Generating Phase Shifts from Pseudostate Energy Shifts

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A simple way to generate low energy phase shifts for elastic scattering using bound-state calculations is postulated, validated, and applied to the problem of $e^+\text{-Mg}$ scattering. The essence of the method is to use the energy shift between a small reference calculation and the largest possible calculation of the lowest energy pseudostate to tune a semiempirical optical potential. The $\ell = 1$ partial wave for $e^+\text{-Mg}$ scattering is predicted to have a shape resonance at an energy of about 0.13 eV. The value of $Z_{\text{eff}}$ at the center of the resonance is about 1500.

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Generating Phase Shifts from Pseudostate Energy Shifts

One of the most technically demanding problems in quantum physics is the scattering problem, i.e., the prediction of the reaction probabilities when two objects collide [1]. The underlying difficulty lies in the unbounded nature of the wave function. This leads to a variety of computational and analytic complications that are simply absent in bound-state calculations, e.g., the Schwartz singularities that occur in the Kohn variational method for scattering [2,3].

One approach to solve scattering problems is to use bound-state methods. There are many examples of such approaches, one of the most popular being the $R$-matrix methods that use the solutions of the Schrödinger equation in a finite sized cavity to determine the behavior of the wave function in the interaction region [1]. The total wave function is then constructed by splicing the inner wave function onto the asymptotic wave function.

However, despite the considerable activity in this area, there are a number of problems that are beyond resolution. The $e^+$-atom problem is a notoriously hard numerical problem since the atomic electrons tend to localize around the positron, thus giving a very slowly convergent partial wave expansion of the wave function inside the interaction region (this should not be confused with the partial wave expansion of the wave function inside the interaction region) [4–7]. For example, the dimensionality of the equations to be solved to achieve a given accuracy are about 5 times larger for $e^+\text{-H}$ scattering than for $e^-\text{-H}$ scattering. At present, there are a number of positron collision problems that are simply inaccessible with existing approaches [7].

This Letter had its origin in a particular scattering problem, namely, the determination of the near threshold phase shifts for positron scattering from magnesium. The dimensions of the secular equations for bound-state calculations on group II atoms are very large, for example, a configuration interaction (CI) calculation of the $e^+\text{Ca}^\text{2P^o}$ state had equations of dimension 874 448 [8]. The idea behind the current method lies closest to the box $R$-matrix method [9] which is exploited in quantum Monte Carlo (QMC) calculations of scattering [10]. In the QMC calculations, one extracts the phase shift by comparing the zero point energy of a finite size cavity to the energy of the system wave function in the same cavity. In the present method, the phase shift is extracted from the energy shift when a reference wave function is enlarged in size to account for short and long range correlations. The approach does depend on the ability to obtain the lowest eigenvalues of large symmetric matrices that arise in electronic structure calculations [11].

An alternative would be to use the CI-Kohn approach [12] to determine the phase shifts. Application to $e^+\text{-Mg}$ scattering in the $2P^o$ channel leads to linear equations that are simply too large ($\approx 1\times10^6$) to be solved by direct methods. Iterative methods do exist, but there are no robust methods that absolutely guarantee convergence [13]. It might be eventually possible to develop an efficient linear solver for the class of problems that arise from a basis set treatment of quantum scattering. However, this approach was not explored since it proved possible to extract the phase shifts from the Mg ground state and $e^+\text{-Mg}$ pseudostate energies with very little effort. The energy shift method as applied to $e^+\text{-Mg}$ scattering in the $2P^o$ symmetry was able to predict the existence of a prominent shape resonance at 0.13 eV. This is noteworthy since shape resonances are currently unknown in $e^+$-atom or $e^+$-molecule scattering [14].

Our method proceeds as follows. The initial calculation uses a reference CI wave function of product form, viz.

$$\Psi_0 = \Phi_{gs}(X)\phi_0(r).$$

The wave function of the parent atom is $\Phi_{gs}(X)$, where $X$ is the collective set of target coordinates. The wave function of the projectile is $\phi_0(r)$ and is constructed from a linear combination of a finite number of square-integrable functions, $\{\Omega_i(r)\}$, designed to give a good representation
of the wave function in a bounded interaction region. The energy expectation, \( E_0 \), is given by
\[
E_0 = \langle \Psi_0 | H_{\text{exact}} | \Psi_0 \rangle. \tag{2}
\]

The wave function \( \Psi_0 \) is then augmented by a very large number of additional functions to represent the correlations between the projectile and the target constituents. This augmented trial function is
\[
\Psi_1 = \Phi_{\text{gs}}(X) \phi_0(r) + \sum_{i,j} c_{ij} \Phi_i(X) \phi_j(r). \tag{3}
\]

The trial wave function \( \Psi_1 \) is used to diagonalize \( H_{\text{exact}} \) giving an energy of \( E_1 \). The additional functions do not include any that have the same subasymmetries as those comprising \( \Psi_0 \).

Next, a semiempirical potential of the form
\[
V_{\text{pol}} = -\frac{\alpha_d}{2r^6}[1 - \exp(-r^6/\rho^6)] \tag{4}
\]
is added to \( H_{\text{exact}} \) (\( \alpha_d \) is the dipole polarizability). This potential only acts on the scattering projectile. Then \( \Psi_0 \) is used to diagonalize \( H_{\text{exact}} + V_{\text{pol}} \) giving \( E_{\text{pol}} \). The wave function, \( \Psi_0' = \Phi_{\text{gs}}(X) \phi_0'(r) \), is constructed with \( \phi_0'(r) \) chosen as a linear combination of \( \{\Omega_i(r)\} \). The parameter \( \rho \) in Eq. (4) is adjusted until \( E_{\text{pol}} = E_1 \). Figure 1 is a schematic diagram outlining this procedure.

In the final stage, the basis \( \{\Omega_i(r)\} \) is enlarged to permit continuum solutions, giving
\[
\Psi_{\text{continuum}} = \Phi_{\text{gs}}(X) \phi_{\text{continuum}}(r). \tag{5}
\]
The phase shifts of \( H_{\text{exact}} + V_{\text{pol}} \) are then obtained by using \( \Psi_{\text{continuum}} \) as the scattering wave function.

The method is verified by computing the low energy phase shifts and annihilation parameters for \( s \)-wave \( e^+\)-H scattering. The reference wave function, \( \Psi_0 \), consisted of the hydrogen atom ground state multiplied by a positron basis of 30 \( \ell = 0 \) Laguerre type orbitals. The energy and annihilation rate of \( \Psi_0 \) are given in Table I.

A sequence of successively larger calculations with \( L \) (the maximum \( \ell \) value of any orbital included in the basis) were done up to \( L = 12 \). The energies at a given \( L \), \( \langle E \rangle_L \), and annihilation rates, \( \langle \Gamma \rangle_L \), are given in Table I. A major problem affecting CI calculations of positron-atom interactions is the slow convergence of the energy with \( L \) [5,6,15]. One way to determine the \( L \rightarrow \infty \) energy, \( \langle E \rangle_\infty \), is to make use of an asymptotic analysis. It has been shown that successive increments, \( \Delta E_L = \langle E \rangle_L - \langle E \rangle_{L-1} \), to the energy can be written as an inverse power series [6,16–20], viz.
\[
\Delta E_L = \frac{A_E}{(L + \frac{1}{2})^4} + \frac{B_E}{(L + \frac{1}{2})^5} + \frac{C_E}{(L + \frac{1}{2})^6} + \ldots \tag{6}
\]

The \( L \rightarrow \infty \) limits have been determined by fitting sets of \( \langle E \rangle_L \) values to asymptotic series with either 1, 2, or 3 terms. The factors, \( A_E, B_E, \) and \( C_E \) for the 3-term expansion are determined at a particular \( L \) from 4 successive energies \( \langle E \rangle_{L-3}, \langle E \rangle_{L-2}, \langle E \rangle_{L-1}, \) and \( \langle E \rangle_L \). The series is summed to \( \infty \) once the linear factors have been determined and the \( L \rightarrow \infty \) limits are given in Table I.

The trial function \( \Psi_0 \) was then used to diagonalize the Hamiltonian with an additional polarization potential (\( \alpha_d = 4.5a_0^6 \)). The energy from this calculation matches the 3-term extrapolation in Table I when \( \rho = 2.0495a_0 \). This value of \( \rho \) is close to a value of \( \rho = 2.051a_0 \) that was obtained when a polarization potential of this form was tuned to an exact phase shift in a semiempirical investigation of \( e^+\)-H scattering [21]. The phase shifts obtained by integrating the Schrödinger equation for the model Hamiltonian with \( \rho = 2.0495a_0 \) are depicted in Fig. 2 and the level of agreement with the close to exact phase shifts could hardly be better.

Besides obtaining phase shifts, this procedure was used to determine the annihilation parameter, \( Z_{\text{eff}} \). In this case, the extrapolation to the \( L \rightarrow \infty \) limit was done with an asymptotic series similar as Eq. (6) but with the leading order starting as \( A_{\Gamma}/(L + 1/2)^2 \). The ratio between the annihilation rates calculated with \( \Psi_0 \) and \( \Psi_1 \) can be equa-

| Table I. | Results of CI calculations for the \( ^1S^\pi \) symmetry of \( e^+\)H for a series of \( L \). The number of electron (\( N_e \)) and positron (\( N_p \)) orbitals are listed. The total number of two-body functions in the CI basis are in the \( N_{\text{CI}} \) column. Energies are given in Hartree while the spin-averaged annihilation rates (\( \Gamma \)) are given in units of \( 10^9 \) s\(^{-1} \). The energy values for the tuned \( \Psi_0 \) is for the tuned \( V_{\text{pol}} \).
<table>
<thead>
<tr>
<th>( L )</th>
<th>( N_e )</th>
<th>( N_p )</th>
<th>( N_{\text{CI}} )</th>
<th>( \langle E \rangle_L )</th>
<th>( \langle \Gamma \rangle_L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Psi_0 )</td>
<td>1</td>
<td>30</td>
<td>30</td>
<td>-0.49772560</td>
<td>0.00089605</td>
</tr>
<tr>
<td>9</td>
<td>250</td>
<td>259</td>
<td>6511</td>
<td>-0.49797210</td>
<td>0.0040914253</td>
</tr>
<tr>
<td>10</td>
<td>274</td>
<td>283</td>
<td>7087</td>
<td>-0.49797276</td>
<td>0.0042047713</td>
</tr>
<tr>
<td>11</td>
<td>298</td>
<td>307</td>
<td>7663</td>
<td>-0.49797255</td>
<td>0.0042994659</td>
</tr>
<tr>
<td>12</td>
<td>322</td>
<td>331</td>
<td>8239</td>
<td>-0.49797236</td>
<td>0.0043795165</td>
</tr>
</tbody>
</table>

The extrapolations to the \( L \rightarrow \infty \) limits use Eq. (6).
ted with the enhancement factor, \( G \), for s-wave \( e^+\)-H scattering [21]. The enhancement factor of \( G = 5.95 \) is within 1.5% of the enhancement factor chosen by normalization to an accurate \( T \)-matrix close coupling calculation [21,22]. The predicted \( Z_{\text{eff}} \), although not shown, lie within 5% of those of Bhatia et al. [23] over the \( k \in [0, 0.7]a_0^{-1} \) range.

This approach to computing the phase shifts was applied to the determination of \( e^+\)-Mg scattering in the \( L_T = 1 \) partial wave. The treatment of Mg requires the use of a frozen core approximation whose details have been discussed elsewhere [6,24], so only a brief description is given here. The model Hamiltonian is based on a Hartree-Fock (HF) wave function for the Mg ground state. The impact of the direct and exchange part of the HF core interactions on the active particles are computed exactly. One- and two-body core-polarization potentials are then added to the potential. The adjustable parameters of the core-polarization potential are defined by reference to the spectrum of Mg\(^{2+}\) [24].

The \( e^+\)Mg CI basis was constructed by letting the two electrons and the positron form all the possible configurations with a total angular momentum of \( L_T = 1 \), with the two electrons in a spin-singlet state, subject to the selection rules,

\[
\max(\ell_0, \ell_1, \ell_2) \leq L, \quad \min(\ell_1, \ell_2) \leq L_{\text{int}}, \quad (-1)^{(\ell_0 + \ell_1 + \ell_2)} = -1. \tag{9}
\]

In these rules \( \ell_0 \), \( \ell_1 \), and \( \ell_2 \) are, respectively, the orbital angular momenta of the positron and the two electrons.

The Hamiltonian for the \( e^+\)Mg \( ^2P^o \) state was diagonalized in a CI basis constructed from a large number of single particle orbitals, including orbitals up to \( \ell = 14 \). The two electrons were in a spin-singlet state. There was a minimum of 14 radial basis functions for each \( \ell \). There were 20 \( \ell = 1 \) positron orbitals. The largest calculation was performed with \( L = 14 \) and \( L_{\text{int}} = 3 \). The parameter \( L_{\text{int}} \) was set to \( L_{\text{int}} = 3 \) since this is mainly concerned with describing the more quickly converging electron-electron correlations [24]. The secular equations were solved with the Davidson algorithm [11].

First, it is necessary to get the Mg ground state energy in this basis. The limitation \( L_{\text{int}} = 3 \) means that only a single electron in the model atom can have \( \ell > 3 \). Translating this to an equivalent CI calculation for the Mg ground state resulted in an energy of \( E = -0.83285190 \) Hartree (energy given relative to the Mg\(^{2+}\) core).

The energy and annihilation rate of the \( e^+\)Mg \( ^2P^o \) state as a function of \( L \) are given in Table II. Figure 3 shows the running estimates of \( \langle E \rangle_\infty \) with the \( L \rightarrow \infty \) extrapolations as a function of \( L \). None of calculations indicate the existence of a bound state, but the energy shift algorithm has to be applied to determine whether this is due to the finite basis size.

A polarization potential given by Eq. (4) with \( \alpha_p = 72a_0^3 \) [21,24] (the Mg ground state polarizability) was added to the original Hamiltonian and \( \rho \) was tuned until an energy shift of 0.003588 (= -0.82886332 + 0.82525710) Hartree was achieved. Figure 4 shows the elastic cross section for \( e^+\)-Mg scattering below the Ps-formation threshold (at \( k = 0.25a_0^{-1} \)). The cutoff parameters in Eq. (4) were set to \( \rho = 3.032a_0 \) for the s-wave [21] and \( \rho = 2.573a_0 \) (derived here) for all the other partial waves. The elastic cross section in this energy region is almost completely dominated by a \( p \)-wave shape resonance with its center near \( k = 0.10a_0^{-1} \).

The existence and position of the resonance is independent of the exact form of \( V_{\text{pol}} \). Alternate calculations were done using

\[
V_{\rho,s} = -\frac{\alpha_p}{2r^4}[1 - \exp(-r^4/\rho^4)] - \frac{\alpha_p}{2r^4}[1 - \exp(-r^4/\rho^4)]
\]

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The existence and position of the resonance is independent of the exact form of \( V_{\text{pol}} \). Alternate calculations were done using

\[
V_{\rho,s} = -\frac{\alpha_p}{2(r^2 + \rho^2)^3}
\]

TABLE II. Results of CI calculations for the \( ^2P^o \) state of \( e^+\)Mg. The threshold for binding is \( -0.83285190 \) Hartree. Most aspects of the table follow those of Table I.

<table>
<thead>
<tr>
<th>( L )</th>
<th>( N_e )</th>
<th>( N_p )</th>
<th>( N_{\text{CI}} )</th>
<th>( \langle E \rangle_L )</th>
<th>( \langle \Gamma \rangle_L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Psi_0 )</td>
<td>20</td>
<td>20</td>
<td>0.82525710</td>
<td>0.029828</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>172</td>
<td>174</td>
<td>651006</td>
<td>-0.82806307</td>
<td>0.12800208</td>
</tr>
<tr>
<td>12</td>
<td>186</td>
<td>188</td>
<td>724506</td>
<td>-0.82817969</td>
<td>0.14306354</td>
</tr>
<tr>
<td>13</td>
<td>200</td>
<td>202</td>
<td>798006</td>
<td>-0.82827695</td>
<td>0.15662562</td>
</tr>
<tr>
<td>14</td>
<td>214</td>
<td>216</td>
<td>871506</td>
<td>-0.82835799</td>
<td>0.16873961</td>
</tr>
</tbody>
</table>

\( L \rightarrow \infty \) extrapolations

1-term Eq. (6) | -0.82871101 | 0.338475 |
2-term Eq. (6) | -0.82884022 | 0.373490 |
3-term Eq. (6) | -0.82886332 | 0.315877 |
The directly calculated energy is shown as the solid line while
the $L \rightarrow \infty$ limits using Eq. (6) with 1, 2, or 3 terms are shown
as the dashed lines. The Mg + $e^+$ dissociation threshold is shown
as the horizontal line.

where $\alpha_q = 814a_0^3$ [25] is the quadrupole polarizability.
The three different calculations (see Fig. 4) give a resonance at the same position. Using an enhancement factor of
$G = 12.5 = 0.3735/0.02983$ for valence annihilation gave a value of Z_eff = 1500 at the resonance peak.

To summarize, a novel technique has been used to
demonstrate the existence of a shape resonance in $e^+\text{Mg}$
scattering which has the virtue of being readily detectable.
The phase shift calculations were performed using a semi-
empirical method [21] with a tuned potential. The tuning of
an optical potential to features such as bound-state energies
and resonance positions is well known. The novel feature
of the present approach is that the optical potential is tuned
to the energy shift of a positive energy pseudostate. This
approach to the calculation of phase shifts can be applied to
other scattering systems which are inaccessible with exist-
ing techniques.

The calculations were performed on Linux clusters
hosted at the SDSU Computational Sciences Research Center and the South Australian Partnership for
Advanced Computing. The authors would like to thank to
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Dr. R. McEachran for a critical reading of the manuscript.

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