

Reply to “Possibility of distinguishing between identical particles in quantum collision processes”

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Bencze and Chandler, in the preceding paper, are highly critical of the convergent close-coupling method as applied to the calculation of differential ionization processes. We argue that the criticism is unwarranted and arises from a misunderstanding of the close-coupling theory. [S1050-2947(99)03404-6]

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There are many criticisms offered by Bencze and Chandler of the convergent close-coupling (CCC) approach to the calculation of electron-impact ionization of atoms. In order to address these with maximal clarity we will enumerate and restate (in *italics*) them first, give a brief response, and follow up with a more detailed one later.

(i) *The CCC method does not yield results consistent with the symmetrization postulate, but should due to the presented analytical formalism.* It is true that the CCC ionization amplitudes do not satisfy the symmetrization postulate, nor should they. The analytical formalism presented by Bencze and Chandler resembles, but is not, the CCC method.

(ii) *The step-function hypothesis was introduced to restore the consistency of the CCC amplitudes with the symmetrization postulate.* Not true: the “step-function hypothesis” has nothing to do with the CCC approach to ionization. It is inconsistent with the symmetrization postulate, but is applicable to all implementations of the close-coupling theory.

(iii) *The CCC method does not include long-range effects of the Coulomb interaction.* There are only one-electron Coulomb phases in the CCC application to ionization.

(iv) *The CCC method is a mixture of classical and quantum mechanical ideas.* Not true: only a consistent usage of quantum mechanics is applied.

Now let us address the points in more detail. Before doing so, it is important that some terminology is clearly defined. First, there is the close-coupling theory that began with Massey and Mohr [1], which presently has many numerical implementations such as the *R*-matrix approach of Burke and Robb [2], the variational approach of Callaway [3], the intermediate-energy *R*-matrix method of Burke, Noble, and Scott [4], the eigenchannel *R*-matrix method of Greene [5], the *R*-matrix method with pseudostates of Bartschat *et al.* [6] and Badnell and Gorczyca [7], the pseudostate approach of van Wyngaarden and Walters [8], the hyperspherical close-coupling method of Watanabe, Hosada, and Kato [9], the CCC method of Bray and Stelbovics [10], and others. If the electron-atom scattering wave function at total energy E is expanded using the same set of square-integrable states $\phi_n^{(N)}$, then all these methods should yield the same results. Traditionally these methods were applied to the calculation

of only discrete transitions, but following the pioneering work of Curran and Walters [11] we have taken the CCC method further and applied it to differential ionization processes. Thus, we wish to distinguish between the close-coupling theory, of which the CCC method is one of many examples, and the CCC specific application to ionization. It is the latter that Bencze and Chandler criticize so strongly.

Let us first concentrate on the CCC implementation of the close-coupling theory. For each total spin S , solution of the close-coupling equations [10] yields scattering amplitudes $F_S^{(N)}$ for the excitation of the states $\phi_n^{(N)}$ with energy $\epsilon_n^{(N)}$ ($n=1, \dots, N$) from some initial state $\phi_1^{(N)}$,

$$F_S^{(N)}(\mathbf{k}_f, n, \mathbf{k}_i) = \langle \mathbf{k}_f \phi_n^{(N)} | T_S(E + i0) | \phi_1^{(N)} \mathbf{k}_i \rangle, \quad (1)$$

with antisymmetry of the total wave function fully implemented, i.e., $F_S^{(N)}$ is a coherent combination of the corresponding direct and exchange amplitudes as S dictates. Note, we use our usual convention that the target-space electron is on either side of the T operator, unlike Bencze and Chandler. The result in Eq. (1) is independent of the numerical implementation of the close-coupling theory. The total energy E is related to the energies of the electrons (atomic units assumed) in the initial and final states via

$$E = \epsilon_1^{(N)} + k_i^2/2 = \epsilon_n^{(N)} + k_f^2/2, \quad (2)$$

and so $\epsilon_n^{(N)} \leq E$. The total cross section σ_T may be obtained via the optical theorem (close-coupling is a unitary theory) or as a sum of all cross sections,

$$\begin{aligned} \sigma_T^{(N)}(S) &= \int d\Omega_f \sum_{n: \epsilon_n^{(N)} \leq E} |F_S^{(N)}(\mathbf{k}_f, n, \mathbf{k}_i)|^2 \\ &= \int d\Omega_f \left(\sum_{n: \epsilon_n^{(N)} < 0} |F_S^{(N)}(\mathbf{k}_f, n, \mathbf{k}_i)|^2 \right. \\ &\quad \left. + \sum_{n: 0 \leq \epsilon_n^{(N)} \leq E} |F_S^{(N)}(\mathbf{k}_f, n, \mathbf{k}_i)|^2 \right) \\ &= \sigma_{\text{NB}}^{(N)}(S) + \sigma_I^{(N)}(S), \end{aligned} \quad (3)$$

where σ_{NB} is the total nonbreakup cross section and σ_I is the total ionization cross section. It is the spectacular agreement between the CCC-calculated σ_I and experiment for the e -H

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system [12] that encouraged us to look in the area of ionization in more detail. The above relations are also used in other implementations of the close-coupling theory with equal success [13–15].

Now, let us closely examine the definition of $\sigma_I^{(N)}(S)$. Let us suppose that the energies $\epsilon_n^{(N)}$ happen to be symmetric about $E/2$ (in practice this almost never happens and some interpolation is required [16]), i.e., for every pair $(\epsilon_n^{(N)}, k_f^2/2)$ there is another pair $(\epsilon_f^{(N)}, k_n^2/2)$ for $f \neq n$ with $\epsilon_f^{(N)} = k_f^2/2$ and hence $\epsilon_n^{(N)} = k_n^2/2$. Then we may write

$$\begin{aligned} \sigma_I^{(N)}(S) &= \int d\Omega_f \sum_{n: 0 \leq \epsilon_n^{(N)} \leq E} |F_S^{(N)}(\mathbf{k}_f, n, \mathbf{k}_i)|^2 \quad (4) \\ &= \int d\Omega_f \sum_{n: 0 \leq \epsilon_n^{(N)} \leq E/2} (|F_S^{(N)}(\mathbf{k}_f, n, \mathbf{k}_i)|^2 \\ &\quad + |F_S^{(N)}(\mathbf{k}_n, f, \mathbf{k}_i)|^2). \quad (5) \end{aligned}$$

Both terms in Eq. (5) have one electron with energy $k_f^2/2$ and the other with $k_n^2/2$. However, they have very different origins. The first term comes from the excitation of the pseudostate with energy $\epsilon_n^{(N)} = k_n^2/2 < E/2$ and the boundary condition that the faster $k_f^2/2$ electron is a plane wave shielded completely from the atom by the slow electron. The second term comes from excitation of the pseudostate with energy $\epsilon_f^{(N)} = k_f^2/2 > E/2$ and the unphysical boundary condition where the slow $k_n^2/2$ electron is a plane wave shielded completely by the fast electron. The incoherent sum in Eq. (5) indicates the theoretical distinguishability of the two processes. In fact, in the close-coupling theory all amplitudes $F_S^{(N)}(\mathbf{k}_f, n, \mathbf{k}_i)$, which are a coherent combination of the direct and the exchange amplitude depending on the total spin S , are distinguishable from $F_S^{(N)}(\mathbf{k}_{f'}, n', \mathbf{k}_i)$ for $n \neq n'$.

The distinguishability is not due to an incorrect imposition of antisymmetry since both amplitudes in Eq. (5) are already a coherent combination of their own direct and exchange amplitudes, but due to the inelastic scattering (discrete excitation) boundary conditions imposed by the close-coupling theory irrespective of the energy of the target state $\phi_n^{(N)}$. The close-coupling “detector” positioned at “infinity” only detects the true continuum electron $|\mathbf{k}|$. The step-function hypothesis [17], deduced from a numerical investigation, says that for infinite N the second term in Eq. (5) is zero. The consequence of this is that the distinguishability between the two electrons disappears, since for infinite N even the functions $\phi_n^{(N)}$ also extend to infinity. This hypothesis, if true, is a complete reconciliation of Eq. (5) with formal ionization theory, where the total ionization cross section is obtained with the energy integration over the interval $[0, E/2]$. For finite N we have to use both terms in Eq. (5) as dictated by Eq. (4). In practice, the second term is usually much smaller than the first, but considerable unphysical oscillation in the $F_S^{(N)}(\mathbf{k}_f, n, \mathbf{k}_i)$ as a function of N typically occurs at small to intermediate E , and accurate convergence is only able to be achieved at large E where the cross section at $E/2$ is very small [16,18].

All of the discussion thus far has related solely to the close-coupling theory and with no reference to classical

ideas. Now we turn to the extension of the close-coupling theory to the calculation of differential ionization cross sections. The CCC approach to differential ionization [16] defines the ionization amplitudes as

$$F_S^{(N)}(\mathbf{k}_f, \mathbf{k}_n, \mathbf{k}_i) = \langle \chi^{(-)}(\mathbf{k}_n) | \phi_n^{(N)} \rangle F_S^{(N)}(\mathbf{k}_f, n, \mathbf{k}_i), \quad (6)$$

where $\chi^{(-)}(\mathbf{k}_n)$ is, in the case of hydrogen, a pure Coulomb wave of energy $k_n^2/2 = \epsilon_n^{(N)}$. In other words, ionization is identified with excitation of the positive-energy pseudostates with the overlap in Eq. (6) restoring the true continuum normalization and introducing a one-electron Coulomb phase. This definition is then used in a manner consistent with Eq. (5), i.e., cross sections are defined using

$$\frac{d^3 \sigma_S^{(N)}}{d\Omega_f d\Omega_n dE_f} = |F_S^{(N)}(\mathbf{k}_f, \mathbf{k}_n, \mathbf{k}_i)|^2 + |F_S^{(N)}(\mathbf{k}_n, \mathbf{k}_f, \mathbf{k}_i)|^2. \quad (7)$$

After integration over Ω_n in Eq. (7), and taking care over the normalization, we recover the two terms in Eq. (5). Spin-averaged results are obtained using the usual statistical weights.

Now, let us return to the criticisms of Bencze and Chandler. For clarity of reference we will label their equations n as BC(n).

(i) The analytic formalism that begins with BC(2) and ends at BC(20) is entirely irrelevant. Consider BC(2) and the claim that the CCC amplitudes are given by BC(6). Compare this with Eq. (6) above. The two are very different. For example, we have specified close-coupling boundary conditions for the evaluation of $F_S^{(N)}(\mathbf{k}_f, n, \mathbf{k}_i)$, i.e., the same as for inelastic scattering. This point is ignored by Bencze and Chandler, and is very different from having two continuum electrons in the outgoing channels. Rudge [19] shows that the definition BC(2) yields divergent phase factors, and thus we have stated [16] that we do not believe that the CCC ionization amplitudes (6) converge to BC(2). There is no requirement for the amplitudes in Eq. (6) to satisfy the symmetrization postulate. In the limit of infinite N we would only obtain nonzero $F_S^{(\infty)}(\mathbf{k}_f, \mathbf{k}_n, \mathbf{k}_i)$ for $k_n \leq k_f$. These have all of the information about all possible ionization processes. The correct implementation of antisymmetry in evaluating Eq. (1) ensures that the numerical results become restricted to the energy range $\epsilon_n^{(\infty)} \in [0, E/2]$. One could make a definition analogous to BC(25), but why? We know that antisymmetry has already been imposed in the solution of the close-coupling equations. We have all we need for $\epsilon_n^{(\infty)} \in [0, E/2]$. There is no new information in trying to construct amplitudes that satisfy the symmetrization postulate by taking what has been calculated to the bigger energy range $\epsilon_n^{(\infty)} \in [0, E]$.

(ii) We have explained here that the “step-function hypothesis” applies to all implementations of the close-coupling method, whether applied to calculate ionization or just elastic scattering. It suggests that for $\epsilon_n^{(N)} > k_f^2/2$ the excitation amplitude $\langle \mathbf{k}_f \phi_n^{(N)} | T_S(E + i0) | \phi_1^{(N)} \mathbf{k}_i \rangle$ goes to zero with increasing N as calculated within the close-coupling theory. We invite the interested reader to attempt to prove this.

(iii) It is true that there are only one-electron Coulomb phases in the CCC amplitudes, which come from the overlap in Eq. (6), and which have an enormous effect on the angular distributions. It is also true that there are other theories which show how the introduction of the three-body Coulomb phases considerably improve angular agreement with experiment. However, we typically find that the CCC theory gets even better angular agreement with experiment, and thus we find this criticism somewhat curious.

(iv) The accusation of the imposition of classical ideas comes from our Eq. (7). The suggestion is that it is used to somehow remedy an incorrect symmetrization procedure. Not so. All stems from the simple relation (4). In the close-coupling theory electron flux is distributed between all states with $\epsilon_n^{(N)} \leq E$ without any double-counting problems. Thus, there are always two independent estimates of the ionization kinematics on either side of $E/2$. The incoherent combination of these is just a consistent application of the close-coupling theory to ionization processes. Just because Eq. (7) looks like a classical statement does not mean that it was derived using classical ideas. Objection to Eq. (7) is an objection to Eq. (4), and so the ability of the close-coupling theory to obtain correct total ionization cross sections [12].

The criticisms of Bencze and Chandler are very general and so may be refuted by taking specific counterexamples. Take the triplet ($S=1$) part of the model e -H ionization problem presented in Fig. 2 of Ref. [17]. Excellent convergence is demonstrated, with the “step-function hypothesis” being trivially satisfied for all N due to the fact that correct antisymmetrization ensures that the size of the step is zero. A similar result is also obtained using the R matrix with pseudostates implementation of the close-coupling theory [21]. The lack of symmetry in the presented cross section clearly indicates incompatibility with the symmetrization postulate. So, is the implementation of the close-coupling theory wrong? No, what is wrong is Bencze and Chandler’s attempt to relate the close-coupling amplitudes on either side of $E/2$ via the symmetrization postulate. A correct interpretation of

the close-coupling amplitudes (1) for $\epsilon_n^{(N)} > E/2$ is that they are (if nonzero) numerical “leftovers” due to an incomplete convergence with N .

Another counterexample is obtained by taking large E , so that Eq. (1) may be accurately obtained by the Born approximation. In other words, we may readily drop exchange without significantly altering the results of the close-coupling theory or the CCC approach to ionization (see Fig. 7 of Ref. [16], for example). Convergence for the dominant cross sections at $\epsilon_n^{(N)} \ll E/2$ is readily obtained as the cross section at $E/2$ is particularly small. Without imposition of antisymmetry in the total wave function, the symmetrization postulate cannot be satisfied but the results are still correct, and this is why we say that Eq. (7) has to be used irrespective of whether exchange is or is not included in the close-coupling part of the calculation.

The biggest misunderstanding exhibited by Bencze and Chandler is that of the close-coupling theory. This theory treats all excitations as if they were just inelastic scattering with only one electron being allowed to escape to true infinity. As such, any direct comparison with theories that have two electrons in the continuum is very difficult. The fact that the CCC approach to ionization works better than any other existing theory is simply a reflection of the fact that the ionization information is extracted consistently from the close-coupling method, which attempts to solve the equations governing the electron-atom scattering system. For the case of ionization it is not without problems [17], but current indications are that it is able to yield accurate ionization cross-section angular distributions in all kinematical regions, from near [20] to far [16] from threshold, from asymmetric to symmetric energy-sharing [18]. The problem of a lack of convergence in the magnitude is due to the inability of a finite N calculation to describe a step function which has a substantial step size. This has been discussed in detail previously and may be remedied approximately semiempirically [17]. This latter part is the weakest point of the CCC application to ionization, and not any criticisms raised by Bencze and Chandler.

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