Close-Coupling Theory of Ionization: Successes and Failures

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We suggest that the close-coupling (CC) approach to ionization requires an infinite expansion of square-integrable pseudostates to completely solve the e-H three-body breakup problem. The slow convergence is due to the fact that the single-differential cross section, arising in CC calculations, should have a step at the point where the two outgoing electrons have the same energy. However, all discrete transitions, including total ionization, as well as angular differential ionization profiles, are able to be described accurately in calculations using relatively small finite expansions of the total wave function. [S0031-9007(97)03327-9]

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In recent times the convergent close-coupling (CCC) method for the calculation of electron-impact excitation and ionization of atoms has proved to be extremely successful. It was developed initially for the e-H system by Bray and Stelbovics [1] and demonstrated that the discrete excitation and total ionization transitions could be accurately obtained at any projectile energy by expanding the total wave function with a sufficiently large number N of square-integrable states obtained from an orthogonal Laguerre basis.

A critical test of the method is provided by the application to the Temkin-Poet model [2,3] of e-H scattering [4]. This model retains the complexity of a true three-body problem, but is simpler than the full problem in that it treats only states with zero orbital angular momentum. The ability to obtain accurate total ionization cross sections (TICS) has attracted a great deal of interest, and there is now almost complete agreement between various numerical approaches [4–10].

The successful application to the Temkin-Poet model has also led to success when applied to real scattering problems. The CCC theory yields good agreement with very detailed electron-impact discrete excitation data in the case of sodium [11] and helium [12]. The experimental electron-impact total ionization cross sections have been reproduced in the case of atomic hydrogen at a broad energy range [13] and near threshold [14], He^+ ion [15], sodium [16,17], and helium [12].

The ability to obtain accurate total ionization cross sections has led to the extension of the CCC method to the calculation of differential ionization cross sections [18]. At a single projectile energy of 100 eV it was demonstrated that a single CCC calculation yielded accurate differential cross sections for electron-impact excitation of the ground state of helium to states with principal quantum number $n \leq 3$, as well as single- (SDCS), double- (DDCS), and triple-differential (TDCS) ionization cross sections [19]. Such an unprecedentedly successful result tempted the authors to wonder if the CCC method was a "complete scattering theory." Here we report that while this may be so at say energies of four or more times the ionization threshold, at lower energies a systematic problem arises.

As the total energy E is decreased we find that convergence in the SDCS is not obtained. This does not affect the accuracy of the CCC results for the discrete transitions, but leads to increasingly incorrect magnitudes in the case of the DDCS and TDCS. However, in the latter case the theory is still able to achieve correct angular distributions in all kinematical regions, even when the two outgoing electrons have similar energy.

This is an astounding state of affairs that is contrary to our initial expectations. We know that the CCC theory obtains correct TICS at all energies, yet the distribution in energy (SDCS), which yields TICS upon integration, does not converge for small-enough E as the number of expansion states N is increased. Then, if this least detailed of the differential ionization cross sections is unstable, how can the more detailed ones (DDCS and TDCS) be accurate in angular profile yet yield magnitudes that are incorrect by a single (for a given ejected electron energy) multiplicative constant? Furthermore, the CCC theory of ionization [18] is inconsistent with formal ionization theory due to the fact that the cross sections are obtained from an incoherent sum of two pairs of coherently summed direct and exchange amplitudes, which, however, is crucial for obtaining good agreement with experimental angular profiles in the equal-energy sharing kinematical region [20].

The purpose of this work is to shed some light on the above-mentioned anomalies. The details of the CCC approach to ionization have been given by Bray and Fursa [18]. The idea is almost unaltered from application to discrete processes. The total wave function is expanded in a set of N negative- and positive-energy square-integrable states, obtained by diagonalizing the target Hamiltonian with a truncated orthogonal Laguerre basis. As N is increased the negative-energy states converge to the true discrete eigenstates of the target, and the positive-energy states provide an increasingly dense integration rule for the target continuum [21]. The basis has been chosen so that we could be sure of "completeness" of the expansion as $N \to \infty$. Upon solution of the coupled equations, scattering amplitudes, which are coherent combinations of a direct and an exchange part, are generated for all open $N_o \leq N$ states. Amplitudes for the negative-energy states may be used directly to calculate discrete transition observations. The amplitudes for the positive-energy states are placed onto the continuous scale by multiplying them by the overlap of the pseudostate with the true continuum wave function of the same energy. This transforms the sum over open positive-energy states to an integral over secondary electron energy from 0 to E. At a specified secondary energy e (other electron has energy $E - e$) the ionization amplitudes $f(e, E - e)$ are then obtained by interpolation over the amplitudes available at the discrete energies of the pseudostates for each target symmetry. However, as the CCC theory distinguishes between the ionization events on either side of $E/2$ we combine the amplitudes $f(e, E - e)$ and $f(E - e, e)$ incoherently when making comparison with experiment. This idea follows from obtaining TICS by simply summing the cross sections for excitation of the positive-energy pseudostates [22].

It is truly remarkable that the simple Temkin-Poet model can be used to address nearly all of the above-mentioned anomalies. Let us begin first by resolving why the TICS may be stable while the corresponding SDCS is not. In Fig. 1 we present the results of CCC(N) calculations ($N = 10, \ldots, 50$) of the singlet and triplet TICS in the Temkin-Poet model at the total energy $E = 2$ Ry. We chose this energy because it is near the peaks of both cross sections [23]. We see that with as few as ten states relatively accurate estimates are obtained, but the rate (with N) of convergence is rather slow. Nevertheless, it is clear that the CCC method is numerically stable and is able to handle as many as 50 states of the same target symmetry. This is a very important strength of the method that allows us to perform the present study.

Now let us see the corresponding SDCS, given in Fig. 2. Concentrating on the triplet case first, we see very good convergence in this SDCS. The individual points are at the energies of the pseudostates with the cross section (for the excitation of the pseudostate) being put onto the continuous scale by multiplying by the absolute value of the square of the overlap of the pseudostate and the Coulomb wave of same energy [22]. The integral over the secondary energy should yield the result given in Fig. 1. A point to note here is that the triplet SDCS vanishes at $E/2$, as must be the case by the Pauli principle, but in addition, remains zero at higher energies. This is a welcome result because the physics on either side of $E/2$ is identical, and double-counting problems have been avoided numerically by yielding nonzero SDCS(e) for only $e < E/2$. In experiment, a symmetric (about $E/2$) SDCS would be measured, but to avoid double counting the TICS is defined as the integral from 0 to $E/2$. So we see that in the close-coupling approach to ionization we obtain convergent triplet TICS and SDCS, and there are no formal theory problems, since an incoherent combination of amplitudes on either side of $E/2$ simply involves adding zero to a nonzero cross section.

Now let us consider the singlet case. There is a clear lack of convergence in going from 10 to 50 states. Yet the integral for each N should yield the stable result given in Fig. 1. Note that the integration rule associated

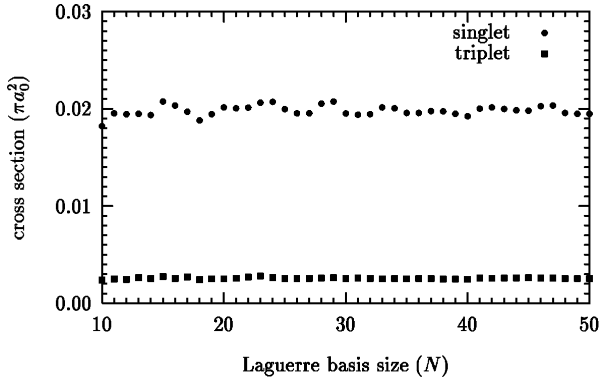

FIG. 1. The total ionization cross section in the Temkin-Poet model of e-H scattering at total energy $E = 2$ Ry, calculated with the given number of states N. Spin weights have been included in the cross sections.

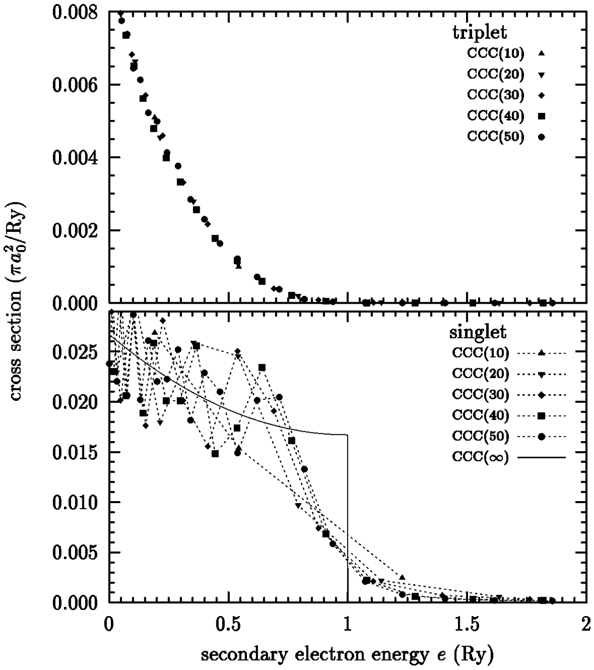

FIG. 2. The triplet and singlet single-differential cross sections in the Temkin-Poet model at total energy $E = 2$ Ry arising in the CCC(N) calculations. The singlet result denoted by CCC(∞) is an educated guess; see text for detail. The integral over the SDCS, available at discrete points only, should approximate the results given in Fig. 1. The points have been connected with straight lines to help guide the eye.

with the discrete points, at which the SDCS is calculated, must be known [24], or else an accurate interpolation must be implemented. The cross section at $E/2$ is small but not zero, and diminishes further past $E/2$. The immediate conclusion is that the CCC theory is unable to obtain the correct singlet SDCS for any finite N, and we suspect neither can any other theory based on the time-independent close-coupling formalism [10]. By contrast, the time-dependent approach [25] appears not to have such problems.

From the simple model singlet SDCS results presented here we can explain all of the problems alluded to above. The convergence in the TICS is assured by unitarity of the close-coupling formalism. Since the total cross section (TCS) may be obtained by the optical theorem we only require convergence in the elastic amplitude to have an accurate TCS. Subtracting the true discrete transitions, which also converge rapidly with N, yields a convergent TICS. However, there is no requirement for convergence within the SDCS. We have demonstrated earlier the strength of unitarity in obtaining convergent TICS without convergent partial angular momentum contributions [16]; here the same argument applies to yield convergent TICS without convergent SDCS.

Also given in Fig. 2 is a curve CCC(∞) which we guess would be the true singlet SDCS in this model if we were able to take $N \rightarrow \infty$. We hypothesize that there should be a step at $E/2$ with the SDCS being zero past $E/2$. There are two reasons for this. The first is numerical. As the number of states is increased we see that the slope of the SDCS at $E/2$ becomes increasingly vertical and the magnitude of the SDCS past $E/2$ diminishes. We checked that this behavior also occurs at lower, near threshold energies. The second is that as in the triplet case we need the SDCS to be zero past $E/2$ in order to avoid the incoherent combination of cross sections on either side of $E/2$. Given that the singlet SDCS is not zero at $E/2$, we must have a step at this point. If this is so then it is clear why for any finite N we do not obtain the correct SDCS. An infinite discretization would be required to obtain a step function. The choice for the CCC(∞) curve is constrained by having to give the correct TICS upon integration and, just as for true SDCS, must have zero slope as $e \rightarrow E/2$ (from below). We took the functional form to be quadratic.

The step function hypothesis also explains why the SDCS, DDCS, and TDCS obtained from full CCC calculations are too small, when compared with experiment, at the $E/2$ point by factors that increase with decreasing E [26]. At smaller E the true SDCS flattens out with the corresponding CCC(∞) step at $E/2$ being particularly large. The "averaging" by the discrete pseudostates over the neighborhood around $E/2$ leads to a much too small result. On the other hand, it also explains why the CCC theory yields very good results for large E. In this case the true SDCS at $E/2$ is particularly small with the step that should arise in the CCC calculations being relatively less significant.

The last thing we need to do is explain why the CCC theory is able to obtain accurate angular DDCS and TDCS profiles given the lack of convergence in the SDCS. These profiles arise from distribution of electron flux in various angular momentum channels. These include target-space and projectile-space channels. With sufficiently large (in angular momentum) calculations there is no problem in obtaining convergence in the angular momentum channels for most of the angular regions of the cross sections. The error in the SDCS is fixed once a particular N has been taken, and is the same irrespective of the partial wave. Since in practice we use the same set of states for all partial waves the error propagates in the same manner for all of them and we are left with the TDCS and DDCS results being in error by a single multiplicative constant which may be obtained by comparison of the experimental and the calculated SDCS. If, on the other hand, we chose a different set of states for each partial wave, then there would not be any convergence in the angular profiles.

There is one feature of the presented results that is also true in realistic calculations [20] that we are unable to explain. This is the fact that there is apparent convergence in the SDCS at $E/2$. Though the slope of the singlet SDCS varies at $E/2$ as a function of N, the SDCS value at $E/2$ (after interpolation) appears relatively stable. The apparent convergence is unfortunate as it is to the wrong value, and has led us to needlessly suspect the accuracy of experimental absolute value determination. Detailed joint experimental and theoretical study of e-He ionization at a broad range of total and secondary energies makes the problem with the CCC results clear [26].

To summarize, the CCC theory yields correct results for all discrete transitions including total ionization at all energies. Problems arise in the CCC calculations of the SDCS whenever the true result at $E/2$ is of substantial magnitude. Since we believe that the SDCS obtained in the CCC calculations as $N \rightarrow \infty$ should be zero past $E/2$, a finite N calculation may be in substantial error depending on the size of the step at $E/2$. Thus, the inconsistency with formal ionization theory arises due to the finite size of the calculation. However, if the same N states are used in each partial wave, as is typically the case, then correct DDCS and TDCS may be obtained if these are scaled by the ratio of the experimental to the calculated SDCS.

Some years ago we had set out to understand just what it means to expand the total wave function in a large set of square-integrable states. We developed numerical techniques towards this end, and together with the continued growth in computational power, have finally been able to complete our original goals. We now can state with some confidence what the close-coupling approach to electron impact scattering will and will not get right. Resolution of the discrepancy with formal ionization theory depends on the contentious hypothesis that the SDCS calculated via the close-coupling approach should be a step function, thus requiring an infinite number of expansion states. It may not come as a surprise to a number of readers that the convenience of the square-integrable approach, employing the same boundary conditions for the discrete and ionization channels thereby doing away with the three-body boundary conditions [27], has resulted in the necessity for taking an infinite basis size in order to completely solve the problem. Nevertheless, for practical purposes finite basis CCC calculations still yield an amazing and unsurpassed amount of accurate information.

It will be very interesting to see the SDCS arising in other theories. We are particularly looking forward to the application of the time-dependent approaches as these should be free of the difficulties encountered here using the time-independent close-coupling method.

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