e-H scattering *S*-wave model for initial excited states

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Electron-hydrogen scattering, within the *S*-wave model, is considered at total energies ranging from 1 through to 7 Ry. Scattering cross sections are presented from initial ground and excited states with particular attention given to the case where the initial state is in the continuum. An unexpected minimum is found in the elastic free-free cross section.

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I. INTRODUCTION

The 1990s saw immense progress in the field of electron-atom collision calculations. To a large extent this is due to the ever-growing computational resources. Ideas that were developed many years earlier could finally be thoroughly tested with the availability of sufficient computational power. For example, the close-coupling (CC) method is reputed to have began with the classic work of Massey and Mohr [1]. Yet only today do we appreciate the full power of this formalism. With the landmark contribution of Yamani and Reinhardt [2] that showed how continuum states may be treated with the use of L^2 states the CC approach is now readily applied to both discrete and ionizing collisions. The convergent close-coupling (CCC) method [3] owes much of its success due to the preceding references combined with modern-day computation facilities.

The fundamental goal of developing the CCC theory has been to provide a general electron-atom scattering theory that is valid at all energies and for all transitions, including ionization. To check whether this is indeed the case immense comparison with experiment has been undertaken, in the knowledge that a single discrepancy is a candidate for the invalidation of the formalism. Generally, agreement with experiment is excellent, but not always. We do not wish to detail all of the successful comparisons of the CCC theory with experiment, but rather bring to the attention of the reader the current controversy regarding electron-impact ionization of atomic hydrogen at 15.6 and 17.6 eV. The CCC theory predicts that the experiment is a factor a little in excess of 2 too high [4,5]. Yet, Rescigno *et al.* [6] claim that they have solved the *e*-H ionization problem and agree with the 17.6-eV experiment. However, having shown that the CCC theory solves the corresponding, but more complicated, *e*-He problem we are confident of the accuracy of CCC for the simpler *e*-H problem [7].

How is it that we can be so confident of the CCC approach to electron-atom collisions? Primarily because CCC is very simple conceptually, though computationally intensive. The total wave function is expanded in a set of N near-complete orthonormal states $\phi_n^{(N)}(\epsilon_n^{(N)})$, defining the CC equations for some total energy E. Solution of these yields amplitudes for excitation of each state from any other. For comparison with experiment the amplitudes are multiplied by the overlap of the final state and the true eigenstate of same energy [8]. For discrete transitions $\epsilon_n^{(N)}<0$ this overlap is just unity, but for ionization it is a complex number restoring the required normalization and introducing a one-electron Coulomb phase. The resultant amplitudes $f_E^{(N)}(\epsilon_n^{(N)})$ have a formal dependence on N, but convergence with N is sufficiently fast computationally whenever $\epsilon_n^{(N)}<0$, and $\epsilon_n^{(N)}=E/2$ when $E>0$. In the latter case convergence is to half the required amplitude. In fact, the $f_E^{(N)}(\epsilon_n^{(N)})$ behave like coefficients of a Fourier expansion of a step function, with $\lim_{N\to\infty} f_E^{(N)}(\epsilon_n^{(N)})=0$ for $E/2<\epsilon_n^{(N)}\leqslant E$ [9]. The requirement for an underlying step-function behavior was recognized some time ago [10]. This reconciled the apparent problem of double counting in a unitary theory with $f_E^{(N)}(\epsilon_n^{(N)})$ and $f_E^{(N)}(E-\epsilon_n^{(N)})$ being two independent estimates of the same ionization process. Demonstration of the fact that $f_E^{(N)}(E/2)$ converges to half the required amplitude is more recent, see Stelbovics [9] and Bray [5] for hydrogen and Bray, Fursa, and Stelbovics [7] for helium. As a consequence of the latter result, in the case of *e*-He ionization the CCC theory is able to yield absolute agreement with all published $E_A=E_B=E/2$ measurements of triply differential cross sections.

Given the claimed successes of the CCC theory, it is interesting to look at some of the internal details in order to better understand how the theory works in practice. In addition, we hope to be of help to others by providing accurate results, which may be used to test other theory. Thus far we have concentrated predominantly on excitation of the atomic ground state. Yet excitation of metastable initial states is of practical importance and agreement between the CCC theory and experiment is not always what it should be [11]. The aim of this paper is to provide comprehensive accurate *S*-wave model results for excitation and ionization of the atomic hydrogen-excited states, including one in the continuum.

The *S*-wave or Temkin-Poet model is one of the great treasures in the field of electron-atom scattering computation. It reduces the complexity of the full *e*-H problem by considering only states with zero orbital angular momentum. It was first considered in detail by Temkin [12] and then by Poet [13]. The model retains most of the numerical difficulties associated with treating the target continuum and antisymmetry of the total wave function. The success of the

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CCC theory began by showing convergence to the known results for this model [14]. Since that time the model continued to attract immense attention, and only very recently has been effectively solved *ab initio* [9,15]. Incidentally, the CCC method cannot claim to solve this problem fully *ab initio* for transitions with $0<\epsilon_n^{(N)}<E/2$ owing to the step-function behavior of the underlying amplitudes. However, a relatively accurate estimate of the true solution may always be readily obtained due to the knowledge how Fourier expansions of step functions behave.

In the following section we give an outline of the CCC theory and bring to the fore issues we consider of interest, and first raised in the preliminary report of this work [16]. Subsequently, results on a broad range of energies are presented and discussed.

II. THEORY

Since we will concentrate solely on the *S*-wave model, all orbital angular momenta will be set to zero and linear momenta will be written as scalars. Thus, the *T*-matrix elements of the electron-hydrogen scattering system may be obtained from the close-coupling equations [3]

$$\langle k_f\phi_f|T_S|\phi_i k_i\rangle=\langle k_f\phi_f|V_S|\phi_i k_i\rangle+\sum\!\!\!\!\!\!\int_n d\epsilon_n\int dk \times\frac{\langle k_f\phi_f|V_S|\phi_n k\rangle\langle k\phi_n|T_S|\phi_i k_i\rangle}{E+i0-\epsilon_n-k^2/2}. \quad (1)$$

Here the projectile electron is modeled by plane waves k and the target electron is modeled by true eigenstates ϕ of the hydrogen Hamiltonian. The total energy and spin are E and S, respectively. The interaction potential V_S includes symmetrization in operator form. The notation $+i0$ indicates outgoing spherical wave boundary conditions.

In the given form (1) is yet to be solved. The problem is that in order to close the equations for T, the final channel must be allowed to have the same range as the intermediate summation and integral. In this case V-matrix elements arise in which both the initial and final channels are in the continuum. Such elements may not exist, though once integrated over $(dk,d\epsilon_n)$ the T matrix should exist. However, the lack of a compact kernel renders Eq. (1) not computationally solvable.

To solve Eq. (1) numerically, a finite set $n=1,\ldots,N$ of pseudostates $\phi_n^{(N)}$ is employed to replace the true eigenstates ϕ_n. Following the work of Yamani and Reinhardt [2] and others, these states are obtained by diagonalizing the target Hamiltonian in a Laguerre basis. In the CCC method [3] we use the orthonormal basis

$$\xi_n(r)=\left(\frac{\alpha}{2}\frac{(n-1)!}{(n+1)!}\right)^{1/2}(\alpha r/2)\exp(-\alpha r/4)L_{n-1}^2(\alpha r/2), \quad (2)$$

where $L_{n-1}^2(\alpha r/2)$ are the associated Laguerre polynomials. The parameter α is a free variable and is usually set so that roughly half the states had negative energies. We may vary it slightly so that some desired positive-energy state was obtained. This allows writing

$$|\phi(\epsilon_n)\rangle=\lim_{N\to\infty}|\phi_n^{(N)}\rangle\langle\phi_n^{(N)}|\phi(\epsilon_n)\rangle, \quad (3)$$

where $\epsilon_n^{(N)}=\epsilon_n$. For negative-energy states the overlap in Eq. (3) converges quickly to unity as N increases. However, for positive energies the overlap tends to infinity.

The usage of pseudostates modifies Eq. (1) trivially to yield

$$\langle k_f\phi_f^{(N)}|T_S^{(N)}|\phi_i^{(N)}k_i\rangle =\langle k_f\phi_f^{(N)}|V_S^{(N)}|\phi_i^{(N)}k_i\rangle +\sum_{n=1}^{N}\int dk\frac{\langle k_f\phi_f^{(N)}|V_S^{(N)}|\phi_n^{(N)}k\rangle\langle k\phi_n^{(N)}|T_S^{(N)}|\phi_i^{(N)}k_i\rangle}{E+i0-\epsilon_n^{(N)}-k^2/2}, \quad (4)$$

which may now be solved computationally. Upon solution the cross sections are defined by

$$\sigma_{fi}^{(SN)}\equiv\frac{k_f}{k_i}\left|\langle\phi(\epsilon_f)|\phi_f^{(N)}\rangle\langle k_f\phi_f^{(N)}|T_S^{(N)}|\phi_i^{(N)}k_i\rangle\langle\phi_i^{(N)}|\phi(\epsilon_i)\rangle\right|^2, \quad (5)$$

where $\epsilon_f=\epsilon_f^{(N)}$ and $\epsilon_i=\epsilon_i^{(N)}$. For $\epsilon_f>0$ it is convenient (to use $d\epsilon$ in energy integration) to define the singly differential cross section (SDCS) by

$$\frac{d\sigma_i^{(SN)}}{d\epsilon}(\epsilon_f)=\sigma_{fi}^{(SN)}/\sqrt{2\epsilon_f}. \quad (6)$$

The total cross section is then given by

$$\sigma_{\rm tot}^{(SN)}=\sum_{f:\epsilon_f^{(N)}<0}\sigma_{fi}^{(SN)}+\sum_{f:0<\epsilon_f^{(N)}<E}\sigma_{fi}^{(SN)} =\sum_{f:\epsilon_f^{(N)}<0}\sigma_{fi}^{(SN)}+\int_0^E\frac{d\sigma_i^{(SN)}}{d\epsilon}(\epsilon)d\epsilon. \quad (7)$$

The latter term above gives the total ionization cross section (TICS). This converges rapidly with N, but not the SDCS itself. If we write the true SDCS as $d\sigma_i^{(S)}/d\epsilon$ then for $0<\epsilon<E$

$$\lim_{N\to\infty}\frac{d\sigma_i^{(SN)}}{d\epsilon}(\epsilon)=\begin{cases}\dfrac{d\sigma_i^{(S)}}{d\epsilon}(\epsilon) & \text{if } \epsilon<E/2\\ \dfrac{1}{4}\dfrac{d\sigma_i^{(S)}}{d\epsilon}(\epsilon) & \text{if } \epsilon=E/2\\ 0 & \text{if } \epsilon>E/2.\end{cases} \quad (8)$$

The above is effectively the consequence of the work by Stelbovics [9]. How practical is Eq. (8) for realistic values of N? For the case $\epsilon=E/2$ convergence is very fast, see Bray [10] for example. However, for $\epsilon<E/2$ the SDCS shows

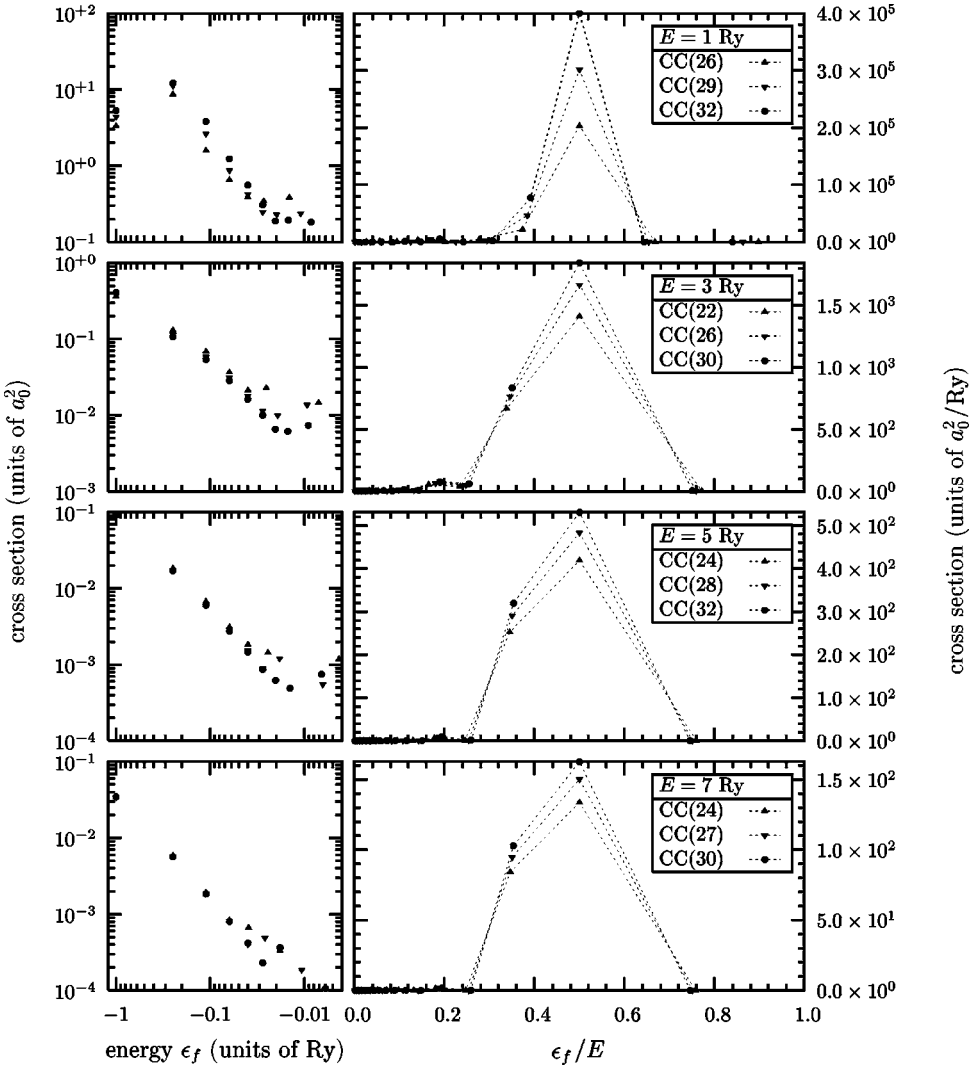

FIG. 1. The *S*-wave model *e*-H singlet cross sections (5) and (6) generated from *V*-matrix elements of Eq. (4) for the case where the initial state has energy $\epsilon_i = E/2$. The total energies are specified by *E*.

N-dependent oscillations. This is a fundamental limitation of the CC theory, yet it does not diminish our ability to estimate relatively accurate SDCS. This is because of the functional form that is expected to decrease monotonically as $\epsilon \to E/2$ from the maximum $d\sigma_i^{(S)}/d\epsilon(0)$ to the minimum $d\sigma_i^{(S)}/d\epsilon(E/2)$. The reason for this is simple. The SDCS represents the probability of detecting an electron with energy ϵ. The bigger this energy is (to $E/2$ maximum) the greater the energy loss is incurred by the incident electron. To our mind it would be rather unphysical if in the continuum a greater initial energy loss resulted in a greater cross section. This notion, together with the fact that the TICS and the SDCS at $E/2$ are known, allows us to make the estimate

$$\frac{d\sigma_i^{(S)}}{d\epsilon}(\epsilon) \approx a|\epsilon - E/2|^n + 4\frac{d\sigma_i^{(SN)}}{d\epsilon}(E/2), \tag{9}$$

where a is determined uniquely from TICS once n has been chosen. Note that we do not force $a > 0$ (monotonic decrease from 0 to $E/2$), but in practice this has always happened thus far. When E is small, i.e., just above the ionization threshold, we can take $n=1$ or $n=2$ without much difference. As the energy increases a higher power is more appropriate. The key is to end up with a curve that adequately averages out over the oscillations, and does so for various values of *N*. Examples of this will be given in the following figures.

III. RESULTS

The *e*-H *S*-wave model is considered for total energies $E \in [1,7]$ Ry. We wish to study convergence in both the discrete and the continuous subspaces and hence present three calculations of various *N* at every energy. Particular attention is paid to convergence when one of the positive energies $\epsilon_f^{(N)} = E/2$. Accordingly, some careful choices of α and *N* in Eq. (2) need to be made. In addition to having $\epsilon_f^{(N)} = E/2$ we also require that $E \approx (\epsilon_n^{(N)} + \epsilon_{n+1}^{(N)})/2$ for some $n \geqslant f$. The latter ensures that the integration weight associated with the last open state ends the integration at E [17]. We take those values of *N* where the above requirements are able to be fulfilled reasonably accurately. Generally, we took *N* to be between 22 and 32, with the resultant overlaps being approximately 3 ± 1.

To gauge the difficulty of the calculations, in Fig. 1 we give the singlet cross sections (5) and (6) when the initial state has the energy $\epsilon_i^{(N)} = E/2$, evaluated from the *V*-matrix

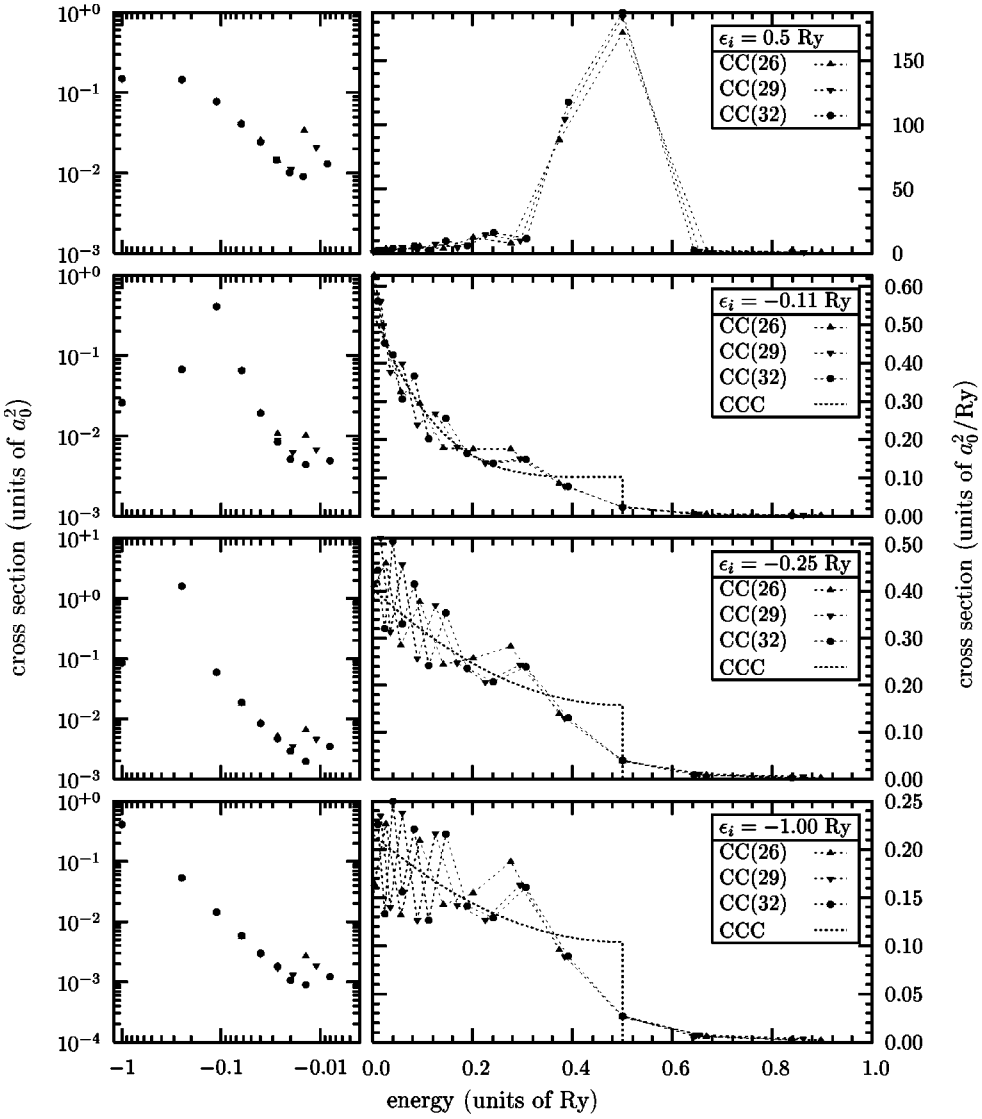

FIG. 2. The singlet e-H scattering cross sections in the S-wave model at the total energy of 1 Ry. The lowest three discrete ($1S$, $2S$ and $3S$) initial states and the $\epsilon_i = 0.5$ Ry state from the target continuum are presented. The CCC curve represents a step-function estimate of CC(N) as $N \rightarrow \infty$.

elements, i.e., the first term on the right-hand side of Eq. (4). These represent the starting point in the solution of Eq. (4) for the specified initial state i. We see that for all four total energies considered, the elastic free-free cross section rises substantially with increasing N. The magnitude for the lowest energy considered $E=1$ Ry is of order 10^5. Such large magnitudes make the solution of Eq. (4) very difficult owing to the associated ill conditioning, but still possible. The elastic free-free matrix elements do not exist as $N \rightarrow \infty$, and the behavior seen in Fig. 1 shows why calculations cannot be performed for arbitrarily high N. Note that it may seem somewhat artificial that we have taken such an unrealistic choice for i. However, even when i represents the ground state, the considered free-free matrix elements occur in the second term of Eq. (4) when the final state has $\epsilon_f^{(N)} = E/2$. So the problem is a general one, but is conveniently illuminated in Fig. 1 by taking i with $\epsilon_i^{(N)} = E/2$.

A. Singlet cross sections

Starting with $S=0$, the results for the $E=1$ Ry total energy are presented in Fig. 2. Discrete excitation involving states with $n \leqslant 6$ display convergent cross sections. Elastic scattering dominates for all four initial states. For the highest lying final discrete states the cross section should decrease by the n^{-3} scaling rule. However, we see that for the last few states the cross section rises. This occurs because the most negative-energy states are not true eigenstates but mimic the collective behavior of all higher discrete eigenstates. Turning our attention to the continuum, as was found earlier [16], the oscillations in the SDCS for initial discrete states diminish with increasing energy of the initial state. This is due to the reduced relative significance of the SDCS at $E/2$. For these states we have given, using Eq. (9), a step-function estimate of what the CC(N) calculations would converge to for infinite N. Lastly, given the variation of the elastic free-free cross sections in Fig. 1 the apparent convergence when using the corresponding T is remarkable, even if not perfect. Although the 26-state calculation is a little lower than the others, the 29- and 32-state calculations yield much the same cross section. The elastic free-free transition yields the maximum cross section even though it is only one-fourth of the true value. This suggests that the true SDCS in this case is very narrowly peaked at $E/2$.

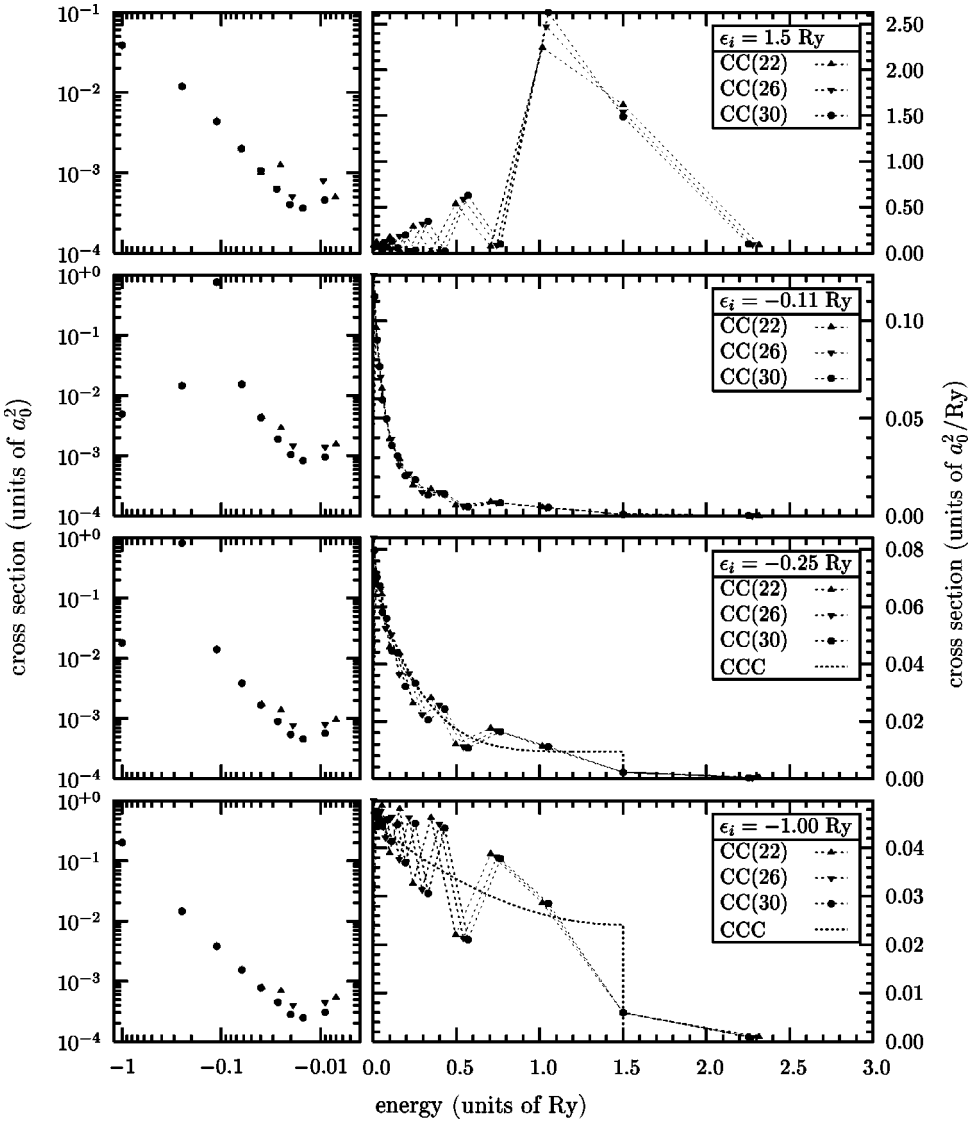

FIG. 3. Same as for Fig. 2 except at a total energy of 3 Ry.

In Fig. 3 the singlet results are presented at a total energy of 3 Ry. Discrete excitations behave qualitatively similar to the 1-Ry case. The SDCS are smaller than for the 1-Ry case. The SDCS for the 1*S* initial state shows substantial oscillation as before, due to the relative magnitude of the SDCS at $E/2$. However, this SDCS diminishes in significance for 2*S* and 3*S* initial states, and the calculated SDCS oscillations diminish substantially. For the free-free case the SDCS at $E/2$ appears to be slowly converging. The elastic free-free cross section is now less dominant than was the case at 1 Ry, and is no longer the dominant presented cross section. It would become the biggest again after multiplication by 4, but the width of the elastic peak is substantially broadened. It can also be noted that the free-free SDCS at $E/2$ marginally decreases with increasing N. Although divergence for higher N cannot be ruled out, this further suggests that this SDCS is finite at $E/2$.

The corresponding results at 5 and 7 Ry are given in Figs. 4 and 5, respectively. The SDCS at $E/2$ have relatively diminished for all three initial discrete states, thereby resulting in smaller oscillations. What is particularly curious is that the free-free elastic cross section has increased at 5 Ry relative to the case at 3 Ry, and again dominates the SDCS as in the 1-Ry total energy case.

To study this further calculations were performed for more intermediate E, concentrating near the minimum. In Fig. 6 the free-free elastic SDCS are presented as a function of the total energy. We see a minimum form around $E = 2.5$ Ry, explaining the change in the behavior observed as the total energy changes from 1 to 3 to 5 Ry. The fact that the present calculations interpolated well amongst the others is indicative, though not conclusive, that we are seeing genuine convergent structure. As with all numerical studies it may be that convergence is particularly slow and apparent convergence may always be slow divergence or bounded oscillation.

To study the origin of the minimum in Fig. 6 we now consider the corresponding TICS, presented in Fig. 7. This also displays a minimum in the same position and the two figures have a similar shape. However, the minimum for the SDCS is deeper than for the TICS. Together, these two figures display interesting and somewhat unexpected results for the model considered.

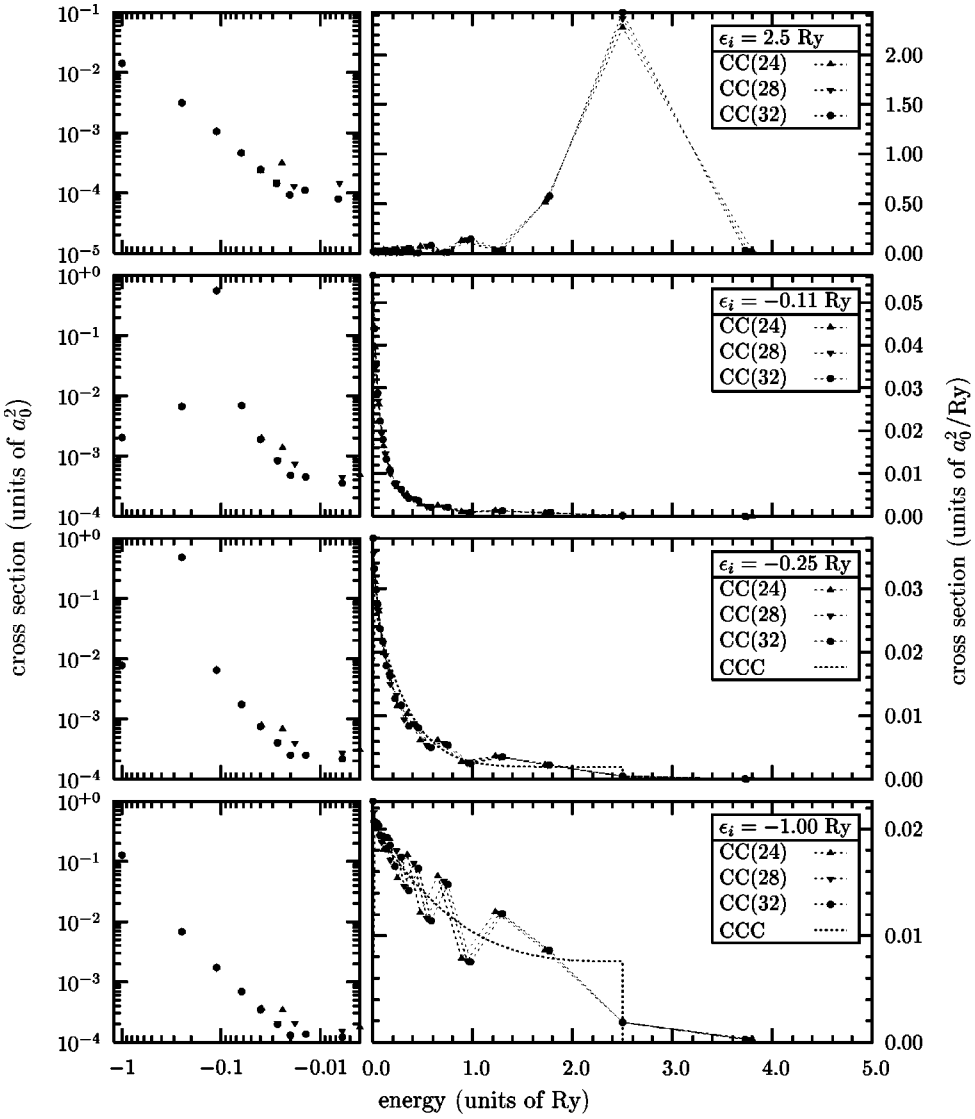

FIG. 4. Same as for Fig. 2 except at a total energy of 5 Ry.

We explain the minimum in the following way. Going down in energy from the high energies the TICS reaches a maximum and then begins to diminish, as expected for any discrete initial state. It is the very large effect of coupling [second term of the right-hand side of (4)] that keeps the cross sections down, compared to the first-order term of Eq. (4), given in Fig. 1. However, with further decrease of energy the magnitude of the first-order term rises so sharply that its dominance can no longer be counteracted by the coupling. Accordingly, the SDCS($E/2$), and hence the TICS, rise sharply as the energy decreases towards threshold. We expect this behavior to be present in not just this model, but also in full electron-atom scattering problems since the fundamental free-free matrix elements given in Fig. 1 occur generally.

B. Triplet cross sections

The triplet e-H cross sections in the S-wave model are much less interesting than their singlet counterparts. Here, the SDCS at $E/2$ should be zero by the Pauli principle, which forbids the elastic free-free transitions of the kind discussed above. Nevertheless, the step-function hypothesis [10] is just as important here as it is for the single case. The step has zero size, but it is vital that this be evaluated accurately numerically, and that the SDCS remains zero for $E/2 < \epsilon_f^{(N)} < E$.

In Figs. 8, 9, 10, and 11 the triplet results are presented corresponding to total energies 1, 3, 5, and 7 Ry. We present them primarily for completeness. They indicate excellent convergence and very good reproduction of the step-function behavior at all energies. No oscillations are present in the SDCS due to the zero SDCS at $E/2$.

Though the triplet case appears less interesting it is important to note that it is not trivial to calculate. For example, the elastic cross section is very large, yet the SDCS are relatively small. Yielding convergence for the SDCS is indicative of an accurate numerical method.

IV. CONCLUSIONS

The S-wave model of e-H scattering has been considered on a broad range of energies with an emphasis on ionization from excited initial states, including an initial state in the

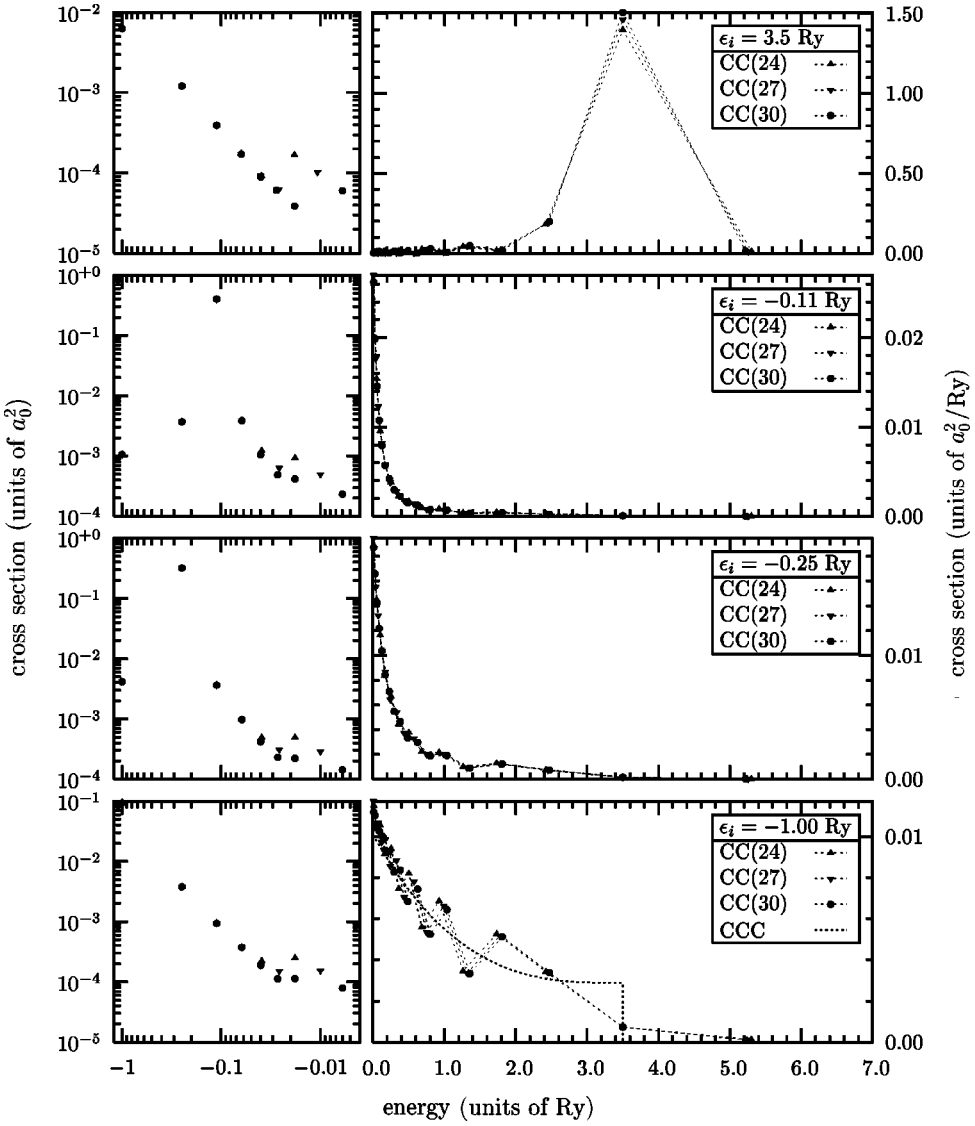

FIG. 5. Same as for Fig. 2 except at a total energy of 7 Ry.

target continuum. The emphasis on a continuum initial state comes from the fact that the underlying free-free potential matrix elements are divergent, which has been the major stumbling block in the numerical development of the close-coupling theory since its inception. However, the present study suggests convergence in the corresponding cross sections on a broad energy range, supporting the earlier finding at a single energy [16]. This demonstrates the immense power of the Laguerre-based approach to treating true continuum functions within the close-coupling method. It ensures a compact kernel allowing all integrals to exist, and

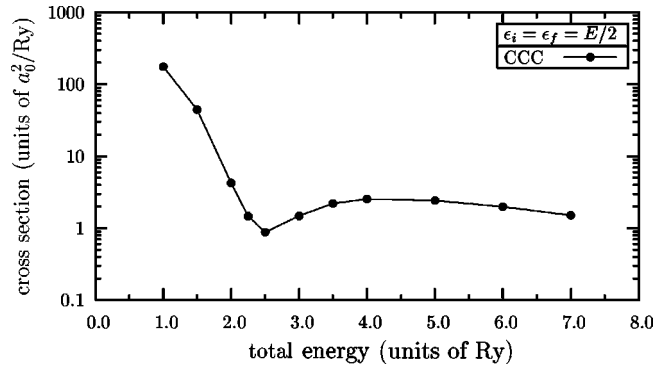

FIG. 6. The singlet *e*-H singly differential cross section in the *S*-wave model for elastic free-free transitions with $\epsilon_f = \epsilon_i = E/2$. The curve connects the indicated points at which calculations were performed.

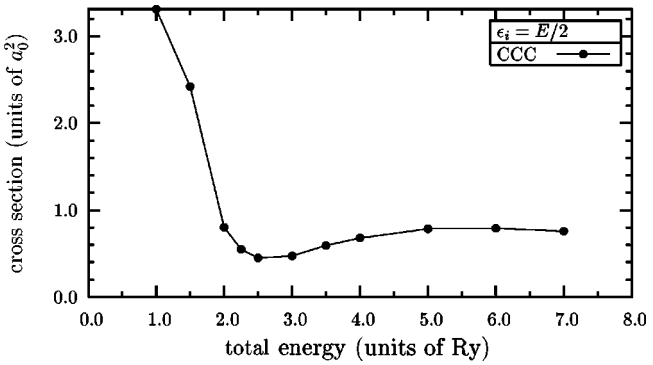

FIG. 7. As for Fig. 6 except for the total ionization cross section.

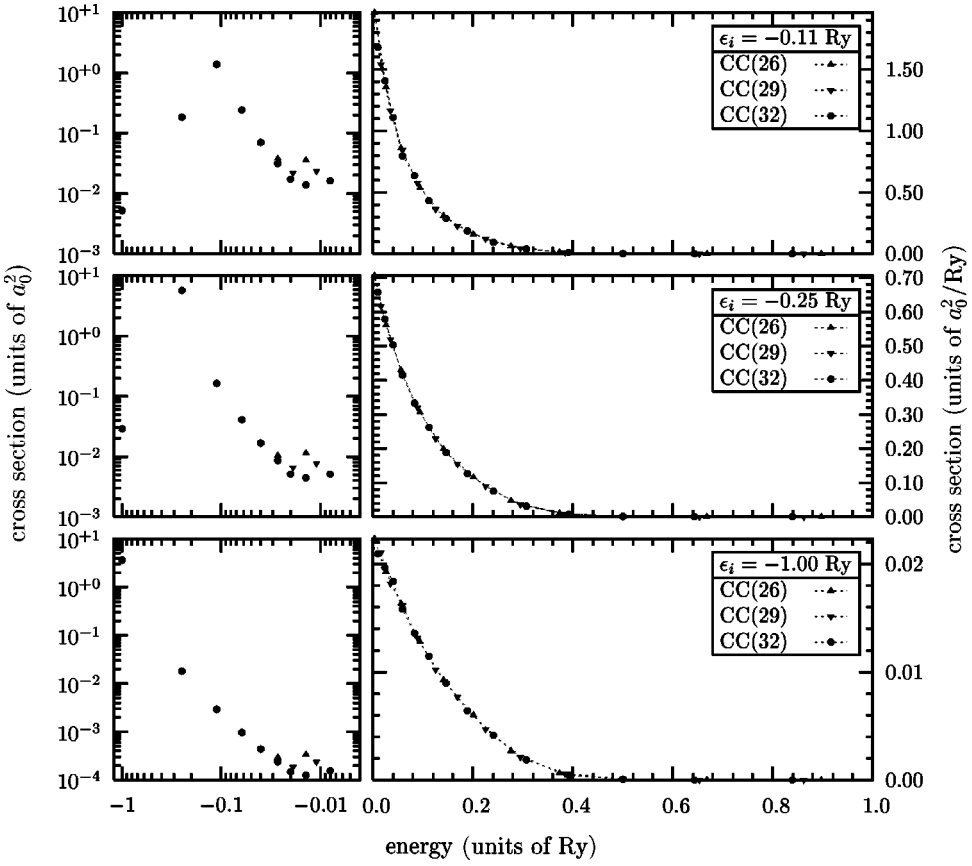

FIG. 8. Same as for Fig. 2 except for the triplet case. No result is given for scattering from the $\epsilon_i = 0.5$ Ry state as these cross sections must be zero due to the Pauli exclusion principle.

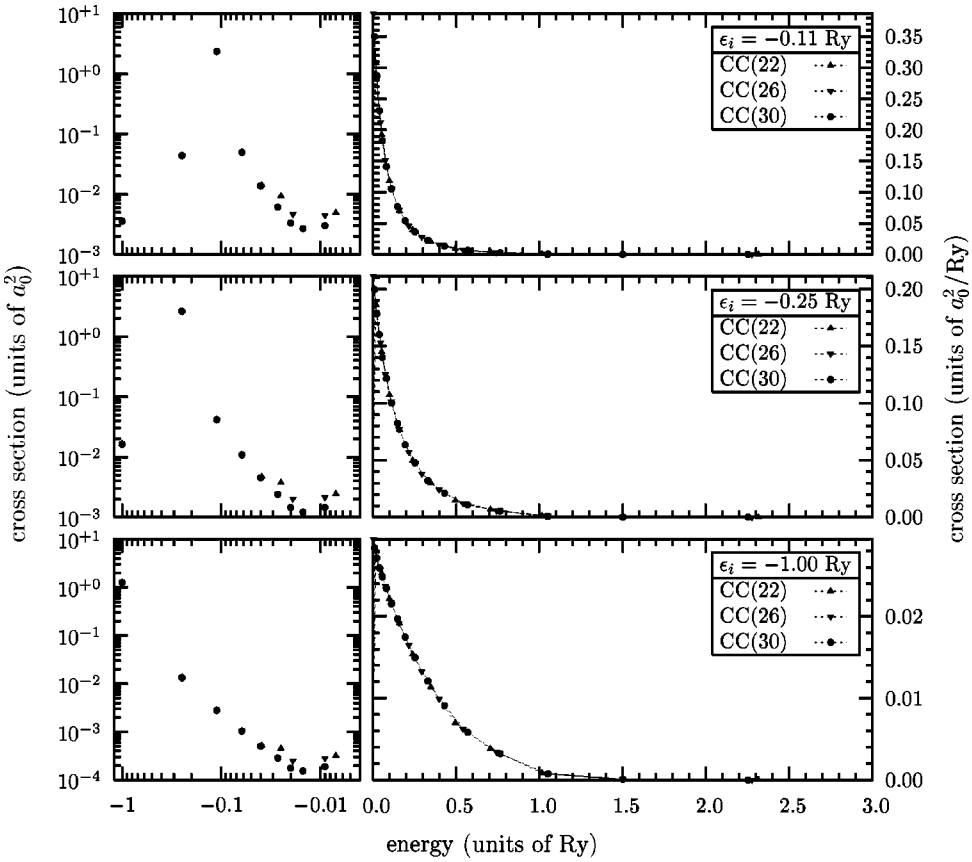

FIG. 9. Same as for Fig. 8 except at a total energy of 3 Ry.

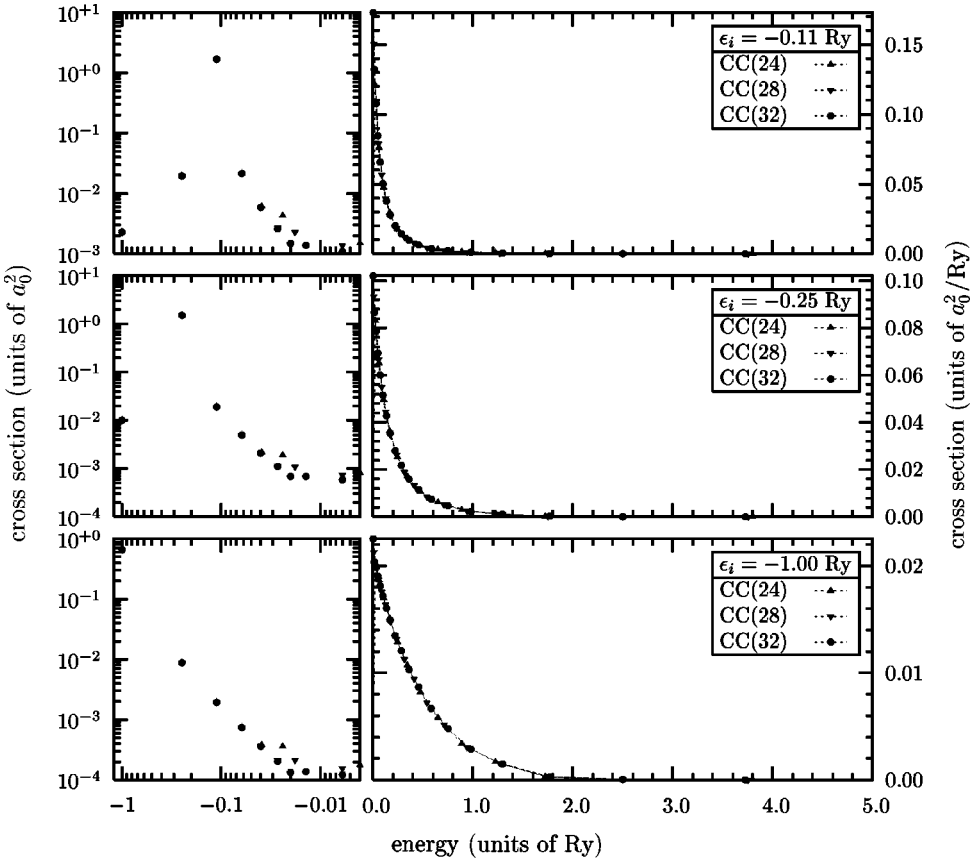

FIG. 10. Same as for Fig. 8 except at a total energy of 5 Ry.

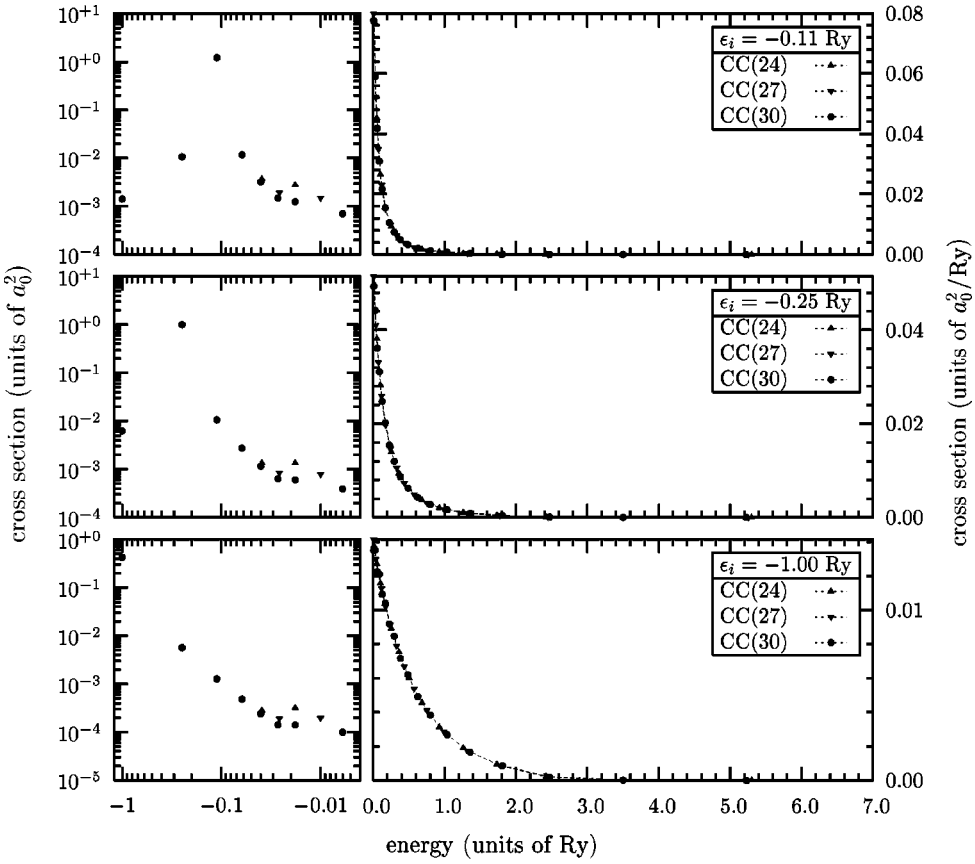

FIG. 11. Same as for Fig. 8 except at a total energy of 7 Ry.

apparently converge, for a sufficiently large, but numerically tractable N.

The study as a function of energy allowed the identification of unexpected structure in both the elastic free-free cross section and in the total ionization cross section when the initial state energy is half the total energy. The structure has been explained by reference to the free-free potential matrix elements, and hence we suspect will also occur in full electron-atom scattering problems.

Convergence has been tested by presenting results for calculations of various basis sizes. While it appears that there is indeed convergence for the considered free-free transitions even larger CC calculations would be desirable. However, we have shown why calculations with large N are so difficult. The free-free V-matrix elements have very large magnitudes particularly at small energies. They occur in all calculations even if we are interested in scattering only from the ground state. They also occur for all incident energies since the V-matrix elements are fully off shell and hence always have combinations where the initial and final energies are small.

We hope that the presented results will be of help to others who wish to check their numerical methods of e-atom scattering, for both initial discrete states and those in the continuum.

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