Reexamination of tests of the Wannier threshold law for two-electron escape

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Recent experimental studies of the spin dependence in electron-impact ionization of atomic hydrogen revealed the presence of deviations from the predictions of the conventional Wannier threshold theory of two-electron escape. We provide some insight into the possible origin of these deviations and reexamine the results of previous work that had claimed consistency with the Wannier theory but, with added statistical analysis, also seem to show deviations.

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The threshold law for double escape of two electrons from a charged center [1] has been the subject of extensive theoretical [2–9] and experimental [10–19] investigation for almost four decades. Until recently, all experimental evidence appeared to be consistent with the conventional Wannier approach, which predicts that the total ionization cross section σ varies according to the relation $\sigma \propto E'^{m}$, where E' is the kinetic energy available for double escape and m is given by [20] 1.127 for a residual ionic center of net charge $+e$. As Rau [1] has noted, the relative simplicity of all threshold laws derives from an assumption, originally advanced by Wigner [21], that the energy dependence of the cross section in the threshold region is insensitive to a detailed knowledge of the "reaction zone," a region of space in which the particles are close together and hence highly interactive. This assumption, also known as the ergodic hypothesis, permits an analysis of threshold behavior to be restricted to the mechanics of the escape process alone, instead of requiring a detailed understanding of the dynamics of the collision as a whole. Such a statistical or classically chaotic approach to the early stages of the break-up of an atomic system near threshold has been challenged by Temkin and his co-workers [9] and is undergoing further scrutiny by quantum chaos [22] and atomic collision theorists [23,24].

Recently we reported on a study of the spin dependence in electron-impact ionization of atomic hydrogen [19,25], in which we used crossed beams of polarized particles to measure the ionization counting-rate asymmetry Δ, which by construction is proportional to the cross-section asymmetry A given by

$$A=(\sigma_s-\sigma_t)/(\sigma_s+3\sigma_t)\ , \tag{1}$$

where σ_s is the singlet cross section and σ_t is the triplet cross section. In the conventional Wannier theory, the cross-section asymmetry A, and hence the counting-rate asymmetry Δ, should be constant throughout the energy region for which the threshold law is valid. Our data contained two features that contradicted the Wannier prediction. First, structure was present over the full 1.7-eV range investigated. Second, within the first 0.5 eV above threshold, a range for which previous cross-section studies had claimed to verify the Wannier power-law behavior [10], the asymmetry had a generally positive slope. These features suggest that three-body dynamics affect the behavior of the asymmetry in the threshold region, calling into question the ergodic ansatz of Wigner [21] and the predictions of the Wannier law, which rely only on the asymptotic behavior of the wave function. While the origin of the structure [23] may be complex and difficult to trace in detail, we believe that a crude plausibility argument can be made for the positive slope.

From the definition of Δ and A and their relationship to the singlet and triplet cross sections expressed by Eq. (1), we see that an increase in the value of Δ requires that the singlet cross section increase faster than the triplet. Moreover, when $\Delta=0$, the singlet and triplet cross sections are equal. This latter condition is well known to occur at high values of the incident electron energy, a kinematic regime for which the two electrons have distinctly different characteristics in configuration space. Under these circumstances, spin symmetry or antisymmetry is not required to satisfy the Pauli exclusion principle, a result that contrasts with that of the ground state of the helium atom, where the two bound electrons have identical configuration-space properties, and the spinor is constrained to be antisymmetric under exchange.

Let us now somewhat imprecisely divide the ionizing collision into two separate processes, one involving the dynamic reaction of the atom to the incident electron and the other involving the momentum transfer from the incident to the bound electron resulting in ionization. In the case of the first process, the atom reacts by becoming polarized, the degree to which depends upon the atomic polarizability and the time-averaged electric field the atom experiences during the collision. If the polarization is large, as is the case for low-velocity collisions, the two electrons will have only a small probability of sharing the same configuration-space properties when ionization

occurs. As the collision velocity increases, however, the collision time shrinks, the time-averaged electric field becomes smaller, the polarization declines, and the probability for similar configuration-space properties increases. (Although this argument is far from rigorous and does not properly consider the role of angular momentum or parity [6], we suggest, nonetheless, that it has general applicability.) Thus, just above threshold, singlet scattering grows relative to that of triplet scattering, and the asymmetry Δ assumes a positive slope. As the incident energy continues to rise, the momentum transfer from the incident to the atomic electron has a steadily decreasing probability of providing the same configuration-space character for the two final-state electrons, leading ultimately to the equality of σ_s and σ_t. The prominence and location of the resulting peak in Δ should depend upon the specific characteristics of the atom. As we showed in a previous paper [25], for hydrogen the peak is clearly visible and occurs at an incident electron energy slightly greater than 15 eV. For lithium [15] and cesium [18], peaks are also visible, but for sodium and potassium [14,15,26] they seem to be absent at the level of the experimental precision.

Motivated by our observations for hydrogen, we reexamined the conclusions reached in three other threshold experiments [13,16,17]. The original results of two double photodetachment studies, one for K^- and one for H^-, are shown in Figs. 1(a) and 2(a) along with the best fits of the Wannier power law presented in the published papers. In each of these studies the experimenters applied a χ^2 analysis in an attempt to discriminate between the Wannier and Coulomb-dipole theories. In each case they found that their data could not be used to make such a distinction. In the present discussion we will focus solely on the conclusions they drew about the Wannier law.

The experimenters [17] who were studying K^-, Bae and Peterson, obtained a power-law exponent of 1.16 ± 0.05, in good agreement with the Wannier prediction of 1.127. The reduced χ^2 for the Wannier fit was 0.69 for 34 degrees of freedom, corresponding to a 91% confidence level. (We note that with 50% representing an ideal confidence level, the 91% value suggests that the uncertainties for the K^- data points might have been overestimated.) The experimenters [13] who were studying H^-, Donahue *et al.*, obtained a power-law exponent of 1.15 ± 0.04, also in good agreement with the Wannier prediction of 1.127. The reduced χ^2 for the Wannier fit in their case was 1.15 for 66 degrees of freedom, corresponding to a confidence level of 19%. Both the K^- and H^- experimenters concluded that their results were consistent with the Wannier threshold law, the validity of the claim resting solely on the respective χ^2 analyses.

A visual examination of the results presented in Figs. 1(a) and 2(a), however, suggests that the functional form of the power law may be inappropriate, since "structure" appears to be present in the data that is not accounted for by a simple exponential behavior. Recognizing that a χ^2 analysis is a "one way" test, that is, it is a sufficient test for ruling out a fit, but it is not a sufficient test for justifying a fit, we examined the normalized residuals $e_i=\delta_i/\sigma_i$ of each experiment for evidence of nonrandom ordering,

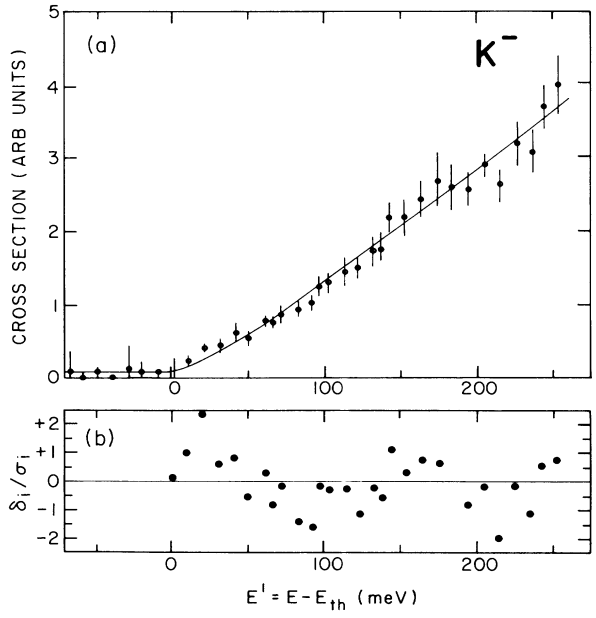

FIG. 1. (a) Cross section for double photodetachment of the K^- ion as a function of excess photon energy $E'=E-E_{th}$ above threshold, taken from Ref. [17], where E is the photon energy and E_{th} is the threshold energy. The curve is a least-squares fit of the Wannier power-law function, also taken from Ref. [17]. (b) Normalized residuals corresponding to the data points in (a).

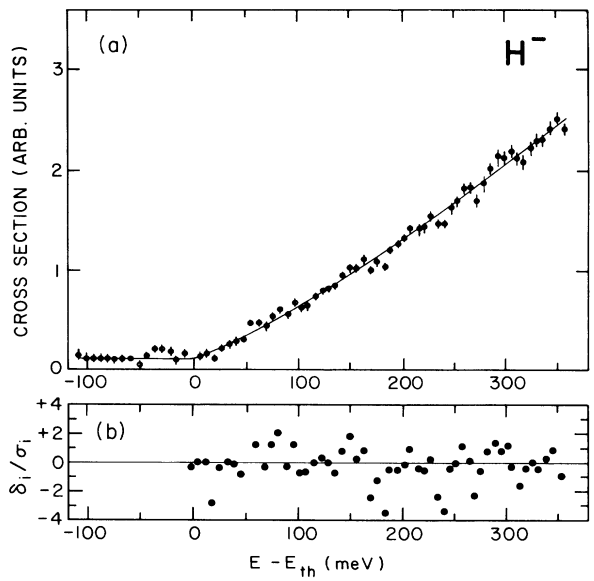

FIG. 2. (a) Cross section for double photodetachment of the H^- ion as a function of excess photon energy $E'=E-E_{th}$ above threshold, taken from Ref. [13]. The curve is a least-squares fit of the Wannier power-law function, also taken from Ref. [12]. (b) Normalized residuals corresponding to the data points in (a).

where σ_i represents the uncertainty and δ_i the residual for each data point i shown in Figs. 1(a) and 2(a). The normalized residuals e_i are plotted in Figs. 1(b) and 2(b).

We carried out a quantitative analysis of the ordering for both experiments by applying four different statistical tests: a runs test [27], an analysis of the Durbin-Watson statistic [28], and two searches for autocorrelation in the normalized residuals [27]. Each test is sensitive to different manifestations of nonrandomness. All four tests should confirm randomness if the residuals are truly randomly distributed.

Tests based on the occurrence of "runs" are widely used in the assessment of the randomness of series. In our application, a run is defined as the sequence of residuals (ordered on the independent variable E') that are consistently above or below a "cut point" (in our case, the median) of the residuals. Sequences of values that show too many or too few runs are indicative of nonrandom ordering. For the K^- data, we found [29] a two-tailed probability of randomness p of only 0.0235, while for the H^- data, we found a p value of 0.217, the former showing strong evidence and the latter only weak evidence for nonrandom ordering.

The Durbin-Watson test is often used in economic analysis to detect nonrandom behavior in the modeling of "time series." The test is particularly sensitive to nonrandomness associated with first-order serial correlation; that is, when the maximum nonrandom association among residuals occurs with respect to successive measurements. In our application, the existence of serial residual correlation is indicative of a specific type of serial model violation. The Durbin-Watson statistic d is defined by the relation

$$d=\sum_{i=1}^{n}(e_i-e_{i-1})^2\Big/\sum_{i-1}^{n}e_i^2\ , \tag{2}$$

where n is the number of observations. By comparing the calculated values of d, 1.27 for the K^- data of Fig. 1 and 1.48 for the H^- data of Fig. 2, with the tabulated [28] 1%, 2.5%, and 5% significance points for d, we found that the p value for randomness in each case was less than 0.035.

We carried out two additional searches for nonrandom behavior of the residuals, both of which tested for autocorrelations. In the first test, we expressed the ith normalized residual e_i in the linear form

$$e_i=b_j^0 e_{i-j}+c_j^0\ , \tag{3}$$

where the lag j was examined for values between 1 and 16. For the K^- data we found compelling evidence for autocorrelation, with four coefficients b_1^0, b_2^0, b_7^0, and b_{15}^0, all exceeding their two-standard error (2σ) limit. For the H^- data we also found evidence for autocorrelation with the b_1^0 and b_5^0 coefficients nonzero at the 1.9σ and 1.6σ limits, respectively. In the second test, generally regarded as more sensitive, we searched for autocorrelation in the differences $D_i=e_i-e_{i-1}$ of successive normalized residuals by expressing D_i in the form

$$D_i=b_j^1 D_{i-j}+c_j^1 \tag{4}$$

for $j=1,2,\ldots,16$. For the K^- data we again found substantial evidence for autocorrelation, with the b_1^1 and b_2^1 coefficients nonzero at the 2.9σ and 2.4σ limits, respectively. For the H^- data we found nonzero values for b_1^1 and b_5^1 at the 2.5σ and 1.8σ limits, respectively. Conservatively, we therefore deduce that evidence exists for autocorrelation of the residuals at the approximate lower limits of 2.5σ for the K^- data and 2.0σ for the H^- data, corresponding to p values of 0.014 and 0.046, respectively.

Combining all four statistical tests, we conclude that the K^- and H^- experiments both show strong evidence for nonrandom ordering of the residuals, the former with a probability of at least 97% and the latter, with at least 95%. (Had the uncertainties for the K^- data not been overestimated, the K^- probability would rise from 97% to 99%.) Thus the results of both experiments reveal the presence of structure, contradicting the conclusions reached in both cases that the results were in agreement with the Wannier power law. In fact, if we treat the H^- and K^- studies as independent tests of the same physical principle, we conclude that the two experiments support the Wannier law with a joint probability of only 1.5×10^{-3}, a conclusion that perhaps is not so startling in light of theoretical work that suggests that deviations from the Wannier law may become visible for hydrogen at energies only slightly higher than 1 meV above threshold [30]. The observed structure strongly argues for further experimental studies that emphasize greater precision and freedom from systematic effects.

In spite of experimental deviations from the Wannier predictions, it must be acknowledged that the theory provides an excellent approximation for the observables in two-electron escape. Whether it captures the essence of the underlying dynamics, however, is the subject of some debate. In the case of doubly excited resonances of He or H^-, for example, the analog to the Wannier prediction for two-electron escape is provided by a symmetric stretch motion in which the two electrons maintain the equality of their radial magnitudes thereby moving along the so-called "Wannier ridge." Although the ridge-state characterization of these resonances has succeeded [31] quite well in predicting the values of the representative energies, Ezra *et al.* [22] recently showed that the underlying dynamics are radically different from the presumed symmetric stretch motion. Instead, according to Ezra *et al.*, the resonances are represented by an asymmetric stretch behavior in which the classical orbits may be visualized as crossing the Wannier ridge perpendicularly rather than traveling along it. While the dynamics are radically different, the predictions for the observables do not display major departures from those given by the ridge-state picture.

Small departures from the predictions of the Wannier theory may thus provide important signatures of major differences in the dynamical behavior of the highly correlated two-electron system. From this perspective, we also reexamined the results of the energy-partitioning studies carried out by Hammond *et al.* [16] for electron-impact ionization of He. Those studies measured the distribution function $f(x)$ for the fraction of excess energy

$x = E_1/E'$ carried away by either one of the outgoing electrons. Since the two electrons may be considered to be indistinguishable, $f(x)$ in the domain $0 \leq x \leq 1$ is constrained to be symmetric about the equal-energy-sharing point $x = 0.5$ ($E_1 = E'/2$). By the time the experiment was reported, Read had already carried out an elegant analysis using the Wannier theory which showed that $f(x)$ should be approximately 5% higher at $x = 0.5$ than at $x = 0$ ($E_1 = 0$) or $x = 1$ ($E_1 = E'$). The results obtained by Hammond *et al.* displayed a small but statistically very significant deviation from this prediction, which the authors speculated might be attributable to a systematic error that could have caused the low-energy data points to be shifted asymmetrically with respect to the $x = 0.5$ symmetry point. While such a systematic shift may have occurred, we could find no statistical evidence for it since the data could be extremely well represented (reduced χ^2 value of 1.02 for 12 degrees of freedom, corresponding to a nearly ideal confidence level of 51%) by a quartic test function constrained to be symmetric about $x = 0.5$ Thus, while the deviations observed in the experiment could have been related to systematic effects, they could also have represented a true signature of a departure from the assumed dynamics in the Wannier picture. New studies are clearly warranted.

In conclusion, we note that we have discussed our findings with several members of the original experimental groups including J. B. Donahue and H. C. Bryant (H^-) [13], J. Peterson (K^-) [17], and F. H. Read (He) [16].

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