

Two spectra of ejected electrons associated with two different kinds of Sturmians are displayed in Fig. 1. Figure 1(a) shows a spectrum related to the S promotion for $v = 0.4$ a.u. The spectrum has two cusp peaks at $k_\perp = 0$ and $k_\parallel = \pm v/2$ in the center-of-mass frame. That the S-promotion mechanism gives cusp electrons can be understood from the corresponding classical trajectories given by Abramov, Ovchinnikov, and Solov'ev [8]. These authors show that the S-promotion classical orbits circle both protons an infinite number of times. Since the electron spends a large fraction of its time near the protons, the electron distribution peaks at $\mathbf{k} = \pm\mathbf{v}/2$. The energy distribution of the fast electrons is exponential. Figure 1(b) shows a spectrum related to the T promotion of the $2p\pi$ state for $v = 0.4$ a.u. The two peaks at zero center-of-mass velocity are associated with the π symmetry of the T_{01} promotion. This agrees with calculations reported in Ref. [2]. The distribution in Fig. 1(b) corresponds to $R_{\text{ion}} \approx 110$ a.u. in good agreement with $R_{\text{ion}} = 50/v$ used in Ref. [2].

Our formulation in terms of outgoing wave Sturmian eigenfunctions presents a complete *ab initio* theory of ionization in low-energy ion-atom collisions. First calculations show that two previously identified ionization mechanisms give dramatically different electron distributions. The T-promotion mechanism gives a peak at the center-of-mass velocity, equal to $v/2$ in lab frame, as in earlier calculations, but without arbitrary adjustable parameters. The S-promotion mechanism gives rise to two cusps where electron velocities match the ion velocities. These calculations show how measured electron distributions may be interpreted in terms of T and S mechanisms.

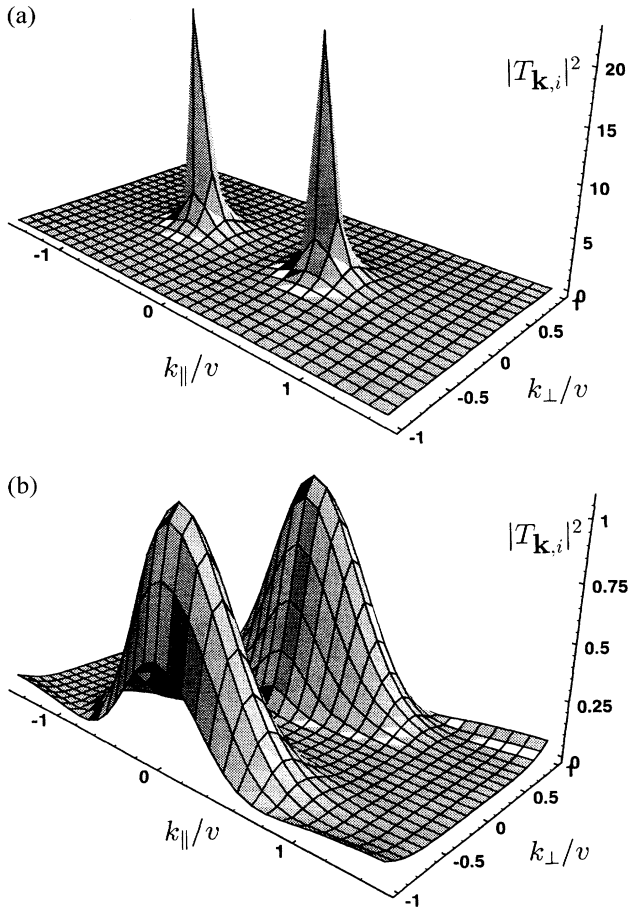

FIG. 1. The differential ionization probabilities $|T_{\mathbf{k},i}|^2$ at $v = 0.4$ a.u. and $b = 0$ (a) for S promotion, (b) for T promotion.

If measurements of the electron-energy and angular distributions of emitted electrons could be performed for small impact parameters b, then these calculations for $b = 0$ can be quantitatively compared with spectra presented in Fig. 1. However, measurements of cross sections integrated over impact parameters should still show the feature described here.

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*Permanent address: Ioffe Physical Technical Institute, St. Petersburg, Russia.

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