

Calculation of atomic photoionization using the nonsingular convergent close-coupling method

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The convergent close-coupling method for atomic photoionization is modified by treating the singularity in the Green's function analytically. The resultant close-coupling equations are then free of any singularities, and can be solved at all incident energies including at the exact thresholds. The utility and superiority of the approach is demonstrated by considering single photoionization of the ground state of helium at photoelectron energies from the ionic $n = 1, 2, 3$ thresholds through to 1 keV. For completeness, the double photoionization cross section is also presented.

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I. INTRODUCTION

The problem of atomic photoionization is very closely linked to electron scattering on the corresponding singly charged atomic ion. The photon is absorbed by an atomic electron, which then proceeds to scatter elastically, inelastically, or ionize the residual ionic target. Elastic scattering corresponds to photoionization leaving the residual ion in the ground state. Inelastic scattering corresponds to photoionization with excitation of the ion. Lastly, ionization corresponds to double photoionization.

The convergent close-coupling (CCC) method was initially developed for the electron-hydrogen scattering problem [1], and was then readily modified to the closely related electron scattering on the He^+ ion [2]. Application to photoionization with excitation and double photoionization of helium and its isoelectronic sequence of ions was presented by Kheifets and Bray [3]. Detailed reviews of the application of the CCC method to photon and electron-impact ionization processes are given in Refs. [4,5].

The CCC method [1] relies on solving the close-coupling equations in momentum space as outlined initially by McCarthy and Stelbovics [6]. This approach involves numeric integration over the Green's function, which contains a singularity for open reaction channels. While this has been a manageable numerical difficulty, it is particularly problematic near, or at, excitation thresholds. Furthermore, the subtraction and addition of large numbers on either side of the singularity leads to ill-conditioned linear equations due to potential precision loss. The latter is particularly problematic in positron scattering [7].

To address the deficiencies associated with the numerical treatment of the singularity in the Green's function an analytical approach to the problem was implemented. This was done first for the S -wave model electron-hydrogen problem [8], then a full problem involving positron scattering on hydrogen [9,10], and then further extended to scattering involving charged targets [11]. Here, we show how this development is also advantageous for calculating single and double photoionization of He. An earlier demonstration has already been made for the H^- ion [12].

II. THEORY

The CCC method for calculation of helium photoionization has been given in detail by Kheifets and Bray [3]. The general idea is that the initial helium ground state is described by a sizable Hylleraas expansion, while the final scattering state is obtained from a CCC calculation of electron scattering on the $\text{He}^+(1s)$ ion. Single photoionization is associated with discrete excitation of the $\text{He}^+(nl)$ ion of energy $-Z^2/n^2$ Ry. Double photoionization is associated with excitation of positive-energy pseudostates included in the CCC calculations. The expansions must be sufficiently large to ensure that the three gauges of the dipole operator, length, velocity, and acceleration, all yield much the same result. Here we concentrate solely on the CCC calculated final state. Atomic units will be used throughout unless specified otherwise.

Assuming reduced matrix element notation, we first obtain target (pseudo)states nl by diagonalizing the target Hamiltonian H_T in a Laguerre basis [1] for orbital angular momentum $l \leq l_{\max}$ to yield

$$\langle n_f | H_T | n_i \rangle = \delta_{fi} \epsilon_{n_i}. \quad (1)$$

Then, as in the original CCC approach the projectile states kL are obtained from solving the Schrödinger equation

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{L(L+1)}{2r^2} + \frac{z_p Z_a}{r} - \epsilon_k \right) \langle r | kL \rangle = 0, \quad (2)$$

where the asymptotic charge $Z_a = +1$ (for He^+ target) and $z_p = -1$ for the electron projectile.

The partial wave expanded Lippmann-Schwinger equations in electron scattering from a charged target within the CCC formalism can be written as

$$\begin{aligned} & \langle L_f k_f l_f n_f | T_{S_J} | n_i l_i k_i L_i \rangle \\ &= \langle L_f k_f l_f n_f | V_{S_J} | n_i l_i k_i L_i \rangle \\ &+ \sum_{l, L} \sum_{n=1}^{N_i} \int dk \frac{\langle L_f k_f l_f n_f | V_{S_J} | n l k L \rangle}{E + i0 - \epsilon_n - \epsilon_k} \\ &\times \langle L k l n | T_{S_J} | n_i l_i k_i L_i \rangle. \end{aligned} \quad (3)$$

Here k_f and L_f (k_i and L_i) are the projectile final (initial) linear and angular momentum respectively. Similarly we have n_f and l_f (n_i and l_i) for the He^+ target electron final (initial) principle quantum number and angular momentum. N_l is the size of the Laguerre basis for a given l . The energy of the projectile and target electron are denoted as ϵ_k and ϵ_n , respectively. The notation $i0$ is used to indicate the limit of ix as positive $x \rightarrow 0$ included to ensure outgoing spherical wave boundary conditions. The total spin and orbital angular momentum of the system are respectively S and J , V_{SJ} are the interaction potentials, and T_{SJ} are the required transition amplitudes.

In order to work with purely real arithmetic we define the K matrix

$$\begin{aligned} & \langle L_f k_f l_f n_f | K_{SJ} | n_i l_i k_i L_i \rangle \\ &= \sum_{l,L} \sum_{n=1}^{N_l^o} \langle L_f k_f l_f n_f | T_{SJ} | n l k L \rangle \\ & \quad \times (\delta_{l_i l} \delta_{L_i L} \delta_{n_i n} + i\pi k_n \langle L k l n | K_{SJ} | n_i l_i k_i L_i \rangle), \end{aligned} \quad (4)$$

where N_l^o is the number of open channels. With this definition the coupled Lippmann-Schwinger equations (3) can be written for this quantity as

$$\begin{aligned} & \langle L_f k_f l_f n_f | K_{SJ} | n_i l_i k_i L_i \rangle \\ &= \langle L_f k_f l_f n_f | V_{SJ} | n_i l_i k_i L_i \rangle \\ & \quad + \sum_{l,L} \sum_{n=1}^{N_l} \mathcal{P} \int dk \frac{\langle L_f k_f l_f n_f | V_{SJ} | n l k L \rangle}{E - \epsilon_n - \epsilon_k} \\ & \quad \times \langle L k l n | K_{SJ} | n_i l_i k_i L_i \rangle, \end{aligned} \quad (6)$$

where the \mathcal{P} is used to denote the Cauchy principle value component of the integral.

The above formulation, which has a singularity in the Green's function, encounters a numerical complication whenever the denominator $E - \epsilon_n - \epsilon_k$ goes through zero. For scattering on a neutral target $\epsilon_k = k^2/2$. However, for charged targets, bound states of the projectile introduce an additional countably infinite number of negative energies. Until recently we were unaware that the CCC formulation for electron-ion scattering had intractable problems in the vicinity of thresholds [11]. This is particularly problematic because the electron-ion scattering excitation cross sections are nonzero at thresholds.

For electron scattering on charged targets (presently He^+), to address the singularity in the numerical implementation of the Green's function we utilize the relation [[13], Eq. (130.10), p. 537, followed by a partial wave expansion]

$$\begin{aligned} G_n^L(r', r'') &= \mathcal{P} \int dk \frac{\langle r' | k L \rangle \langle k L | r'' \rangle}{E - \epsilon_n - \epsilon_k} \\ &= \text{Re} \left[\frac{-\pi}{k_n} f_L(k_n r_{<}) [g_L(k_n r_{>}) + i f_L(k_n r_{>})] \right], \end{aligned} \quad (7)$$

where $k_n^2/2 = E - \epsilon_n$. For open channels k_n is real, purely imaginary for closed channels, and exactly zero at thresholds. The $f_L(kr) = \langle r | k L \rangle$ and $g_L(kr)$ are the regular and irregular

solutions of Eq. (2) (Coulomb functions [14] for $Z_a > 0$), respectively. Asymptotically, they are oscillatory for open channels ($E - \epsilon_n > 0$), and exponentials for closed channels ($E - \epsilon_n < 0$); see the Appendix. At the exact thresholds ($k_n = 0$), we utilize the relations

$$\begin{aligned} \lim_{k_n \rightarrow 0} f_L(k_n r) / \sqrt{k_n} &= \sqrt{\pi r} J_{2L+1}(\sqrt{8r}), \\ \lim_{k_n \rightarrow 0} g_L(k_n r) / \sqrt{k_n} &= -\sqrt{\pi r} Y_{2L+1}(\sqrt{8r}), \end{aligned} \quad (8)$$

where J and Y are (cylindrical) Bessel functions of the first and second kind, respectively ([15], Eqs. 96, 98, normalization differs by $\sqrt{2/\pi}$). We also have to take care of the limit $k_n \rightarrow 0$ in the definition of cross sections. For neutral ($Z_a = 0$) targets the f and g become Riccati-Bessel functions, and for $k_n = 0$ a nonzero cross section is only obtained for the $L = 0$ elastic channel (to yield the scattering length).

We now define

$$\begin{aligned} & \langle L_f k_f l_f n_f | V'_{SJ} | n l k L \rangle \\ &= \int_0^\infty dr' \int_0^\infty dr'' \sum_{n'=1}^{N_k} \\ & \quad \times \langle L_f k_f l_f n_f | V_{SJ} | n l k_n' L \rangle \\ & \quad \times \langle L k_n' | r' \rangle G_n^L(r', r'') \langle r'' | k L \rangle, \end{aligned} \quad (9)$$

which leads to the nonsingular formulation of Eq. (6)

$$\begin{aligned} & \langle L_f k_f l_f n_f | K_{SJ} | n_i l_i k_i L_i \rangle \\ &= \langle L_f k_f l_f n_f | V_{SJ} | n_i l_i k_i L_i \rangle \\ & \quad + \sum_{l,L} \sum_{n=1}^{N_l} \sum_{n'=1}^{N_k} \langle L_f k_f l_f n_f | V'_{SJ} | n l k_n' L \rangle \\ & \quad \times \langle L k_n' l n | K_{SJ} | n_i l_i k_i L_i \rangle. \end{aligned} \quad (10)$$

Here the $\langle r | k_n' L \rangle$ are N_k box-based solutions of (2) which are zero at $r = R_k$, and are set to zero for $r > R_k$. They are normalized such that $\langle k_n | k_n' \rangle = \delta_{nn'}$. The usage of box-based states as forming a complete set ensures that all integrals in (9) exist, with the final results needing to be stable for sufficiently large R_k and N_k .

To calculate photoionization amplitudes within the CCC formalism [3] we write the following set of equations for the D -matrix elements:

$$\begin{aligned} & \langle L_f k_f l_f n_f | D_{SJ} | n_i l_i k_i L_i \rangle \\ &= \langle L_f k_f l_f n_f | d_{SJ} | n_i l_i k_i L_i \rangle \\ & \quad + \sum_{l,L} \sum_{n=1}^{N_l} \int dk \frac{\langle L_f k_f l_f n_f | T_{SJ} | n l k L \rangle}{E + i0 - \epsilon_n - \epsilon_k} \\ & \quad \times \langle L k l n | d_{SJ} | n_i l_i k_i L_i \rangle. \end{aligned} \quad (11)$$

Here d_{SJ} is the uncorrelated dipole matrix element and T_{SJ} is the half off-shell transition amplitude of the associated electron scattering process. In the case of photoionization of the helium atom this associated process is the scattering of an electron on the He^+ ion in the dipole singlet channel ($S = 0, J = 1$).

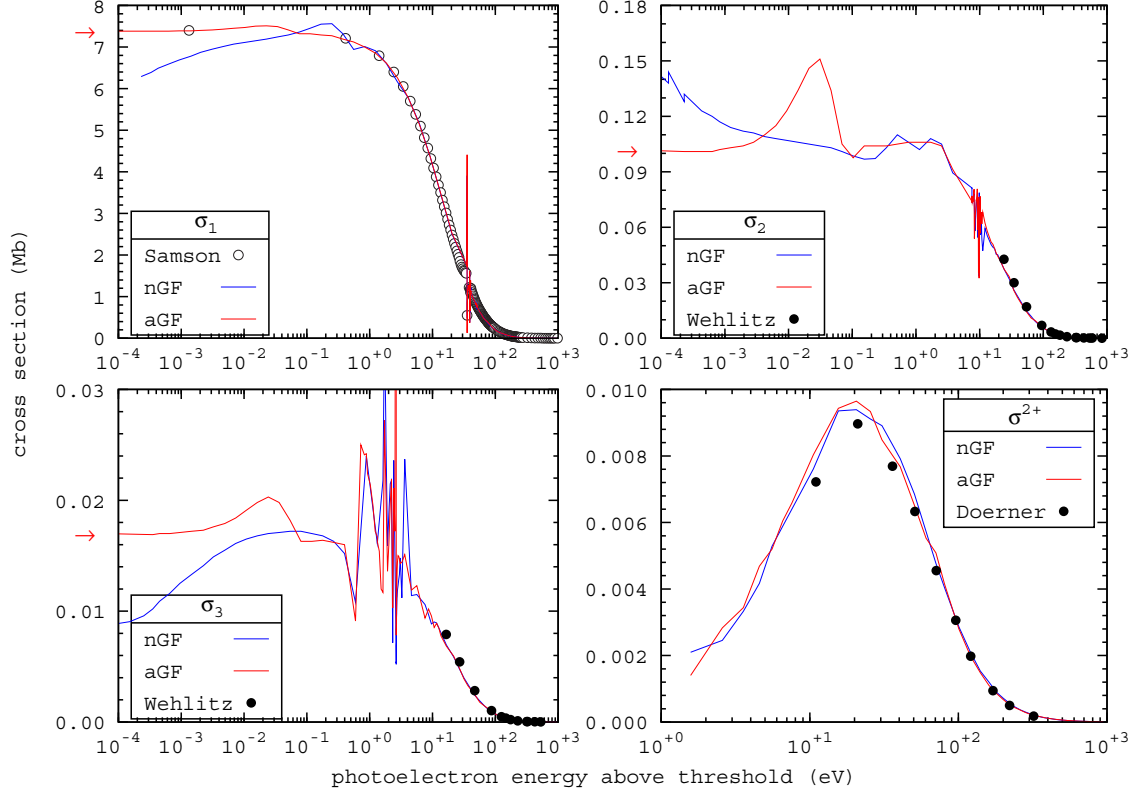


FIG. 1. Photoionization cross sections σ_n of the ground state of helium leaving the residual ion in a state of the specified principal quantum number n calculated with the CCC method using a numerical treatment of the Green's function (nGF) and an analytic treatment (aGF). The arrows indicate the calculated result when the outgoing electron energy is set to exactly zero, available for aGF only. The corresponding double photoionization cross section σ^{2+} is also presented. Experimental data are due to Samson *et al.* [16], Wehlitz *et al.* [17], and Dörner *et al.* [18].

We now introduce a nonsingular treatment for the D -matrix elements in a similar fashion as for (6). We define

$$\begin{aligned} & \langle L_f k_f l_f n_f | d'_{S_J} | n l k L \rangle \\ &= \int_0^\infty dr' \int_0^\infty dr'' \sum_{n'=1}^{N_k} \\ & \times \langle L_f k_f l_f n_f | d_{S_J} | n l k_n L \rangle \\ & \times \langle L k_n | r' \rangle G_n^L(r', r'') \langle r'' | k L \rangle, \end{aligned} \quad (12)$$

using which we rewrite (11) as

$$\begin{aligned} & \langle L_f k_f l_f n_f | D_{S_J} | n_i l_i k_i L_i \rangle \\ &= \langle L_f k_f l_f n_f | d_{S_J} | n_i l_i k_i L_i \rangle \\ & + \sum_{l,L} \sum_{n=1}^{N_l} \sum_{n'=1}^{N_k} \langle L_f k_f l_f n_f | T_{S_J} | n l k_n L \rangle \\ & \times \langle L k_n | n | d'_{S_J} | n_i l_i k_i L_i \rangle. \end{aligned} \quad (13)$$

The solution of (13) allows for the calculation of photoionization amplitudes avoiding the aforementioned complications associated with numerical integration over the Green's function.

III. RESULTS

To test the nonsingular implementation of the CCC method for atomic photoionization we set the target to be the ground state of helium. For this system there is immense reliable experimental data and theory for both photoionization with or without excitation and double photoionization (see Refs. [19–21] for detailed reviews). Our primary goal is to contrast the original numerical implementation of the Green's function (nGF) and the present analytical treatment of the Green's function (aGF) implementation of the CCC method. In addition we compare with experiment where available.

To yield convergence in the cross sections of interest, with respect to the expansion of the total wave function in a Laguerre basis, we take states with orbital angular momentum $l \leq l_{\max} = 2$ and $N_l = 20 - l$, all with exponential falloff parameter $\lambda = 2$. Both sets of calculations have been performed for a range of photoelectron energies from 10^{-4} eV to 10^3 eV above threshold of the photoionization plus excitation channels. Additionally, the aGF calculations have been performed at the exact thresholds. In the case of double photoionization obtaining accurate results in the near threshold region is problematic due to the requirement of large N_l to yield many low-energy positive target states. This is not a focus of the present work. Their presentation is solely to demonstrate that the aGF approach works equally well in this case.

The results of the calculations are presented in Fig. 1, where the energy is on a logarithmic scale to enhance the near

threshold regions. We see substantial discrepancy between the two calculations below 1 eV. The nGF results, at energies below 1 eV, are not stable with respect to the numerical integration and sum over the virtual momenta in Eq. (6). One such typical result is presented. The aGF results at all energies have been obtained by taking $N_k = 400$ and $R_k = 200a_0$, and have been checked to be numerically stable. The evaluation of aGF at the exact thresholds utilizing Eq. (8) is indicated by the arrows, which are clearly consistent with the near-threshold aGF results and the one near-threshold experimental point. Away from thresholds both methods yield much the same results and are in very good agreement with experiment. Note that both methods yield correct results in the resonance regions, which can be compared with the detailed studies presented some time ago by Salomonson *et al.* [22].

IV. CONCLUSIONS

We have implemented an analytical treatment of the Green's function in the CCC equations with application to photoionization of atoms that is valid at all energies, including at exact thresholds. By utilizing the example of the ground state of helium as the target, the extra utility of the approach over the one used previously has been demonstrated. This benefit is primarily at, and near, the thresholds. Such utility is indispensable for threshold studies, in particular the study of threshold behavior utilizing attosecond chronoscopy [12].

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APPENDIX

In generating the component functions of Eq. (7) we utilize the computational program COULCC of Thompson and Barnett [14] with $\eta = z_p Z_a / \sqrt{2\varepsilon_k}$ (η is purely imaginary for negative

TABLE I. $L = 0$ expressions for $G_n^L(r', r'')$ of (7) for neutral targets ($Z_a = 0$) with energies $\varepsilon_n = k_n^2/2$. Note that for $k_n^2/2 < 0$ we write $k_n = ik'_n$, and that $r_< \equiv \min(r', r'')$ and $r_> \equiv \max(r', r'')$.

Energy	$L = 0$
$k_n^2/2 > 0$	$\frac{-\pi}{k_n} \sin(k_n r_<) \cos(k_n r_>)$
$k_n^2/2 = 0$	$-\pi r_<$
$k_n^2/2 < 0$	$\frac{-\pi}{2k'_n} [\exp(k'_n r_<) - \exp(-k'_n r_<)] \exp(-k'_n r_>)$

energies). We do not alter the normalization of the resultant functions, which require a different mode depending on whether the energy is positive (including zero) (MODE1=2 yields f and g) or negative (MODE1=12 yields f and $h^+ = g + if$). Whether $\eta = 0$ for neutral targets or nonzero for charged targets, the resultant functions are used in exactly the same way.

In Table I explicit expressions for the neutral $L = 0$ cases are given for positive, zero, and negative energies. Note how the zero energy limit is readily obtained from the positive or negative energy side. Note also how the positive energy results transform to those of the negative upon $k \rightarrow ik'$ in Eq. (7).

In the case of a charged target ($Z_a \geq 1$) we are not able to use elementary functions to express $G_n^L(r', r'')$ even for $L = 0$. However, the asymptotic behavior is much the same as for $\eta = 0$ except for the extra complexity of the Coulomb term $\theta_L = -\eta \ln(2k_n r) + \sigma_L$, where σ_L is the Coulomb phase. For positive energies ($k_n^2/2 > 0$) and large r we have $f_L(k_n r) \rightarrow \sin(k_n r - L\pi/2 + \theta_L)$, and $g_L(k_n r) = \cos(k_n r - L\pi/2 + \theta_L)$. For negative energies ($k_n = ik'_n$), the f and h^+ are both complex, but their individual phases have no r dependence with their product being always i , leading to k'_n in the denominator of Eq. (7). For large r the function of $r_<$ grows as $\exp(k'_n r_<)$ and the function of $r_>$ behaves as $\exp(-k'_n r_>)$.

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