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Close-coupling approach to electron-impact ionization of helium

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The close-coupling theory of electron-impact ionization of helium is studied. It is found that the ''raw'' convergent close-coupling equal-energy-sharing amplitudes converge to half the required amplitudes. As in the e-H case, solving the close-coupling equations yields amplitudes that behave as results of a finite Fourier expansion of a step function. We argue that the close-coupling formalism readily solves the e-He ionization problem with equal-energy outgoing electrons at all practical incident energies, and demonstrate it at the most difficult kinematic case of 2 eV above threshold.

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Recently Rescigno *et al.* [1] stated ''A framework for solving ionization problems in many areas of chemistry and physics is finally provided . . . .'' As evidence of their claim, they presented first absolute agreement between their external complex scaling (ECS) theory with experiment for the fixed $\theta_{AB}=\theta_B-\theta_A$ subset of triply differential cross section (TDCS) measurements available for 17.6 eV e-H ionization with 2 eV outgoing electrons, where $0°\leqslant\theta_A\leqslant 180°$ and $-180°\leqslant\theta_B\leqslant 180°$ are the positions of the two detectors. For the large θ_{AB} cases, which yield the biggest cross sections, the ECS results are almost exactly a factor of 2 greater than the convergent close-coupling (CCC) results [2]. Given the work of Stelbovics for electron-hydrogen ionization [3], who showed how to reconcile the apparent inconsistency of the CCC approach to ionization [4] and formal theory, we are puzzled by the discrepancy with the ECS results.

In establishing the computational accuracy of a general theory by comparison with experiment, it is vital to have a large body of accurate absolute data. In the case of electron-impact ionization of atoms, this is provided for the helium atom. In contrast, the atomic hydrogen target, while ideal for theorists, is very difficult for experimentalists. We are aware of only two absolute experiments with equal-energy outgoing electrons, and these have large (40%) error bars [5]. This is not so for helium, where highly detailed absolute data are given at total energy $E=2$, 8, 20, and 40 eV above threshold, with relative and absolute errors of 5% and 20%, respectively. Accordingly, the electron-helium ionization problem forms the ideal testing ground of general ionization theories, of which the CCC method [4] is one.

The CCC approach to ionization is particularly easy to state as it is much the same for ionization as say elastic scattering. The total wave function is expanded using $n=1,\ldots,N$ square-integrable target states $\phi_{ns}^{(N)}$, of spin s and energies $\epsilon_{ns}^{(N)}$, obtained by diagonalizing the target Hamiltonian in an orthogonal Laguerre basis. The idea relies on the completeness of the basis so that merely increasing N ensures improved accuracy of the expansion. Once the target atom and the states $\phi_{ns}^{(N)}$ have been defined, solving the close-coupling equations yields scattering amplitudes for excitation of states $\phi_{fs_f}^{(N)}$ from $\phi_{is_i}^{(N)}$ by incident electrons of momentum $\boldsymbol{k}_i$, with $E=\epsilon_{fs_f}^{(N)}+k_f^2/2=\epsilon_{is_i}^{(N)}+k_i^2/2$ in atomic units. Formally, it does not matter which numerical implementation is used to solve the time-independent close-coupling equations. In our calculations, we solve coupled Lippmann-Schwinger equations

$$\begin{aligned}\langle \boldsymbol{k}_f\phi_{fs_f}^{(N)}|T_S|\phi_{is_i}^{(N)}\boldsymbol{k}_i\rangle &= \langle \boldsymbol{k}_f\phi_{fs_f}^{(N)}|V_S|\phi_{is_i}^{(N)}\boldsymbol{k}_i\rangle \\ &\quad+\sum_{n=1}^{N}\int d^3k\frac{\langle \boldsymbol{k}_f\phi_{fs_f}^{(N)}|V_S|\phi_{ns_n}^{(N)}\boldsymbol{k}\rangle\langle \boldsymbol{k}\phi_{ns_n}^{(N)}|T_S|\phi_{is_i}^{(N)}\boldsymbol{k}_i\rangle}{E+i0-\epsilon_{ns_n}^{(N)}-k^2/2},\end{aligned} \tag{1}$$

where S is the total spin and V_S are the interaction potentials that include implementation of antisymmetry; see Refs. [6,7] for hydrogen and helium, respectively. For hydrogen $S=0,1$ and $s_f=s_i=s_n=\frac{1}{2}$, whereas for helium with $s_i=0$, we have $S=\frac{1}{2}$ and $s_f,s_n=0,1$. The $(e,2e)$ amplitude for ionization of the ground state is then defined [4] simply as

$$f_{Ss}^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B)=\langle \phi_{fs}^{(-)}(\boldsymbol{k}_B)|\phi_{fs}^{(N)}\rangle\langle \boldsymbol{k}_A\phi_{fs}^{(N)}|T_S|\phi_{is_i}^{(N)}\boldsymbol{k}_i\rangle, \tag{2}$$

where $\phi_{fs}^{(-)}(\boldsymbol{k}_B)$ is the target eigenstate of energy $k_B^2/2=\epsilon_{fs}^{(N)}$. In the case of hydrogen, $\phi_{fs}^{(-)}$ is a pure Coulomb wave; for helium it is an antisymmetric wave function with one orbital being the $1s$ of He^+ and the other being Coulomblike. The effect of the overlap in Eq. (2), which arises from expansion of the channel functions [4], is to change the unity normalization of states $\phi_{fs}^{(N)}$ to that of the continuum and to introduce the very important one-electron Coulomb phase.

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While such amplitudes are no more difficult to calculate than excitation amplitudes, their interpretation is more subtle. The first problem is that due to the fact that the Green's function in Eq. (1) contains the total energy $E=k_A^2/2+k_B^2/2$ and not $E/2$. Hence, two independent amplitudes $f_{Ss}^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B)$ and $f_{Ss}^{(N)}(\boldsymbol{k}_B,\boldsymbol{k}_A)$ arise for what should be a single-ionization process. They are independent because for $k_A \neq k_B$ excitation of the state of energy $k_A^2/2$ is independent of excitation of the state of energy $E-k_A^2/2$. There appears to be double-counting of ionization processes, yet the theory is unitary and yields excellent total ionization cross sections [8]. No resolution of the apparent conflict was given, and in order to maintain consistency and unitarity, Bray and Fursa [4] suggested that cross sections should be obtained as

$$\frac{d^3\sigma_S^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B)}{d\Omega_A d\Omega_B E_B}=(2\pi)^4\frac{k_A k_B}{k_i}\sum_s\,[|f_{Ss}^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B)|^2 + |f_{Ss}^{(N)}(\boldsymbol{k}_B,\boldsymbol{k}_A)|^2]. \tag{3}$$

Subsequently, a detailed study of the e-H, S-wave model problem (momentum vectors may be replaced by scalars) suggested a resolution of the apparent inconsistency with formal theory. It was hypothesized that with increasing N the term with $k_A<k_B$ in Eq. (3) should converge to zero, as was almost the case in finite calculations [9]. Thus, the amplitudes (2) should converge to a step function, being zero for $k_A<k_B$. For a finite N unphysical oscillations were noted owing to the difficulty associated with obtaining step functions numerically. However, this did not explain why the prescription (3) yielded excellent convergent shape agreement with e-He measurements with 20 eV [10], 10 eV [11], and 4 eV [12] outgoing electrons, but was uniformly a factor of around 2 too low in magnitude.

Stelbovics [3] attempted to understand the origin of the step-function behavior as did Rescigno *et al.* [13]. Due to antisymmetry of the total wave function, the true e-H ionization amplitude F_S (we may drop s from the notation) must satisfy

$$F_S(\boldsymbol{k}_A,\boldsymbol{k}_B)=(-1)^S F_S(\boldsymbol{k}_B,\boldsymbol{k}_A). \tag{4}$$

By studying the same model problem, Stelbovics showed that the required amplitudes may be obtained from those calculated via Eq. (2) as

$$F_S^{(N)}(k_A,k_B)=f_S^{(N)}(k_A,k_B)+(-1)^S f_S^{(N)}(k_B,k_A), \tag{5}$$

but only if $f_S^{(N)}(k_B,k_A)=0$ for $k_A>k_B$. This is entirely consistent with the step-function idea [9]. For $k_A=k_B$,

$$F_{S=0}^{(N)}(k_A,k_A)=2f_{S=0}^{(N)}(k_A,k_A), \quad F_{S=1}(k_A,k_A)=0, \tag{6}$$

identically. Note that $f_{S=1}^{(N)}(k_A,k_A)\approx 0$ numerically [9]. Hence, the CCC-calculated $k_A=k_B$ amplitudes were half the required values. A similar conclusion was reached by Rescigno *et al.* [13]. Stelbovics suggested that the close-coupling amplitudes (2) behaved similarly to a Fourier expansion of a step function with convergence at the step to half the step height. As a consequence, the cross section according to Eq. (3) is exactly a factor of 2 too low. For the model problem, the CCC-calculated amplitudes satisfy Eq. (4), but only for $k_A=k_B$.

The same conclusions translated to the full e-H problem, where it was shown that for $k_A=k_B$,

$$f_S^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B)=(-1)^S f_S^{(N)}(\boldsymbol{k}_B,\boldsymbol{k}_A)+\delta_S^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B), \tag{7}$$

with δ being small for sufficiently large calculations [2]. In this case it follows that

$$|F_S^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B)|^2=2[|f_S^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B)|^2 + |f_S^{(N)}(\boldsymbol{k}_B,\boldsymbol{k}_A)|^2-\tfrac{1}{2}|\delta_S^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B)|^2]. \tag{8}$$

Thus, again the $k_A=k_B$ amplitudes (2) converge to half the required value, and the cross section of Eq. (3) converges even quicker, but to a result a factor of 2 too small. Thus, the same Fourier-expansion-of-a-step-function picture holds for the full e-H ionization problem.

Now consider the substantially more complicated case of electron-helium ionization. Unlike the case of hydrogen, where the target spin decouples readily, for helium we need to carry the target spin in the analysis, with $S=1/2$ (which we now drop from the notation) and $s=0,1$. Then it can be shown that analogous to Eq. (4)

$$F_s(\boldsymbol{k}_A,\boldsymbol{k}_B)=-\frac{1}{2}(-1)^s F_s(\boldsymbol{k}_B,\boldsymbol{k}_A)-\frac{\sqrt{3}}{2}F_{\bar{s}}(\boldsymbol{k}_B,\boldsymbol{k}_A), \tag{9}$$

where $\bar{s}\neq s$. Applying the ideas in the work of Stelbovics [3] to helium leads to the relation, analogous to Eq. (5),

$$F_s^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B)=f_s^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B) -\frac{1}{2}(-1)^s f_s^{(N)}(\boldsymbol{k}_B,\boldsymbol{k}_A)-\frac{\sqrt{3}}{2}f_{\bar{s}}^{(N)}(\boldsymbol{k}_B,\boldsymbol{k}_A), \tag{10}$$

for $k_A=k_B$, and if the last two terms are zero also for $k_A>k_B$.

In sufficiently large calculations we find that for $k_A=k_B$

$$f_s^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B)=-\frac{1}{2}(-1)^s f_s^{(N)}(\boldsymbol{k}_B,\boldsymbol{k}_A) -\frac{\sqrt{3}}{2}f_{\bar{s}}^{(N)}(\boldsymbol{k}_B,\boldsymbol{k}_A)+\delta_s^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B), \tag{11}$$

where δ is small. In other words, similarly to the e-H case, the e-He CCC-calculated amplitudes satisfy the required symmetry relation (9), but only at $k_A=k_B$. It follows, after considerable algebra, that

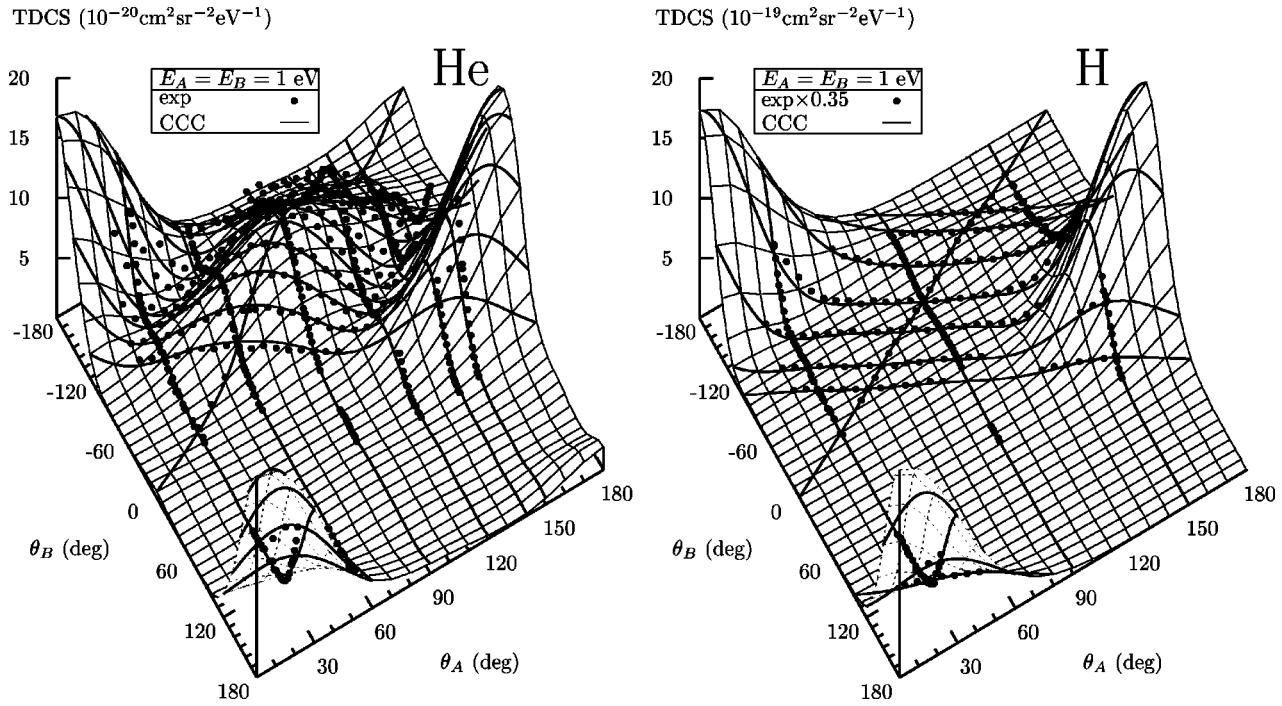

FIG. 1. Triply differential cross sections for e-He and e-H ionization with 1 eV outgoing electrons. The thick solid lines are given to aid the eye in the comparison of theory and experiment. The e-He experiment, with an estimated uncertainty of 22%, is due to Rösel *et al.* [14]. The e-He CCC calculation is outlined in the text, while the e-H calculation, evaluated according to Eq. (8), is due to Bray [18]. The e-H experiment is due to Röder *et al.* [5], and references therein.

$$\sum_s |F_s^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B)|^2 = 2\sum_s [|f_s^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B)|^2 + |f_s^{(N)}(\boldsymbol{k}_B,\boldsymbol{k}_A)|^2 - \tfrac{1}{2}|\delta_s^{(N)}(\boldsymbol{k}_A,\boldsymbol{k}_B)|^2]. \tag{12}$$

Once again, as in the case of e-H ionization, the CCC-calculated $k_A = k_B$ amplitudes (11) converge to half the required amplitudes (10), and the prescription (3) yields an even more rapidly converging cross section, but a factor of exactly 2 too small. For $k_A \neq k_B$, Eq. (3) suffices whenever only one of the two terms contributes significantly.

Equation (12) is thus the correct prescription for e-He ionization and explains why the CCC theory based on prescription (3) yielded TDCS a factor of 2 lower than experiment [10–12], which we now claim to describe fully *ab initio*, and hence do not present here. The only remaining published similar experiment is for the most difficult kinematic case of 1 eV outgoing electrons [14], which we now consider.

The CCC calculations were performed in the frozen-core model, where one of the target electrons is described by the $1s$ orbital of He^+ [7]. The total number of states $N = \Sigma_{s,l \leqslant l_{\max}} N_l$ is 125, arising from $l_{\max} = 5$ and $N_l = 13 - l$. We compare the CCC-calculated TDCS via Eq. (12) with the full set of available measurements in Fig. 1. Generally, excellent agreement between theory and experiment is found. We note some minor inconsistency in the measurements in the region of large $\theta_A = -\theta_B$, where the fixed θ_{AB} data are below the fixed $\theta_A = 120°$ data. These problems are not of the same magnitude identified for 17.6 eV e-H ionization [2]. Theory is not perfect either. The asymmetric treatment of the two outgoing electrons makes it difficult to obtain zero cross section along the $\theta_A = \theta_B$ line. Given the frozen-core approximation used in the calculations, we find the agreement between theory and experiment very satisfying.

From Fig. 1, and application of Eq. (12) to the previously published results [10–12], we infer that the CCC method has effectively solved, fully *ab initio*, the problem of electron-impact ionization of helium with equal-energy outgoing electrons and He^+ in the ground state, for all incident energies of practical interest. The case of asymmetric energy sharing requires considerable discussion. It is our present opinion that here the CCC theory can be made no less predictive than for the case of equal energy sharing. For example, in the double photoionization case [15], CCC suggested that an experiment was in error for both shape and magnitude. Subsequent remeasurement was found to be in agreement with the CCC theory [16]. A detailed analysis of ionization with asymmetric energy sharing will be given following this publication.

Another very important consequence of the present work is that it sheds light on what is happening for the simpler e-H ionization problem, especially in regard to the 17.6-eV results alluded to in the introduction. One advantage of working in the near-threshold region is that accurate total ionization cross sections (TICS) put a severe constraint on the absolute values of the TDCS. In the present e-He case, the TICS is made up of ionization processes with initial energy losses ranging from the minimum of 24.6 eV to the maximum of 25.6 eV, only a 4% difference. Intuitively, we do not

expect the singly differential cross section (SDCS) to vary much as a function of secondary energy from 0 to 1 eV. Indeed this is found in the present calculations. The present CCC-calculated TICS is 2.1×10^{-20} cm^2, while the SDCS($E/2$) is 1.9×10^{-20} cm^2/eV. Therefore, the SDCS is marginally concave ($1.9\times1<2.1$). For the corresponding e-H case, the initial energy loss varies from the minimum of 13.6 eV to the maximum of 14.6 eV, a 7% difference, leading to a more concave CCC-calculated SDCS [TICS is 1.1×10^{-17} cm^2, SDCS($E/2$) is 7.8×10^{-18} cm^2/eV] [17], as might be expected. Yet even a flat SDCS was shown to require the uniform reduction of the e-H experiment by more than two, while yielding excellent angular profiles [18], as shown in Fig. 1. It would be very unphysical, indeed, for the maximum initial energy loss SDCS to be many times greater than for the minimum initial energy loss, as would have to be the case to yield the known TICS upon integration. Thus, we see that in the case of the helium target, theory and experiment behave consistently, but not so for the hydrogen target. Given the extra (over helium) difficulties associated with determining absolute e-H ionization TDCS with around $\pm40\%$ uncertainty [5], and that the e-H system is much simpler to calculate than the e-He one, we are confident that the CCC theory is accurate for both the hydrogen and helium targets. Hence, we suggest that the ECS theory of Rescigno *et al.* [1] is a factor of 2 too high for the dominant large θ_{AB} geometries. We hope this work will stimulate new experimental and theoretical investigation of the fundamental e-H ionization problem.

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