Threshold Behavior of e-H Ionizing Collisions

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We present accurate *ab initio* numerical solutions of the full Schrödinger equation for the electron-impact ionization of hydrogen near threshold using the propagating exterior complex scaling method. They provide strong support for the Wannier threshold law [Phys. Rev. **90**, 817 (1953)], giving $\sigma \propto E^{1.122\pm0.015}$, and also give the energy dependence of the electrons' angular distribution as $(\pi - \theta_{12})_{\mathrm{FWHM}} \approx 3.0E^{1/4}$, in general agreement with classical and semiclassical predictions.

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In 1953, Wannier [1] proposed an ionization threshold law for *all* ionizing collisions leading to two free electrons and a charged atomic ion in the final state. It relates the total ionization cross section (TICS) to the total system energy by $\sigma \propto E^{\eta}$ near ionization threshold, where η is a constant that depends on the charge of the ion and can be expressed analytically. For the electron impact of a hydrogen target $\eta = (\sqrt{91/3} - 1)/4 \approx 1.127$. Wannier's threshold law applies to a vast range of atomic collisions, and consequently it continues to attract considerable interest five decades later. Experiments [2,3] have given support to this threshold law, and numerous semiclassical and quantal studies [4–10], which utilize approximations to the Schrödinger equation, are in agreement with Wannier's conjecture. Wannier theory also predicts that the ionized and scattered electrons emerge in opposite directions ($\theta_{12} = \pi$) at threshold. As system energy approaches threshold, θ_{12} is predicted to have a Gaussian probability distribution, centered at $\theta_{12} = \pi$, with a full width at half maximum related to system energy by $(\pi - \theta_{12})_{\mathrm{FWHM}} \propto E^{1/4}$ [11]. Later investigations [8,9,12,13] support this prediction though they give a range of values for the constant of proportionality. However, an *ab initio* investigation of these laws using a direct numerical solution of the full Schrödinger equation for the electron-hydrogen (e-H) system has been a rather remote goal until now due to the sheer scale of the computations.

Semiclassical and quantal investigations have given important insights into near-threshold collisions, but have relied on one or more *a priori* assumptions to make the computations tractable: They (a) consider only collisions with zero total angular momentum (L=0) and use semiclassical arguments [6,7,14] for similar scaling of the higher angular momentum states, (b) use Wannier's conjecture that the interaction is limited to the region where the Coulomb potential dominates the kinetic energy of the escaping electrons, thus restricting calculations to the "Coulomb zone" where $RE \approx 1$ ($R = \sqrt{r_1^2 + r_2^2}$ is the hyper-radius and r_1, r_2 are the radial coordinates of the outgoing electrons.), (c) assume that the potential ridge at $\theta_{12} = \pi$ and $r_1 \approx r_2$ dominates the interaction, or (d) include a semiclassical approximation of the final-state wave function.

To-date, several state-of-the-art fully quantal numerical methods have been used to explore near-threshold e-H ionizing collisions [15,16]. Yet, none of these methods have been implemented with the necessary precision to calculate η or the energy dependence of θ_{12} for the full e-H collision. The most comprehensive set of calculations thus far [17,18] incorporate assumptions (a) and (c) and support the Wannier threshold law.

The purpose of this Letter is to report fully quantal *ab initio* near-threshold calculations for e-H ionizing collisions, obtained without simplifying assumptions. To this end we solve the time-independent Schrödinger equation using the propagating exterior complex scaling (PECS) method, which accurately computes numerical solutions to the scattering wave functions on a finite hypercube of length $R_{\max}$ in coordinate space. Previously, we have used this method to obtain accurate solutions for e-H collisions at intermediate energies [19,20] and model e-H problems near threshold [18]. The computational efficiency and low-energy stability of PECS has allowed a detailed and accurate examination of the e-H threshold region. PECS uses the exterior complex scaling (ECS) ansatz pioneered by Rescigno, Baertschy, McCurdy and coworkers [21,22], and originally proposed by Nicolaides and Beck [23] and independently by Simon [24].

We performed calculations at 261 system energies between 0.01–0.10 a.u., spaced at 0.000 25 a.u. intervals below 0.05 a.u., and 0.0005 a.u. above. The TICS are converged, with respect to grid spacing and angular momenta, to around $\pm 1\%$ over the energy range. In Fig. 1(a) we plot our spin-weighted TICS and include several higher-energy calculations from our previous publications [19,20] to demonstrate the deviation from near-linear behavior above system energy $E = 0.05$ a.u. The present calculations use the same grid spacing and grid size ($R_{\max} = 180$ a.u.), and include six partial waves ($L \leq 5$) to achieve the stated convergence. The cross

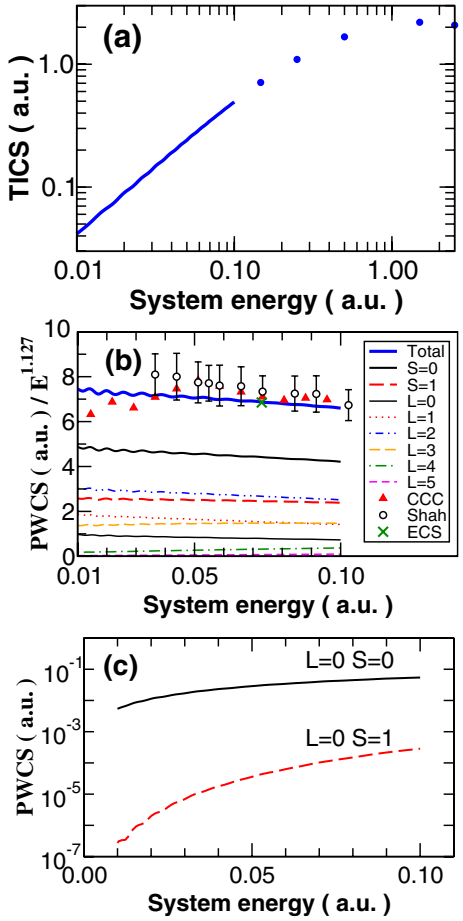

FIG. 1 (color online). (a) TICS results for $E = 0.01$ to 2.50 a.u. (b) TICS and separate partial-wave cross section (PWCS) contributions from $S = 0$ and $S = 1$, and separate PWCS for $L \leq 5$ ($S = 0$ and $S = 1$ combined). TICS are also presented for CCC [26], ECS [22], and experiment [25]. All results are scaled by $E^{1.127}$. (c) Spin-state contributions to the $L = 0$ PWCS.

sections were extracted using a standard surface integral method [19,22], which can be applied at any hyperradius R within our grid size $R_{\max}$. The extracted cross sections contain smooth R-dependent oscillations that diminish with increasing R. In a similar manner, for fixed R and varying energy there are slight E-dependent oscillations, visible in Fig. 1(b), that range from $\pm 0.2\%$ at 0.10 a.u., $\pm 0.5\%$ at 0.05 a.u., and reach $\pm 1.5\%$ at the lowest energy presented. Increasing $R_{\max}$ to allow larger R reduces these oscillations, but vastly increases computational effort. Overall, our estimated TICS error ranges between $\pm 1.5\%$ at 0.10 a.u. to $\pm 3\%$ at 0.01 a.u. Our results match the ECS calculation [22] at 0.0735 a.u. (15.6 eV) and are in good agreement with experiment [25] and convergent close-coupling (CCC) calculations [26] (with significantly reduced scatter).

Semiclassical studies [6,7,14] predicted that the TICS contribution from each LS partial wave separately obeys the Wannier threshold law (with same η), with the exception of the $L = 0$ triplet partial wave. This partial wave is highly suppressed due to the Pauli exclusion principle and was predicted [7,14] to have $\eta \approx 3.88$, but later corrected by [27] to $\eta \approx 3.38$.

In Fig. 1(b) we present the TICS, and separate contributions of the angular momentum states (L) and spin states (S) to the TICS, divided by $E^{1.127}$ to emphasize the low-energy results. With this scaling we would expect the curves to become linear (ignoring E-dependent oscillations) if the Wannier threshold law is valid as threshold is approached. This is indeed the case and confirms that both the TICS and the L and S contributions to the TICS are consistent with Wannier's threshold law. It is also evident that the relative contribution of higher partial waves diminishes as threshold is approached. The singlet and triplet spin-weighted ionization cross sections for the $L = 0$ partial wave shown in Fig. 1(c) demonstrate the suppression of the $L = 0$ triplet state due to the Pauli exclusion principle and different scaling law as threshold is approached.

In order to estimate the threshold power laws we performed nonlinear fitting of our results presented in Fig. 1 to the function $E^{\eta} \sum_{j=0}^{j_{\max}} c_j E^j$. This method has been used previously [17,18] and has the advantage that it extracts accurate information near threshold by fitting to a finite energy interval thus allowing for deviations from the power law further from threshold. The fitting function coefficients and their errors are sensitive to both $j_{\max}$ and the energy range chosen. We chose the largest $j_{\max}$ that minimized χ^2 without resulting in exponential increases in c_j or large errors in $c_{j_{\max}}$. Our calculations were fitted over several ranges of energies (0.01–0.03 a.u. through 0.01–0.10 a.u., in 0.01 a.u. increments) and the average and standard deviation of η for these fits are shown in Table I. This table includes fits for the TICS and the separate spin state S and angular momentum state L contributions to the TICS.

TABLE I. Mean and standard deviation of η for the nonlinear fitting of: TICS, separate spin-state partial-wave cross sections (over all L), and separate L (spin-weighted $S = 0$ and $S = 1$ combined).

	η
TICS	1.122 ± 0.015
$S = 0$	1.107 ± 0.040
$S = 1$	1.120 ± 0.038
$L = 0$	1.092 ± 0.018
$L = 1$	1.102 ± 0.030
$L = 2$	1.109 ± 0.031
$L = 3$	1.166 ± 0.015
$L = 4$	1.131 ± 0.048
$L = 5$	1.117 ± 0.032

Our results for the summed partial cross sections give $\sigma \propto E^{1.122\pm0.015}$, and hence provide strong support for the Wannier threshold law. The individual partial-wave and spin-state results are also consistent with the Wannier threshold law, though the standard errors of our $L = 0$ and $L = 3$ partial-wave fitting appear low. Separate calculations for the $L = 0$ singlet partial wave at $R_{\max} = 400$ a.u. give $\eta = 1.124 \pm 0.016$, providing strong evidence that these variations in η would be resolved by calculations with larger $R_{\max}$. However, a significantly larger $R_{\max}$ for the full problem is beyond our present computational resources. It is worth noting that $L = 2$ and $L = 1$ provide the majority contribution in this energy range rather than $L = 0$ and $L = 3$. Nonlinear fitting of the $L = 0$ triplet PWCS gives $\sigma \propto E^{3.36\pm0.02}$, in agreement with [27].

The energy sharing behavior of the outgoing electrons is shown in Fig. 2(a) by normalizing the single-differential cross sections (SDCS) at several system energies. As threshold is approached the dominance of the asymmetric energy sharing diminishes. Earlier calculations [4,11] had suggested that the SDCS should become independent of energy sharing near threshold. At 0.04 a.u. this is essentially correct, but as the energy is further decreased to 0.01 a.u. the $E_1 = 0$ normalized contribution drops to 0.96. This result is consistent with our previous e-H model calculations [18] and other classical [9] and semiclassical [10] predictions.

Classical mechanics is unable to predict spin asymmetry (A_s) as spin is a quantum-mechanical concept.

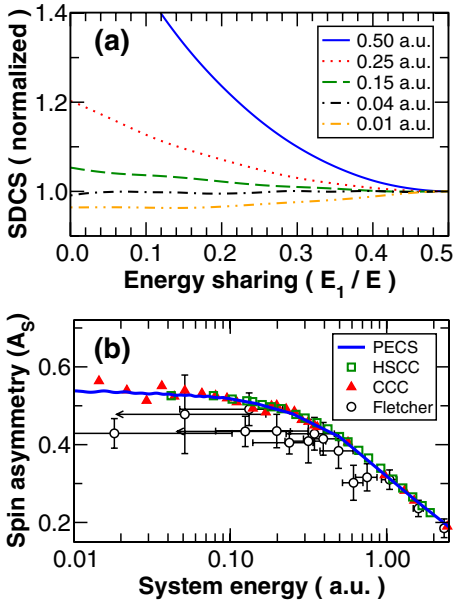

FIG. 2 (color online). (a) SDCS (with respect to E_1) normalized to 1.00 at $E_1 = E/2$. Results for $E = 0.01$ and 0.04 a.u. were calculated at $R = 360$ a.u. (b) Spin asymmetry: PECS, CCC [26], and hyperspherical close-coupling (HSCC) [15] calculations and experiment [28].

Semiclassical analysis [14] indicates that A_s should be independent of energy near threshold, based on the argument that singlet and triplet channels (except $L = 0$) have the same Wannier power-law exponent. Though recent quantal calculations [15,26] are consistent with this energy independence, their scatter or insufficient penetration into the threshold region leads to uncertainty in the value at threshold. We present our results along with experiment [28] and other calculations for A_s in Fig. 2(b). They confirm a linear, nearly energy-independent behavior below 0.05 a.u. suggesting the spin asymmetry approaches the limiting value $A_s = 0.54 \pm 0.01$.

The remaining important prediction of the Wannier models that we investigate is the angular dependence of the outgoing electrons. Many semiclassical calculations assume a Gaussian shape for the θ_{12} SDCS (as in [5] but in disagreement with [9]) and are limited to $L = 0$. Our SDCS results exhibit an approximate Gaussian shape, but deviate systematically from this shape with increasing RE. The range of the Coulomb zone, which is fundamental to Wannier and semiclassical derivations, scales as a function of energy, so it is reasonable to expect that RE is a suitable radial measure when investigating long-range interactions. The SDCS, with respect to θ_{12}, are presented in Fig. 3(a) at several system energies and constant $RE = 1.8$. The cross sections peak at $\theta_{12} = \pi$ and the position of the half maxima (shown with filled circles) moves towards $\theta_{12} = \pi$ as the energy diminishes. This is consistent with classical [11] and semiclassical [8,9,12] calculations, which report the relationship between system energy and the full width at half maximum as $(\pi - \theta_{12})_{\mathrm{FWHM}} = \alpha E^{1/4}$.

In Fig. 3(b) we present $(\pi - \theta_{12})_{\mathrm{FWHM}}/E^{1/4}$ as a function of RE at several system energies. If our results support the $E^{1/4}$ power law, then each curve within the threshold energy region should converge to the same constant α. Though we cannot demonstrate complete radial convergence at all energies due to our limited $R_{\max}$, all the curves overlap and have the same convergence behavior with respect to RE, which suggests that α converges to approximately 3.0 for $E \leq 0.05$ a.u. There is a slight deviation for the $E = 0.10$ a.u. curve, but we consider that this is outside of the applicable energy range of the threshold law. In order to demonstrate full convergence at 0.01 a.u. we estimate that our calculations need to be extended to at least $RE = 20$ ($R_{\max} = 2000$ a.u.). As the computational effort of PECS scales as $O(N^4)$, where N is the number of grid points along one dimension, these calculations are well beyond the capacity of our present supercomputing facilities. However, we have undertaken larger calculations for the $L = 0$ and $L = 2$ singlet partial waves at $E = 0.01$ a.u. ($R_{\max} = 720$ a.u. and 360 a.u., respectively), which confirm that the converging trend demonstrated in Fig. 2(b) continues at larger RE.

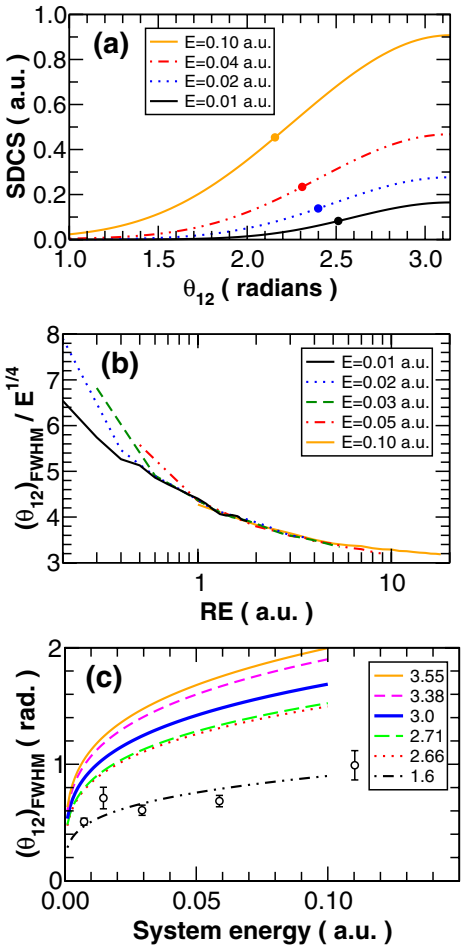

FIG. 3 (color online). (a) SDCS (with respect to θ_{12}) at $RE = 1.8$ a.u. (b) Convergence of $(\theta_{12})_{\mathrm{FWHM}}$ with respect to RE, scaled by $E^{1/4}$. (c) $(\theta_{12})_{\mathrm{FWHM}}$ energy dependence: Experiment for He [3] and best fit $\alpha = 1.6$, PECS $\alpha = 3.0$, and semiclassical predictions for α: 2.66 [13], 2.71 [8], 3.38 [12], 3.55 [9].

Semiclassical calculations for α are reported as 2.66 [13], 2.71 [8], 3.38 [12], and 3.55 [9], and are markedly different from experiment 1.6 ± 0.1 [3]. Reasons for disagreement with experiment have been given as possible experimental error [9] and that the single plane of measurement (90° to the incident electron) is not representative of the full problem [13]. Our calculations support the $E^{1/4}$ energy dependence of the FWHM, and our fit of α lies within the midrange of semiclassical calculations, shown in Fig. 3(c).

In summary, we have undertaken a wide-ranging investigation into e-H ionization collisions at energies very close to threshold using the PECS method. Our calculations provide strong support for Wannier's threshold law for e-H ionizing collisions, support classical and semiclassical predictions for the $E^{1/4}$ dependence of the angular distribution of the outgoing electrons, and give insight into the electron energy distribution and spin asymmetry near threshold. The accurate numerical solution of the time-independent Schrödinger equation near threshold has proven to be an enormous computational task but has at last provided convincing support for these classically and semiclassically derived relationships.

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