Threshold ionization laws for electron-hydrogen scattering and their dominant region of configuration space

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(Received 19 November 2002; published 23 September 2003)

DOI: 10.1103/PhysRevA.68.030701 PACS number(s): 34.80.Dp, 34.10.+x

The validity of the Wannier [1] threshold law for the electron-hydrogen total ionization cross section (TICS) has experimental [2] and theoretical support, e.g., Refs. [3–8]. However, several interesting questions remain. The semiclassical and quantal derivations of Peterkop and Liepinsh [9] and Rau [3] assume that the region of configuration space in the neighborhood of \( r_1 \approx r_2 \) is dominant. Temkin [10] suggested that, on the contrary, the dominant region is the one where \( r_1 \) and \( r_2 \) are highly asymmetric. This assumption leads to a quite different threshold behavior. Interestingly, no fully quantal calculation has established which regions of the wave function are dominant for electron-hydrogen ionization. Also, the Wannier threshold law is based on arguments concerning the form of the three-body wave function in the region \( r_1 \approx r_2 \). The major contributions are from those three-body partial waves that do not vanish in this region. For example, if we consider the \( L = 0 \) partial wave, quantum mechanically the singlet scattering provides the law although \( ^3S \) ionization may occur but should be suppressed relative to the singlet on account of the Pauli principle. What is the nature of the threshold law when there is no classical analog? Finally, the experimental work of McGowan and Clarke [2] indicates that the region is less than 0.4 eV above the ionization threshold. The computations of Kato and Watanabe [7] provided some weight for this conclusion but further work is warranted.

The purpose of this paper is to investigate these questions within the Wannier model of near-threshold ionization where the two electrons escape in the opposite directions. This model provides the essential features leading to the Wannier threshold law of the full problem near the ionization threshold. Its simpler collinear nature allows us to compute the three-body wave function with great accuracy since the electron-electron potential becomes just \( 1/(r_1 + r_2) \) to second order in the deviation of the mutual angle from \( \pi \).

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of 0.2% in the total ionization cross sections was maintained. At 0.2 a.u. this criterion required \( R_0 = 600 \) a.u., and at 0.04 a.u. \( R_0 = 1400 \) a.u. Below 0.04 a.u., \( R_0 \) was set to 1400 a.u. due to limits on our computational resources. As a result, the estimated error of these very low-energy calculations increased to 0.5–1.0%.

The TICS was extracted from the scattered wave function using the relationships [9,18]

\[
\sigma(E) = \int_0^{E/2} \frac{16}{\pi k_1 k_2 k_3} |f(k_1, k_2, R)|^2 dE, \tag{3}
\]

\[
f(k_1, k_2, R) = \frac{R}{2} \int_0^{\pi/2} d\alpha \left[ \hat{\phi}_0(k_1, r_1) \hat{\phi}_0(k_2, r_2) \frac{\partial}{\partial R} \psi(r_1, r_2) - \psi(r_1, r_2) \frac{\partial}{\partial R} \hat{\phi}_0(k_1, r_1) \hat{\phi}_0(k_2, r_2) \right], \tag{4}
\]

where \( E = k_1^2/2 + k_2^2/2 = E_1 + E_2 \), \( R = \sqrt{r_1^2 + r_2^2} \) and \( \alpha = \tan^{-1}(r_2/r_1) \) are the hyperradius and hyperangle, and \( \hat{\phi}_0(k, r) \) is the hydrogenic Coulomb function for \( l = 0 \).

Though Eq. (4) is derived in the limit \( R \rightarrow \infty \), it can be used for finite but large hyperradius by choosing \( R_0 \) as described to achieve good convergence of the single-differential cross section (SDCS). This method of extracting ionization cross sections was recently employed by McCurdy, Horner, and Rescigno [13] for model hydrogen problems and by Baertschy, Rescigno, and McCurdy [19] for the full hydrogen problem.

First, we examine the regions of configuration space of the scattering wave function responsible for the threshold law. According to Wannier [1] and Rau [3], it is the region \( r_1 \approx r_2 \) in the so-called “Coulomb zone,” where \( RE \approx 3\sqrt{2} \) which dominates the threshold behavior. On the other hand, Temkin [10] stated that the dominant contribution to the threshold behavior is from the region where \( r_1 \geq r_2 \), that is, \( \alpha \approx \alpha_T = \tan^{-1}(1/2) \approx 26^\circ \). Since these regions are complementary, a straightforward way to examine their contribution is to let \( f = f_T + f_W \), where the Temkin and Wannier amplitudes are obtained by adjusting the integration limits in Eq. (4) to \([0, \pi/2) + (\pi/2, \alpha_T + (\pi/2)] \) and \([\alpha_T, (\pi/2) - \alpha_T) \), respectively. Noting that \( |f|^2 = |f_T|^2 + |f_W|^2 + 2 Re(f_T^* f_W) \), the contributions to the TICS from the Wannier and Temkin regions can be derived from Eq. (3). The interference term \( 2 Re(f_T^* f_W) \) will also contribute to the TICS.

Figure 1 shows the contribution to the TICS for the singlet wave function. Our computed TICS are labeled \( \sigma(R_0) \). The corresponding Wannier and Temkin cross sections, extracted from our calculated wave functions, are labeled \( \sigma_W(R_0) \) and \( \sigma_T(R_0) \), respectively. It is worth reiterating that in order to achieve the high accuracy stated, we used hyperradius values \( R_0 \) ranging from 600 a.u. at \( E = 0.2 \) a.u. \( (R_0E = 120) \) to 1400 a.u. at \( E = 0.04 \) a.u. \( (R_0E = 56) \). At all lower energies \( R_0 = 1400 \) and at the smallest energy studied, 0.005 a.u., this gives \( R_0E = 7 \). In all cases this places \( RE \approx 3\sqrt{2} \), so our surface integrals are probing the wave function well outside the Coulomb zone although it is being approached at the lowest energy. It appears that the dominance of \( \sigma_W \) is diminished as we leave this zone. In order to quantify this further, we calculated TICS for the fixed value of \( RE = 7 \) over the whole energy range. The TICS with this setting for \( R \) have not converged, of course, to the same accuracy as previously, now having errors up to 5% at the higher energies. As is evident from Fig. 1, the dominance of the Wannier region as the Coulomb zone is neared is firmly established by our calculations. It is also evident that at constant \( RE \) the dominance of \( \sigma_W \) over \( \sigma_T \) increases from one order of magnitude at 0.2 a.u. to two orders of magnitude at 0.005 a.u., demonstrating the increasing dominance of the Wannier region as the ionization threshold is approached. Using our method for calculating the hyperradius \( R_0 \) required to achieve convergence of our results to within 0.2%, we estimate that \( R_0 \) would only fall within the Coulomb zone for energies below \( 10^{-5} \) a.u. It is only in this region that the arguments of Rau will rigorously hold and give TICS to the specified accuracy. It is also worth pointing out that the convergence of the TICS is much more rapid with \( R \) than for \( \sigma_W \) and \( \sigma_T \) separately, as evidenced from Figs. 1 and 2.

The TICS for the \(^3S\) case was calculated using a hyperradius of 800 a.u. for all energies, and is presented in Fig. 2. Near threshold they are similarly influenced by the contributions from the Wannier region, but to a lesser extent than the singlet TICS, due to the suppression of the amplitude at...
$r_1 = r_2$. Maintaining a constant energy-dependent hyperradius of $RE = 7$ for the triplet case also maintains the dominance of the Wannier region at all energies considered. Like the singlet case, this gives evidence that the $r_1 = r_2$ region, though suppressed, is also dominant within the Coulomb zone.

In Fig. 3, the shape of the SDCS at various energies is shown. At 0.22 a.u. the SDCS is flat, apart from very slight oscillations. Below this energy, there is an increasing reduction in the SDCS at unequal energy sharing as the total energy approaches threshold. At 0.12 a.u., the reduction of 3% is consistent with the semiclassical calculations of Rost [20]. However at higher energies, the SDCS remains flatter than that calculated by Rost. Our calculations were performed at similar energies to Rost to facilitate comparison with his publication. The relatively flat SDCS presented here are in line with the predictions of Rau [3].

Plotted in Fig. 4 are our singlet TICS calculations, where all datasets have been divided by $E_{1.127}^3$ to emphasize their threshold behavior. There is good agreement between our results and those of Kato and Watanabe [7] above 0.02 a.u., and our results showed significantly reduced energy-dependent fluctuations. Also shown are the recent ECS calculations of McCurdy, Horner, and Rescigno [13] and time-dependent calculations of Robicheaux, Pindzola, and Plante [21].

In order to determine the near-threshold law for the TICS, we employed the same procedure as Kato and Watanabe [7], and fitted to the function $\sigma = E^n g(E)$, where an $n$th-order series expansion of $g(E)$ was used. The value of $n$, and its error, is dependent upon both $n$ and the error estimate given to each point. Kato and Watanabe did not provide details of their error estimating procedure. We performed a nonlinear fit based upon the estimated maximum errors from our convergence testing, and then partitioned the points into four energy regions. The standard deviation of the points in each region was used as an improved estimate for their absolute error. The fitting procedure was performed iteratively, using the latest error estimates, until convergence of the coefficients was obtained. The resultant nonlinear fit for the $^1S$ TICS is

$$\sigma_{S=0} = E^{1.128 \pm 0.004} \left[ (0.386 \pm 0.007) - E(1.69 \pm 0.08) + E^2(4.1 \pm 0.5) - E^3(4.6 \pm 1.1) \right].$$

The fit presented above was made for the energy range 0.005–0.20 a.u., which matched nonlinear fits of subsets of the data over the energy ranges 0.005–0.10 a.u. and 0.005–0.05 a.u. It also matched linear least-squares fits of the transformed data over these energy ranges, within their calculated standard errors. With higher-order fitting functions, the higher-order coefficients became very large, with significant errors, which indicated that the fitting procedure was overly influenced by numerical errors in our results. The leading term for the singlet TICS is $E^{1.128 \pm 0.004}$ which is very close to the classical Wannier [1] result of $E^{1.127}$, with a threefold improvement in the standard error compared with Kato and Watanabe’s calculation. It accounts for 96% of the cross section at $E = 0.01$ a.u. rising to 99% at $E = 0.0025$ a.u. The conclusion of McGowan and Clarke [2] that the Wannier [1] region is within 0.4 eV of threshold is, within experimental error, consistent with our calculations.

These fitting procedures were performed, for completeness, on the other datasets shown in Fig. 4. The results for our fits are $E^{1.228 \pm 0.074}$ for McCurdy, Horner, and Rescigno [13] and $E^{1.197 \pm 0.01}$ for Robicheaux, Pindzola, and Plante [21]. The fit published by Kato and Watanabe [7] was $E^{1.124 \pm 0.013}$.

Due to the highly suppressed TICS of the $L=0$ triplet at low energies, linear fitting procedures were used on the transformed data in preference to nonlinear methods, giving an estimated threshold behavior of $E^{3.37 \pm 0.02}$, which is in excellent agreement with the semiclassical calculation by Peterkop [22] of $E^{3.38}$. The estimated error is larger than the singlet error due to the limited hyperradii used for the low-energy calculations.

In conclusion, our fully quantal study has yielded several new insights into the physics of the near-threshold ionization. We explored the regions of configuration space which are important in obtaining accurate TICS and were able to confirm that the important region that emerges from a fully quantal calculation is the $r_1 = r_2$ one, but only while in the Coulomb zone. However, the evaluation of the surface integrals to obtain accurate amplitudes requires hyperradii well

FIG. 3. Collinear $^1S$ SDCS, normalized to 1.00 at $\varepsilon_1 = \varepsilon_2$.

FIG. 4. Singlet $L=0$ TICS for the collinear model with spin weighting (divided by $E^{1.127}$). These results are compared with those of Kato and Watanabe [7], McCurdy, Horner, and Rescigno [13], and Robicheaux, Pindzola, and Plante [21].
outside the Coulomb zone. We have provided further evidence for the Wannier threshold law for $^1S$ scattering and its range of applicability given by Eq. (5). In particular, the nonzero linear term with $E$ indicates that the $E^{1.127}$ functional form is only valid strictly at the threshold, which is consistent with the analysis of Rost [20]. The accuracy of our numerical methods enabled us to describe the nonclassical threshold behavior of $^3S$ scattering. A theoretical understanding of the emergence of a Wannier-like threshold behavior for $^3S$ TICS, with exponent three times the Wannier value, has been given by Peterkop [22]. Finally, we provided an independent confirmation of the ECS methodology and demonstrated that it can yield extremely accurate TICS near threshold.

The authors would like to acknowledge Aaron Temkin for providing the stimulus for the work, the support of the Australian Research Council, the Australian Partnership for Advanced Computing, and the Western Australian Interactive Virtual Environment Center.