LETTER TO THE EDITOR

Electron-impact ionization of atomic hydrogen at 2 eV above threshold

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Abstract. The convergent close-coupling method is applied to the calculation of fully differential cross sections for ionization of atomic hydrogen by 15.6 eV electrons. We find that even at this low energy the method is able to yield predictive results with small uncertainty. As a consequence, we suspect that the experimental normalization at this energy is approximately a factor of two too high.

At the base of all electron–atom scattering and ionization problems is the fundamental, yet unsolved, three-body problem of an electron interacting with atomic hydrogen. This problem occupies a special place in the set of unsolved problems of interest to physicists due to its fundamental nature in the realm of atomic physics. It represents a class of Coulomb three-body problems which includes electron interaction with the single positive ion of helium, and hence the problem of helium double photoionization.

For heavier atoms the complexity of the Coulomb three-body problem may be masked by the collective behaviour of the many target electrons. Similarly, for high incident electron energies the complicated role played by the long-ranged Coulomb interaction is also somewhat hidden. The problem exhibits all of its complexities at energies a little above the ionization threshold for the simplest atomic target, namely hydrogen. Here we have the possibility of exciting a countably infinite number of the hydrogen discrete states as well as the three-body continuum of two very slow strongly interacting electrons. In this letter we consider the e–H problem at the incident electron energy of 15.6 eV, i.e. only 2 eV above the ionization threshold.

To solve the e–H problem at a total energy $E$ (presently 2 eV) and spin $S = 0$, 1 means to correctly predict all of the possible scattering amplitudes $f_{nl}^S(k)$ for discrete excitation of target eigenstates with energy $\epsilon_{nl} < 0$ with $\epsilon_{nl} + k^2/2 = E$, and ionization amplitudes $f^S(k_A, k_B)$ with $k_A^2/2 + k_B^2/2 = E$. For the discrete transitions the close-coupling methods have proved to be the most successful, particularly at low energies. These rely on expanding the total wavefunction in a set of orthonormal states. From the landmark work of Yamani and Reinhardt (1975), followed by Broad (1978), Stelbovics (1989) and others, it became clear that the set of orthonormal states obtained by diagonalizing the target Hamiltonian in a Laguerre basis formed an unusual equivalent-quadrature rule. The states thus obtained provide a quadrature rule that incorporates both the infinite set of true target discrete states and the true target continuum. This is an immensely powerful result and forms the basis of the

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convergent close-coupling (CCC) method for the calculation of electron–atom scattering (Bray and Stelbovics 1992, Bray 1994, Fursa and Bray 1995). The idea relies on simply increasing the number of expansion states \( N = \sum_{l=1}^{l_{\text{max}}} N_l \) until convergence in the amplitude of interest \( f^{SN}_{nl}(k) \) is obtained to an acceptable accuracy, just like with standard numerical quadrature. This approach has proved to be very successful for the discrete transitions at all energies. In the rare case of substantial discrepancy with experiment (Bray and Stelbovics 1992) subsequent new measurements were found to be in agreement with the CCC theory (Yalim et al. 1997).

Obtaining reliable scattering amplitudes for the discrete transitions is a good start, but what about ionization? The square-integrable expansion states \( \phi_{nl}(l \leq l_{\text{max}}, n = 1, \ldots, N_l) \), obtained by diagonalizing the target Hamiltonian in a Laguerre basis of size \( N_l \), have both negative and positive energies \( \epsilon_{nl}^{N} \). With increasing \( N \) the negative-energy states converge to the true eigenstates \( (\epsilon_{nl}^{N} = \epsilon_{nl}^{N}, \phi_{nl}^{N} \rightarrow \phi_{nl}) \), and the positive-energy states yield an increasingly dense discretization of the continuum. By summing the integrated cross sections, obtained upon solution of the close-coupling equations, for just the positive-energy states yields excellent agreement with the measurements of the e–H total ionization cross section (TICS) (Bray and Stelbovics 1993, Kato and Watanabe 1995, Scott et al. 1997). Though this is the least informative ionization process it is an encouraging first step. The question is: do the scattering amplitudes for the excitation of the positive-energy \( \phi_{nl}^{A} \) contain all of the detailed ionization information?

Before proceeding further let us define some convenient notation. Suppose we are interested in describing an experiment where the two outgoing electrons have momenta \( k_A \) and \( k_B \) with \( k_B \leq k_A \). When performing the diagonalizations we ensure, by varying the exponential fall-off parameter \( \lambda_l \) (Bray and Stelbovics 1992), that for each \( l \) we have a state \( \phi_{nl}^{N} \) whose energy is \( \epsilon_{nl}^{N} = k_B^2/2 \). We will refer to these states collectively as \( \phi_B^{N} \) with energy \( \epsilon_{nl}^{N} = k_B^2/2 \). Though it is rarely practical, let us further suppose that the same diagonalizations have resulted in states \( \phi_{nl}^{N} \) whose energies \( \epsilon_{nl}^{N} = k_A^2/2 \). We shall collectively refer to these states as \( \phi_A^{N} \) with energy \( \epsilon_{nl}^{N} = k_A^2/2 \). Similarly, the scattering amplitudes \( f^{SN}_{nl}(k) \) for the excitation of the states \( \phi_B^{N} \) and \( \phi_A^{N} \) arising upon solution of the \( N \)-state close-coupling equations, we write as \( f^{SN}_{nl}(k_A) \) and \( f^{SN}_{nl}(k_B) \), respectively. Note that the close-coupling formalism ensures that the total wavefunction is expanded explicitly antisymmetrically using the states \( \phi_{nl}^{N} \), with the arising equations solved separately for each total spin \( S \). Thus, each \( f^{SN}_{nl}(k) \) may always be thought of as a combination of the direct \( F \) and exchange \( G \) amplitudes, e.g. \( f^{SN}_{nl}(k) = F + (-1)^S G \) for hydrogen. The close-coupling boundary conditions assume that only one electron is ever allowed to escape to true infinity, asymptotically as a plane wave. It is helpful to keep in mind that the energies \( \epsilon_{nl}^{N} \leq \epsilon_{nl}^{N} \) are symmetrically on either side of \( E/2 \), and that the summation of the integrated cross sections to obtain TICS includes both sets of amplitudes \( f^{SN}_{nl}(k_A) \) and \( f^{SN}_{nl}(k_B) \) combined as cross sections. For equal-energy sharing \( \epsilon_{nl}^{N} = \epsilon_{nl}^{N} = E/2 \), which we consider as the limit \( \epsilon_{nl}^{N} \rightarrow \epsilon_{nl}^{N} \).

The work of Bray and Fursa (1996a) attempted to provide a correct interpretation of the already calculated positive-energy-state scattering amplitudes, with some surprising and controversial results. It was shown that the \((e, 2e)\) ionization amplitudes may be defined from the \( f^{SN}_{nl}(k_A) \) by

\[
f^{SN}(k_A, k_B) = \langle k_B^{(-)} | \phi_B^{N} | f^{SN}_{nl}(k_A) \rangle
\]

where \( k_B^{(-)} \) is a Coulomb wave (in the case of a H target) of energy \( k_B^2/2 = \epsilon_{nl}^{N} \). This definition is, in fact, a simplification of the pioneering work of Curran and Walters (1987). The overlap has the effect of changing the unity normalization of \( \phi_B^{N} \) to that of the true continuum, as well as introducing a one-electron Coulomb phase. The controversy (Bencze and Chandler 1999) arises not from the above definition, but from the subsequent use of (1) to define the triply
differential cross section (TDCS) by

\[
\frac{d^3\sigma^{SN}(k_A, k_B)}{d\Omega_A d\Omega_B dE_A} = |f^{SN}(k_A, k_B)|^2 + |f^{SN}(k_B, k_A)|^2.
\] (2)

The second term above looks like an exchange term, but it is not. The amplitudes \( f^{SN}_B(k_A) \), and hence \( f^{SN}(k_A, k_B) \), are already a coherent combination of their own direct and exchange amplitudes as determined by \( S \). The two terms have a very different origin. The amplitudes \( f^{SN}_B(k_A) \) arise from the excitation of the states \( \phi^N_B \), with the boundary condition that the ‘\( k_A \)’ electron exits as a plane wave totally shielded from the ion by the bound \( \phi^N_B \) electron. For \( \epsilon_B^N < k_A^2/2 \) this is the physically sound shielding approximation, as used in the Born approximation where the slow electron is modelled by a Coulomb wave and the fast one by the plane wave. However, the boundary conditions for the amplitude \( f^{SN}_A(k_B) \) are unphysical (low-energy outgoing plane wave shielded by a higher-energy bound state). Yet, these two theoretically distinguishable amplitudes correspond to the same ionization process since \( E = \epsilon_A^N + \epsilon_B^N \).

From (2) we see that close-coupling yields twice as many amplitudes as we may expect from formal ionization theory. In the often used language of direct and exchange amplitudes we have two such pairs \( f^{SN}_B(k_A, k_B) = F_1 + (-1)^5 G_1 \) and \( f^{SN}_B(k_B, k_A) = F_2 + (-1)^5 G_2 \), which are very different for \( \epsilon_B^N \neq \epsilon_A^N \). Note, there is no symmetrization relation between the close-coupling theory calculated \( f^{SN}_B(k_A, k_B) \) and \( f^{SN}_B(k_B, k_A) \) as claimed by Bencze and Chandler (1999). In forming the TDCS we have \( F_i G_i \) and cross terms \( G_i F_i \), generally very different for each \( i = 1, 2 \). A careful numerical study of the problem led to the suggestion that with increasing \( N \) the second term in (2) and hence both \( F_2 \) and \( G_2 \) converge to zero (Bray 1997). This allows for consistency with formal ionization theory except that the \( f^{SN}(k_A, k_B) \) are obtained only for \( \epsilon_B^N \leq \epsilon_A^N \). However, for finite \( N \) a consistent interpretation (compatible with the definition of TICS) of the close-coupling approach to ionization requires the use of both terms. A further consequence of the numerical study (Bray 1997) is that the close-coupling method is unable to obtain convergence to a satisfactory accuracy in the singly differential cross section (SDCS) whenever the true SDCS at equal energy sharing is substantial. Nevertheless, it was argued that if the true SDCS was known then accurate angle-differential ionization cross sections could still be predicted. Here we test this claim at just 2 eV above threshold, where the SDCS may be conveniently denoted by \( \text{CCC}(20^N) \).

The concept of convergence with increasing \( N = \sum_{l=0}^{\lambda l} N_l \) involves both the increase of \( l_{\text{max}} \) and \( N_l \). We performed a series of calculations for various \( N \). The ones presented may be conveniently denoted by \( \text{CCC}(N_0, \lambda_{\text{max}}) \) with \( N_l = N_0 - l \). To examine the rate of convergence we present two vastly different calculations \( \text{CCC}(20, 5) \) and \( \text{CCC}(13, 4) \), which require approximately 2 Gb and 500 Mb of computer RAM, respectively. In both cases the Laguerre exponential fall-off parameter was \( \lambda_l \approx 0.6 \) with the variation performed to ensure that for each \( l \) there was a state \( \phi^N_{nl} \) with energy \( \epsilon^N_{nl} = \epsilon^N_{n l} = 1 \) eV. In the present equal energy-sharing case the two terms in (2) are evaluated using the same set of amplitudes, assuming a continuous limit of \( \epsilon_B^N \to \epsilon_A^N \).

The first test of the calculations is the comparison of the total ionization cross section and its spin asymmetry \( A_f \) with the highly accurate measurement (Shah et al 1987) of TICS 1.08 \((10^{-17} \text{ cm}^2)\) and the \( A_f \approx 0.5 \) measurements (Fletcher et al 1985, Crowe et al 1990). The \( \text{CCC}(20, 5) \) and \( \text{CCC}(13, 4) \) results for the TICS, \( A_f \) are 1.18, 0.50 and 0.91, 0.51, respectively. Thus, we see that both calculations attribute approximately the correct amount of electron flux to the two spin ionization channels. The TICS results from other calculations typically varied around the experimental value. The reliability of various close-coupling-based theories for the calculation of the TICS at low energies has been discussed in detail by Scott et al (1997).
The difficulty of the problem of obtaining accurate ionization amplitudes at this energy is indicated by the fact that the total cross section is more than 40 times larger, 4.7, 4.8 and 4.6 ± 0.1 \((10^{-16} \text{ cm}^2)\), respectively, for the CCC(20, 5), CCC(13, 4) and experiment of Zhou et al (1997).

Next we consider the energy distribution within the ionization channels, i.e. the SDCS, defined by

\[
\frac{d\sigma^{SN}}{de}(e) = \int d\Omega_A d\Omega_B |f^{SN}(k_A, k_B)|^2.
\]

The TICS \(\sigma^{SN}_I\) is obtained by performing the integration

\[
\sigma^{SN}_I = \int_{E_0}^{E} \frac{d\sigma^{SN}}{de}(e) \, de
\]

\[
= \int_{E/2}^{E_0} \frac{d\sigma^{SN}}{de}(e) + \frac{d\sigma^{SN}}{de}(E - e) \, de.
\]

The integral in (4) is equivalent to the sum of the integrated cross sections for the excitation of the positive-energy states. The step function hypothesis (Bray 1997) says that the second term in (5) converges to zero with increasing \(N\). The origin of the two terms in (2) are the two terms in (5). We think of the second term as numerical ‘left-overs’ from an incomplete convergence with \(N\), due to its minor contribution (past 1 eV) to the TICS. Integration of (2), for a given secondary energy \(e\), over the angular variables yields the integrand of (5).

\[\text{Figure 1.} \] The singly differential cross sections arising in the CCC\((N_0, l_{\text{max}})\) (see text) calculations. The step function labelled by CCC\((\infty, 5)\) is an integral-preserving estimate.

In figure 1 the spin-averaged SDCS are presented. We see that there is no convergence in the CCC(20, 5) and CCC(13, 4) results, though the integral of both is much the same. The step function CCC\((\infty, 5)\) is an estimate of what the CCC-calculated SDCS would converge to for \(N_l \to \infty\) (there are no problems in obtaining convergence with increasing \(l_{\text{max}}\)). In other words, we assume that at this low energy the true SDCS is approximately flat. Since the close-coupling theory is unitary we cannot have double counting of the TICS, and hence suppose that with increasing \(N\) the SDCS defined in (3) becomes non-zero only for \(0 \leq e \leq E/2\). In experiment the observed SDCS is symmetric about \(E/2\) with the TICS being obtained upon integration to \(E/2\). Comparison with the experimental SDCS requires both terms of (5). For the substantially asymmetric energy-sharing kinematics only the first term contributes significantly, but both are necessary at equal energy sharing. From figure 1 it is clear that the angular distributions determined by (2) will be much too small in magnitude. In order that the integration of (2) over the angular variables, the endpoint of the integrand in (5), yielded
Figure 2. The coplanar triply differential cross sections, in the indicated geometries, for electron-impact ionization of atomic hydrogen with 1 eV outgoing electrons. The absolute experiment of Röder et al (1997b) has been scaled by a factor of 0.45 for best visual fit to the rescaled CCC data, see text. The DWBA calculations are due to Jones et al (1992).
the estimated SDCS of 1.08 \(10^{-17} \text{ cm}^2 \text{ eV}^{-1}\) we will multiply the equal energy-sharing CCC-calculated TDSC by 1.08/(0.2 \times 2) = 2.7.

In figure 2 we present the TDSCS calculated by the two CCC models and compare these with experiment and the previously overall best agreement-yielding theory, the distorted-wave Born approximation (DWBA) of Jones et al (1992). The relative measurements were initially presented by Brauner et al (1991), but were remeasured and put on an absolute scale, with an estimated 35% uncertainty, by Röder et al (1997b). The DWBA calculations (Jones et al 1992) work relatively well at this low energy since they utilize the effective charge formalism of Rudge (1968) in the distorting potentials. For an example of a more common DWBA approach and the 3C theory see Rouet et al (1996) and Brauner et al (1991), respectively.

In the TDSCS figure we use the convenient, for the coplanar geometry, convention that the negative scattering angles are on the opposite side of the incident beam (z-axis) to the positive scattering angles. For best visual comparison with the rescaled CCC calculations we have multiplied all of the experimental values by the single constant of 0.45. Having done so, we see excellent agreement between the two CCC calculations and experiment for all geometries, which is a considerable improvement on the comparison with the DWBA calculation. The quality of the agreement gives us confidence that the rescaling of the experiment has brought it into consistency with the estimated SDCS value at 1 eV of 1.08 \(10^{-17} \text{ cm}^2 \text{ eV}^{-1}\). Should the true SDCS prove to be a little convex (concave) then the experimental rescaling should be done by a factor a little greater (smaller) than 0.45. Perhaps the experimentally determined normalization is an indication that the SDCS is more convex than concave. As a consequence, we do not believe that the theory of Pan and Starace as presented by Röder et al (1997b) is a factor of two too low at 15.6 eV, and may indeed be accurate at all energies. Though not presented their theory is almost indistinguishable from the \(\theta_{AB} = 180^\circ\) rescaled CCC(20, 5) TDSCS.

Let us turn specifically to the case where the two detectors are kept \(\theta_{AB} = 80^\circ\) apart. Though no experiment is available for this case we present it because it shows the greatest difference between the two CCC calculations, but is still experimentally measurable. In fact, smaller \(\theta_{AB}\) geometries yield even greater differences. Such geometries, first suggested by Whelan et al (1993), are an excellent test of the CCC theory because the cross sections fall rapidly with decreasing \(\theta_{AB}\). We see that the bigger calculation yields the smaller cross section for \(\theta_{AB} = 80^\circ\). This is an important indication of how well the CCC theory is working. For the other presented cases the fact that the shapes of the two calculations are much the same, even though one requires four times as much computational resources as the other, suggests rapid shape convergence for the largest cross sections. On the other hand, almost identical overall magnitude suggests that convergence to the true correct SDCS is extremely slow.

So how is it that the CCC theory yields such good TDSCS angular distributions? To help answer this question let us have a look in more detail at the symmetric geometry. Given the good agreement between CCC(13, 4) and CCC(20, 5) TDSCS one would imagine that one may readily interchange the partial wave amplitudes of \((1) \langle kl|\phi_{Nl}^N \rangle f_{Nl}^SN(k)\) in the two calculations. The curve labelled by CCC(mix) was generated by taking the \(1 \text{ eV} \ l = 1\) partial wave amplitude of the CCC(20, 5) calculation and using it with the other \(l\) CCC(13, 4) amplitudes. Whereas one may reasonably expect the CCC(mix) calculated TDSCS to be between the other two, it differs substantially when the two electrons emerge close together. This is an indication of the importance of treating all partial waves in a consistent manner. The Laguerre basis choice \(N_l = N_0 - l\) with similar \(\lambda_0\) results in much the same integration rule over the true continuum for each \(l\). In other words, the number of positive energy states and their separation is similar for each \(l\). We also use the same set of states for each partial wave of total orbital angular
momentum $J$. Thus, for each $J$, the error in the energy distribution is also very similar for each $l$, and this is why the CCC($N_0, l_{\text{max}}$) calculations yield good TDCS angular distributions whose magnitude is in error by a single constant.

What have we learned from this and preceding studies? The CCC approach to e–H scattering has not fully solved this Coulomb three-body problem. Given the complexity of the problem it is not surprising that the close-coupling approach should run into an intractable problem. Whereas we are confident of obtaining accurate discrete scattering amplitudes \textit{ab initio} at all energies, this is not so for the ionization amplitudes. Accurate ionization amplitudes may require too many states, depending on the incident energy, for practical implementation of the CCC theory. However, we have suggested two empirical prescriptions that still allow the CCC-calculated ionization amplitudes to be useful and predictive, though with some uncertainty. The first, demonstrated here, ensures rapid convergence in the angular distributions. It relies on taking a similar quadrature rule in the continuum for all target space $l$, total orbital angular momentum $J$ and total spin $S$. Defining $N_l = N_0 - l$ with $\lambda_l \approx \lambda$ for each $J$ and $S$ achieves this. There may be other more efficient approaches that use a different basis as in say the intermediate-energy $R$-matrix method (Burke \textit{et al} 1987). A sensible choice for $\lambda$ is also important. The second prescription, necessary at low energies when the true SDCS is substantially large at $E/2$, is that of rescaling the cross sections according to the ratio of the estimated true SDCS and the close-coupling-calculated SDCS. At high-enough energies no such rescaling is necessary and most aspects of the problem may be obtained accurately \textit{ab initio} (Bray and Fursa 1996a, b). Given the general structure of the true SDCS at low energies, and that the close-coupling-based theories obtain the correct TICS, estimating the true SDCS is likely to yield only a minor error. Furthermore, in some cases accurate SDCS are available from experiment and other theories. With these two empirical prescriptions the close-coupling approach to ionization has practical application at all incident energies, energy sharing and geometries of the two detectors.

There are a number of opinions relating to improving the close-coupling-calculated ionization amplitudes in an \textit{ab initio} manner such as by matching the calculated total wavefunction to the correct asymptotic three-body boundary conditions. However, we note that once the close-coupling equations have been solved the electron flux may be incorrectly distributed within the ionization channels. This information will be hidden in the total wavefunction and we suspect may require empirical correction of some kind prior to matching.

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