Excited States of Positronic Atoms

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Generating phase shifts from pseudo state 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^+-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 pseudo-state to tune a semi-empirical optical potential. The $\ell = 1$ partial wave for e^+-Mg scattering is predicted to have a shape resonance at an energy of about 0.13 eV. The value of $Z_{\rm eff}$ at the center of the resonance is about 1500.

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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 Schrodinger equation in a finite sized cavity to determine the behaviour 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 asymptotic wave function) [4–7]. For example, the dimensionality of the equations to be solved to achieve a given accuracy are about 5 times larger for e^+-H scattering than for e^--H scattering. At present, there are a number of positron collision problems that are simply inaccessible with existing approaches [7].

This article had its origin in a particular scattering problem, namely the determination of the near threshold phase shifts for positron scattering from the di-valent group II and IIB atoms. The dimension of the secular equations for bound state calculation on such systems are very large, for example a CI calculation of the e^+Ca ^{2}P$^{\rm o}$ state resulted in equations of dimension 874,448 [8]. Application of the CI-Kohn approach [9] to determine the phase shifts for e^+-Mg scattering in the ^{2}P$^{\rm o}$ channel would result in linear equations that are simply too large ($\approx 1,000,000$) to be solved by direct methods. Iterative methods do exist, but there are no robust methods that absolutely guarantee convergence [10]. It is likely that the development of an efficient linear solver for the class of problems that arise from a basis set treatment of quantum scattering would involve a good deal of initial effort and experimentation. There is, however, a great deal of experience in obtaining the lowest eigenvalues of the large symmetric matrices that arise in electronic structure calculations [11].

The idea behind the current method lies closest to the trivial R-matrix method [12] which is exploited in Quantum Monte Carlo (QMC) calculations of scattering [13]. In the QMC, 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 method is applied to e^+-Mg scattering in the ^{2}P$^{\rm o}$ symmetry and used to predict the existence of a prominent shape resonance at 0.13 eV incident energy. 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

$$\Psi_0 = \Phi_{\rm gs}(\mathbf{X})\phi_0(\mathbf{r}) \ . \tag{1}$$

The wave function of the parent atom is $\Phi_{\rm gs}(\mathbf{X})$ where $\mathbf{X}$ is the collective set of target coordinates. The wave function of the projectile is $\phi_0(\mathbf{r})$ and is constructed from a linear combination of a finite number of square-integrable functions, $\{\Omega_i(\mathbf{r})\}$ designed to give a good representation of the wave function in a bounded interaction region. The energy expectation, E_0 is given by

$$E_0 = \langle\Psi_0|H_{\rm exact}|\Psi_0\rangle. \tag{2}$$

The wave function Ψ_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

$$\Psi_1 = \Phi_{\rm gs}(\mathbf{X})\phi_0(\mathbf{r}) + \sum_{i,j} c_{i,j}\Phi_{\rm i}(\mathbf{X})\phi_j(\mathbf{r}) \ . \qquad (3)$$

The trial wave function Ψ_1 is used to diagonalize $H_{\rm exact}$ giving an energy of E_1. The additional functions do not include any that have the same sub-symmetries as those comprising Ψ_0.

Next, a semi-empirical potential of the form

$$V_{\rm pol} = -\frac{\alpha_d}{2r^4}\left(1-\exp(-r^6/\rho^6)\right) \ , \qquad (4)$$

is added to $H_{\rm exact}$ (α_d is the dipole polarizability). This potential only acts on the scattering projectile. Then Ψ_0' is used to diagonalize $H_{\rm exact} + V_{\rm pol}$ giving $E_{\rm pol}$. The wave function, $\Psi_0' = \Phi_{\rm gs}(\mathbf{X})\phi_0'(\mathbf{r})$ is constructed with $\phi_0'(\mathbf{r})$ chosen as a linear combination of $\{\Omega_i(\mathbf{r})\}$. The parameter ρ in eq. (4) is adjusted until $E_{\rm pol} = E_1$. Figure 1 is a schematic diagram outlining this procedure.

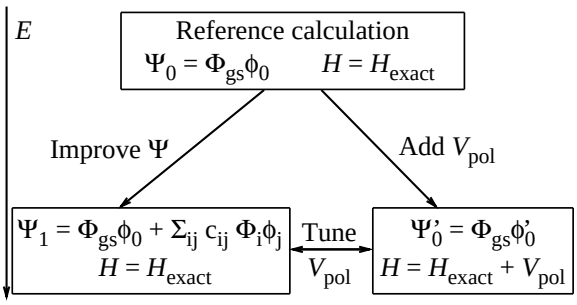

FIG. 1: Schematic diagram showing the strategy used to tune the semi-empirical optical potential.

In the final stage, the basis $\{\Omega_i(\mathbf{r})\}$ is enlarged to permit continuum solutions, giving

$$\Psi_{\rm continuum} = \Phi_{\rm gs}(\mathbf{X})\phi_{\rm continuum}(\mathbf{r}) \ . \qquad (5)$$

The phase shifts of $H_{\rm exact} + V_{\rm pol}$ are then obtained by using $\Psi_{\rm continuum}$ 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, Ψ_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 Ψ_0 are given in Table I.

A sequence of successively larger calculations with L (the maximum ℓ 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

TABLE I: Results of CI calculations for the $^1{\rm S}^{\rm e}$ 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_{CI} column. Energies are given in Hartree while spin-averaged annihilation rate (Γ) are given in units of 10^9 s^{-1} (Γ for Ψ_0 is for the tuned $V_{\rm pol}$). The extrapolations to the $L\to\infty$ limits use eq. (6).

L	N_e	N_p	N_{CI}	$\langle E\rangle_L$	$\langle\Gamma\rangle_L$
Ψ_0	1	30	30	-0.49772560	0.00089605
9	250	259	6511	-0.49797210	0.0040914253
10	274	283	7087	-0.49797276	0.0042047713
11	298	307	7663	-0.49797325	0.0042994659
12	322	331	8239	-0.49797360	0.0043795165
$L\to\infty$ extrapolations					
1-term eq. (6)				-0.49797439	0.005341190
2-term eq. (6)				-0.49797509	0.005334089
3-term eq. (6)				-0.49797509	0.005264739

$L\to\infty$ 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 written as an inverse power series [6, 16–20], viz

$$\Delta E_L \approx \frac{A_E}{(L+\frac{1}{2})^4} + \frac{B_E}{(L+\frac{1}{2})^5} + \frac{C_E}{(L+\frac{1}{2})^6} + \dots \ . \qquad (6)$$

The $L\to\infty$ 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 ∞ once the linear factors have been determined and the $L\to\infty$ limits are given in Table I).

The trial function Ψ_0 was then used to diagonalize the Hamiltonian with an additional polarization potential ($\alpha_d = 4.5\ a_0^3$). The energy from this calculation matches the 3-term extrapolation in Table I when $\rho = 2.0495\ a_0$. This value of ρ is close to a value of $\rho = 2.051\ a_0$ that was obtained when a polarization potential of this form was tuned to an exact phase shift in a semi-empirical investigation of e^+-H scattering [21]. The phase shifts obtained by integrating the Schrodinger equation for the model Hamiltonian with $\rho = 2.0495\ a_0$ are depicted in Figure 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, $Z_{\rm eff}$. In this case the extrapolation to the $L\to\infty$ limits were 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 Ψ_0 and Ψ_1 can be equated 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 cho-

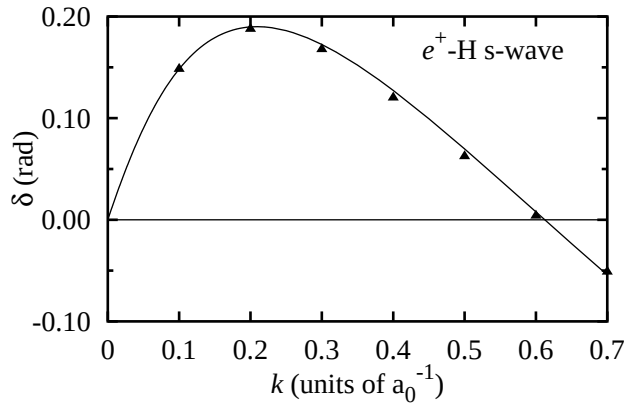

FIG. 2: The phase shift for e^+-H scattering in the s-wave as a function of k (in units of a_0^{-1}). The solid line shows the results of the present calculation while the triangles show the close to exact phase shifts of Bhatia *et al* [22].

sen by normalization to an accurate T-matrix close coupling calculation [21, 23]. The predicted $Z_{\rm eff}$, although not shown, lie within 5% of those of Bhatia *et al* [24] 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, 25], 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^+ [25].

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

$$\max(\ell_0, \ell_1, \ell_2) \;\le\; L \;, \tag{7}$$

$$\min(\ell_1, \ell_2) \;\le\; L_{\rm int} \;, \tag{8}$$

$$(-1)^{(\ell_0+\ell_1+\ell_2)} \;=\; -1 \;. \tag{9}$$

In these rules ℓ_0, ℓ_1 and ℓ_2 are respectively the orbital angular momenta of the positron and the two electrons.

The Hamiltonian for the e^+Mg ^{2}P^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 ℓ. There were 20 $\ell = 1$ positron orbitals. The largest calculation was performed with $L = 14$ and $L_{\rm int} = 3$. The parameter $L_{\rm int}$ was set to $L_{\rm int} = 3$ since this is mainly concerned with describing the more quickly converging electron-electron correlations [25]. The secular equations were solved with the Davidson algorithm [11].

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

L	N_e	N_p	N_{CI}	$\langle E\rangle_L$	$\langle\Gamma\rangle_L$
Ψ_0		20	20	-0.82525710	0.029828
11	172	174	651006	-0.82806307	0.12800208
12	186	188	724506	-0.82817969	0.14306354
13	200	202	798006	-0.82827695	0.15662562
14	214	216	871506	-0.82835799	0.16873961
$L \to \infty$ 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

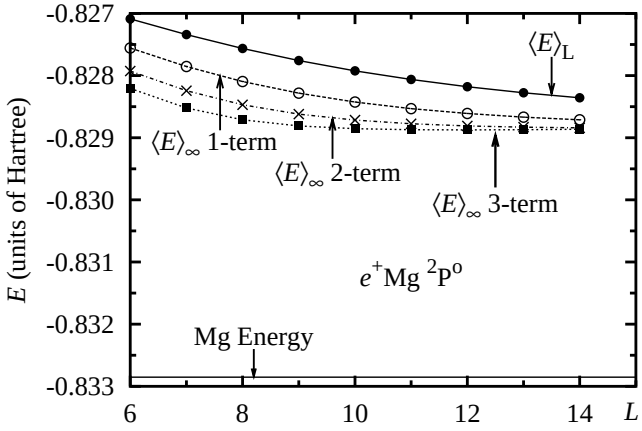

FIG. 3: The energy of the ^{2}P^o state of e^+Mg as a function of L. The directly calculated energy is shown as the solid line while the $L \to \infty$ limits using eq. (6) with 1, 2 or 3 terms are shown as the dashed lines. The Mg + e^+ dissociation threshold is shown as the horizontal line.

First, it is necessary to get the Mg ground state energy in this basis. The limitation $L_{\rm int} = 3$ 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 of $E = -0.83285190$ Hartree (energy given relative to the Mg^{2+} core).

The energy and annihilation rate of the e^+Mg ^{2}P^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 $L \to \infty$ 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 $\alpha_d =$

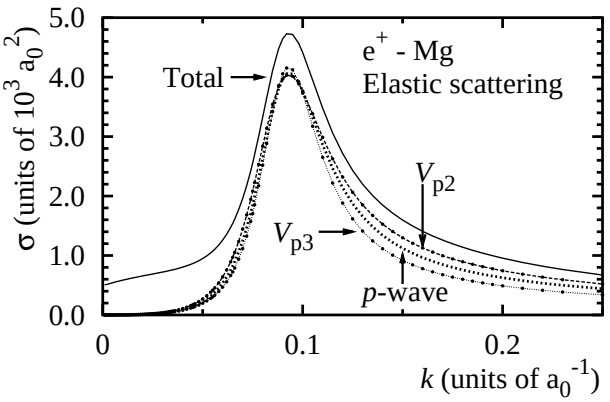

FIG. 4: The elastic scattering cross section for e^+-Mg scattering in the energy region below the Ps-formation threshold. The solid line shows the total cross section while the dashed curves shows the $\ell = 1$ partial cross section. The curves labelled $V_{\rm p2}$ and $V_{\rm p3}$ give the $\ell = 1$ partial cross section using alternate forms of the polarization potential.

72 a_0^3 [21, 25] (the Mg ground state polarizability) was added to original Hamiltonian and ρ 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 $k \approx 0.25\ a_0^{-1}$). The cutoff parameters in eq. (4) were set to $\rho = 3.032\ a_0$ for the s-wave [21] and $\rho = 2.573\ a_0$ (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 $k \approx 0.10\ a_0^{-1}$.

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

$$V_{\rm p2} = \frac{-\alpha_d}{2r^4}(1-\exp(-r^6/\rho^6)) - \frac{\alpha_q}{2r^6}(1-\exp(-r^8/\rho^8))$$
$$V_{\rm p3} = \frac{-\alpha_d r^2}{2(r^2+\rho^2)^3}\ , \qquad (10)$$

where $\alpha_q = 814\ a_0^5$ [26] is the quadrupole polarizability. The three different calculations (see Figure 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 $Z_{\rm eff} \approx 1500$ at the resonance peak.

To summarize, a novel technique has been used to demonstrate the existence of a shape resonance in e^+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 pseudo-state. This approach to the calculation of phase shifts can be applied to other scattering systems which are inaccessible with existing techniques.

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