# Practical calculation of amplitudes for electron-impact ionization

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An integral expression that is formally valid only for short-range potentials is applied to the problem of calculating the amplitude for electron-impact ionization. It is found that this expression provides a practical and accurate path to the calculation of singly differential cross sections for electron-impact ionization. Calculations are presented for the Temkin-Poet and collinear models for ionization of hydrogen by electron impact. An extension of the finite-element approach using the discrete-variable representation, appropriate for potentials with discontinuous derivatives like the Temkin-Poet interaction, is also presented.

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## I. INTRODUCTION

The formulation in the 1960s by Peterkop [1] and by Rudge and Seaton [2] of the quantum theory of electron-impact ionization of atoms focused on difficulties in the collisional breakup problem that are unique to the case when Coulomb forces act between all the particles [3]. The resulting asymptotic form, only recently completely elucidated [4], is sufficiently difficult to have thus far prevented its explicit use as a boundary condition for solving the Schrödinger equation. In addition, the integral expression required by the formal theory for extracting the ionization amplitudes from the scattering wave function is awkward because of the presence of effective charges connected with the asymptotics of the three-body Coulomb problem.

In a series of papers [5–9] we have successfully developed a procedure for solving the Schrödinger equation for the correct wave function without explicit use of the complicated formal boundary conditions. However, we have been left in the Coulomb case with a quandary that is somewhat unusual in quantum-mechanical calculations. In our efforts to date, we have avoided using the asymptotic boundary conditions, not only in computing accurate wave functions (over a finite volume) for the breakup process, but also in the procedures used to extract collisional-ionization cross sections from them. To accomplish the latter, we relied on a direct evaluation of the quantum-mechanical flux through a finite (hyper)surface that bounds the region where we know the wave function. This procedure requires the use of grids large enough to allow the physical region inhabited only by the ionization part of the wave function to be distinguished from the region where channels that describe scattering into discrete states of the target contribute appreciably. To obtain physical cross sections, the ionization flux must then be extrapolated to infinite volume. While the straightforward evaluation of quantum-mechanical flux has the appeal that it corresponds to the most basic formal definition of the cross sections, it is not as efficient, even for simple inelastic scattering, as the calculation of scattering amplitudes via matrix elements that depend only on the range of the interaction potential.

That fact motivated us recently to explore the subject of optimal methods to extract the breakup amplitudes from the wave functions in the context of short-range interactions [10]. We found that some formally correct expressions are strikingly impractical, while others are both efficient and accurate. A key finding in that work was that the flux approach can require grids that span a region well beyond the range of the potential, while the most efficient calculations can be done on smaller grids by evaluating matrix elements that depend only on the range of the two-body interaction between the two outgoing particles.

In this paper we explore the subject of practical integral expressions for the calculation of collisional-breakup amplitudes in the Coulomb case with a step that we believe addresses the computation of at least the singly differential cross section for electron-impact ionization of atoms. The organization of this paper is as follows. In the next section we very briefly summarize the exterior complex scaling approach to computing the scattering wave function while avoiding use of the formal asymptotic form. In Sec. III, we describe the integral expression we propose to use for computing the singly differential cross section and discuss its possible limitations in light of the formal theory [1,2]. In Sec. IV, we apply this procedure to compute the singly differential and total ionization cross sections for the Temkin-Poet and collinear models for electron-impact ionization of hydrogen. We conclude with a summary and speculation about applications to other differential cross sections for ionization in Sec. V.

## II. COMPUTING THE WAVE FUNCTION FOR ELECTRON-IMPACT IONIZATION

We will specialize our discussion to electron-hydrogen collisions in this section, and later we will further specialize to two-dimensional models of that system. Generalization of the formalism to other systems is straightforward, and the two-dimensional formulation is a model for the partial wave quantities of the full problem. In this approach we solve for $\Psi_{sc}$, the scattered portion of the full scattering wave function $\Psi^{(+)}$,

 

$$\Psi^{(+)}=\Psi_{\rm sc}+\Phi_0, \tag{1}$$

where $\Phi_0$ is the initial, unperturbed state,

$$\Phi_0=\frac{1}{\sqrt{k_0}}[e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\varphi_0(\mathbf{r}_2)\pm e^{i\mathbf{k}_0\cdot\mathbf{r}_2}\varphi_0(\mathbf{r}_1)], \tag{2}$$

$\mathbf{k}_0$ is the incident-electron momentum, and $\varphi_0$ is the initial state of the atom. The scattered wave satisfies the driven Schrödinger equation

$$[E-H]\Psi_{\rm sc}=[H-E]\Phi_0. \tag{3}$$

The next step is to make the exterior complex scaling [11] transformation on the radial coordinates of the two electrons:

$$r\rightarrow\begin{cases} r, & r<R_0 \\ R_0+(r-R_0)e^{i\eta}, & r\geqslant R_0 \end{cases}. \tag{4}$$

Because $\Psi_{\rm sc}$ contains only outgoing waves, it decays exponentially on the complex part of the exterior scaling contour in Eq. (4). Thus Eq. (3) can be solved by applying only the boundary condition that $\Psi_{\rm sc}$ vanish at large distances. On the real part of the contour, $\Psi_{\rm sc}$ is the correct physical wave function from which all scattering information can be extracted, provided it is extracted in the region of real coordinates. The only subtlety is that because Eq. (2) contains incoming waves interaction potentials must be truncated at large distances, but only on the right-hand side of Eq. (3). Thus for the case of Coulomb interactions the final results must be extrapolated as a function of that cutoff, and that procedure has been investigated extensively in earlier work [5,6,8,9], including showing that the direction-dependent logarithmic phase of the $\Psi_{\rm sc}$ is correctly reproduced [9].

After expansion of $\Psi_{\rm sc}$ in coupled (two-particle) spherical harmonics, Eq. (3) can be solved using finite-difference or finite-element methods in the remaining radial variables. The calculations we present here were performed using an implementation of the finite-element method using the so-called ''discrete-variable representation'' or DVR. The DVR was originally introduced to provide a discretization method that combined the accuracy of an underlying analytic basis with a representation in terms of grid points in the coordinates [12,13]. We have found [14] that its application within the context of a finite-element approach provides an extremely efficient discrete representation of the radial equations of this problem.

## III. INTEGRAL EXPRESSIONS FOR THE BREAKUP AMPLITUDE

### A. Short-range potentials

Formal rearrangement theory [15,16] allows one to construct classes of exact integral expressions for scattering amplitudes that involve distorted waves. Recently Lucey, Rasch, and Whelan [17] have extensively explored a family of such ''two-potential'' integral expressions for collisional breakup amplitudes, neatly deriving them in the context of evaluating ''ansatz'' approximations that use assumed forms of the scattering wave function. From a different perspective we have recently shown [10] that, given the numerically ''exact'' representation of the scattered portion of the wave function in a problem with short-range interactions, at least one of those two-potential formulas provides an efficient, stable, and accurate path to the breakup cross section. That is the procedure we explain here and extend to the Coulomb case in the following section.

For simplicity we will specialize this discussion to two-dimensional models of the electron–hydrogen-atom collision problem. The Hamiltonian for these models is

$$H=-\frac{1}{2}\frac{\partial^2}{\partial r_1^2}-\frac{1}{2}\frac{\partial^2}{\partial r_2^2}+V(r_1,r_2). \tag{5}$$

If we write the complete interaction for a system with two active particles as a sum of one-body and two-body parts,

$$V=V_1+V_2, \tag{6}$$

with $V_1=v(r_1)+v(r_2)$, the scattered wave satisfies

$$\begin{aligned}[E-H]\Psi_{\rm sc}(r_1,r_2)&\\ =\frac{1}{\sqrt{k_0}}\{&[v(r_1)+V_2(r_1,r_2)]\\ &\times\sin(k_0r_1)\varphi_0(r_2)\pm[v(r_2)+V_2(r_1,r_2)]\\ &\times\sin(k_0r_2)\varphi_0(r_1)\}.\end{aligned} \tag{7}$$

Then in general, for short-range interactions, we can write the breakup amplitude in terms of the solution of Eq. (7) as

$$f(k_1,k_2)=\langle\Phi_{k_1}^{(-)}\phi_{k_2}^{(-)}|E-T-V_1|\Psi_{\rm sc}\rangle, \tag{8}$$

where the distorted waves $\phi_k^{(-)}$ (with incoming-wave boundary conditions and momentum normalization) satisfy

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial r^2}+v(r)\right]|\phi_k^{(-)}\rangle=\frac{k^2}{2}|\phi_k^{(-)}\rangle. \tag{9}$$

With these definitions, the singly differential cross section (SDCS) is related to the amplitude by

$$\sigma(k_1,k_2)=\frac{8\pi^2}{k_0^2}\frac{1}{k_1k_2}|f(k_1,k_2)|^2. \tag{10}$$

This was the method for extracting the singly differential cross section from the scattered wave that we explored in Ref. [10]. We found that, in contrast to the formally equivalent relation in terms of undistorted functions $\phi_k^0=\sqrt{2/\pi}\sin(kr)$,

$$f(k_1,k_2)=\langle\phi_{k_1}^0\phi_{k_2}^0|V|\Psi^{(+)}\rangle, \tag{11}$$

Eq. (8) was stable and accurate, and that the difference was due to the distinct ways in which the contributions of the discrete channels vanish as the integration volume is increased. The two-potential formula greatly facilitates numerical separation of the ionization contributions from those

of the discrete channels, which integrate to zero in both cases, because the distorted waves are orthogonal to the target-channel eigenfunctions.

The two-potential formula of Eq. (8) also has an equivalent surface integral representation, which appears upon the application of Green's theorem,

$$f(k_1,k_2)=\frac{1}{2}\int_S(\phi_{k_1}^{(+)}\phi_{k_2}^{(+)}\nabla\Psi_{\rm sc}-\Psi_{\rm sc}\nabla\phi_{k_1}^{(+)}\phi_{k_2}^{(+)})\cdot\hat{\mathbf{n}}\,dS. \tag{12}$$

We found this form to be the most convenient in numerical calculations. This representation makes it obvious that Eq. (8) depends only on the asymptotic form of $\Psi_{\rm sc}$.

Moreover, Eq. (8) and its surface integral form Eq. (12) can be shown to require integration only over the range of the interaction potential $V_2$. To see this, we rewrite Eq. (8) equivalently [10] as

$$f(k_1,k_2)=\langle\phi_{k_1}^{(-)}\phi_{k_2}^{(-)}|T+V_1-E|\Phi_0\rangle + \langle\phi_{k_1}^{(-)}\phi_{k_2}^{(-)}|V_2|\Psi^{(+)}\rangle. \tag{13}$$

If $V_1$ is chosen to be a sum of one-body potentials such that the initial target state $\varphi_0$ in Eq. (7), also satisfies Eq. (9), then the first term in Eq. (13) vanishes by orthogonality. So we see by the remaining term that the integration volume need be only the range of the interaction potential between the outgoing particles. Equation (13) also suggests how the orthogonality relations satisfied by the distorted waves eliminate terms involving one-body potentials that appear in Eq. (11).

### B. Coulomb interactions

For problems with Coulomb interactions between all the particles, we propose to employ Eq. (8) or Eq. (12) by replacing $\phi_k^{(+)}$ by momentum-normalized Coulomb functions, so that the distorting potential is

$$V_1=-1/r_1-1/r_2. \tag{14}$$

In the following section we will demonstrate that the results of doing so are entirely stable and produce accurate values for the singly differential cross section for the two-dimensional models we treat here.

However, the formal theory [1–3] clearly states that expressions like Eq. (12) should have a divergent phase as the volume of integration becomes infinite. In his review of the subject, Rudge [3] defines the integral

$$I=-\frac{1}{2}\lim_{S\to\infty}\int[\Psi\nabla\phi(z_1,-\mathbf{k}_1|\mathbf{r}_1)\phi(z_2,-\mathbf{k}_2|\mathbf{r}_2) - \phi(z_1,-\mathbf{k}_1|\mathbf{r}_1)\phi(z_2,-\mathbf{k}_2|\mathbf{r}_2)\nabla\Psi]\cdot\hat{\mathbf{n}}\,dS \tag{15}$$

to calculate the amplitude for the full six-dimensional problem for two electrons, so that the integral is over a five-dimensional bounding surface. The functions $\phi(z,-\mathbf{k}|\mathbf{r})$ are Coulomb functions with effective charge $z$.

This surface integral is precisely analogous to Eq. (12) in our two-dimensional examples. Doing the integral in Eq. (15) using the stationary-phase approximation reveals a divergent phase dependent on the radius of the bounding surface. To eliminate that phase, the formal theory requires that the effective charges $z_1$ and $z_2$ satisfy the so-called Peterkop relation [18], which is a momentum- and direction-dependent equation,

$$\frac{z_1}{k_1}+\frac{z_2}{k_2}=\frac{1}{k_1}+\frac{1}{k_2}-\frac{1}{|\mathbf{k}_1-\mathbf{k}_2|}. \tag{16}$$

With this condition the electron-impact ionization amplitude is then given by

$$f(\mathbf{k}_1,\mathbf{k}_2)=-(2\pi)^{-5/2}\exp[i\Delta(\mathbf{k}_1,\mathbf{k}_2)] \times\int\Psi(H-E)\phi(z_1,-\mathbf{k}_1|\mathbf{r}_1)\phi(z_2,-\mathbf{k}_2|\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 \tag{17}$$

with the finite phase

$$\Delta(\mathbf{k}_1,\mathbf{k}_2)=2\left[\left(\frac{z_1}{k_1}\right)\ln\left(\frac{k_1}{K}\right)+\left(\frac{z_2}{k_2}\right)\ln\left(\frac{k_2}{K}\right)\right], \tag{18}$$

where $K=\sqrt{k_1^2+k_2^2}$.

In our calculations the enclosed integration volume for Eq. (12) is always finite and so the phase must be also. Any volume-dependent overall phase does not contribute to the singly differential cross section in Eq. (10) of course, so one would not expect a problem in the two-dimensional examples we present here. As we will discuss in the Conclusion, in the complete problem with its six dimensions, the singly differential cross section is a sum of terms like the one in Eq. (10). However, other cross sections, like the triply differential cross section giving the angular as well as energy dependence of the two emerging electrons, are coherent sums of such amplitudes for various partial-wave contributions, and in those cases the situation may be different if partial-wave expansions are used.

In spite of the fact that it is formally correct, Eq. (15) appears to have some practical numerical pathologies when applied using finite integration volumes. In attempts to apply Eq. (15) or Eq. (17) to the Coulomb problems discussed in the next section, we found that one-body terms arise from using effective charges ($z_1$ and $z_2$) not equal to unity. These give contributions to the integral from discrete inelastic channels that persist at all finite box sizes. Spurious oscillations in the singly differential cross sections resulted. We observed similar behavior in our earlier work on short-range potentials [10] when we applied Eq. (11) in numerical calculations.

We should note that in their exploration of integral expressions like Eq. (8) for the electron-impact ionization amplitude, Lucey *et al.* [17] also ignored these results of the formal theory, reasoning that it would be alarming ''if the physical results of interest were dependent on the environment outside the experimental apparatus.''

## IV. NUMERICAL EXAMPLES

We have performed exploratory calculations using the Coulomb version of the two-potential formula in Eq. (12) on two models of electron–hydrogen-atom collisions. One of those is the Temkin-Poet model [19,20], for which the potential in Eq. (5) is

$$V=-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{r_>}. \tag{19}$$

This potential has a discontinous first derivative, so the discrete-variable representation method we discussed previously [14] requires some modification to treat it accurately, and that modification is discussed in the Appendix.

In our calculations the right-hand side (rhs) of Eq. (7) was cut off at $R_0$ as discussed above and in our earlier work using exterior complex scaling. In the case of short-range potentials, it is not necessary to cut off $V_2$ on the lhs. However, in the Coulomb case we found that failure to smoothly cut off $V_2$ on the lhs resulted in small diffraction effects, less extreme than but similar to those seen by Kato and Watanabe [21] in their calculations. These are apparently due to the finite grids being employed, and in the absence of cutoffs they subside with increasing box size. Therefore, we cut off $V_2$ on the lhs in these calculations just short of the point where the hyperradius $\rho=\sqrt{r_1^2+r_2^2}$ equals $R_0$, using the function

$$h(\rho)=\exp[-(\rho/R_0)^{\mathrm{Int}[R_0/3]}]. \tag{20}$$

The use of exact Coulomb functions as distorted waves makes it unnecessary to cut off the one-body potential $V_1$ on the lhs of Eq. (7). The largest value of $R_0$ for which we did calculations for this model, and for the collinear model discussed below, was $396a_0$. We used finite elements of length $12a_0$ up to $R_0$. On the complex portion of the contour, we used five elements with sizes of $12a_0$, $12a_0$, $24a_0$, $24a_0$, and $48a_0$, respectively. The DVR grids employed in these calculations used 15 DVR points (basis functions) in each element. A scaling angle $\eta$ in Eq. (4) of 40° was found to be adequate, and the results are completely insensitive both to varying the scaling angle from 25° to 45° and to lengthening the complex part of the countour at the energies we have considered here.

Figure 1 compares the results of these calculations with the benchmark calculations of Jones and Stelbovics [22] and of Baertschy *et al.* [7]. Baertschy *et al.* used the direct evaluation of outgoing flux to compute their results and extrapolated the SDSC in both box size ($R_0$) and in the hyperangle $\alpha$ that determines the energy of one of the electrons via

$$\epsilon_1=K^2\sin^2(\alpha)/2. \tag{21}$$

The results show convincingly that the application of Eq. (8) or Eq. (12) produces the correct SDCS for this problem. In particular, there is no problem obtaining accurate results when the energy fraction $\epsilon_1/E$ approaches 0 or 1, where extrapolation of the ionization flux is complicated by contamination from discrete excitation channels.

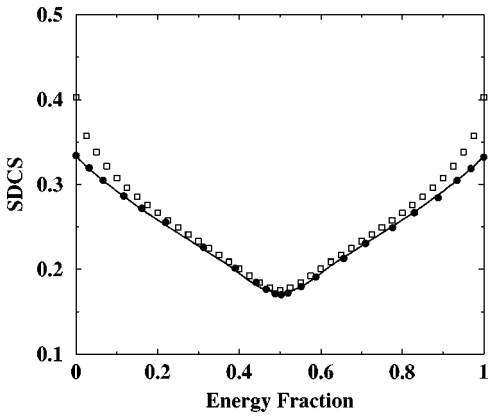


FIG. 1. Singlet SDCS (units of $a_0^2$/hartree) vs energy fraction $\epsilon_1/E$ for Temkin-Poet model at 40.8 eV incident-electron energy. Solid curve, present results; filled circles, Jones and Stelbovics [22]; open squares, Baertschy *et al.* [7].

The total ionization cross section is given by the integral of the SDCS's. To test this approach further we computed total ionization cross sections at low energies to explore the threshold region. In this region the finite values of $R_0$ we employed obviously become a limiting factor. By examining the dependence of the total ionization cross section on $R_0$ over a range of ≈150 bohr, we found that we could reliably extrapolate the calculated values to infinite box size as a linear function of $1/R_0^2$. Figure 2 shows the total ionization cross section given by integrating the SDSC's according to

$$\sigma_{\mathrm{ion}}(E)=\int_0^E \sigma(\sqrt{2\epsilon},\sqrt{2(E-\epsilon)})d\epsilon. \tag{22}$$

We also show fits to our data using the forms $\sigma(E)\propto E^2$ and $\sigma(E)\propto E^{3/2}$. For comparison, we have also plotted the intermediate energy *R*-matrix (IERM) results of Scott *et al.* [23], which were carried out using a box radius of 150 bohr. A

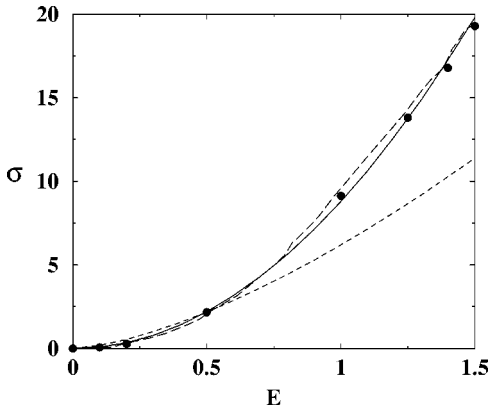


FIG. 2. Singlet total ionization cross section for the Temkin-Poet problem, in units of $10^4\pi a_0^2$ vs total energy (in eV). Dots, present results, computed and extrapolated from finite box size as described in text; solid curve, $E^2$ least-squares fit to the calculated data; short-dashed curve, $E^{3/2}$ power law, fit to data at 0.5 eV; long-dashed curve, calculated IERM values (multiplied by 0.9) from Ref. [23].

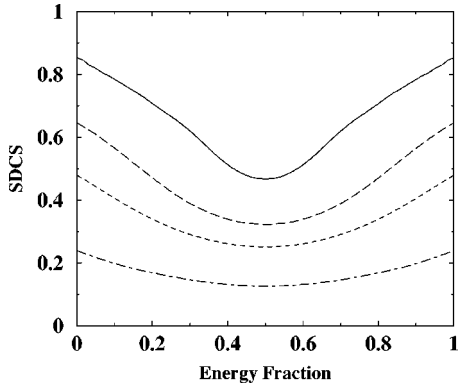


FIG. 3. Singlet SDCS (units of $a_0^2$/hartree) for the Temkin-Poet model. Dash-dotted line, 0.5 eV; short-dashed line, 1.0 eV; long-dashed line, 1.5 eV; solid line, 10.0 eV.

scale factor of 0.9 brings the IERM results into good accord with our values. This small discrepancy can probably be explained by our having extrapolated to infinite grid size while the radius of the *R*-matrix ''box'' in the IERM calculations was finite. We observed, as Scott *et al.* found, that the threshold law due to Macek and Ihra [24], $\sigma(E) \propto \exp(-11.916E^{-1/6})$, fits the data as well as $E^2$ at the energies at which we were able to do these calculations. The threshold behavior for this example is $E^2$, just as though it were a short-range problem [25]. Even though the one-body potentials are evidently Coulomb potentials, the total potential is $-1/r_<$ so the outer electron is always completely shielded from the nucleus by the inner electron.

In Fig. 3, we show the SDCS for the Temkin-Poet model for several values of the total energy between 0.5 and 10 eV. It is interesting to note that the ''notch'' in the SDCS at $E/2$, corresponding to the Wannier ridge, is clearly visible at 10 eV. The notch broadens as the energy decreases, but the SDCS continues to show a minimum at $E/2$, even as the energy approaches threshold.

Because the Temkin-Poet model does not have all the properties of the three-body Coulomb problem, we performed calculations on a second example, the so-called collinear model. In this case the potential is

$$V(r_1,r_2) = -\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_1+r_2}. \tag{23}$$

This is a genuine long-range potential problem displaying essentially all the mathematical features of the physical electron-hydrogen ionization problem [21,26], including the $\sigma(E) \propto E^{1.127}$ threshold behavior that characterizes the physical system [27,28]. Figure 4 shows total ionization cross sections we calculated from threshold to 1 eV total energy. The data are clearly well represented by a $\sigma(E) \propto E^{1.127}$ curve down to 0.3 eV. The fact that the calculated values begin to deviate from that curve at lower energies should not be taken to signal a deviation from the Wannier threshold law. We have verified that at the lowest energies we could not reliably extrapolate our cross sections without performing calculations on much larger grids. The SDSC for the collinear model is plotted in Fig. 5 at incident energies of 2, 10, and

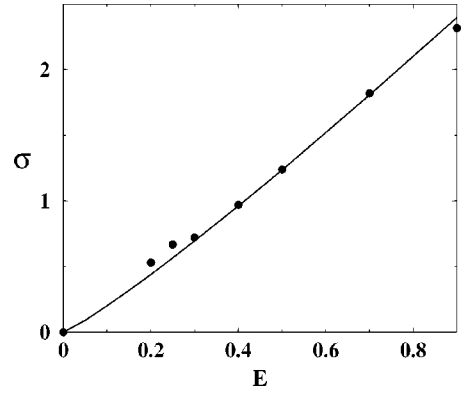


FIG. 4. Singlet total ionization cross section for the collinear model, in units of $10^3 \pi a_0^2$ vs total energy (in eV). Calculated values (dots) are plotted along with a Wannier curve [$\sigma(E) \propto E^{1.127}$], fitted to the data at 0.4 eV.

20 eV above the ionization threshold. In contrast to the results of the Temkin-Poet model, the SDCS is relatively flat, as expected from the analysis that leads to the Wannier threshold law.

## V. CONCLUSION

The question we have tried to address here is, given an accurrate numerical representation of the scattering wave function over a finite region of space, what is the best way to extract from it physical information pertaining to breakup collisions? We have proposed a method for computing ionization amplitudes based on the formal theory of rearrangement collisions and, by examining two different two-dimensional models that involve Coulomb interactions, demonstrated that it gives accurate singly differential cross sections. However, our results here have not ruled out the presence of a finite, volume-dependent phase factor.

Our use of Coulomb functions, without effective charges that satisfy the Peterkop relation as distorted waves, does not follow the prescriptions dictated by the formal theory of ionization. Nevertheless, the results we obtain are very accurate, even for collision energies close to the ionization threshold. We hasten to point out that there is no issue about divergent

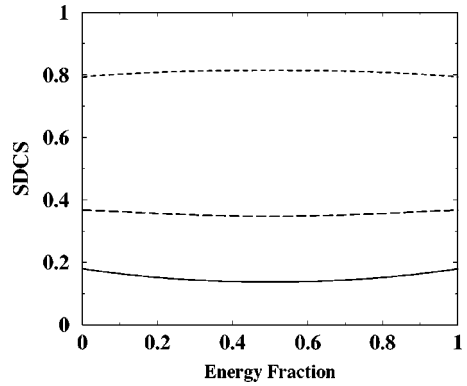


FIG. 5. Singlet SDCS (units of $a_0^2$/hartree) for the collinear model at total energies of 2 (short-dashed curve), 10 (long-dashed curve), and 20 (solid curve) eV.

phase factors in our procedure, since the amplitudes are contructed from matrix elements over a finite volume.

The methods we have discussed here offer significant advantages over the direct evaluation of the quantum-mechanical flux. Except for energies close to threshold, the procedures outlined here yield useful results with modest-sized grids and no extrapolation and, in contrast to the flux method, are stable over the entire range of ejected-electron energy.

We believe that the integral expression for the ionization amplitude [Eq. (12)] can also be used to compute the SDCS in the full electron-impact ionization problem, because the SDCS is an incoherent sum of partial-wave contributions and involves no quantum interference between those terms. When an expansion of $\Psi_{\rm SC}$ in partial waves is employed, the SDSC for the full electron-hydrogen problem is given by the sum

$$\sigma(k_1,k_2)=\frac{8\pi^2}{k_0^2}\frac{1}{k_1k_2}\sum_{l_1,l_2,L}\left|\frac{1}{2}\int_S(\phi^{(+)}_{l_1,k_1}\phi^{(+)}_{l_2,k_2}\nabla\Psi^L_{\rm sc}-\Psi^L_{\rm sc}\nabla\phi^{(+)}_{l_1,k_1}\phi^{(+)}_{l_2,k_2}).\hat{\mathbf{n}}\,dS\right|^2. \tag{24}$$

In contrast to the SDCS, the triply (and doubly) differential ionization cross sections involve coherent sums of the partial-wave amplitudes. Further investigation will be needed to see if the procedures discussed here will prove useful in computing such observables.

## ACKNOWLEDGMENTS

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## APPENDIX: DISCRETE-VARIABLE REPRESENTATION FOR THE TEMKIN-POET POTENTIAL

The combination of the discrete-variable representation with the finite-element method was designed [14] to treat systems with continuously differentiable potentials. In that context it has all the advantages of the discrete-variable method [12,13]. In particular, the representation of the potential energy is completely diagonal. However, in the case of the Temkin-Poet potential, and in partial-wave expansions for electron-atom scattering, potentials of the form $r_<^l/r_>^{l+1}$ appear, and their derivatives are discontinuous. Thus the underlying Gauss quadrature, upon which the discrete-variable representation relies for its accuracy, can fail seriously [29]. It is that problem that we address in this Appendix. Further details of the DVR finite-element method can be found in Ref. [14].

Our implementation [14] of the discrete-variable representation uses Lagrange interpolating polynomials as basis functions, with mesh points derived from a Gauss-Lobatto quadrature. Gauss-Lobatto quadrature is similar to the more familiar Gauss-Legendre quadrature, both of which approximate integrals as

$$\int_a^b F(x)dx\simeq\sum_{i=1}^n F(x_i)w_i\,. \tag{A1}$$

In Gauss-Lobatto quadrature two of the points are constrained to coincide with the end points, which means that Eq. (A1) can be made exact when $F(x)$ is a polynomial of degree $\leqslant 2n-1$.

We define normalized DVR basis functions as

$$f_i(x)=w_i^{-1/2}\prod_{j\neq i}\frac{x-x_j}{x_i-x_j}. \tag{A2}$$

These functions, when evaluated at the quadrature points, clearly have the property that

$$f_i(x_j)=\delta_{i,j}/\sqrt{w_i}, \tag{A3}$$

and are thus orthonormal under Gauss-Lobatto integration:

$$\int_a^b f_i(x)f_j(x)dx\simeq\sum_{k=1}^n f_i(x_k)f_j(x_k)w_k=\delta_{i,j}\,. \tag{A4}$$

Although they behave as $\delta$ functions under Lobatto integration, we emphasize that Eq. (A2) defines a continuous representation for the DVR functions.

Since Gauss-Lobatto quadrature explicitly includes the end points as quadrature points, it is possible to combine this particular DVR with the finite-element method. For each independent variable $r$, we choose a grid of nodes $0\leqslant r^{(1)}<r^{(2)}<\cdots<r^{(N)}$ and define a set of DVR functions in each interval, in a notation where $f_i^m(r)$ refers to the $i$th DVR function in the $m$th element. We can impose continuity conditions across elements by combining the end-point functions on adjacent intervals into single ''bridging'' functions $\chi_i$,

$$\chi_i(r)=[f_n^i(r)+f_1^{i+1}(r)]/\sqrt{w_n^i+w_1^{i+1}}. \tag{A5}$$

We can impose the boundary conditions that the wave function vanish at the grid boundaries by excluding the basis functions centered on the first and last nodes. For simplicity in the following discussion, we will drop the index that labels the finite elements. The notation is further simplified by combining the DVR functions in the various finite elements and the associated bridging functions into a single basis $[\phi_i]$ of $M=N(n-1)-1$ functions.

The DVR has the desirable feature that any local operator $V(r)$ has a diagonal matrix representation

$$\int_0^{r^{(N)}}\phi_i(r)V(r)\phi_{i'}(r)dr=\delta_{i,i'}V(r_i) \tag{A6}$$

when the Gauss quadrature rule is used to approximate the integration. For multidimensional problems, we use a product basis of DVR functions in each independent variable.

The DVR can give accurate results, provided that the Gauss quadrature approximation is valid for the potential matrix elements. In the Temkin-Poet model, the two-body electron-electron repulsion term $1/|r_1-r_2|$ is replaced by its spherical average $1/r_>$. This potential has a discontinuous derivative along $r_1=r_2$ so the primitive DVR approximation of Eq. (A6) gives very poor results.

If instead we apply the DVR to solving Poisson's equation for the potential due to the charge distribution corresponding to a product of two of the DVR basis functions, we restore the validity of the underlying Gauss quadrature for this problem. Doing so can provide a natural and consistent extension of the original method to any potential of the form $r_<^l/r_>^{l+1}$, although we discuss only the $l=0$ case here.

We wish to calculate matrix elements of the form

$$\langle ij\|kl\rangle = \int_0^{r^{(N)}} dr_1 \phi_i(r_1)\phi_k(r_1) \int_0^{r^{(N)}} dr_2 \frac{1}{r_>} \phi_j(r_2)\phi_l(r_2)$$

$$\equiv \int_0^{r^{(N)}} dr\, \phi_i(r)\phi_k(r)\frac{1}{r} g_{jl}(r), \tag{A7}$$

which defines the function $g_{jl}(r)$ as $r$ times the potential due to the charge distribution $\phi_j(r)\phi_l(r)$. We use the fact that $1/r_>$ is the Green's function for Poisson's equation [30] to write

$$\frac{d^2}{dr^2} g_{jl}(r) = -\phi_j(r)\phi_l(r)/r, \tag{A8}$$

along with the boundary conditions

$$g_{jl}(0)=0,$$
$$g_{jl}(r^{(N)}) = -\delta_{j,l}. \tag{A9}$$

To solve Eqs. (A8) and (A9), we expand $g_{jl}(r)$ in a DVR basis, which consists of the original basis plus the function $\phi_{M+1}$, which is nonzero at the boundary $r^{(N)}$,

$$g_{jl}(r) = \sum_{k=1}^{M} c_k^{jl}\phi_k(r) - \delta_{j,l}\sqrt{w_{M+1}}\phi_{M+1}(r). \tag{A10}$$

Fixing the coefficient of $\phi_{M+1}$ applies the boundary condition at $r^{(N)}$. Substituting Eq. (A10) into Eq. (A8), closing from the left with another DVR basis function, and integrating (under Lobatto quadrature) gives

$$\sum_{k=1}^{M} T_{ik} c_k^{jl} = \frac{\delta_{j,l}\delta_{j,i}}{r_i\sqrt{w_i}} + \delta_{j,i}\sqrt{w_{M+1}} T_{i,M+1}, \tag{A11}$$

where we have defined

$$T_{ij} = -\int \phi_i(r)\frac{d^2}{dr^2}\phi j(r)dr. \tag{A12}$$

We can solve Eq. (A11) for the expansion coefficients $c_i^{jl}$:

$$c_i^{jl} = \delta_{j,l}\left[\frac{T_{ij}^{-1}}{r_j\sqrt{w_j}} + \sqrt{w_{M+1}}\sum_{k=1}^{M} T_{ik}^{-1}T_{kM+1}\right]. \tag{A13}$$

Note that the inverse in Eq. (A13) is of the $M\times M$ second-derivative matrix.

We now complete the evaluation of Eq. (A7) using Eq. (A13):

$$\langle ij\|kl\rangle = \int_0^{r^{(N)}} dr\, \frac{\phi_i(r)\phi_k(r)g^{jl}(r)}{r}$$

$$= \delta_{i,k}\frac{1}{r_i} g^{jl}(r_i)$$

$$= \delta_{i,k}\delta_{j,l}\left[\frac{T_{ij}^{-1}}{r_i\sqrt{w_i}r_j\sqrt{w_j}} + \frac{\sqrt{w_{M+1}}}{r_i\sqrt{w_i}}\sum_{k=1}^{M} T_{ik}^{-1}T_{kM+1}\right]. \tag{A14}$$

It can be shown that the second term on the right-hand side of Eq. (A14) is equal to $1/r^{(N)}$ so that the final working expression for the two-body potential representation is

$$\langle ij\|kl\rangle = \delta_{i,k}\delta_{j,l}\left[\frac{T_{ij}^{-1}}{r_i\sqrt{w_i}r_j\sqrt{w_j}} + \frac{1}{r^{(N)}}\right]. \tag{A15}$$

If the products $\phi_i\phi_k$ and $\phi_j\phi_l$ lie in different finite elements, then Eq. (A15) reduces to the formula given by the natural application of Eq. (A6):

$$\langle ij\|kl\rangle = \delta_{i,k}\delta_{j,l}/\mathrm{Max}(r_i,r_j). \tag{A16}$$

The prescription of Eq. (A15) and Eq. (A16) is completely symmetric in the basis function indices and is easy to evaluate. In contrast to the primitive use of Eq. (A6), this procedure yields accurate results, and in the calculations reported here behaves as well for the Temkin-Poet model as the original DVR finite-element procedure does for potentials that are continuously differentiable.

Since Eqs. (A15) and (A16) give a diagonal representation of the potential, we can unambiguously apply a cutoff, as in Eq. (20), to the matrix DVR representation of the potential, whereas incorporating a cutoff into the definition of the potential at the outset, that is, trying to make a DVR representation of the potential $V_2=h(\rho)/r_>$, would make it impossible to use Poisson's equation in the formulation.

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