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# Benchmark single-differential ionization cross section results for the *s*-wave model of electron-hydrogen scattering

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Exterior complex scaling enables one to compute the outgoing wave portion of the wave function for three charged particles without explicitly imposing the asymptotic boundary condition for three-body breakup. This technique is used in connection with a high-order finite difference scheme to provide numerically accurate single-differential ionization cross sections for the Temkin-Poet (*s*-wave) model of $e$-H scattering. These benchmark values are compared with results obtained from several recent close-coupling approaches that employ pseudostates to discretize the ionization continuum, but use a strictly two-body scattering formalism. [S1050-2947(99)50507-6]

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Over the past five years, remarkable success has been achieved in combining the use of pseudostates with conventional close-coupling methodology to demonstrate ''convergence'' of the close-coupling expansion in computing excitation and total ionization cross sections for simple atomic systems. Of particular note in this regard are the convergent close-coupling (CCC) method of Bray and Stelbovics [1] and the *R*-matrix plus pseudostate (RMPS) method of Bartschat and co-workers [2]. More recently, these methods have been extended to the calculation of differential ionization cross sections [3,4], but this extension has met with some difficulties and has raised some fundamental questions about aspects of the formalism [5,6]. While initial applications of the CCC method to helium yielded triple-(TDCS), double-(DDCS), and single-(SDCS) differential ionization cross sections in remarkable agreement with experiment for energies above 100 eV [7], it was found that as the total energy was decreased convergence of the SDCS could not be achieved, although the *relative shapes* of the TDCS and DDCS profiles appear to remain accurate [5]. Calculations of differential ionization cross sections for $e$-H in the Temkin-Poet model, in which only the spherical average of the electron-electron repulsion is retained, computed using the CCC and RMPS methods, revealed similar problems with both methods [4].

Pseudostate close-coupling methods employ a strictly two-body formalism, since the target eigenstates, including those with positive eigenvalues, are square-integrable. In that sense, close coupling, when extended to ionization, is a ''distinguishable electron model'' in the sense that only one electron can escape the target: the total wave function will tend asymptotically to zero if two electron coordinates are taken to infinity. This distinguishability should not be confused with a lack of exchange symmetry in the computed wave functions, since the close-coupling methods generally employ properly antisymmetrized expansions. It does, however, lead to certain incompatibilities with formal ionization theory [6,8], notably the symmetrization postulate that guarantees symmetry in the SDCS about $E/2$, where $E$ is the total energy, under interchange of the energies of the scattered and ejected electrons [9]. The SDCS is related to the probability of detecting an electron with energy $\varepsilon$. Since both the primary (scattered) and secondary (ejected) electrons can contribute to this process and since they are experimentally indistinguishable, it has been argued [10] that the ''observable'' SDCS in close-coupling methods should be computed as

$$\frac{d\sigma_{\rm obs}(\varepsilon)}{d\varepsilon}=\frac{d\sigma(\varepsilon)}{d\varepsilon}+\frac{d\sigma(E-\varepsilon)}{d\varepsilon}, \tag{1}$$

where $d\sigma(\varepsilon)/d\varepsilon$ and $d\sigma(E-\varepsilon)/d\varepsilon$ are related to the excitation cross sections corresponding to target pseudostates with energies $\varepsilon$ and $E-\varepsilon$, respectively. The total ionization cross section is then given as

$$\sigma^{i}_{\rm tot}=\int_0^{E/2}\frac{d\sigma_{\rm obs}(\varepsilon)}{d\varepsilon}d\varepsilon, \tag{2}$$

as is the formal theory [8].

Bray [5] has commented recently on the way the SDCS is evaluated in close-coupling theory, and in particular on the fact that the ionization cross section is computed as the incoherent sum of two cross sections corresponding to two physically indistinguishable processes. He argues that, in the limit of a complete basis of pseudostates, the excitation amplitudes will vanish for pseudostates whose energies are greater than $E/2$, and hence either $d\sigma(\varepsilon)/d\varepsilon$ or $d\sigma(E-\varepsilon)/d\varepsilon$ will be zero—at convergence. He argues that this ''step function hypothesis'' explains the lack of convergence in the SDCS in the case of singlet scattering, since no finite analytic basis-set calculation could produce an amplitude that drops discontinuously to zero at $E/2$. (The triplet amplitude, on the other hand, is less problematic, since it must vanish at $E/2$.) Bray offers only numerical evidence to support his step function hypothesis; no mathematical proof is given.

The fact that the close-coupling approach does not yield ionization amplitudes that obey the symmetrization postulate of formal ionization theory does not necessarily mean they are incorrect. Unfortunately, no one to date has succeeded in

 

using the formal theory to carry out accurate numerical or variational calculations of ionization and perhaps no one ever will. Calculations employing three-body Coulomb boundary conditions have been limited to a distorted-wave ansatz [11,12] and so cannot be used to answer fundamental questions about convergence of other *ab initio* methods. This situation has prompted us to provide an independent calculation of the SDCS for $e$-H ionization in the Temkin-Poet model. To address this problem unambiguously, we have devised a method [13,14] that does not employ the two-body formalism of close coupling, yet avoids the intractable prospect of trying to explicitly incorporate the three-body Coulomb boundary condition into the numerical solution of the time-independent Schrödinger equation.

The Temkin-Poet model [15,16] of $e$-H scattering provides a nontrivial test of any method proposed to study the problem of ionization. It retains much of the complexity of a three-body Coulomb problem, yet it simplifies the true problem by treating only states of zero angular momentum, replacing the true electron-electron repulsion $1/|r_1-r_2|$ by its spherical average $1/r_>$. It has thus become something of a testing ground for any new approach to the ionization problem and there is now good agreement on total excitation and ionization cross sections for this problem among a variety of numerical methods.

Our approach to the electron-impact ionization problem was outlined in two previous papers [13,14] and so the essential ideas are only summarized here. In essence, our method consists of two steps. The first is showing that the wave function, or more precisely the scattered wave part of the total wave function, can be computed without recourse to the explicit asymptotic form. The scattered wave function is defined as

$$\Psi_{\rm sc}^{+}=G^{+}(E)(H-E)\Phi_0 \tag{3}$$

or, equivalently, by the differential equation

$$(E-H)\Psi_{\rm sc}^{+}=(H-E)\Phi_0, \tag{4}$$

where $G^{+}(E)$ is the full Green's function corresponding to the Hamiltonian $H$ and $\Phi_0$ is the (antisymmetrized) unperturbed initial state, $\Phi_0=\sin(kr_1)\varphi_{1s}(r_2)+(-1)^S\sin(kr_2)\varphi_{1s}(r_1)$, where $S$ is the total spin. To solve this equation, we introduce an exterior complex scaling transformation [17] on the radial portion of each electron's coordinates, $r\rightarrow R(r)$, which scales those coordinates by a complex phase factor *beyond a radius* $R_0$:

$$R(r)=\begin{cases} r, & r<R_0 \\ R_0+(r-R_0)e^{i\phi}, & r\geqslant R_0. \end{cases} \tag{5}$$

Because $\Psi_{\rm sc}^{+}$ contains only outgoing waves, it decays exponentially on the complex part of the radial contours like an ordinary bound state, thus obviating the need for asymptotic scattering boundary conditions, but in the region where the coordinates are real, $\Psi_{\rm sc}^{+}$ is just the outgoing part of the physical wave function. To solve for this scattered wave function, we introduce a two-dimensional (2D) grid of radial points, $\{R(r_{1,i}),R(r_{2,i}),i=1,\ldots,n\}$, but, unlike in our previous work where we used a basis of finite elements, here the scattering equations are solved directly at the grid points using a high-order finite difference scheme. With the boundary conditions that $\Psi_{\rm sc}^{+}$ vanish at $r_1=r_2=0$ and $R(r_{1,n})$ and $R(r_{2,n})$, Eq. (4) reduces to a large set ($n^2\times n^2$) of complex linear equations. These equations were solved using SuperLU [18], a parallelized direct solver for sparse linear systems.

TABLE I. Single-differential ionization sections $d\sigma/d\varepsilon$ (in units of $\pi a_0^2$/hartree) for the Temkin-Poet model of $e$-H scattering at $E=1.0$ and 1.5 hartrees. The cross sections, which are symmetric about $\varepsilon=E/2$, are given as a function of the energy fraction $\varepsilon/E$. As noted in the text, they are normalized such that the total cross section is obtained by integrating from $\varepsilon=0$ to $E/2$. The total cross sections for singlets and triplets at these energies are 0.020 36($S=0$), 0.002 70($S=1$) and 0.015 36($S=0$), 0.003 39($S=1$)$\pi a_0^2$, respectively.

| | $E=1.0$ | | $E=1.5$ | |
|---|---|---|---|---|
| $\varepsilon/E$ | $S=0$ | $S=1$ | $S=0$ | $S=1$ |
| 0.0 | 0.064 06 | 0.025 48 | 0.037 72 | 0.024 66 |
| 0.025 | 0.056 85 | 0.018 23 | 0.031 26 | 0.016 31 |
| 0.050 | 0.053 79 | 0.015 01 | 0.028 52 | 0.012 82 |
| 0.075 | 0.051 14 | 0.012 48 | 0.026 62 | 0.010 42 |
| 0.100 | 0.048 96 | 0.010 38 | 0.025 14 | 0.008 52 |
| 0.125 | 0.047 10 | 0.008 61 | 0.023 88 | 0.006 96 |
| 0.150 | 0.045 42 | 0.007 11 | 0.022 78 | 0.005 67 |
| 0.175 | 0.043 87 | 0.005 82 | 0.021 80 | 0.004 59 |
| 0.200 | 0.042 42 | 0.004 72 | 0.020 90 | 0.003 68 |
| 0.225 | 0.041 03 | 0.003 77 | 0.020 08 | 0.002 92 |
| 0.250 | 0.039 69 | 0.002 97 | 0.019 32 | 0.002 29 |
| 0.275 | 0.038 38 | 0.002 23 | 0.018 61 | 0.001 76 |
| 0.300 | 0.037 09 | 0.001 73 | 0.017 93 | 0.001 32 |
| 0.325 | 0.035 81 | 0.001 26 | 0.017 28 | 0.000 96 |
| 0.350 | 0.034 53 | 0.000 89 | 0.016 65 | 0.000 67 |
| 0.375 | 0.033 23 | 0.000 59 | 0.016 03 | 0.000 45 |
| 0.400 | 0.031 92 | 0.000 36 | 0.015 43 | 0.000 27 |
| 0.425 | 0.030 63 | 0.000 19 | 0.014 84 | 0.000 15 |
| 0.450 | 0.029 40 | 0.000 08 | 0.014 28 | 0.000 06 |
| 0.475 | 0.028 38 | 0.000 02 | 0.013 83 | 0.000 02 |
| 0.500 | 0.027 92 | 0.0 | 0.013 62 | 0.0 |

Exterior scaling can only be applied when the interaction potentials are of finite range or fall off exponentially at large distances. The reason is that the unperturbed wave function $\Phi_0$ that appears on the right-hand side of Eq. (4) contains plane-wave terms [or, for the Temkin-Poet model, terms involving $\sin(kr)$] that diverge exponentially when the coordinates are made complex. To assure convergence, we therefore zero the potential on the complex portions of the grid beyond $r_1,r_2=R_0$ and solve the scattered wave equation for this finite-range potential. Although the method will converge for any finite value of $R_0$, obtaining the correct physical result requires an extrapolation of the scattering parameters extracted from finite values of $R_0$ to $R_0=\infty$.

The second step consists in showing how the desired scattering information can be extracted from the computed wave function without recourse to the explicit asymptotic form. To compute the total (elastic+excitation+ionization) cross section, we started with the optical theorem and derived the expression [13]

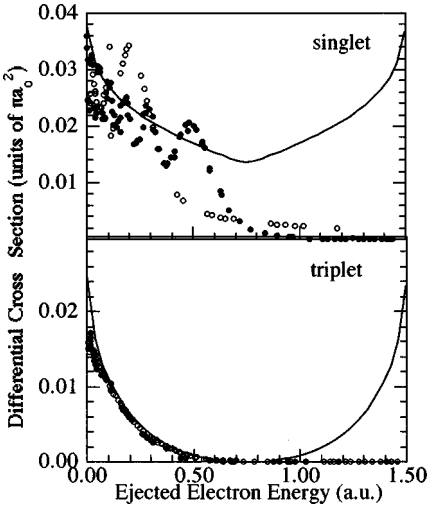


FIG. 1. Single-differential ionization cross section, $d\sigma/d\varepsilon(\pi a_0^2)$, for the Temkin-Poet model of $e$-H scattering at a total energy of 1.5 hartrees. Solid curve, present results; filled circles, CCC results (Ref. [5]); open circles, RMPS results (Ref. [4]).

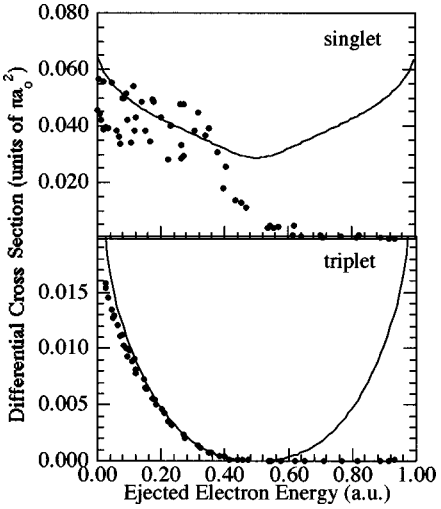


FIG. 2. As in Fig. 1, for $E=1.0$ hartrees.

$$\sigma_{\rm tot} = -\frac{8\pi}{k^2}\,{\rm Im}\langle\Psi_{\rm sc}^{+}|H_0|\Psi_{\rm sc}^{+}\rangle$$
$$= \frac{4\pi}{k^2}\,i\langle\Psi_{\rm sc}^{+}|H_0 - H_0^{+}|\Psi_{\rm sc}^{+}\rangle$$
$$= -\frac{8\pi}{k^2}\,{\rm Im}\int \Psi_{\rm sc}^{-} H_0 \Psi_{\rm sc}^{+} d\mathbf{r}_1 d\mathbf{r}_2, \qquad (6)$$

where $H_0$ is the many-body kinetic-energy operator for the system (not the unperturbed Hamiltonian). There are two things to note about Eq. (6). In evaluating this matrix element, the integration must be confined to the finite volume where both electron coordinates are real, since $\Psi_{\rm sc}^{-}$ (which is the complex conjugate of $\Psi_{\rm sc}^{+}$ only for real $r$) is not well behaved under coordinate rotation. The other key point about Eq. (6) is that it only depends on the asymptotic form of $\Psi_{\rm sc}^{+}$, which is easily seen by using Green's theorem to convert the volume integral to a surface integral. This fact allows a generalization of Eq. (6) in the form of a ''projected optical theorem,'' which gives an expression for the integral cross section for the inelastic process $0\rightarrow\alpha$:

$$\sigma_{0\rightarrow\alpha} = -\frac{8\pi}{k^2}\,{\rm Im}\langle P_\alpha \Psi_{\rm sc}^{+}|H_0|P_\alpha\Psi_{\rm sc}^{+}\rangle, \qquad (7)$$

where $P_\alpha$ projects asymptotically onto target state $\alpha$. The total ionization cross section can be obtained by subtracting the discrete inelastic cross sections from the total cross section. We emphasize again that the cross sections so computed will have an implicit dependence on $R_0$ and have to be extrapolated to $R_0\rightarrow\infty$ to obtain physically correct results.

We use flux operators to compute differential ionization cross sections directly from $\Psi_{\rm sc}^{+}$ without the use of projection operators [14]. The essential quantities are expressed in hyperspherical coordinates $\rho=(r_1^2+r_2^2)^{1/2}$ and $\alpha=\tan^{-1}(r_1/r_2)$. We need to compute the flux due to $\Psi_{\rm sc}^{+}$ at $\rho_0$, and $\alpha$:

$$F(\rho_0,\alpha) = \frac{1}{2i}[(\Psi_{\rm sc}^{+})^{*}\nabla\Psi_{\rm sc}^{+} - \Psi_{\rm sc}^{+}\nabla(\Psi_{\rm sc}^{+})^{*}]_{\rho=\rho_0}. \qquad (8)$$

As $\rho_0\rightarrow\infty$, $\alpha$ also determines the ratio of the two momenta $k_1,k_2$ of the outgoing electrons, $\alpha=\tan^{-1}(k_1/k_2)$. The differential cross section $\sigma_{\rho_0}(\alpha)$ is defined in terms of the flux in the direction of $\hat{\rho}$,

$$\sigma_{\rho_0}(\alpha) = \frac{4\pi}{k_0^2}\,\mathbf{F}(\boldsymbol{\rho}_0,\alpha)\cdot\boldsymbol{\rho}_0 \qquad (9)$$

and the total ionization cross section is given as

$$\sigma_{\rm tot}^{i} = \lim_{\rho_0\rightarrow\infty}\int_0^{\pi/2}\sigma_{\rho_0}(\alpha)\,d\alpha = \int_0^{E/2}\frac{d\sigma(\varepsilon)}{d\varepsilon}\,d\varepsilon. \qquad (10)$$

We note that since $\Psi_{\rm sc}^{+}(r_1,r_2)=(-1)^{S}\Psi_{\rm sc}^{+}(r_2,r_1)$, the flux is symmetric about $\alpha=\pi/4$, i.e., the symmetrization postulate is automatically satisfied. Since $(2\varepsilon)^{1/2}=K\cos\alpha$, where $K^2/2=E$, a simple change of variable establishes the desired relationship

$$\frac{d\sigma(\varepsilon)}{d\varepsilon} = \frac{2}{K^2\sin\alpha\cos\alpha}\lim_{\rho_0\rightarrow\infty}\sigma_{\rho_0}(\alpha). \qquad (11)$$

We determined the flux from the exterior scaled scattered wave function, letting the hyperradius $\rho_0$ coincide with the parameter $R_0$. Since the flux approaches its asymptotic limit as $1/\rho$ [14], *except* near $\alpha=0$ and $\alpha=\pi/2$, it easy to deduce the limiting values of $\sigma_{\rho_0}(\alpha)$ away from these regions from calculations carried out at several values of $R_0$. The SDCS cannot be calculated near $\alpha=0$ and $\alpha=\pi/2$ directly, since the flux is contaminated by contributions from discrete two-body channels over an angular range near the end points that only vanishes in the limit $\rho_0\rightarrow\infty$. For $R_0=200$ a.u., which represents the largest grid we employed in these calculations (the total number of grid points, and hence the dimension of

the complex linear equations we had to solve in that case was ~750 000), the ionized flux could be calculated to within approximately 8° of $\alpha=0$. To obtain the SDCS for smaller values of $\alpha$, we used the fact that the quantity $\sigma_{\rho_0}(\alpha)/(\sin\alpha\cos\alpha)$, which limits to a finite value at $\alpha=0°$ (and $\alpha=90°$), has such a smooth behavior that it could simply be extrapolated linearly to that limit from the smallest values of $\alpha$ at which $\sigma_{\rho_0}(\alpha)$ could be computed directly. [Note that in Ref. [14] we erroneously stated that $\sigma_{\rho_0}(\alpha)/(\sin\alpha\cos\alpha)^2$ limited to a finite value. This is only true for short-range potentials.]

We have carried out calculations at $E=1.0$ and 1.5 a.u., since these are the energies for which the CCC and RMPS results are available for comparison. Our results are reported in Table I and compared with the CCC and RMPS values in Figs. 1 and 2. By comparing extrapolated results from calculations that used different sized grids, we can estimate the accuracy to be better than 1.5% for the singlets and 1.0% for triplets for relative energies $0.1\leqslant\varepsilon/E\leqslant0.9$. For energies outside this range, the errors are more difficult to estimate. For the triplet spin channel, there is very good agreement between our results and both the CCC and RMPS single-differential cross sections for ejected electron energies between zero and $E/2$. The singlet spin channel, however, is more problematic. Our calculations clearly show that the singlet SDCS is substantial at $\varepsilon=E/2$. The pronounced V shape of the singlet SDCS is caused by the sharp ridge in the Temkin-Poet model potential along $r_1=r_2$, as noted in Ref. [14]. If one accepts the step-function hypothesis of Bray, then a distinguishable electron close-coupling model would be trying to converge to a result that shows a marked discontinuity at $\varepsilon=E/2$ where the cross section must drop abruptly to zero. The fact that the CCC and RMPS cross sections appear to be oscillating about the correct answer suggests that Bray and Stelbovic's step-function hypothesis may indeed be correct, although it by no means proves it.

There are two questions that remain to be answered about the close-coupling approach to ionization. First, does the wave function itself converge to the correct answer for finite values of the electron coordinates? And if it does, would a method such as we have employed for extracting the scattering information from the wave function provide a more reliable and stable way of computing the SDCS for singlets and remove the troubling inconsistencies with formal ionization theory? The recent work of Miyashita *et al.* [19], who have also obtained SDCS results for the Temkin-Poet model by making use of an approximate asymptotic form in calculating the wave function for ionization, supports our speculation that the oscillations found in the CCC and RMPS methods may be tied to the way the ionization information is extracted. We have presented a time-independent method that gives accurate differential ionization cross sections that can be systematically converged and involves no appeal to approximate asymptotic forms.

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