PHYSICAL REVIEW A **70**, 042710 (2004)

Direct calculation of the scattering amplitude without partial-wave analysis. II. Inclusion of exchange

Janine Shertzer
College of the Holy Cross, Worcester, Massachusetts 01610, USA

Aaron Temkin
NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA

(Received 1 August 2003; revised manuscript received 2 June 2004; published 15 October 2004)

The development of a practical method of accurately calculating the full scattering amplitude, *without* making a partial-wave decomposition is continued. The method is developed in the context of electron-hydrogen scattering, and here exchange is dealt with by considering e-H scattering in the static exchange approximation. The Schrödinger equation in this approximation can be simplified to a set of coupled integro-differential equations. The equations are solved numerically for the full scattering wave function. The scattering amplitude can most accurately be calculated from an integral expression for the amplitude; that integral can be formally simplified, and then evaluated using the numerically determined wave function. The results are essentially identical to converged partial-wave results.

DOI: 10.1103/PhysRevA.70.042710 PACS number(s): 34.10.+x, 02.70.Dh

INTRODUCTION

The standard approach to accurate electron-atom scattering calculations involves an expansion of the total wave function into partial waves [1]. This results in a set of coupled radial equations for each angular momentum component (partial wave). For elastic scattering, the resulting phase shifts η_l can be used to construct the total scattering amplitude $f_k(\theta)$. A drawback of this method is the need to require more and more partial waves as the energy increases to achieve convergence. We pursue here the alternative method that does not employ a partial-wave analysis.

The method involves three steps: (i) the analytical reduction of the Schrödinger equation for the scattering problem to a set of coupled two-dimensional partial differential equations; (ii) the numerical solution of these equations using finite element analysis to obtain the full scattering wave function; (iii) the evaluation of the integral expression for the scattering amplitude using the numerical wave function

In a previous paper [2], the method was applied to electron-hydrogen scattering in the static approximation (i.e., without exchange). The results were very accurate and stable and the computational effort was independent of energy. In this paper, we include the effects of exchange. This is a nontrivial generalization, and it is an important step in the direction of a full treatment, which will eventually include the additional correlation in the scattering problem. At long range, this correlation reduces to polarization of the target.

DERIVATION OF THE EQUATIONS FOR *e*-H SCATTERING IN THE STATIC-EXCHANGE APPROXIMATION

In the static exchange approximation for electron scattering from the ground state of hydrogen, the full scattering wave function is approximated by

$$\Psi_k^{\pm}(\vec{r}_1,\vec{r}_2) = \psi_k^{\pm}(\vec{r}_1)R_{10}(r_2)Y_0^0(\theta_2,\phi_2) \pm \psi_k^{\pm}(\vec{r}_2)R_{10}(r_1)Y_0^0(\theta_1,\phi_1), \tag{1}$$

where +/− refers to the singlet and triplet states, respectively. Substituting $\Psi_k^{\pm}(\vec{r}_1,\vec{r}_2)$ into the exact three-body Schrödinger equation and projecting onto $R_{10}(r_1)Y_0^0(\theta_1,\phi_1)$, we obtain an integro-differential equation for $\psi_k^{\pm}(\vec{r})$:

$$[-\nabla^2 + V_h(r) - k^2]\psi_k^{\pm}(\vec{r}) \pm \frac{2e^{-r}}{\pi}\int \frac{e^{-r'}\psi_k^{\pm}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r' \pm (k^2+1)\frac{e^{-r}}{\pi}\int e^{-r'}\psi_k^{\pm}(\vec{r}\,')d^3r' = 0 \tag{2}$$

subject to the boundary condition

$$\psi_k^{\pm}(r\to\infty) \to e^{ikr\cos\theta} + f_k^{\pm}(\theta)\frac{e^{ikr}}{r}. \tag{3}$$

The potential in Eq. (2) is the Hartree potential

$$V_h(r) = -2e^{-2r}\left(1+\frac{1}{r}\right) \tag{4}$$

and k is the incident electron momentum (Rydberg units are used throughout).

Note that the hydrogen ground state $R_{10}(r)Y_0^0(\theta,\phi)$ is a solution to Eq. (2) for the triplet symmetry; hence $\psi_k^-(\vec{r})$ is not unique and any multiple of the ground state can be added to the solution. Since we will solve the equations numerically, we can require $\psi_k^-(\vec{r})$ to be orthogonal to the hydrogen ground state. Thus the second integral in Eq. (2) vanishes for the triplet state and the solution of the modified equation is now unique.

The first integral in Eq. (2) is undesirable from a computational point of view, because it involves a three-dimensional integral which must be evaluated at each value of $\vec{r}$. To eliminate this term, we define

$$\phi_k^{\pm}(\vec{r}) = \frac{1}{\pi}\int \frac{e^{-r'}\psi^{\pm}(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3r' \tag{5}$$

so that Eq. (2) can be rewritten as

$$[-\nabla^2 + V_h(r) - k^2]\,\psi_k^{\pm}(\vec{r}) \pm 2e^{-r}\phi_k^{\pm}(\vec{r}) + (k^2+1)\frac{(1\pm 1)}{2}\frac{e^{-r}}{\pi}\int e^{-r'}\,\psi_k^{\pm}(\vec{r}')d^3r' = 0. \tag{6}$$

To obtain a second partial differential equation involving the two unknown functions, we operate on $\phi_k^{\pm}(\vec{r})$ with ∇^2 and use the identity $\nabla^2(1/|\vec{r}-\vec{r}'|) = -4\pi\delta(\vec{r}-\vec{r}')$to obtain

$$-\nabla^2\phi_k^{\pm}(\vec{r}) - 4e^{-r}\psi_k^{\pm}(\vec{r}) = 0. \tag{7}$$

Equations (6) and (7) constitute the coupled equations for $\psi_k^{\pm}(\vec{r})$and $\phi_k^{\pm}(\vec{r})$. The asymptotic boundary condition on $\phi_k^{\pm}(\vec{r})$ (through order $1/r$) is

$$\phi_k^{\pm}(r\to\infty) \to \frac{c_k^{\pm}}{r} \tag{8}$$

where $c_k^{+} = (1/\pi)\int e^{-r'}\,\psi_k^{+}(\vec{r}')d^3r'$ and $c_k^{-} = 0$.

For this application, we use the fact that the functions are azimuthally symmetric: $\psi_k^{\pm}(\vec{r}) = \psi_k^{\pm}(r,\theta)$ and $\phi_k^{\pm}(\vec{r}) = \phi_k^{\pm}(r,\theta)$, with $m_1 = m_2 = 0$. Carrying out the integration over $d\phi'$ explicitly, Eqs. (6) and (7) reduce to

$$[\hat{T} + V_h(r) - k^2]\psi_k^{\pm}(r,\theta) \pm 2e^{-r}\phi_k^{\pm}(r,\theta) + (1\pm 1)(k^2+1)e^{-r}\int e^{-r'}\,\psi_k^{\pm}(r',\theta')r'^2dr'\,\sin\theta'\,d\theta' = 0 \tag{9}$$

and

$$\hat{T}\phi_k^{\pm}(r,\theta) - 4e^{-r}\psi_k^{\pm}(r,\theta) = 0, \tag{10}$$

where

$$\hat{T} = -\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{d}{dr} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \cot\,\theta\frac{\partial}{\partial\theta}\right)\right].$$

ANALYTICAL REDUCTION OF THE INTEGRAL EXPRESSION FOR THE SCATTERING AMPLITUDE

An integral expression for the scattering amplitude [1] applied to electron-hydrogen scattering is

$$f_k^{\pm}(\theta) = -\frac{1}{4\pi}\iint e^{-i\vec{k}\cdot\vec{r}_1}R_{10}(r_2)Y_0^0(\theta_2,\phi_2) \times\left(-\frac{2}{r_1}+\frac{2}{r_{12}}\right)\Psi_k^{\pm}(\vec{r}_1,\vec{r}_2)d^3r_1\,d^3r_2. \tag{11}$$

In the static exchange approximation, $\Psi_k^{\pm}(\vec{r}_1,\vec{r}_2)$ is given in Eq. (1) and

$$\begin{aligned} f_k^{\pm}(\theta) = &-\frac{1}{4\pi}\iint e^{-i\vec{k}\cdot\vec{r}_1}R_{10}(r_2)Y_0^0(\theta_2,\phi_2)\left(-\frac{2}{r_1}+\frac{2}{r_{12}}\right) \\ &\times\psi_k^{\pm}(\vec{r}_1)R_{10}(r_2)Y_0^0(\theta_2,\phi_2)d^3r_1d^3r_2 \\ &\mp\frac{1}{4\pi}\iint e^{-i\vec{k}\cdot\vec{r}_1}R_{10}(r_2)Y_0^0(\theta_2,\phi_2) \\ &\times\left(-\frac{2}{r_1}+\frac{2}{r_{12}}\right)\psi_k^{\pm}(\vec{r}_2)R_{10}(r_1)Y_0^0(\theta_1,\phi_1)d^3r_1d^3r_2. \end{aligned} \tag{12}$$

The first integral in Eq. (12) is identical in form to the scattering amplitude obtained in the static approximation without exchange. As described in Ref. [2], the integration over the azimuthal angle ϕ_1 can be carried out analytically for states with $m_1 = m_2 = 0$:

$$\int e^{ikr_1\,\sin\,\theta_1\,\sin\,\theta\,\cos(\phi_1-\phi)}\,d\phi_1 = 2\pi J_o(kr_1\,\sin\,\theta_1\,\sin\,\theta). \tag{13}$$

The integration over the coordinates of the second electron can then be carried out analytically.

To evaluate the second integral in Eq. (12), we use the fact that the first term containing $-2/r_1$ is independent of θ_1. Choosing $\hat{z}_1 = \hat{k}$, we carry out the integration over the coordinates of the first electron:

$$\frac{1}{\sqrt{\pi}}\int e^{ikr\,\cos\,\theta_1}\left(-\frac{2}{r_1}\right)e^{-r}\,d^3r_1 = -8\sqrt{\pi}\frac{1}{(k^2+1)}. \tag{14}$$

The second term [in the second integral in Eq. (12)] containing $2/r_{12}$ can be simplified using the definition in Eq. (5),

$$\int R_{10}(r_2)Y_0^0(\theta_2,\phi_2)\frac{2}{r_{12}}\psi_k^{\pm}(\vec{r}_2)d^3r_2 = 2\phi_k^{\pm}(\vec{r}_1), \tag{15}$$

and Eq. (13). Combining the results, we obtain

$$\begin{aligned} f_k^{\pm}(\theta) = &-\frac{1}{2}\int J_0(kr'\,\sin\,\theta'\,\sin\,\theta)e^{-ikr'\,\cos\theta'\,\cos\,\theta}V_h(r') \\ &\times\psi_k^{\pm}(r',\theta')r'^2\,dr'\,\sin\,\theta' d\theta' \mp \int J_0(kr'\,\sin\theta'\,\sin\,\theta) \\ &\times e^{-ikr'\,\cos\theta'\,\cos\,\theta}e^{-r'}\,\phi_k^{\pm}(r',\theta')r'^2\,dr'\,\sin\theta'\,d\theta' \\ &+\frac{4(1\pm 1)}{k^2+1}\int e^{-r'}\,\psi_k^{\pm}(r',\theta')r'^2dr'\,\sin\theta' d\theta'. \end{aligned} \tag{16}$$

Once the functions $\psi_k^{\pm}(r,\theta)$ and $\phi_k^{\pm}(r,\theta)$ are determined, the remaining two-dimensional (2D) integration can be carried out numerically.

There is a great advantage to using the integral formula for the scattering amplitude rather than extracting it from the value of the wave function on the boundary: the main contribution to the integral in Eq. (16) is at small values of r'. The accuracy of the scattering amplitude obtained from the integral formula depends on how well the wave function is approximated in the interaction region where the wave function is not oscillating. Consequently, the scattering amplitude obtained in this way tends to be more stable.

NUMERICAL SOLUTION OF THE SCATTERING EQUATIONS

Equations (9) and (10) were solved using 2D finite element (FE) analysis [3,4]. The coordinate space defined by $0 \leqslant r \leqslant R$ and $0 \leqslant \theta \leqslant \pi$ is discretized into N small regions called elements. In each element n, the unknown functions $\psi_k^{\pm}(r,\theta)$ and $\phi_k^{\pm}(r,\theta)$ are approximated locally with fifth degree polynomials in r and θ:

$$\psi_k^{\pm}(r,\theta)^n = \sum_{j=1}^{36} [\psi_k^{\pm}]_j^n \rho_j^n(r,\theta), \tag{17}$$

$$\phi_k^{\pm}(r,\theta)^n = \sum_{j=1}^{36} [\phi_k^{\pm}]_j^n \rho_j^n(r,\theta). \tag{18}$$

The polynomials $\rho_j^n(r,\theta)$ are chosen in such a way that the 36 unknown expansion coefficients $[\psi_k^{\pm}]_j^n$ and $[\phi_k^{\pm}]_j^n$ are the value of the function and its derivatives ($\partial/\partial r$, $\partial/\partial\theta$, and $\partial^2/\partial r\,\partial\theta$) at nine points in the element (the four corners, the midpoint of each side, and the geometric center). We substitute Eqs. (17) and (18) into Eqs. (9) and (10); projecting onto the FE basis functions, we obtain a set of matrix equations for each element n:

$$\begin{aligned}\sum_{j=1}^{36} \langle\rho_i^n|\hat{T}+V_h-k^2|\rho_j^n\rangle[\psi_k^{\pm}]_j^n \pm 2\sum_{j=1}^{36}\langle\rho_i^n|e^{-r}|\rho_j^n\rangle[\phi_k^{\pm}]_j^n \\ + (1\pm 1)(k^2+1)\langle\rho_i^n|e^{-r}\rangle \sum_{n'=1}^{N}\sum_{j=1}^{36}\langle e^{-r'}|\rho_j^{n'}\rangle[\psi_k^{\pm}]_j^{n'} = 0,\end{aligned} \tag{19}$$

$$\sum_{j=1}^{36} \langle\rho_i^n|\hat{T}|\rho_j^n\rangle[\phi_k^{\pm}]_j^n - 4\sum_{j=1}^{36}\langle\rho_i^n|e^{-r}|\rho_j^n\rangle[\psi_k^{\pm}]_j^n = 0 \qquad i = 1,2,\ldots,36. \tag{20}$$

The equations for the N elements are then "added" together in such a way as to ensure continuity of the functions and their derivatives across the element boundaries. Note that the integral term in Eq. (9) introduces a "nonlocal" term into the FE equations for singlet symmetry; this destroys the banded nature of the final FE matrix equations. However, since convergence is achieved for relatively small grids, this does not pose a problem in terms of computational effort.

At $r=R$, we impose the asymptotic boundary conditions given by Eqs. (3) and (8); $f_k^{\pm}$ (and $df_k^{\pm}/d\theta$) at the grid points where $r=R$ are left as unknowns.

The solution of the resultant equations yields the unknown expansion coefficents $[\psi_k^{\pm}]_j^n$ and $[\phi_k^{\pm}]_i^n$ for all grid points that are not on the boundary; in addition, we obtain the value of $f_k^{\pm}$ (and $df_k^{\pm}/d\theta$) at the grid points where $r=R$. Using the FE basis functions, we can then reconstruct the piecewise continuous analytical functions $\psi_k^{\pm}(r,\theta)$, $\phi_k^{\pm}(r,\theta)$, and $f_k^{\pm}(\theta)$.

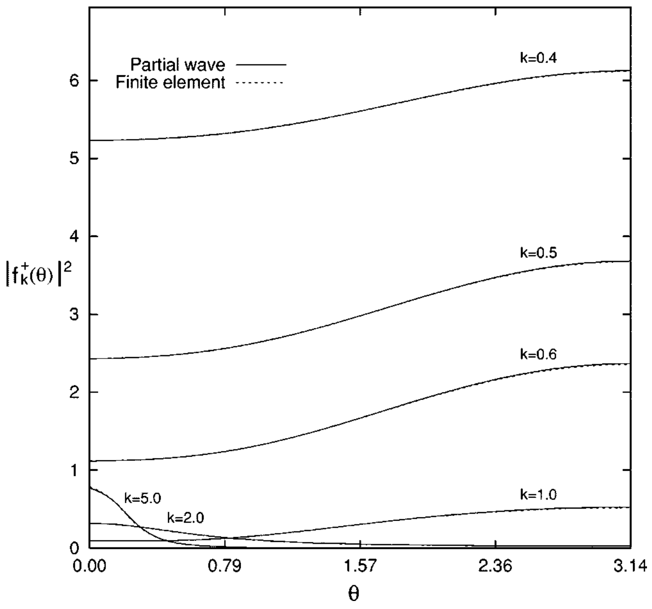

FIG. 1. The scattering amplitude for the singlet state obtained with this method is compared with fully converged partial-wave results.

To evaluate the three integrals in Eq. (16), we carry out the integration over each element using 32 point Gauss quadrature in both coordinates, and sum the contribution from the N elements. At $r \geqslant R$, all three integrals are essentially zero because of the exponential term in each integral.

Extracting the scattering amplitude directly from the solution of the FE equations generally requires a large value for R, and an accurate representation of the wave function in the asymptotic region. In contrast, using the FE representation of the functions $\psi^{\pm}$ and $\phi^{\pm}$ in the integral expression of Eq. (16) yields accurate and stable results at surprisingly small values of R.

RESULTS

The results for the singlet and triplet scattering amplitude $|f_k^{\pm}|^2$are compared with fully converged partial wave results in Figs. 1 and 2. For the partial-wave calculation, the number of partial waves needed for convergence increased with increasing energy, from $l_{\max}=4$ at $k=0.4$ to $l_{\max}=10$ at $k=5.0$. In contrast, the computational effort using this approach is independent of energy.

All results reported in Figs. 1 and 2 were obtained using only 100 elements; no attempt was made to optimize the grid. The radial and angular ranges were both divided into ten equal parts: $\Delta r = R/10$ and $\Delta\theta = \pi/10$. Although elements need not be uniform in size, this allowed for the most systematic study of convergence. The only "free parameter" was the radial cutoff R, where the asymptotic boundary conditions were imposed. As a rule of thumb, we use the condition $2\pi < kR < 5\pi$. The lower limit places the radial boundary beyond one full radial oscillation of the wave function, where $\lambda = 2\pi/k$. The upper limit ensures that there are a sufficient number of basis functions to approximate the oscilla-

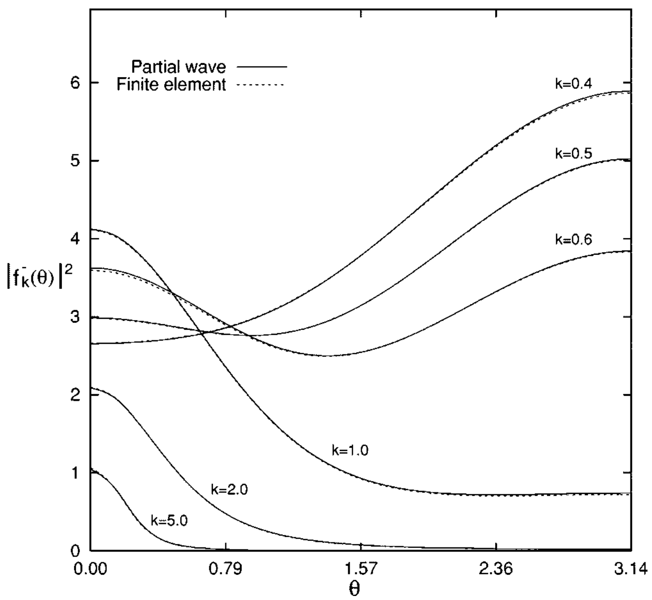

FIG. 2. The scattering amplitude for the triplet state obtained with this method is compared with fully converged partial-wave results.

tory behavior of the wave function in the asymptotic region (i.e., $\Delta r \leqslant \lambda/4$ and $R\Delta\theta/\pi \leqslant \lambda/4$). For $0.4 \leqslant k \leqslant 0.6$ we used $R=20$; for $k=1$, 2, and 5 we used $R=12$, 7, and 3, respectively.

The FE scattering amplitude is considered converged when increasing the number of elements (while holding R fixed) or increasing R (while holding Δr fixed) does not result in any appreciable change ($\leqslant 1\%$) in $|f_k^{\pm}(\theta)|^2$ for $0 \leqslant \theta \leqslant \pi$. Also, the value of the scattering amplitude obtained directly from the solution of the FE equations should be in reasonable agreement with the more accurate result obtained by using the integral formula. Both criteria provided a reliable and consistent way to evaluate the accuracy of the results.

In Table I, we show a convergence study for the triplet case at $k=0.5$, varying both the radial cutoff R and the number of elements N. In Table II we show a similar study for the singlet case at $k=1.0$. Even with a small number of elements, the scattering amplitude is accurate to within a few percent. These results are typical of the triplet and singlet states over the range of energy studied.

CONCLUSIONS

We believe that the above results speak for themselves as to the efficacy of the approach. The next steps are: (i) to include correlation (with exchange) in the total wave function and (ii) to include inelastic channels for $k > 0.866$. Neither of these steps will be easy, but a preliminary analysis has already been made on the inclusion of correlation.

The inclusion of correlation must be done in such a way that we go well beyond the static exchange approximation, so that the results are competitive with the most sophisticated close-coupling and R-matrix calculations for e-H scattering. At the same time, the final equations must be tractable from a computational point of view.

The inclusion of inelastic channels will involve deriving and simplifying integral expressions for the S-matrix elements and imposing more complicated boundary conditions at $r=R$. As with all methods, the rigorous inclusion of ionization at energies above the ionization threshold poses a difficult challenge.

One of the attractive features of this method is that the FE basis set was not designed to treat Coulomb potentials *per se*; the method should work equally well with angular-dependent potentials or model potentials with more complicated structure. Thus this approach may be useful in treating electron scattering from more complicated targets (including the alkalis and molecules.)

In conclusion, it is clear that this is only the second step (Ref. [2] being the first) in the development of a general

TABLE I. Convergence study of the scattering amplitude for the triplet state at $k=0.5$; R is the radial cutoff and N is the number of elements. Results are compared with a partial-wave calculation using six partial waves.

R	N	$\|f^-_{0.5}(0)\|^2$	$\|f^-_{0.5}(\pi/4)\|^2$	$\|f^-_{0.5}(\pi/2)\|^2$	$\|f^-_{0.5}(3\pi/4)\|^2$	$\|f^-_{0.5}(\pi)\|^2$
8	4×4	2.90	2.78	3.18	4.28	4.87
8	6×6	2.87	2.74	3.14	4.23	4.83
8	8×8	2.87	2.74	3.14	4.23	4.83
10	6×6	2.92	2.76	3.14	4.27	4.89
10	8×8	2.92	2.76	3.14	4.27	4.89
10	10×10	2.92	2.76	3.14	4.27	4.89
15	8×8	2.97	2.78	3.14	4.33	4.98
15	10×10	2.98	2.78	3.14	4.33	4.98
15	12×12	2.98	2.78	3.14	4.33	4.98
20	10×10	2.98	2.77	3.14	4.35	5.02
20	12×12	2.98	2.77	3.14	4.35	5.02
25	12×12	2.98	2.77	3.14	4.35	5.02
Partial wave		2.99	2.78	3.14	4.35	5.02

TABLE II. Convergence study of the scattering amplitude for the singlet state at $k=1.0$; R is the radial cutoff and N is the number of elements. Results are compared with a partial-wave calculation using nine partial waves.

R	N	$\lvert f_{1.0}^{+}(0)\rvert^2$	$\lvert f_{1.0}^{+}(\pi/4)\rvert^2$	$\lvert f_{1.0}^{+}(\pi/2)\rvert^2$	$\lvert f_{1.0}^{+}(3\pi/4)\rvert^2$	$\lvert f_{1.0}^{+}(\pi)\rvert^2$
6	4×4	0.087	0.116	0.259	0.385	0.427
6	6×6	0.078	0.120	0.283	0.422	0.468
6	8×8	0.078	0.120	0.284	0.424	0.470
9	6×6	0.078	0.128	0.284	0.424	0.471
9	8×8	0.091	0.130	0.307	0.464	0.518
9	10×10	0.091	0.130	0.306	0.463	0.516
12	8×8	0.104	0.134	0.299	0.448	0.500
12	10×10	0.091	0.127	0.305	0.465	0.521
12	12×12	0.091	0.127	0.305	0.466	0.522
15	12×12	0.091	0.127	0.306	0.468	0.526
Partial wave		0.091	0.126	0.305	0.470	0.528

methodology for calculating the full scattering amplitude directly. The successful inclusion of correlation in electron-hydrogen scattering will constitute the third important step. These studies will hopefully act as a guide to the generalization of these ideas and methods to deal with scattering (elastic and inelastic) from many-electron targets. Such developments will obviously take time and require the work of many investigators. It is clearly naive to expect such developments to be immediately competitive with more mature (partial-wave) methods, such as the R-matrix, which have developed over many years and involved many man-years of work. However, in time it is not unreasonable to think the technology of directly calculating the full scattering amplitude may become one of the standard approaches.

VII. ACKNOWLEDGMENT

We thank Anand Bhatia for providing partial-wave results for the static-exchange approximation.

---

[1] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions*, 3rd ed. (Oxford University, London, 1965).

[2] J. Shertzer and A. Temkin, Phys. Rev. A **63**, 062714 (2001).

[3] K. J. Bathe, *Finite Element Procedures in Engineering Analysis* (Prentice-Hall, Englewood Cliffs, NJ, 1982).

[4] F. S. Levin and J. Shertzer, Phys. Rev. Lett. **61**, 1089 (1988); J. Botero and J. Shertzer, Phys. Rev. A **46**, R1155 (1992); J. Shertzer and J. Botero, *ibid.* **49**, 3673 (1994).