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Direct calculation of the scattering amplitude without partial-wave analysis. III. Inclusion of correlation effects

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In the first two papers in this series, we developed a method for studying electron-hydrogen scattering that does not use partial-wave analysis. We constructed an ansatz for the wave function in both the static and static exchange approximations and calculated the full scattering amplitude. Here we go beyond the static exchange approximation, and include correlation in the wave function via a modified polarized orbital. This correlation function provides a significant improvement over the static exchange approximation: the resultant elastic scattering amplitudes are in very good agreement with fully converged partial-wave calculations for electron-hydrogen scattering. A fully variational modification of this approach is discussed in the conclusion.

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I. INTRODUCTION

The standard approach to electron-atom scattering involves a partial wave (PW) decomposition of the wave function. With increasing energy, more and more partial waves are needed to obtain fully converged scattering amplitudes and cross sections. Even for the simplest system, electron scattering from atomic hydrogen, accurate phase shifts for elastic scattering have been calculated only up to $l=4$. For higher l, approximate phase shifts can be calculated based on an expansion of the long range potential.

In two previous papers [1,2], we developed a method to calculate the scattering amplitude for e-H scattering in the static exchange approximation (SEA) without partial-wave analysis. The two-electron Schrödinger equation was analytically reduced to a set of coupled integro-partial differential equations, which were solved numerically for the scattering wave function. The wave function was then used in the integral formula for the scattering amplitude. In this paper, we go beyond the SEA and include correlation effects in the ansatz for the wave function via a polarized orbital. This new ansatz yields scattering amplitudes that are in good agreement with fully converged partial-wave calculations for e-H scattering.

II. ANALYTIC DERIVATION OF EQUATIONS FOR *e*-H SCATTERING INCLUDING CORRELATION

In the nonpartial wave formulation of the SEA [2], the ansatz for the scattering wave function is

$$\Psi_k^{\pm}(\vec{r}_1,\vec{r}_2) = [1 \pm P_{12}]\phi_{1s}(r_2)\psi_k^{\pm}(r_1,\theta_1), \tag{1}$$

where P_{12} is the symmetrizer $\vec{r}_1 \leftrightarrow \vec{r}_2$. We require

$$\left\langle \phi_{1s}(r_2) \left| \left[\nabla_1^2 + \nabla_2^2 + \frac{2}{r_1} + \frac{2}{r_2} - \frac{2}{r_{12}} + k^2 - 1 \right] \right| \Psi_k^{\pm}(\vec{r}_1,\vec{r}_2) \right\rangle = 0, \tag{2}$$

where the quantity in brackets is $[E\text{-}H]$ in Rydberg units. Equation (2) is solved for the unknown function $\psi_k^{\pm}(r_1,\theta_1)$, subject to the asymptotic boundary condition

$$\psi_k^{\pm}(r_1 \to \infty, \theta_1) \to e^{ikr_1 \cos\theta_1} + f_k^{\pm}(\theta_1)\frac{e^{ikr_1}}{r_1}. \tag{3}$$

The triplet solution $\psi_k^{-}(r_1,\theta_1)$ is not unique, since $\phi_{1s}(r_1)$ is an exact solution to Eq. (2) [3]; therefore, we require $\langle \phi_{1s} | \psi_k^{-} \rangle = 0$ to ensure stability in the numerical solution.

In order to go beyond the SEA and incorporate explicit electron-electron correlation in the wave function, we adapt the method of polarized orbitals introduced by Temkin [4] and applied to e-H scattering by Temkin and Lamkin [5]. We include a perturbative correction to the $1s$ state

$$\Psi_k^{\pm}(\vec{r}_1,\vec{r}_2) = [1 \pm P_{12}]\left[\phi_{1s}(r_2) + \phi_p(r_2)\frac{\phi_c(r_1)}{r_1^2}\cos\theta_{12} \right] \times \psi_k^{\pm}(r_1,\theta_1), \tag{4}$$

where

$$\phi_p(r_2) = -\frac{1}{\sqrt{\pi}}e^{-r_2}\left(r_2 + \frac{1}{2}r_2^2 \right). \tag{5}$$

We refer to this improved ansatz as the static exchange approximation plus polarized orbital (SEA+PO). The function $\phi_p(r_2)\cos\theta_{12}/r_1^2$ is the first-order perturbative correction to the ground state of electron 2 resulting from the presence of electron 1 at a fixed distance $r_1 > r_2$.

The purpose of the *analytically continuous* cutoff function $\phi_c(r_1)$ is to "turn off" the perturbative correction when electron 1 is inside the atomic core ($r_1 < r_2$) and to ensure that $\phi_c(r_1)/r_1^2 \to 0$ as $r_1 \to 0$. In the partial-wave application of polarized orbitals [4,5], the function $\phi_p(r_2)\cos\theta_{12}/r_1^2$ was multiplied by a step function $\varepsilon(r_1,r_2)$

$$\varepsilon(r_1,r_2)=\begin{cases}0, & r_1\leqslant r_2\\ 1, & r_1>r_2.\end{cases} \tag{6}$$

In this nonpartial-wave treatment, the total wave function must be continuous and separable in the coordinates of the two electrons. Therefore, to construct a simple cutoff function that is independent of spin and k, we require

$$\langle\phi_{1s}(r_2)|\phi_p(r_2)\varepsilon(r_1,r_2)\rangle=\langle\phi_{1s}(r_2)|\phi_p(r_2)\rangle\phi_c(r_1). \tag{7}$$

This yields a cutoff function

$$\phi_c(r_1)=1-e^{-2r_1}\left(1+2r_1+2r_1^2+\frac{4}{3}r_1^3+\frac{1}{3}r_1^4\right). \tag{8}$$

Note that this is a parameter-free prescription for the cutoff function. The function $\phi_c(r_1)/r_1^2$ is plotted in Fig. 1; in the limit $r_1\to 0$, $\phi(r_1)/r_1^2\to\frac{1}{3}r_1^2$.

We obtain the scattering equation for $\psi_k^\pm$ by projecting $[E-H]\Psi_k^\pm$ onto the ground state; this is equivalent to using the SEA+PO ansatz of Eq. (4) in Eq. (2), subject to the boundary condition of Eq. (3). Since the SEA+PO reduces to the SEA when both r_1 and r_2 are small, we continue to require that in the triplet case $\langle\phi_{1s}|\psi_k^-\rangle=0$. It is to be noted that when polarization is included in $\Psi_k^\pm$, the calculation is no longer variational. However, as in the partial-wave formulation of the method of polarized orbitals [4,5], this approach is consistent with first-order perturbation theory [6].

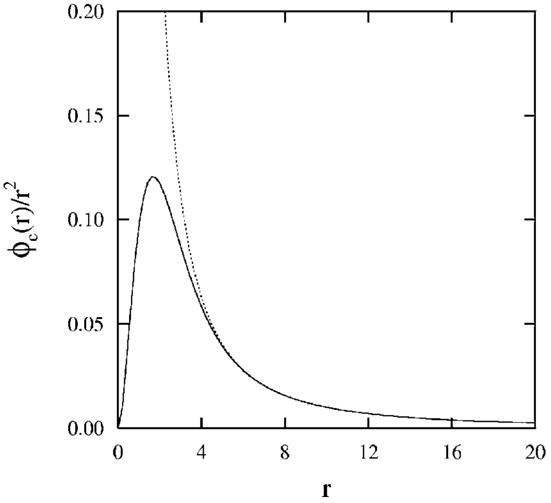

FIG. 1. $\phi_c(r)/r^2$, where $\phi_c(r)$ is the cutoff function given by Eq. (8). (The dashed curve is $1/r^2$.)

Using $[\nabla_2^2+2/r_2-1]\phi_{1s}(r_2)=0$, we obtain from Eq. (2)

$$\left\langle\phi_{1s}(r_2)\left|\nabla_1^2+\frac{2}{r_1}-\frac{2}{r_{12}}+k^2\right|\phi_{1s}(r_2)\right\rangle\psi_k^\pm(r_1,\theta_1)+\left\langle\phi_{1s}(r_2)\left|\nabla_1^2+\frac{2}{r_1}-\frac{2}{r_{12}}+k^2\right|\phi_p(r_2)\cos\theta_{12}\right\rangle\frac{\phi_c(r_1)}{r_1^2}\psi_k^\pm(r_1,\theta_1)$$
$$\pm\left\langle\phi_{1s}(r_2)\left|\nabla_1^2+\frac{2}{r_1}-\frac{2}{r_{12}}+k^2\right|\psi_k^\pm(r_2,\theta_2)\right\rangle\phi_{1s}(r_1)\pm\left\langle\phi_{1s}(r_2)\left|\nabla_1^2+\frac{2}{r_1}-\frac{2}{r_{12}}+k^2\right|\frac{\phi_c(r_2)}{r_2^2}\cos\theta_{12}\psi_k^\pm(r_2,\theta_2)\right\rangle\phi_p(r_1)=0. \tag{9}$$

The first and third terms of Eq. (9) are identical to those we obtained in the SEA [2]; the second and fourth terms are the new contributions due to correlation.

Two of the integrals involving the electron-electron interaction are evaluated analytically:

$$V_{1s1s}(r_1)=\left\langle\phi_{1s}(r_2)\left|\frac{2}{r_1}-\frac{2}{r_{12}}\right|\phi_{1s}(r_2)\right\rangle=2e^{-2r_1}\left(1+\frac{1}{r_1}\right), \tag{10}$$

$$\begin{aligned}V_{1sp}(r_1)&=\left\langle\phi_{1s}(r_2)\left|\frac{2}{r_1}-\frac{2}{r_{12}}\right|\phi_p(r_2)\cos\theta_{12}\right\rangle\\&=\frac{9}{2r_1^2}-e^{-2r_1}\left[r_1^2+5r_1+9+\frac{9}{r_1}+\frac{9}{2r_1^2}\right].\end{aligned} \tag{11}$$

The additional two electron-electron interaction integrals in Eq. (9) which contain the unknown function $\psi_k^\pm(r_2,\theta_2)$ are more difficult to evaluate. The first of these appeared in the SEA; using the approach we introduced in Ref. [2], we define the function $\alpha_k^\pm(r_1,\theta_1)$

$$\alpha_k^\pm(r_1,\theta_1)=\left\langle\phi_{1s}(r_2)\left|\frac{-2}{r_{12}}\right|\psi_k^\pm(r_2,\theta_2)\right\rangle. \tag{12}$$

A partial differential equation for $\alpha_k^\pm(r_1,\theta_1)$ will be given below. The second of these integrals is due to correlation. To proceed further, we use $\cos\theta_{12}=\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2(\cos\phi_1\cos\phi_2+\sin\phi_1\sin\phi_2)$ and express the final electron-electron interaction integral in terms of three functions

$$\begin{aligned}&\left\langle\phi_{1s}(r_2)\left|\frac{-2}{r_{12}}\right|\frac{\phi_c(r_2)}{r_2^2}\psi_k^\pm(r_2,\theta_2)\cos\theta_{12}\right\rangle\\&\quad=\cos\theta_1\beta_k^\pm(r_1,\theta_1)+\sin\theta_1\cos\phi_1\tilde{\gamma}_k^\pm(r_1,\theta_1,\phi_1)\\&\quad+\sin\theta_1\sin\phi_1\bar{\gamma}_k^\pm(r_1,\theta_1,\phi_1),\end{aligned} \tag{13}$$

where

$$\beta_k^\pm(r_1,\theta_1)=\left\langle\phi_{1s}(r_2)\left|\frac{-2}{r_{12}}\right|\frac{\phi_c(r_2)}{r_2^2}\psi_k^\pm(r_2,\theta_2)\cos\theta_2\right\rangle, \tag{14}$$

$$\tilde{\gamma}_k^{\pm}(r_1,\theta_1,\phi_1) = \left\langle \phi_{1s}(r_2) \left| \frac{-2}{r_{12}} \right| \frac{\phi_c(r_2)}{r_2^2} \psi_k^{\pm}(r_2,\theta_2) \sin\theta_2 \cos\phi_2 \right\rangle, \tag{15}$$

$$\bar{\gamma}_k^{\pm}(r_1,\theta_1,\phi_1) = \left\langle \phi_{1s}(r_2) \left| \frac{-2}{r_{12}} \right| \frac{\phi_c(r_2)}{r_2^2} \psi_k^{\pm}(r_2,\theta_2) \sin\theta_2 \sin\phi_2 \right\rangle. \tag{16}$$

Expanding $1/r_{12}$ in coupled spherical harmonics, we can carry out the integration over $d\phi_2$ in Eqs. (15) and (16). We can then re-express $\tilde{\gamma}_k^{\pm}$ and $\bar{\gamma}_k^{\pm}$ in terms of a single unknown function $\gamma_k^{\pm}(r_1,\theta_1)$, which is independent of ϕ_1

$$\tilde{\gamma}_k^{\pm}(r_1,\theta_1,\phi_1) = \cos\phi_1 \gamma_k^{\pm}(r_1,\theta_1), \tag{17a}$$

$$\bar{\gamma}_k^{\pm}(r_1,\theta_1,\phi_1) = \sin\phi_1 \gamma_k^{\pm}(r_1,\theta_1), \tag{17b}$$

where

$$\gamma_k^{\pm}(r_1,\theta_1) = 4\pi \sum_{l=1}^{\infty} P_l^1(\cos\theta_1) \int\int \phi_{1s}(r_2) \frac{r_<^l}{r_>^{l+1}} \times P_l^{-1}(\cos\theta_2) \phi_c(r_2) \psi_k^{\pm}(r_2,\theta_2) \sin^2\theta_2 d\theta_2 dr_2. \tag{18}$$

The explicit form of $\gamma_k^{\pm}(r_1,\theta_1)$ given in Eq. (18) is used only to obtain the asymptotic boundary condition. Using Eqs. (17a) and (17b), we can now substitute into Eq. (13) and thereby obtain an equation in which the ϕ_1 dependence has been eliminated

$$\left\langle \phi_{1s}(r_2) \left| \frac{-2}{r_{12}} \right| \frac{\phi_c(r_2)}{r_2^2} \psi_k^{\pm}(r_2,\theta_2) \cos\theta_{12} \right\rangle = \cos\theta_1 \beta_k^{\pm}(r_1,\theta_1) + \sin\theta_1 \gamma_k^{\pm}(r_1,\theta_1). \tag{19}$$

In order to determine the unknown functions, we operate on $\alpha_k^{\pm}(r_1,\theta_1)$, $\beta_k^{\pm}(r_1,\theta_1)$, and $[\tilde{\gamma}_k^{\pm}(r_1,\theta_1,\phi_1) + \bar{\gamma}_k^{\pm}(r_1,\theta_1,\phi_1)]$ with ∇_1^2 and use the identity

$$\nabla_1^2\left(\frac{1}{r_{12}}\right) = -4\pi\delta(\vec{r}_1 - \vec{r}_2) \tag{20}$$

to obtain the following coupled differential equations for the functions

$$\nabla_1^2 \alpha_k^{\pm}(r_1,\theta_1) - 8\pi\phi_{1s}(r_1)\psi_k^{\pm}(r_1,\theta_1) = 0, \tag{21}$$

$$\nabla_1^2 \beta_k^{\pm}(r_1,\theta_1) - 8\pi\phi_{1s}(r_1)\frac{\phi_c(r_1)}{r_1^2}\cos\theta_1 \psi_k^{\pm}(r_1,\theta_1) = 0, \tag{22}$$

$$\left[\nabla_1^2 - \frac{1}{r_1^2 \sin^2\theta_1}\right]\gamma_k^{\pm}(r_1,\theta_1) - 8\pi\phi_{1s}(r_1)\frac{\phi_c(r_1)}{r_1^2}\sin\theta_1 \psi_k^{\pm}(r_1,\theta_1) = 0. \tag{23}$$

Taking the limit $r_1 \to \infty$ in Eqs. (12), (14), and (18), we obtain the asymptotic boundary conditions for the three functions (through order $1/r_1$)

$$\alpha_k^{\pm}(r_1 \to \infty, \theta_1) \to -\frac{2}{r_1}\langle \phi_{1s} | \psi_k^{\pm} \rangle, \tag{24}$$

$$\beta_k^{\pm}(r_1 \to \infty, \theta_1) \to -\frac{2}{r_1}\left\langle \phi_{1s} \left| \frac{\phi_c}{r_2^2} \psi_k^{\pm} \cos\theta_2 \right\rangle\right., \tag{25}$$

and

$$\gamma_k^{\pm}(r_1 \to \infty, \theta_1) \to 0. \tag{26}$$

Finally, using Eqs. (10)–(12) and (19), we re-express Eq. (9) as an integro-partial differential equation:

$$\begin{aligned} &\left[\nabla_1^2 + V_{1s1s}(r_1) + V_{1sp}(r_1)\frac{\phi_c(r_1)}{r_1^2} + k^2\right]\psi_k^{\pm}(r_1,\theta_1) \pm \frac{(1 \pm 1)}{2}(k^2+1)\phi_{1s}(r_1)\langle \phi_{1s} | \psi_k^{\pm} \rangle \pm \phi_{1s}(r_1)\alpha_k^{\pm}(r_1,\theta_1) \\ &\pm 2r_1\phi_{1s}(r_1)\cos\theta_1 \left\langle \phi_{1s} \left| \frac{\phi_c}{r_2^2}\cos\theta_2 \psi_k^{\pm} \right\rangle\right. \pm \phi_p(r_1)\cos\theta_1 \beta_k^{\pm}(r_1,\theta_1) \pm \phi_p(r_1)\sin\theta_1 \gamma_k^{\pm}(r_1,\theta_1) \\ &\pm (k^2+1)\phi_p(r_1)\cos\theta_1 \left\langle \phi_{1s} \left| \frac{\phi_c}{r_2^2}\cos\theta_2 \psi_k^{\pm} \right\rangle\right. = 0. \end{aligned} \tag{27}$$

Equations (21), (22), (23), and (27) and the corresponding boundary conditions Eqs. (24), (25), (26), and (3) constitute the set of four coupled integro-partial differential equations for *e*-H scattering. We solve the equations for the functions $\psi_k^{\pm}(r_1,\theta_2)$, $\alpha_k^{\pm}(r_1,\theta_2)$, $\beta_k^{\pm}(r_1,\theta_2)$, and $\gamma_k^{\pm}(r_1,\theta_2)$ with the finite element method (see Sec. IV). One also obtains the scattering amplitude $f_k^{\pm}(\theta)$; however, that result for $f_k^{\pm}(\theta)$ is sensitive to the wave function in the asymptotic region. A more accurate value of the scattering amplitude can be obtained from an integral formula involving the functions $\psi_k^{\pm}(r_1,\theta_2)$,

$\alpha_k^{\pm}(r_1,\theta_2)$, $\beta_k^{\pm}(r_1,\theta_2)$, and $\gamma_k^{\pm}(r_1,\theta_2)$. This is described in detail in the next section (Sec. III).

In summary, in the SEA+PO approach, the final equations to describe e-H scattering are independent of ϕ_1: they are *two-dimensional* integro-partial differential equations. All the terms have been simplified analytically without any approximation and we have made tractable the difficult integrals involving $1/r_{12}$.

III. INTEGRAL FORMULA FOR THE SCATTERING AMPLITUDE

As was previously shown [1,2], we can greatly improve the accuracy of the scattering amplitude by using an integral formula for $f_k^{\pm}(\theta)$. For e-H scattering, the integral formula for the scattering amplitude is

$$f_k^{\pm}(\theta) = \frac{1}{4\pi}\int\int e^{-i\vec{k}\cdot\vec{r}_1}\phi_{1s}(r_2)\left(\frac{2}{r_1}-\frac{2}{r_{12}}\right)\Psi_k^{\pm}(\vec{r}_1,\vec{r}_2)d^3r_1d^3r_2. \tag{28}$$

In general, Eq. (28) is not practical because of the difficulty of carrying out the six-dimensional integration analytically or numerically for any realistic $\Psi_k^{\pm}$. In our formulation, we can carry out the integration over four variables analytically, by exploiting the fact that we have determined the functions $\alpha_k^{\pm}(r,\theta)$, $\beta_k^{\pm}(r,\theta)$, and $\gamma_k^{\pm}(r,\theta)$ in addition to $\psi_k^{\pm}(r,\theta)$. The integrals containing $1/r_{12}$ are replaced by functions which have already been determined.

Using the SEA+PO ansatz of Eq. (4) in Eq. (28), we have, to begin with

$$\begin{aligned} f_k^{\pm}(\theta) = {}& \frac{1}{4\pi}\int\int e^{-i\vec{k}\cdot\vec{r}_1}\phi_{1s}(r_2)\left(\frac{2}{r_1}-\frac{2}{r_{12}}\right)\phi_{1s}(r_2)\psi_k^{\pm}(r_1,\theta_1)d^3r_1d^3r_2 + \frac{1}{4\pi}\int\int e^{-i\vec{k}\cdot\vec{r}_1}\phi_{1s}(r_2)\left(\frac{2}{r_1}-\frac{2}{r_{12}}\right)\phi_p(r_2)\frac{\phi_c(r_1)}{r_1^2} \\ & \times\cos\,\theta_{12}\psi_k^{\pm}(r_1,\theta_1)d^3r_1d^3r_2 \pm \frac{1}{4\pi}\int\int e^{-i\vec{k}\cdot\vec{r}_1}\phi_{1s}(r_2)\left(\frac{2}{r_1}-\frac{2}{r_{12}}\right)\phi_{1s}(r_1)\psi_k^{\pm}(r_2,\theta_2)d^3r_1d^3r_2 \\ & \pm\frac{1}{4\pi}\int\int e^{-i\vec{k}\cdot\vec{r}_1}\phi_{1s}(r_2)\left(\frac{2}{r_1}-\frac{2}{r_{12}}\right)\phi_p(r_1)\frac{\phi_c(r_2)}{r_2^2}\cos\,\theta_{12}\psi_k^{\pm}(r_2,\theta_2)d^3r_1d^3r_2. \end{aligned} \tag{29}$$

The first and third integrals are equivalent to the results from the SEA, although the function $\psi_k^{\pm}$ is obviously different. Carrying out the integrations over d^3r_2 and $d\phi_1$, we can reduce Eq. (29) to

$$\begin{aligned} f_k^{\pm}(\theta) = {}& \frac{1}{2}\int e^{-ikr_1\cos\,\theta_1\cos\,\theta}J_o(kr\sin\,\theta_1\sin\,\theta)\left[V_{1s1s}(r_1)+V_{1sp}(r_1)\frac{\phi_c(r_1)}{r_1^2}\right]\psi_k^{\pm}(r_1,\theta_1)\sin\,\theta_1\,d\theta_1r_1^2dr_1 \\ & \pm\frac{1}{2}\int e^{-ikr_1\cos\,\theta_1\cos\,\theta}J_o(kr\sin\,\theta_1\sin\,\theta)\Bigg((1\pm 1)\frac{\phi_{1s}(r_1)}{r_1}\langle\phi_{1s}|\psi_k^{\pm}\rangle + 2\frac{\phi_p(r_1)}{r_1}\cos\,\theta_1\left\langle\phi_{1s}\middle|\cos\,\theta_2\frac{\phi_c}{r_2^2}\psi_k^{\pm}\right\rangle + \phi_{1s}(r_1)\alpha_k^{\pm}(r_1,\theta_1) \\ & +\phi_p(r_1)\cos\,\theta_1\beta_k^{\pm}(r_1,\theta_1)+\phi_p(r_1)\sin\,\theta_1\gamma_k^{\pm}(r_1,\theta_1)\Bigg)\sin\,\theta_1\,d\theta_1r_1^2dr_1. \end{aligned} \tag{30}$$

The integral terms $\langle\phi_{1s}|\psi_k^{\pm}\rangle$ and $\langle\phi_{1s}|\phi_c\cos\,\theta_{12}\psi_k^{\pm}/r_2^2\rangle$ are the same ones that appeared in Eq. (27) and they are easily evaluated. The final integration over dr_1 and $d\theta_1$ is carried out numerically.

IV. PARTIAL-WAVE RESULTS

In order to determine the accuracy of our approximation, we first obtain near exact scattering amplitudes for e-H scattering from fully converged partial-wave results. For $l=0$ and $l=1$, we use the extremely accurate variational phase shifts of Bhatia and Temkin [7,8]. For $2\leqslant l\leqslant 4$, we employ coupled-state phase shifts of Gien, which were obtained using the Harris-Nesbet method [9]. Gien's results are in good agreement with other calculations [10–14] for $l=2$ and $l=3$; they are the only published results for $l=4$. There are no variational or coupled-state results for $l\geqslant 5$.

For higher partial waves, we use an approximation based on the long-range interaction of the electron and the induced multipoles of the neutral target. The first two terms in the long-range potential (in Rydberg units) are

$$V(r) = -\frac{\alpha_d}{r^4}-\frac{\alpha_q}{r^6}, \tag{31}$$

where in this case, $\alpha_d=4.5$ and $\alpha_q=15$ are the static dipole and quadrupole polarizabilities of hydrogen. In the limit $k\rightarrow 0$, the spin-independent phase shifts are given approximately by [15–18]

$$\tan \eta_l = \frac{\pi\alpha_d k^2}{(2l+3)(2l+1)(2l-1)} + \frac{\pi\alpha_d^2 k^4[15(2l+1)^4 - 140(2l+1)^2 + 128]}{(2l+5)(2l+3)^3(2l+1)^3(2l-1)^3(2l-3)} + \frac{3\pi\alpha_q k^4}{(2l+5)(2l+3)(2l+1)(2l-1)(2l-3)} + \cdots . \qquad (32)$$

The term proportional to k^2 is the first Born contribution to the r^{-4} term in the expansion of the long-range potential. The two terms proportional to k^4 are the second Born contribution to the r^{-4} term and the first Born contribution to the r^{-6} term.

There is some question as to whether an additional nonadiabatic correction should also be included in the long-range potential. For hydrogen in the field of either a positron or electron, this term is repulsive. To include the correction to the phase shift, one replaces α_q with $(\alpha_q - 6\beta_1)$ in Eq. (32), where $\beta_1 = 43/8$ for hydrogen [19]. It has been suggested by Callaway *et al.* [20] that the correction is too repulsive, and lowers the phase shift too much for $k > 0.5$.

To address this issue further, we compare the $l=4$ coupled-state phase shifts $[\eta_4^{\mathrm{Gien}}]$ with the approximate phase shifts retaining only the k^2 term $[\eta_4^{O(k^2)}]$, and including the k^4 term with $[\eta_4^{O(k^4)+ad}]$ and without $[\eta_4^{O(k^4)}]$ the adiabatic correction. At low k, the contribution to the phase shifts from the k^4 term is negligible. At higher values of k, $\eta_4^{O(k^4)} > \eta_4^{O(k^2)} > \eta_4^{O(k^4)+ad}$. Specifically at $k=0.8$, $\eta_4^{O(k^4)} = 0.014\,45$, $\eta_4^{O(k^2)} = 0.013\,06$, and $\eta_4^{O(k^4)+ad} = 0.011\,68$, compared to the coupled-state result $\eta_4^{\mathrm{Gien}} = 0.0124$. Retaining only the k^2 term gives the best agreement. Therefore, we calculated all partial-wave phase shifts for $l \geqslant 5$ retaining only the k^2 term in Eq. (32).

To obtain the scattering amplitude from the partial-wave phase shifts, we use

$$f_k^{\pm}(\theta) = \frac{1}{k}\sum_{l=0}^{l_{\max}} (2l+1)e^{i\eta_l} \sin \eta_l P_l(\cos\theta). \qquad (33)$$

We systematically increase $l_{\max}$ until $|f_k^{\pm}(\theta)|^2$, $0 \leqslant \theta \leqslant \pi$ is converged to about 1%. The number of partial waves needed for convergence increases with energy; near the inelastic threshold, we use $l_{\max} = 12$. The scattering amplitude converges much more rapidly at intermediate angles; the contribution of the higher partial waves has the greatest impact on $|f_k^{\pm}(\theta)|^2$ near $\theta=0$, and to a lesser degree, near $\theta=\pi$. For large k, the resultant error in the value of $|f_k^{\pm}(\theta)|^2$ due to the neglected higher order terms in the expansion of $\tan \eta_l$, $l \geqslant 5$ is at most a few percent near $\theta=0$, and less at larger angles.

V. SEA+PO RESULTS

In the SEA+PO approach, we solve Eqs. (21), (22), (23), and (27) with the finite element method [21]. The coordinate space $0 \leqslant \theta \leqslant \pi$ and $0 \leqslant r \leqslant r_{\max}$ is discretized into N_{el} elements of equal size. Within each element, we approximate the unknown functions with a local basis set. We vary $r_{\max}$ with respect to k in order to ensure that we impose the asymptotic boundary conditions at about one de Broglie wavelength outside the atomic core; for higher values of k, we need to keep $r_{\max}$ sufficiently large so that the contribution from the polarized orbital term is negligible on the boundary. Keeping $kr_{\max}$ relatively constant also ensures that we have a sufficient number of basis functions to approximate the oscillatory nature of the asymptotic wave function in both the radial and angular coordinates [2]. To test convergence, we increase $r_{\max}$ (keeping the element size the same), and increase the number of elements (keeping $r_{\max}$ fixed). No attempt is made to finetune the grid for each value of k. For purposes of this calculation, the results are considered sufficiently converged when $|f_k^{\pm}(\theta)|^2$ obtained with the integral formula is stable to within a few percent. Although the integral terms in Eq. (27) destroy the banded nature of the finite element matrices, the order of the matrices is sufficiently small that this does not pose a problem. The finite element parameters for each value of k are given in Table I.

TABLE I. The finite element parameters for the SEA+PO calculation. The number of elements N_{el} and $r_{\max}$ are the only free parameters in the numerical calculation. N is the order of the finite element matrix.

k	N_{el}	$r_{\max}$	N
0.1	8×8	60	4388
0.2	8×8	30	4388
0.3	8×8	20	4388
0.4	8×8	20	4388
0.5	8×8	20	4388
0.6	8×8	16	4388
0.7	10×10	16	6764
0.8	10×10	16	6764

In Fig. 2 we compare fully converged PW and SEA+PO singlet results for $|f_k^{+}(\theta)|^2$. The lower energy results are shown on a separate plot, where the scale is four times greater. In Fig. 3 we compare the PW and SEA+PO triplet results for $|f_k^{-}(\theta)|^2$; the results are shown in two plots (with the same scale) to avoid multiple overlaps of the curves. For the triplet case, the shape of the curve changes dramatically with increasing energy. The results show that the inclusion of a correlation function which depends on $\cos\theta_{12}$ is an extremely efficient way to capture the physics of many partial waves.

In Table II, we compare the singlet (σ_k^{+}), triplet (σ_k^{-}), and spin-averaged $\left(\sigma_k = \frac{1}{4}\sigma_k^{+} + \frac{3}{4}\sigma_k^{-}\right)$, total cross sections for the PW calculation and the SEA+PO. The SEA+PO total cross section is accurate to within 5%, except near the excitation threshold.

VI. CONCLUSION

The purpose of this calculation is to establish the effect of including a correlation function that depends explicitly on

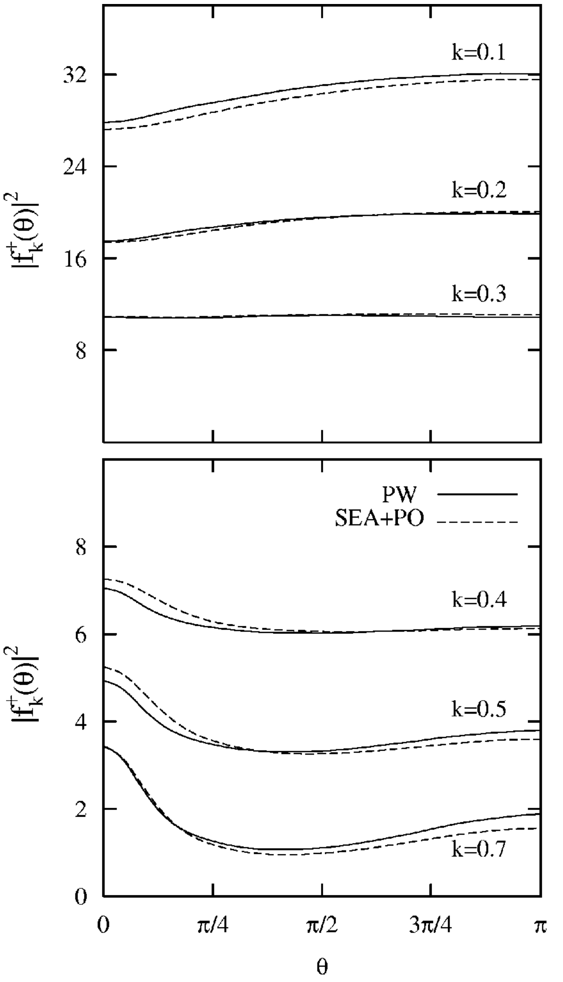

FIG. 2. Comparison of partial-wave (PW) and static exchange approximation plus polarized orbital (SEA+PO) results for $|f_k^+(\theta)|^2$ in Rydberg units.

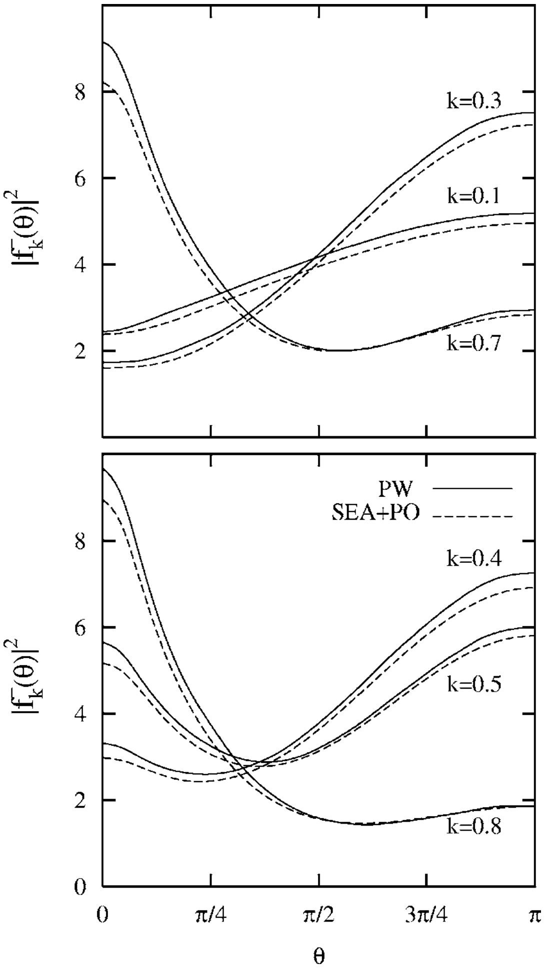

FIG. 3. Comparison of partial-wave (PW) and static exchange approximation plus the polarized orbital (SEA+PO) results for $|f_k^-(\theta)|^2$ in Rydberg units.

cos θ_{12} in the nonpartial wave methodology. By using a wave function based on the method of polarized orbitals, and introducing a parameter-free cutoff function, we obtain scattering amplitudes that are in good agreement with fully converged partial-wave results. We stress that a single calculation yields the combined contribution from all relevant partial waves. The present calculation shows that one can indeed include correlation, as well as exchange, into the nonpartial wave approach to electron-atom scattering.

The next step in this nonpartial-wave approach is to introduce correlation using a variational principle. We propose to use a closely coupled polarized orbital ansatz

$$\Psi_k^{\pm}(\vec{r}_1,\vec{r}_2) = [1 \pm P_{12}][\phi_{1s}(r_2)\psi_k^{\pm}(r_1,\theta_1) + \phi_p(r_2)\cos\theta_{12}\chi_k^{\pm}(r_1,\theta_1)], \qquad (34)$$

where $\chi_k^{\pm}(r_1,\theta_1)$ is a second variational function. This form of the wave function is a nonpartial-wave generalization of the method proposed by Damburg and Geltman [22], and applied to *e*-H excitation by Burke *et al.* [23]. In the nonpartial-wave context, both the scattering state $\psi_k^{\pm}(r_1,\theta_1)$ and the function $\chi_k^{\pm}(r_1,\theta_1)$ are determined from the coupled equations that result from requiring

$$\langle \phi_{1s}(r_2)|(E-H)|\Psi_k^{\pm}(\vec{r}_1,\vec{r}_2)\rangle = 0, \qquad (35)$$

TABLE II. The singlet (σ_k^+), triplet (σ_k^-), and spin-averaged (σ_k), total cross sections for the fully converged partial-wave (PW) calculation and the static exchange approximation plus polarized orbital (SEA+PO) in atomic units.

	σ_k^+ (a_o^2)		σ_k^- (a_o^2)		σ_k (a_o^2)	
k	PW	SEA+PO	PW	SEA+PO	PW	SEA+PO
0.1	387	378	51.5	48.8	135	131
0.2	243	242	55.3	52.2	102	99.7
0.3	138	139	55.0	52.3	75.8	74.0
0.4	76.9	77.6	52.6	50.3	58.7	57.1
0.5	44.0	43.6	48.4	46.8	47.3	46.0
0.6	26.4	25.5	42.8	40.9	38.7	37.0
0.7	17.0	15.4	36.4	34.8	31.6	30.0
0.8	12.6	9.6	30.4	29.0	26.0	24.1

$$\langle \phi_p(r_2)\cos\theta_{12}|(E-H)|\Psi_k^{\pm}(\vec{r}_1,\vec{r}_2)\rangle = 0. \tag{36}$$

Since the cutoff function is optimized at each value of k and for each symmetry, there will be a significant increase in the accuracy of the scattering amplitude, particularly at higher energy. This work is in progress.

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