Theory of Rapidly Oscillating Electron Angular Distributions in Slow Ion-Atom Collisions

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A general expression for the ionization amplitude in slow ion-atom collisions is derived. The expression is inverted to obtain adiabatic electronic wave functions at complex values of the internuclear distance. It is shown that beating between σ and π components of electronic wave functions gives rise to rapid oscillations of electron angular distributions with ion velocity v. These rapid oscillations measure the real part of that eigenvalue whose imaginary part gives the well-known Wannier exponent. [S0031-9007(98)05440-4]

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The cold-target recoil-ion mass-spectrometry (COLTRIMS) imaging technique has been used to obtain energy and angular distributions of electrons ejected from atoms in a variety of atomic processes [1]. Distributions of electrons produced by slow ion-atom collisions are of particular interest since there is as yet no consensus as to the physical mechanisms that transfer energy from heavy, charged ions with velocity v to electrons such that the electrons acquire energy greatly in excess of v^2.

The Sturmian theory [2] and its antecedents [3,4] indicate two or three mechanisms that may operate, but definitive predictions of the electron distributions have proved elusive. Experimental evidence [1,4] qualitatively supports one of the three mechanisms of Ref. [4], namely, electron promotion to continuum states along the top of the potential barrier between target and projective species. In this Letter we develop a general theory for electron distributions and show how to extract key parameters from the data. The theory is used to extract details relevant to Born-Oppenheimer potential energy curves $\varepsilon(R)$ for diatomic molecular energy levels. Here, R is a coordinate measuring the separation between target and projectile cores. Atomic units with $e = m_e = \hbar = 1$ are used throughout.

In slow ion-atom collisions, adiabatic potential curves $\varepsilon_n(R)$ related to bound states may be extracted from the velocity and impact parameter dependencies of inelastic and elastic cross sections [5]. Theory is less well developed for ionization processes. The advanced adiabatic description [3] of fast electron distributions $(k \gg v)$ gives some information about the potential curves $\varepsilon(R)$ in the complex R plane for relatively small R. The simplicity of expressions suggest that several parameters of quasimolecules (i.e., energy of the level coupled with a continuum, effective charge of the core, and characteristic internuclear distances) could be determined directly from analysis of the electron energy spectra [6]. It is important that a determination of most parameters can be made using only relative (not absolute) values of differential cross sections which can be measured very accurately. Some data on parameters of relatively simple diatomic and triatomic quasimolecules have been reported in Ref. [6]. It has been found that the values of parameters of diatomic quasimolecules extracted from experimental data are close to those of the united atom limit. The remarkable similarity in behavior of cross sections and reasonable values of extracted parameters indicate that the range of applicability of the theoretical approach extends far beyond one-electron systems. Ogurtsov and co-workers [6] have shown that it is possible to describe the core of few-electron systems by proper effective charges.

To develop a theory for all electron velocities, note that adiabatic potential curves $\varepsilon_n(R)$ at real R are different sheets of the same analytic function $\varepsilon(R)$ on a multisheeted Riemann surface in the complex R plane, and the analytic function $\varepsilon(R)$ over the complex R plane completely describes collisions. This aspect is exploited in both the advanced adiabatic and the Sturmian theory, but only the Sturmian technique gives a complete description of electron spectra [2]. In this Letter we use the Sturmian theory to solve an inverse problem, namely, we recover potential curves $\varepsilon(R)$ and corresponding adiabatic (Sturmian) eigenfunctions on the Riemann surface in the complex R plane from ionization amplitudes.

As was discussed in Ref. [4], slow electrons are top-of-barrier electrons and are related to the harmonic oscillator region of $\varepsilon(R)$ in the complex R plane. It was shown [7] that the threshold "Wannier law" is associated with the imaginary part of $\varepsilon(R)$. Here, we show that fast oscillations in the electron spectra, "Wannier oscillations," are associated with the real part of $\varepsilon(R)$ in the harmonic oscillator region.

The electron ionization amplitude $A(\mathbf{k})$ is given by the projection of the time-dependent Schrödinger wave function $\Psi(t,\mathbf{r})$ on the time-dependent plane wave

$$A(\mathbf{k}) = \lim_{t\to\infty} \int \Psi(t,\mathbf{r}) \exp(i\mathbf{k}\cdot\mathbf{r} + ik^2t/2)d^3r\,. \quad (1)$$

We assume that nuclear motion can be treated classically, and the time-dependent internuclear distance $R(t) = |\mathbf{R}|$ is defined by the relative motion of the nuclei. The computation of $\Psi(t,\mathbf{r})$ in the Sturmian representation employs several steps.

Firstly, a time-dependent scaling transformation [8] with scaled coordinates $\mathbf{q} = \mathbf{r}/R$ and scaled time $\tau = \int^t R^{-2}(t')dt'$ is introduced. In this space the Galilean invariant solution has the form $\Psi(t,\mathbf{r}) = R^{-3/2}\exp[\frac{ir^2}{2R}\frac{dR}{dt}]\varphi(\tau,\mathbf{q})$. The wave function $\varphi(\tau,\mathbf{q})$ is the solution of a Schrödinger equation with a Hamiltonian that depends on the scaled time τ only through a factor $R(\tau)$ multiplying the potential.

Secondly, the wave function $\Psi(t,\mathbf{r})$ is written as a Fourier transform and expanded in the terms of Sturmian eigenfunctions $S_\nu(\omega;\mathbf{q})$ [7],

$$[H_0(\mathbf{q}) + \rho_\nu(\omega)V(\mathbf{q})]S_\nu(\omega;\mathbf{q}) = \omega S_\nu(\omega;\mathbf{q}), \quad (2)$$

where $\rho_\nu(\omega)$ are the Sturmian eigenvalues. The Sturmians are proportional to the adiabatic wave functions $\Phi_\nu(R;\mathbf{q})$ taken at the specific internuclear distances $R = \rho_\nu(\omega)$,

$$S_\nu(\omega;\mathbf{q}) = \sqrt{d\rho_\nu/d\omega}\,\Phi_\nu(R;\mathbf{q}).$$

The complete time-dependent wave function $\Psi(t,\mathbf{r})$ in the Sturmian representation has the form

$$\Psi(t,\mathbf{r}) = \frac{R^{-3/2}}{\sqrt{-2\pi i v}}\exp\left[\frac{ir^2}{2R}\frac{dR}{dt}\right]\int_{-\infty}^{\infty} d\omega \exp\left[-i\omega\int^t R^{-2}(t')dt'\right]\sum_\nu S_\nu(\omega;\mathbf{r}/R)B_\nu(\omega), \quad (3)$$

where v is the relative collision velocity and $B_\nu(\omega)$ is an expansion coefficient. Taking into account that $R(t) \sim vt \to \infty$, as $t \to \infty$ and using

$$\lim_{\tau\to 0}(2\pi i\tau)^{-3/2}\exp\left[\frac{i}{\tau}(\mathbf{q}-\mathbf{q}_0)^2\right] = \delta^3(\mathbf{q}-\mathbf{q}_0) \quad (4)$$

gives a simple expression for the ionization amplitude,

$$A(\mathbf{k}_v) = \frac{1}{\sqrt{2\pi v}}\lim_{\tau\to 0}\int_{-\infty}^{\infty} d\omega e^{-i\omega\tau}\sum_\nu S_\nu(\omega;\mathbf{k}_v)B_\nu(\omega), \quad (5)$$

where $\mathbf{k}_v \equiv \mathbf{k}/v$. The Galilean invariant cross section is

$$d^3\sigma/dk^3 = |A(\mathbf{k}_v)|^2. \quad (6)$$

The expansion coefficients $B_\nu(\omega)$ are solutions of coupled equations [7]. (For example, in the case of the straight-line approximation, they are coupled difference equations, and if the impact parameter equals zero, they become coupled differential equations.) We write the solutions of the coupled equations in the form

$$B_\nu(\omega) = \frac{1}{\rho_\nu(\omega)}\exp\left[-\frac{i}{v}\int_{-\infty}^{\omega}\frac{d\omega'}{\rho_\nu(\omega')}\right]F_\nu(v;\omega) \quad (7)$$

and introduce a new variable $y = \int_{-\infty}^{\omega}\frac{d\omega'}{\rho_\nu(\omega')}$ in order to obtain

$$A(\mathbf{k}_v) = \frac{1}{\sqrt{2\pi v}}\int_{-\infty}^{\infty} dy e^{-i(1/v)y} \times \sum_\nu S_\nu[\omega(y);\mathbf{k}_v]F_\nu[v;\omega(y)]. \quad (8)$$

Considering that $F_\nu[v;\omega(y)]$ is a slowly varying function of v, called $F_\nu(y)$, and using the inverse Fourier transformation gives the Sturmian functions in terms of a Fourier integral over ionization amplitudes;

$$\sum_\nu F_\nu(y)S_\nu(y,\mathbf{k}_v) = \frac{1}{\sqrt{2\pi}}\int_0^\infty d\left(\frac{1}{v}\right) \times \exp\left(i\frac{1}{v}y\right)A(\mathbf{k}_v)\sqrt{v}. \quad (9)$$

Equation (9) is the solution of the inverse problem in ion-atom collisions; namely, it shows how to recover Sturmian (adiabatic) eigenfunctions from $A(\mathbf{k}_v)$.

Since cross sections relate to $|A(\mathbf{k}_v)|^2$ rather than to $A(\mathbf{k}_v)$ in Eq. (9), it is useful to develop expressions that more directly relate to experiment. In the case of fast electrons ($k \gg v$) we may use adiabatic wave functions at large k_v. They have the form [3]

$$\Phi_\nu(\omega;\mathbf{k}_v) \sim \frac{C(\omega/\rho_\nu^2)\rho_\nu^{1/2}}{k_v}\exp(i\sqrt{2\omega}\,k_v)Y_\nu(\mathbf{k}_v), \quad (10)$$

where $Y_\nu(\hat{\mathbf{k}})$ is the angular part of the wave function. We find that

$$A(\mathbf{k}) = v^{-1/2}\sum_\nu\sqrt{\frac{dR_\nu(\varepsilon)}{d\varepsilon}}\exp\left[\frac{i}{v}\int_{E_\nu(-\infty)}^{\varepsilon}R_\nu(E)dE\right] \times F_\nu(\varepsilon)Y_\nu(\mathbf{k}), \quad (11)$$

where $\varepsilon = k^2/2$ and $R_\nu(E)$ is the function reciprocal to the adiabatic eigenvalue $E_\nu(R)$. This formula coincides with the expression for the electron distribution amplitude $A(\mathbf{k})$ derived by Solov'ev [3], and used in Ref. [6] to extract $\varepsilon(R)$ from the velocity dependence of fast electron spectra.

Since slow electrons ($k \ll v$) are saddle point electrons, consider Eq. (8) in the vicinity of the saddle point. Near the saddle point, the potential has the harmonic oscillator structure

$$V(\mathbf{q}) \approx -C_0 - C_1^2(q_\parallel^2 - q_\perp^2/2), \quad (12)$$

where

$$C_0 = (\sqrt{Z_1} + \sqrt{Z_2})^2 - Z_1Z_2, \qquad C_1 = \frac{(\sqrt{Z_1} + \sqrt{Z_2})^2}{(Z_1Z_2)^{1/4}}, \quad (13)$$

where $\parallel$ and $\perp$ denote components parallel and perpendicular to the internuclear axis, and Z_1 and Z_2 are nuclear charges. The corresponding adiabatic wave functions are just the well-known harmonic oscillator states $\Phi_{n_\xi n_\eta m}(R;\mathbf{q})$. These states are labeled by the harmonic oscillator quantum number n_η corresponding to motion in directions $q_\parallel$ parallel to the internuclear axis, the quantum number n_ξ corresponding to eigenstates in the coordinate $q_\perp$, and the projection m of angular momentum on the internuclear axis. Since $\mathrm{Im}\sqrt{R} > 0$, the wave function

$$\Phi_{00m}(R;\mathbf{k}_v) \approx 2^{1/8}\pi^{-3/4}(C_1\sqrt{R})^{3/4+m/2} \times \exp[iC_1\sqrt{R/2}\,k_\parallel^2]k_\perp^m \times \exp[-(C_1/2)\sqrt{R}\,k_\perp^2] \tag{14}$$

is localized on the potential saddle near $k_v = 0$.

On the real axis the function $\Phi_{n_\xi n_\eta m}(R;\mathbf{k}_v)$ of Eq. (14) is unbounded in $k_\parallel$ and does not satisfy appropriate boundary conditions; thus it does not represent the adiabatic eigenfunction. For sufficiently large $\mathrm{Im}\sqrt{R}$, however, the function is exponentially damped and vanishingly small at the end points. Along the real axis, the function $\Phi(R;\mathbf{k}_v)$ represents the atomic Rydberg states for sufficiently large R. The Rydberg region is separated from the harmonic oscillator region by a series of branch points called the super T^s series [7]. These branch points play an important role, via the stationary phase approximation, in the theory of ionization of atoms by both electron and proton impact near threshold as explained in Ref. [3]. For purposes of computing electron distributions, however, we avoid the stationary phase approximation, thus the branch points play no direct role in the calculation.

In the harmonic oscillator region the adiabatic eigenvalues $\varepsilon_{00m}(R)$ are well represented by the expression

$$\varepsilon_{00m}(R) = -C_0R^{-1} + (m + 1 - i/\sqrt{2})C_1R^{-3/2} + O(R^{-2})\,. \tag{15}$$

The first term is eliminated by a phase transformation in the time-dependent Schrödinger equation, and the equation $\varepsilon(R)R^2 - C_0R = \omega$ with $R = \rho(\omega)$ is solved for $\rho(\omega)$ to obtain

$$\rho_{00m}(\omega) = \omega^2/[(m + 1 - i/\sqrt{2})C_1]^2 + O(\omega)\,. \tag{16}$$

The amplitudes corresponding to different channels are obtained by integrating over y in Eq. (8) using Eqs. (14) and (16) with $F_\nu(y) = 1$. The result is

$$A_{00m}(\mathbf{k}_v) \approx \left(\frac{\sqrt{2}}{\pi}\right)^{5/4}\alpha^{-3/2}\left(\frac{k_\perp}{\alpha}\right)^m X_{1/4+m/2}\left((\gamma/\gamma^*)^{1/2}, (\gamma/\gamma^*)^{-3/2}, \frac{k_\perp^2 + i\sqrt{2}\,k_\parallel^2}{\alpha^2}\right)\exp\left[-\frac{i}{v}\int_0^\infty \frac{d\omega'}{\rho(\omega')}\right], \tag{17}$$

where

$$\alpha^2 = \frac{v}{2C_1^2}[(m + 1)^2 + 1/2]^{-1/2},$$

$$X_\nu(a,b;z) \equiv \left(\frac{a}{z}\right)^{\nu/2}K_\nu(-i\sqrt{az}) - \left(-\frac{b}{z}\right)^{\nu/2}e^{i\pi\nu/2}K_\nu(\sqrt{-bz})\,,$$

$\gamma = 1/\sqrt{2} + i(m + 1)$, and $K_\nu(z)$ is the modified Bessel function. Equation (17) gives a completely *ab initio* description of ionization by a top-of-barrier promotion. To extract the velocity and charge dependence, note that $\mathbf{k}_v$ occurs only in the combination $\mathbf{k}_v/\alpha$; thus, define

$$\mathbf{k}' \equiv \frac{\mathbf{k}_v}{\alpha} \propto \frac{\mathbf{k}}{v^{3/2}}\frac{(\sqrt{Z_1} + \sqrt{Z_2})^2}{(Z_1Z_2)^{1/4}} \tag{18}$$

so that

$$\frac{d^3\sigma}{dk'^3} = f(\mathbf{k}')\left|e^{-i/v}\int_0^\infty \frac{d\omega'}{\rho_\nu(\omega')}\right|^2, \tag{19}$$

where $f(\mathbf{k}')$ is independent of Z_1, Z_2, and v. Equation (19) shows how the distributions scale with charge and velocity. This scaling is a unique feature of the Sturmian theory of top-of-barrier electrons and amenable to experimental investigation.

At the lowest ion velocities the π_u top-of-barrier eigenstate with $n_\xi = 0$, $n_\eta = 0$, and $m = 1$ dominates the spectrum, but as the energy increases, the population of the lowest σ_g mode with $n_\xi = 0$, $n_\eta = 0$, and $m = 0$ becomes comparable. The contributions of the amplitudes corresponding to σ_g and π_u ionization must be added coherently. Adding the two amplitudes coherently gives an electron distribution of the form

$$\frac{d^3\sigma}{dk^3} \propto |A_\sigma(\mathbf{k}_v) + a\exp[i\phi/v]A_\pi(\mathbf{k}_v)|^2\,, \tag{20}$$

where a is an amplitude determined by the expansion coefficient $B_\nu(\omega)$.

The amplitude $A_\sigma = A_{000}$ is nodeless, but $A_\pi = A_{001}$ has a node when $k_\perp = 0$. For this reason, the distribution is not symmetric about the z axis and changes rapidly with ion velocity. This rapid change can be traced to the rapid change of the phase ϕ/v, where

$$\phi = -\mathrm{Re}\int_{R_0}^\infty [\varepsilon_\sigma(R) - \varepsilon_\pi(R)]dR = C_1\int_{R_0}^\infty R^{-3/2}dR = 8/\sqrt{R_0}\,. \tag{21}$$

Our calculations show that $R_0 \approx 2.2$ a.u. and $a \approx 2.2$ a.u. for proton-hydrogen collisions in the 1–15 keV energy range.

The corresponding electron distributions for 5, 10, and 15 keV collisions at an impact parameter of $b = 1.2$ a.u. are shown as density plots in Fig. 1. In these plots, the z axis is taken along the ion velocity so that $k_\parallel + k_z$, and the x axis lies in the scattering plane along the direction of the impact parameter vector. The phase ϕ/v changes by nearly two multiples of π over the 5–15 keV energy range. At 5 keV the electrons are distributed mainly below the $k_\perp = 0$ axis. At 10 keV the distribution

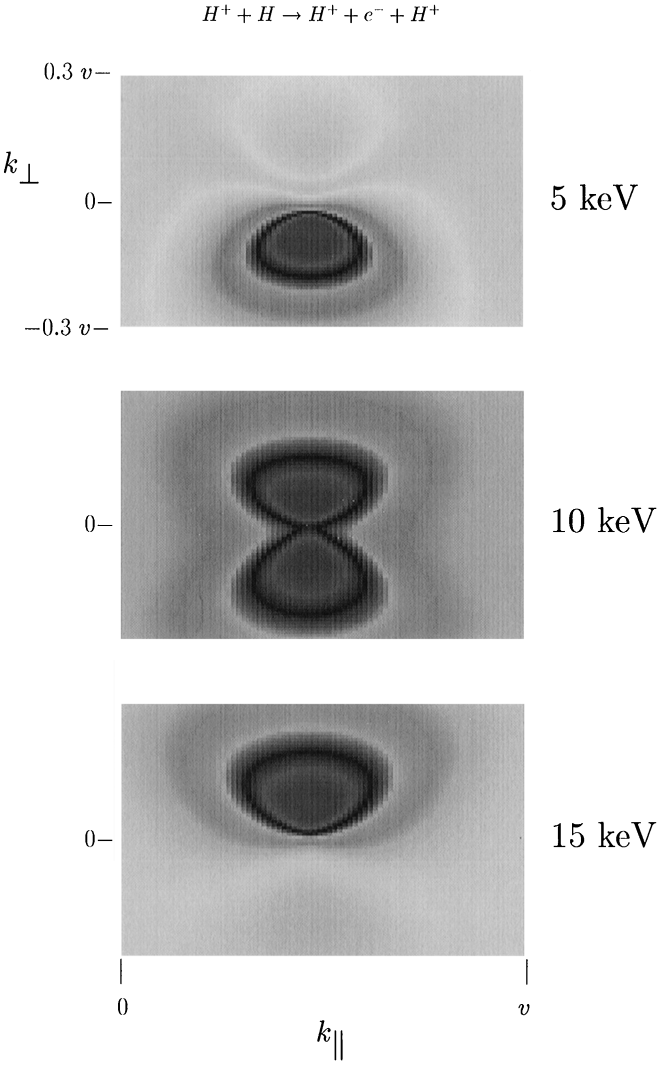

FIG. 1. Density plot of the electron distributions, $\mathbf{k}/v$, for proton impact on atomic hydrogen at fixed impact parameter $b = 1.2$ a.u. and ion energies of 5 keV (top), 10 keV (middle), and 15 keV (bottom).

is symmetric about $k_\perp = 0$, and for 15 keV it shifts to positive $k_\perp$. The observations of rapidly changing electron distributions and their interpretation in terms of the interference of π_u and σ_g amplitudes bring up a novel point concerning the Wannier theory. Usually the focus in this theory is on the Wannier exponent, which relies upon the imaginary part of the $R^{-3/2}$ term in Eq. (15) [9]. In contrast, the interference effect illustrated in Fig. 1 depends upon the real part of these eigenvalues. This suggests that the rapidly changing electron distributions could be exploited to obtain the real part of the top-of-barrier eigenvalues experimentally. Thus, we have the remarkable result that an energy eigenvalue pertaining to complex values of the internuclear distance R, according to Fig. 1, can be extracted from experimental data in much the same way that real energy eigenvalue differences are obtained from Rosenthal and Foley [5] oscillations in excitation cross sections.

In conclusion, we have shown that parameters of potential energy curves for complex values of the coordinate R are obtained from measured electron angle and energy distributions. The $R^{-3/2}$ term in the expansion of the adiabatic eigenvalues $[\varepsilon_\sigma(R) - \varepsilon_\pi(R)]$ in the harmonic oscillator region, which occurs only at complex R, has been identified.

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[1] R. Dörner, H. Khemliche, M. H. Prior, C. L. Cocke, J. A. Gary, R. E. Olson, V. Mergel, J. Ullrich, and H. Schmidt-Böcking, Phys. Rev. Lett. **77**, 4520 (1996).
[2] S. Ovchinnikov and J. Macek, Phys. Rev. Lett. **75**, 2474 (1995).
[3] E. A. Solov’ev, Zh. Eksp. Teor. Fiz. **70**, 872 (1976) [Sov. Phys. JETP **43**, 453 (1976)].
[4] M. Pieksma, S. Y. Ovchinnikov, J. van Eck, W. B. Westerveld, and A. Niehaus, Phys. Rev. Lett. **73**, 46 (1994).
[5] H. Rosenthal and H. M. Foley, Phys. Rev. Lett. **23**, 480 (1969).
[6] G. N. Ogurtsov, A. G. Kroupyshev, M. G. Sargsyan, Yu. S. Gordeev, and S. Yu. Ovchinnikov, Phys. Rev. A **53**, 2391 (1996).
[7] J. H. Macek and S. Yu. Ovchinnikov, Phys. Rev. A **49**, R4273 (1994).
[8] E. A. Solov’ev and S. I. Vinitsky, J. Phys. B **18**, L557 (1985).
[9] A. R. P. Rau, Phys. Rev. A **4**, 207 (1971).