

Variational calculation of positron-atom scattering using configuration-interaction-type wave functions

M. W. J. Bromley* and J. Mitroy†

Faculty of SITE, Northern Territory University, Darwin, Northern Territory 0909, Australia

(Received 18 January 2003; revised manuscript received 27 March 2003; published 20 June 2003)

The Kohn variational method is used with a configuration-interaction (CI)-type wave function to determine the phase shifts and Z_{eff} for positron-copper scattering. The method is first tested for positron-hydrogen scattering and it is found to give phase shifts and Z_{eff} within 1–2% of the best previous calculations. Although the phase shift for Cu converged more slowly with L_{max} (the maximum angular momentum of the electron and positron orbitals included in the short-range basis), it was still possible to get reliable estimates of the phase shifts by including orbitals with $\ell \leq 18$ and the use of an extrapolation technique. Calculation of Z_{eff} was more problematic since the convergence of Z_{eff} with respect to L_{max} was very slow. Despite the uncertainties, it was clear that the p -wave phase shift was showing signs of forming a shape resonance at about 0.5 eV incident energy. This resulted in a p -wave contribution to Z_{eff} that was larger than that of the s wave for $k \geq 0.1 a_0^{-1}$. Speculative calculations based upon a model potential suggest that a p -wave shape resonance centered at thermal energies, e.g., about 0.025 eV, could result in a thermally averaged Z_{eff} exceeding 10 000.

DOI: 10.1103/PhysRevA.67.062709

PACS number(s): 34.85.+x, 36.10.–k

I. INTRODUCTION

In one respect, the calculation of positron-atom scattering is simpler than electron-atom scattering. There is no exchange interaction between the positron and target electrons. But in every other respect, the theoretical treatment of positron-atom scattering is a more difficult proposition than electron-atom scattering. The reason for this lies in the attractive nature of the positron-electron interaction, which leads to very strong electron-positron correlations. These correlations manifest themselves in a close-coupling (CC) expansion that converges much more slowly (than the equivalent electron-atom CC expansion) and furthermore, the formation of an electron-positron bound state, namely, positronium (Ps) is also possible above certain energies.

One way to avoid the slow convergence of the CC expansion is to explicitly include Ps formation channels into the CC expansion. The inclusion of Ps states into the channel space carries its own set of difficulties associated with the calculation of the matrix elements between states in the positron-atom and positronium-(residual ion) groups of channels. In the case of positron-hydrogen scattering, these difficulties have been solved and quite large calculations can now be performed routinely [1–3]. The generalization of such techniques to treat scattering from the alkali atoms is not trivial, one area of difficulty with the Ps channels being the treatment of the exchange interaction between the positronium atom and the residual ion. Existing calculations on these systems have largely ignored these issues [4,5].

In this work, the Kohn variational method is used to study positron-atom scattering with a configuration-interaction

(CI)-type basis that has the electron and positron orbitals centered at the nucleus. The drawback of this approach is the slow convergence of the phase shifts with L_{max} , the maximum ℓ value of the orbitals included in the CC expansion, and the restriction that the method can only sensibly be applied at energies below the Ps-formation threshold. For the positron-hydrogen system it is necessary to explicitly include orbitals with $\ell = 15$ to get the phase shifts that are converged at the 2–3% level [6,7]. The difficulties with slow convergence are handled by simply accepting that the trial wave functions will have a basis of very large dimension and developing procedures to perform the necessary calculations as accurately and efficiently as possible. This turned out to be not too difficult since an existing CI program developed to study positronic atoms in a single-center basis was readily adapted to perform the necessary calculations [8].

The restriction that the method can only be sensibly applied at energies below the Ps-formation threshold is not a cause for great concern since there are very few high precision calculations of positron-atom scattering in the low energy region, and therefore any information that can be obtained is extremely useful. Quite simply, apart from hydrogen and helium [9–11], it is difficult to name another atom for which it could be asserted that the positron scattering length is known with an accuracy of $\pm 5\%$. Indeed, some of the most reliable estimates of positron atom scattering lengths are derived a simple model potential analysis of group II and group IIB elements [12,13]. These calculations are believed to be reliable since the model potentials were tuned to the positron affinities obtained from some large scale bound-state calculations [13,14]. Put succinctly, the ability to calculate the scattering observables for target systems with ionization potentials greater than 6.8 eV (the Ps binding energy) will lead to an improved understanding of the dynamics of positron-atom interactions at thermal energies. The advantage of the single-center basis is that the matrix elements of the scattering Hamiltonian can be evaluated without any approximations. Therefore, the present calcula-

*Present address: Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA; Email address: bromley@phys.ksu.edu

†Electronic address: jxm107@rsphysse.anu.edu.au

tions are not subject to the same degree of uncertainty as previous calculations on the alkali atoms [4,5].

Calculations upon two systems are reported in this work. The initial calculation for the positron-hydrogen system was used to validate our computer programs since the phase shifts and annihilation parameter Z_{eff} for this system had previously been calculated to a high degree of accuracy by a number of authors [2,9,15–19].

The other calculation on the positron-copper system was done for a number of reasons. First, this system supports a bound state, so it was worthwhile to check whether Z_{eff} was abnormally large for the system. Next, copper is a system with an ionization potential of 7.7 eV, which is not much larger than the Ps-ionization potential. So it provides a rather exacting test of the basis-set requirements to achieve convergence with respect to L_{max} . It should be noted that we had previously solved the Kohn-variational equations for e^+ -Cu scattering at zero energy [8]. In the present work those calculations are extended to 0.5 eV incident energy and the p -wave contributions to the cross section and Z_{eff} are also determined.

II. DETAILS OF THE CALCULATION

A. The model Hamiltonian

The model Hamiltonian previously used to model the positron-copper system has been discussed previously [8], so only a brief description is given here (note, the Hamiltonian for the simpler positron-hydrogen system is well known and is not detailed here). The calculations were done in the fixed core approximation and the model Hamiltonian is

$$H = -\frac{1}{2}\nabla_0^2 - \frac{1}{2}\nabla_1^2 + V_{\text{dir}}(\mathbf{r}_1) + V_{\text{exc}}(\mathbf{r}_1) + V_{p1}(\mathbf{r}_1) - V_{\text{dir}}(\mathbf{r}_0) + V_{p1}(\mathbf{r}_0) - \frac{1}{r_{01}} + V_{p2}(\mathbf{r}_1, \mathbf{r}_0). \quad (1)$$

The direct potential (V_{dir}) represents the interaction with the core, which was derived from the Hartree-Fock (HF) wave function of the neutral copper ground state computed with the program of Mitroy [20] using the optimized Slater Type Orbital (STO) set of Koga and Thakkar [21]. The core potential is attractive for an electron and repulsive for a positron. The exchange potential (V_{exc}) between the valence electrons and the HF core was computed without approximation.

The one-body polarization potential (V_{p1}) is a semiempirical polarization potential derived from an analysis of the spectrum of the parent atom. It has the functional form

$$V_{p1}(r) = \sum_{\ell m} -\frac{\alpha_d g_\ell^2(r)}{2r^4} |\ell m\rangle \langle \ell m|. \quad (2)$$

The factor α_d is the static dipole polarizability of the core and $g_\ell^2(r)$ is a cutoff function designed to make the polarization potential finite at the origin. The same cutoff function was adopted for both positron and electron and it was defined to be

$$g_\ell^2(r) = 1 - \exp(-r^6/\rho_l^6). \quad (3)$$

The Cu^+ core polarizability was chosen as $5.36a_0^3$ [22] and the cutoff parameters, ρ_l were set as $\rho_0 = 1.988a_0$, $\rho_1 = 2.03a_0$, $\rho_2 = 1.83a_0$, $\rho_3 = 1.83a_0$. For all $l > 3$, ρ_l is set to $1.91a_0$. The two-body polarization potential (V_{p2}) was

$$V_{p2}(\mathbf{r}_i, \mathbf{r}_j) = \frac{\alpha_d}{r_i^3 r_j^3} (\mathbf{r}_i \cdot \mathbf{r}_j) g_{p2}(r_i) g_{p2}(r_j), \quad (4)$$

where ρ_{p2} was set to $1.91a_0$.

B. The Kohn variational method and trial wave function

The Kohn variational method [23–25] is a commonly used method to solve the Schrodinger equation for low-energy scattering problems. It can be regarded as the continuum variant of the Rayleigh-Ritz variational method so often used for bound-state problems. The formalism presented here closely follows that outlined in the monograph of Burke and Joachain [26].

The trial wave function, with net orbital angular momentum L , adopted for the present Kohn variational calculations has the form

$$|\Psi_i; LS\rangle = \alpha_0 |\Phi_s; LS\rangle + \alpha_1 |\Phi_c; LS\rangle + \sum_{i,j} c_{ij} |\Phi_{ij}; LS\rangle, \quad (5)$$

where the first two terms are the continuum functions that are equal to the regular and irregular solutions of the free particle Schrödinger equation at large distances from the origin. They are written as

$$|\Phi_s; LS\rangle = \sum_{m_{gs}, m_s} \sum_{\mu_{gs}, \mu_s} \langle \ell_{gs} m_{gs} \ell_s m_s | LM_L \rangle \times \langle \frac{1}{2} \mu_{gs} \frac{1}{2} \mu_s | SM_S \rangle \phi_{gs}(\mathbf{r}_1) \theta_s(\mathbf{r}_0), \quad (6)$$

$$|\Phi_c; LS\rangle = \sum_{m_{gs}, m_c} \sum_{\mu_{gs}, \mu_c} \langle \ell_{gs} m_{gs} \ell_c m_c | LM_L \rangle \times \langle \frac{1}{2} \mu_{gs} \frac{1}{2} \mu_c | SM_S \rangle \phi_{gs}(\mathbf{r}_1) \theta_c(\mathbf{r}_0). \quad (7)$$

In this expression $\phi_{gs}(\mathbf{r}_1)$ is the ground-state wave function of the target atom, while $\theta_s(\mathbf{r}_0)$ and $\theta_c(\mathbf{r}_0)$ are the continuum functions. They have the radial forms

$$\theta_s(r_0) = j_\ell(kr_0), \quad (8)$$

$$\theta_c(r_0) = [1 - \exp(-\beta r_0)]^{2\ell+1} n_\ell(kr_0). \quad (9)$$

The $[1 - \exp(-\beta r_0)]$ factor is used to make the irregular solution $\theta_c(r_0)$ go to zero as $r_0 \rightarrow 0$. The factor β was set to 2.0 for the present calculations. The scattering lengths and Z_{eff} were insensitive to the precise value chosen for β . For calculations at zero energy, one is only interested in the $\ell = 0$ partial wave and in this case the continuum functions can be written as

$$\theta_s(r_0) = r_0, \quad (10)$$

$$\theta_c(r_0) = [1 - \exp(-\beta r_0)]A, \quad (11)$$

where A is the scattering length. The short-range functions are

$$|\Phi_{ij}; LS\rangle = \sum_{m_i, m_j} \sum_{\mu_i, \mu_j} \langle \ell_i m_i \ell_j m_j | LM_L \rangle \times \langle \frac{1}{2} \mu_i \frac{1}{2} \mu_j | SM_S \rangle \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_0), \quad (12)$$

where $\phi_i(\mathbf{r}_1)$ and $\phi_j(\mathbf{r}_0)$ are L^2 functions written as a linear combination of an Laguerre Type Orbitals (LTOs) or as a linear combination of LTOs and STOs. All the basis functions so far, except $|\Phi_s; LS\rangle$ and $|\Phi_c; LS\rangle$, are identical in functional form to the basis functions used in earlier CI calculations of positronic copper. Therefore, the amount of work required to adapt the program to perform scattering calculations was minimal. The major practical change was the extension of the radial grid to a maximum radius of $625a_0$. This was needed to correctly handle the long-range dipole coupling between the ground state and the first np excited state. More details about the specifics of the basis sets used for the calculations on hydrogen and copper are presented later.

The asymptotic form of the scattering wave functions can be written with a number of different normalizations depending on the form adopted for α_0 and α_1 [27]. These conditions can be written as

$$\alpha_0 = \cos \tau - \alpha_t \sin \tau, \quad (13)$$

$$\alpha_1 = \sin \tau + \alpha_t \cos \tau, \quad (14)$$

$$\alpha_t = \tan(\delta_t - \tau), \quad (15)$$

where δ_t is the phase shift of the trial wave function and $\tau \in [0, \pi/2]$. When $\tau = 0$, α_t reduces to $\tan(\delta_t)$, which is just the K -matrix element. The choice $\tau = \pi/2$ gives $\alpha_t = \cot(\delta_t)$, which is just the reciprocal of the K -matrix element. This choice of τ is sometimes called the inverse-Kohn method [28].

Besides the normalizing condition, there is another area where there is flexibility in the choice of the continuum functions. This concerns whether the functions θ_s and θ_c are orthogonalized to the short-range L^2 radial basis functions. Either choice is permissible, but we chose to orthogonalize since this simplified the evaluation of the matrix elements.

The generalized Kohn functional $\alpha_v = \tan(\delta_v - \tau)$ is given by [29]

$$\alpha_v = \alpha_t - 2 \langle \Psi_t | H - E | \Psi_t \rangle. \quad (16)$$

Applying the Kohn condition that the Kohn functional is stationary with respect to the linear variational parameters in the trial wave function leads to the linear equations

$$\frac{\partial \alpha_v}{\partial \alpha_t} = 0, \quad (17)$$

$$\frac{\partial \alpha_v}{\partial c_i} = 0. \quad (18)$$

These equations are solved to determine α_t and c_i . The error in α_v upon solving the set of $(n+1)$ linear equations is of second order with respect to variations in the trial wave function.

The annihilation parameter Z_{eff} is calculated from the scattering wave function by the identity [18,30,31],

$$Z_{\text{eff}} = 4N_e \int d^3 r_0 d^3 \tau |\hat{O}^S \Psi(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_{N_e})|^2 \delta(\mathbf{r}_0 - \mathbf{r}_1), \quad (19)$$

where $\Psi(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_{N_e})$ is the total wave function of the system and $d^3 \tau$ represents the integration over all electron coordinates. Operator \hat{O}^S is a spin projection operator that only permits annihilation to occur for electrons and positrons in a spin singlet state. In the plane-wave Born approximation, the positron wave function is written as a plane wave and the annihilation parameter is equal to the number of atomic electrons, i.e., $Z_{\text{eff}} = N_e$.

The L^2 basis was constructed by populating all the possible configurations that could be formed by letting the electron and positron populate all the orbitals subject to the selection rules,

$$\max(\ell_0, \ell_1) \leq L_{\text{max}}, \quad (20)$$

$$|\ell_0 - \ell_1| \leq L, \quad (21)$$

$$(-1)^{\ell_0 + \ell_1} = (-1)^L. \quad (22)$$

In these expressions ℓ_0 is the positron angular momentum and ℓ_1 is the electron angular momentum. It is necessary to choose a basis with a large value of L_{max} in order to obtain results close to convergence. It is well known that the attractive interaction between the electron and positron leads to localization of the atomic electrons in the vicinity of the positron [32,33]. The formation of something akin to a virtual Ps cluster leads to very slow convergence with ℓ . The convergence of Z_{eff} with respect to L_{max} is typically much slower than the phase shift [8,31].

The slow convergence of the phase shift and annihilation rate with increasing L_{max} means that an extrapolation technique must be used to estimate the $L_{\text{max}} \rightarrow \infty$ limit. Making the assumption that the successive increments to any physical observable, X_L scale as $1/L^p$ for sufficiently large L , one can write

$$X_\infty = \lim_{L_{\text{max}} \rightarrow \infty} \left(\sum_{L=0}^{L_{\text{max}}} X_L + \Delta \sum_{L=L_{\text{max}}+1}^{\infty} \frac{1}{L^p} \right). \quad (23)$$

The power series is easy to evaluate, the coefficient Δ is defined as

$$\Delta = X_{L_{\text{max}}} (L_{\text{max}})^p, \quad (24)$$

and the exponent p can be derived from

$$\left(\frac{L_{max}}{L_{max}-1}\right)^p = \frac{X_{L_{max}-1}}{X_{L_{max}}}. \quad (25)$$

Recently Gribakin and Ludlow [34] used second-order perturbation theory to show that the energy exponent p_E should be 4, while the exponent for the annihilation rate, p_Γ should be 2. Translating these results to the scattering region, this suggests that p_δ should be 4, while p_Z should be 2. In practice the exponents obtained in calculations are usually slightly smaller in magnitude than the expected values [8,13]. The extrapolation of Z_{eff} for e^+ -Cu scattering was somewhat problematic and it was not possible to directly extrapolate Z_{eff} . This point is discussed later.

For evaluating the core and valence electron contributions to Z_{eff} from Eq. (19), the following identities are used. The core annihilation rate is

$$Z_{\text{eff}}^{\text{core}} = N_k \sum_{c=1}^{N_{\text{core}}} 2(2\ell_c + 1) \sum_{i,j}^{N_p} \rho_{ij}^p \int r^2 \phi_c^2(r) \phi_i(r) \phi_j(r) dr, \quad (26)$$

where ρ_{ij}^p is the one-body positron density matrix. The density matrix is defined by

$$\begin{aligned} \rho_{ij}^p &= \langle \Psi; LS | a_i^\dagger a_j | \Psi; LS \rangle \\ &= \sum_{I,J=1}^{N_{CI}} c_I c_J \langle \Phi_{I_e, I_p}; LS | a_i^\dagger a_j | \Phi_{J_e, J_p}; LS \rangle \\ &= \sum_{I,J=1}^{N_{CI}} c_I c_J \delta_{I_e, J_e} \delta_{I_p, i} \delta_{J_p, j}. \end{aligned} \quad (27)$$

The index I_e denotes the electron orbital in configuration I . The sum over configurations includes all terms from Eq. (5) and c_I is the coefficient for configuration Φ_{I_e, I_p} . The positron indices i, j run over all the positron orbitals. The valence annihilation rate for the L partial wave is

$$\begin{aligned} Z_{\text{eff}}^{\text{valence}(L)} &= N_k \sum_{I,J=1}^{N_{CI}} c_I c_J \int r^2 \phi_{I_e}(r) \phi_{J_e}(r) \phi_{I_p}(r) \phi_{J_p}(r) dr \\ &\times \sum_{k=k_{\min}}^{k_{\max}} (2k+1) \\ &\times \langle \phi_{I_e} \phi_{I_p}; LS | \mathbf{C}^k(\hat{\mathbf{r}}_1) \cdot \mathbf{C}^k(\hat{\mathbf{r}}_0) | \phi_{J_e} \phi_{J_p}; LS \rangle. \end{aligned} \quad (28)$$

The normalization factor N_k in Eqs. (26) and (28) for $k > 0$ with the asymptotic wave functions defined by Eqs. (8) and (9) is

$$N_k = \frac{(2\ell+1)}{k(\alpha_0^2 + \alpha_1^2)}. \quad (29)$$

At $k=0$ with asymptotic wave functions written as Eqs. (10) and (11) the normalization constant is unity.

In an earlier work [8], the core and the valence annihilation parameter were presented separately. In the present work this distinction is not made. We adopt the notation that $Z_{\text{eff}}^{(L)}$ will be used to denote the contribution to the annihilation rate from the L partial wave including both core and valence contributions. We then denote Z_{eff} to be the contribution from the summed $L=0$ and $L=1$ partial waves.

C. Real or complex boundary conditions

One of the problems of the Kohn variational method as originally formulated lies in the presence of spurious singularities (sometimes called Schwartz singularities) [35] when the K -matrix is plotted as a function of energy. A good deal of attention has been devoted to the development of procedures to eliminate or otherwise handle these singularities (refer to the extensive discussions in Refs. [24,25]). One of the more ingenious ideas is to formulate the scattering problem with complex (i.e., S -matrix) boundary conditions rather than real (i.e., K -matrix) boundary conditions [36,37]. Since the complex-Kohn variational method does not seem to possess these spurious singularities it has been increasingly applied to a variety of scattering problems in the last decade [38]. The complex-Kohn method does have two drawbacks. The first is the annoyance of dealing with complex arithmetic and the second relates to the fact that the resulting S -matrix cannot be guaranteed to be unitary (it is expected to satisfy the unitarity condition with increasing accuracy as the trial wave functions is increased in size and sophistication).

The K -matrix version of the Kohn method was adopted in this work as it was found that any problems with singularities became increasingly unimportant as the size of the basis used to represent the scattering function was enlarged (Nesbet has previously commented on this point [25,39]). To illustrate this, the results of some test calculations using a model potential are presented. These are based on the earlier research of Brownstein and McKinley [40], who investigated the behavior of the Kohn variational phase shift for an attractive square well with a short-range basis consisting of a small number of STOs.

Here, a real Woods-Saxon-type potential [41] is chosen as the model potential. A square-well potential has a discontinuity, which can lead to unnecessary complications when looking at the fine details of the convergence of the Kohn solution to the exact answer. The Woods-Saxon potential is given by

$$V(r) = - \frac{V_0}{1 + \exp\left(\frac{(r-R_0)}{a}\right)}, \quad (30)$$

where we chose $V_0 = 2$, $R_0 = 1$, and $a = 0.05$.

Calculations were performed with two sets of short-range basis functions. The first was a set with four LTOs, which has exactly the same exponents as the $r^n \exp(-\lambda r)$ ($n = 1, 2, 3, 4$) STO basis of Brownstein and McKinley [40]. Since the LTO and STO basis sets span the same space, they are effectively equivalent. The second set with 28 LTOs was able to give phase shifts very close to convergence. Although the LTOs have a common exponent ($\lambda = 1.0$) and are thus mutually orthogonal, the two continuum orbitals were sub-

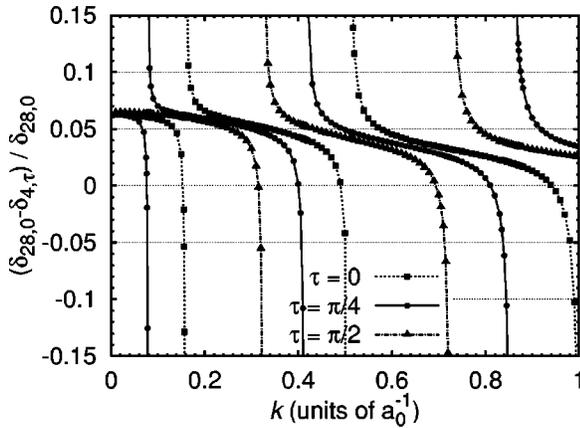


FIG. 1. Investigations of Schwartz singularities using for potential scattering from an attractive Woods-Saxon Potential. The phase shifts of three $N=4$ calculations with Kohn normalization conditions: $\tau=0$, $\pi/4$, and $\pi/2$, as a function of incident particle momentum k . The phase shifts are plotted relative to the $\delta_{28,0}$ phase shift.

jected to a Gram-Schmidt orthogonalization to ensure that they were orthogonal to the LTO set.

For the present model potential the variation in the phase shift with incident particle momenta k was investigated. First of all it should be mentioned that the K -matrix elements were insensitive to the specific value chosen for β , the parameter in the cutoff function used to make the irregular part of the long-range solution finite at the origin. The results hardly changed for $\beta \in [0.5, 4]$ and the value of $\beta=2.0$ was adopted for all the calculations reported in this article. These observations are consistent with those made by Lucchese [42] for the complex-Kohn method. The phase shifts will be insensitive to β as long as there is some degree of overlap between the L^2 orbitals and the continuum orbital $\theta_c(r)$.

In order to exhibit the properties of the variational solution, the phase shifts from calculations with $\tau=0, \pi/4$ and $\pi/2$ are shown in Figs. 1 and 2. The differences between the

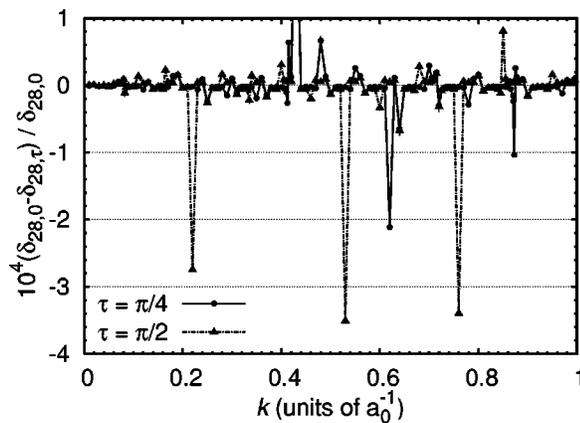


FIG. 2. The phase shifts of two $N=28$ calculations with Kohn normalization conditions, $\tau=\pi/4$ and $\pi/2$, are plotted as a function of incident particle momentum k . The phase shifts are plotted relative to $\delta_{28,0}$. The exact energy dependence of the phase shifts in the vicinity of the spikes was not determined.

three calculations with different τ can be used to gauge the uncertainty in the phase shifts for the calculations with the $N=4$ and $N=28$ LTO basis sets. The phase shift for a given N and τ is denoted as $\delta_{N,\tau}$. In order to demonstrate the variations amongst different calculations, the phase shifts from the $N=28, \tau=0$ calculation, $\delta_{28,0}$ are taken as the reference set. The deviation in each phase shift is calculated relative to $\delta_{28,0}(k)$, and shown in Figs. 1 and 2.

The three calculations with $N=4$ shown in Fig. 1 clearly exhibit the occurrence of the Schwartz singularities as the incident moment is changed. There are at least two singularities for each of the three values of τ in the range of k investigated. The deficiencies in the L^2 basis are exhibited most clearly in the fact that the phase shift plateaus are consistently 5% larger than the $\delta_{28,0}(k)$ phase shift. Figure 1 is very reminiscent of the figures previously published by Schwartz [35] and Brownstein and McKinley [40].

A completely different picture emerges when the L^2 part of the basis is enlarged to include 28 LTO basis functions. The variations of the $\tau=\pi/4$ and $\pi/2$ $\delta(k)$ calculations relative to the normal Kohn formulation, $\tau=0$, are shown in Fig. 2. The first thing to note is that the variations in the relative difference, $(\delta_{28,\tau} - \delta_{28,0}) / \delta_{28,0}$, have been multiplied by a factor of 10 000 in order to make the difference visible. Although there are one or two spikes where the relative difference reaches 3×10^{-4} , there is no feature that could be unambiguously identified as a Schwartz singularity. It is not possible to completely rule out the possibility that singularities may be present in the $k \in [0.0, 1.0] a_0^{-1}$ range. Narrow singularities could very well exist in this momentum range. However, it was decided not to actively search for singularities as long as they did not manifest themselves in an overt manner and detract from the accuracy of the calculations.

It is worth noting that spurious resonances above the ionization threshold have long been a feature of close-coupling calculations of electron-hydrogen scattering that have used a pseudostate basis [43,44]. However, it has been found that the impacts of these spurious resonances are less noticeable when the dimension of the pseudostate basis sets used in CC calculations of electron-hydrogen scattering are enlarged [45,46]. The pseudostate basis used for the CC calculations was a LTO basis identical in construction to the basis adopted for the present series of calculations. An interesting thing amongst all of this is that the spurious features so prominent in calculations using a small *ad hoc* pseudostate basis [43,44] seem to diminish in importance as the dimension of the Laguerre basis is increased.

The reliability of the Kohn and inverse-Kohn variational methods for this model problem persuaded us to use the standard Kohn method with real boundary conditions for our calculations upon H and Cu. The subsequent calculations upon these atoms, which were performed for $\tau=0, \pi/4$, and $\pi/2$, did not show any trace of a Schwartz singularity and, furthermore, the three Kohn variants gave phase shifts and Z_{eff} that generally agreed to within 0.1%.

D. Semiempirical model of e^+ -Cu scattering

In this section, details of a simple semiempirical model of positron-Cu scattering are described. The purpose behind the

model potential was to put the results of the CI-Kohn calculations into perspective, and also to highlight the possible impact that p -wave shape resonances will have on the system. Since the model potential has been previously described and applied to positron-Cu scattering, only a short description is given here.

The model potential approximates the Hamiltonian by

$$H = -\frac{1}{2}\nabla_0^2 + V_{dir}(\mathbf{r}_0) + V_{pol}(\mathbf{r}_0). \quad (31)$$

The repulsive direct potential V_{dir} is computed from the HF wave function of the target atom. The polarization potential has the functional form given by Eq. (2) with $\alpha_d = 40.0a_0^3$ and $\rho = 1.974a_0$ [12]. The value of ρ was set by tuning to the e^+ Cu binding energy of $\varepsilon = 0.005597$ hartree obtained in the fixed-core stochastic variational method (FCSVM) [8,12,32].

The annihilation of positrons was modelled by the equation

$$Z_{\text{eff}} = \int d^3r [G_v \rho_v(\mathbf{r}) + G_c \rho_c(\mathbf{r})] |\Phi(\mathbf{r})|^2, \quad (32)$$

where $\rho_c(\mathbf{r})$ and $\rho_v(\mathbf{r})$ are the electron densities associated with the core and valence electrons of the target atom, and $\Phi(\mathbf{r})$ is the positron-scattering function. The enhancement factors G are introduced to take into consideration the influence that electron-positron correlations will have upon the annihilation rate. The enhancement factor for valence and core electrons is treated differently. For core orbitals, G_c is simply set to 2.5 due to reasons outlined in [12]. The valence enhancement factor G_v was computed by the simple identity

$$G_v = \frac{\Gamma_v^{FCSVM}}{\Gamma_v^{model}}, \quad (33)$$

where Γ_v^{FCSVM} was the annihilation rate of the positron with the valence orbital as given by the FCSVM calculation [8,12], and Γ_v^{model} is the valence annihilation rate predicted by the model potential calculation with $G_v = 1$. This factor was set to 18.2 [12].

These semiempirical distorted wave calculations will be referred to as the DW calculations.

III. THE SCATTERING OF POSITRONS FROM ATOMIC HYDROGEN

The calculations upon atomic hydrogen were performed mainly to validate the analytical and numerical details of the program used to perform the calculations. They were also done to give information about the convergence of the phase shift and Z_{eff} with increasing L_{max} .

The initial calculation was designed to be equivalent to a three state $H(1s,2s,2p)$ close-coupling calculation. The phase shifts and Z_{eff} for the $\ell=0$ and 1 partial waves are listed in Table I. The results are in very good agreement with previous calculations in this model space [18,47]. The agreement with the values of Z_{eff} computed using the momentum space T -matrix method are particularly impressive. The results in this table can usefully serve as benchmark values of

TABLE I. The phase shifts and $Z_{\text{eff}}^{(L)}$ for positron scattering from hydrogen in the $H(1s,2s,2p)$ three-state model. The column k reports momentum in a_0^{-1} . The $L=0$ entry for the $k=0$ phase shift gives the scattering length.

k	δ	δ [47]	$Z_{\text{eff}}^{(L)}$	$Z_{\text{eff}}^{(L)}$ [18]
$L=0$				
0.0	-0.185		0.6593	-
0.1	-0.0049	-0.0048	0.6200	0.6200
0.2	-0.0424	-0.0421	0.5665	0.5666
0.3	-0.0934	-0.0929	0.5196	0.5196
0.4	-0.1475	-0.1471	0.4802	0.4801
0.5	-0.1994	-0.1986	0.4465	0.4464
0.6	-0.2466	-0.2465	0.4171	0.4169
0.7	-0.2880	-0.2876	0.3908	0.3907
$L=1$				
0.1	0.0047	0.0047	0.0143	0.0143
0.2	0.0134	0.0134	0.0535	0.0535
0.3	0.0203	0.0203	0.1080	0.1080
0.4	0.0222	0.0221	0.1662	0.1663
0.5	0.0185	0.0184	0.2199	0.2199
0.6	0.0102	0.0099	0.2649	0.2650
0.7	-0.0014	-0.0016	0.3005	0.3005

Z_{eff} for solutions of the Schrödinger equation in the $H(1s,2s,2p)$ model.

One aspect about the calculation that should be mentioned was the need to include a large basis of L^2 functions for the positron partial wave which is coupled to the $H(2p)$ excitation. The interaction between the $H(1s)$ and $H(2p)$ channels decays as $1/r^2$ at large r and to represent the virtual excitation to the $H(2p)$ state requires a rather large L^2 basis. This is especially true at energies close to threshold. The calculation for the s wave had 33 short-range positron $\ell=0$ and 50 $\ell=1$ LTO. For p -wave scattering, the number of positron LTOs for $\ell=0, 1$, and 2 were 48, 33, and 48, respectively.

Some much larger calculations were also done to determine whether the present single center Kohn-variational calculations could give scattering parameters accurate at the 1% level. These calculations are reported in Tables II and III. These calculations included about 20 LTOs for small values of ℓ , either 48 or 50 LTOs for the positron channels that are dipole coupled to the entrance channel, and 15 electron and 18 positron LTOs for orbitals with $\ell > 3$.

The s -wave phase shifts for the explicit calculation with $L_{max} = 12$ are accurate to about 0.002–0.003 rad. When the extrapolation of the phase shift is performed, the agreement with the variational phase shifts of Drachman and co-workers [9,48] could hardly be better. Values of Z_{eff} are generally a few percent smaller than the T -matrix calculations of Ref. [18] and the variational calculations of Ref. [17]. This is expected for two reasons. As mentioned earlier, the attractive interaction between the electron and positron leads to the formation of a virtual Ps cluster, resulting in very slow convergence with ℓ . To put the slow convergence in perspective, we estimate that L_{max} would have to be at least as large as 25

TABLE II. Phase shifts for positron scattering from hydrogen at various values of momenta (k in a_0^{-1}). The column δ_{12} reports the phase shift from the calculation with $L_{max}=10$, while the phase shift in the δ_∞ column includes the corrections from the $L_{max}\rightarrow\infty$ extrapolation. The entry for $k=0$ reports the scattering length.

k	δ_{12}	δ_∞	CC(13,8) [2]	Variational [9,15,48]
$L=0$				
0.0	-2.067	-2.088		-2.104
0.1	0.1463	0.1480	0.1474	0.1483
0.2	0.1851	0.1875	0.1868	0.1877
0.3	0.1648	0.1672	0.1667	0.1677
0.4	0.1176	0.1198	0.1191	0.1201
0.5	0.0604	0.0623	0.0621	0.0624
0.6	0.0021	0.0036	0.0031	0.0039
0.7	-0.0528	-0.0516	-0.0518	-0.0512
$L=1$				
0.1	0.008835	0.00886	0.00887	
0.2	0.0326	0.0328	0.0327	0.0338
0.3	0.0652	0.0658	0.0657	0.0665
0.4	0.0993	0.1004	0.1002	0.1016
0.5	0.1291	0.1307	0.1306	0.1309
0.6	0.1524	0.1546	0.1542	0.1547
0.7	0.1741	0.1776	0.1788	0.1799

to ensure that Z_{eff} was within 10% of its converged value at most energies. Second, the Kohn-variational principle is variational with respect to the phase shifts and there is no guarantee that other expectation values of the wave function will be fully optimized.

The agreement of the p -wave phase shifts with earlier high accuracy calculations [2,15] is also very good. The present calculations with $L_{max}=12$ gave phase shifts within

TABLE III. The annihilation parameter $Z_{\text{eff}}^{(L)}$ as a function of k (in a_0^{-1}) for positron scattering from hydrogen.

k	$L_{max}=12$	$L_{max}\rightarrow\infty$	CC(13,8) [18]	Variational [16,17]
$L=0$				
0.0	7.102	8.565		8.868
0.1	5.935	7.143	7.388	7.363
0.2	4.483	5.363	5.539	5.538
0.3	3.452	4.093	4.232	4.184
0.4	2.757	3.232	3.332	3.327
0.5	2.275	2.633	2.753	2.730
0.6	1.928	2.200	2.302	2.279
0.7	1.666	1.874	1.952	1.950
$L=1$				
0.1	0.1023	0.1398	0.141	0.130
0.2	0.3985	0.5409	0.556	0.540
0.3	0.8340	1.120	1.148	1.124
0.4	1.317	1.746	1.786	1.763
0.5	1.769	2.313	2.382	2.339
0.6	2.169	2.808	2.916	2.850
0.7	2.665	3.544	3.904	3.670

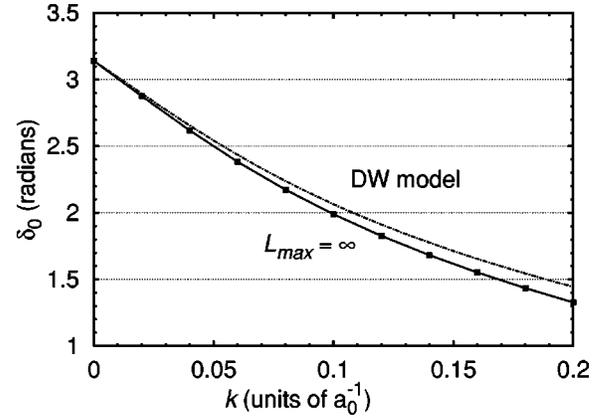


FIG. 3. The s -wave phase shift δ_0 as a function of k (in a_0^{-1}) for positron scattering from copper. Included are the phase shifts with the $L_{max}\rightarrow\infty$ correction, and the DW phase shifts of Mitroy and Ivanov [12].

a few percent of earlier calculations. When the extrapolation correction is made, the agreement with the earlier calculations is generally better than 1%. Somewhat surprisingly, the convergence of Z_{eff} with L_{max} appears to be slower for the p wave than the s wave. Only about 70% of the estimated $Z_{\text{eff}}^{(1)}$ comes from the explicit calculation with $L_{max}=12$. About 80% of $Z_{\text{eff}}^{(0)}$ for the s wave came from the explicit calculation.

IV. THE SCATTERING OF POSITRONS FROM Cu

The L^2 basis was almost the same as the basis used for previous CI calculations of positronic copper [8] and so only the differences in the basis from that earlier calculation are mentioned here. The major change was the inclusion of additional positron LTOs for the $\ell=0, 1$, and 2 orbitals. A total of 25, 50, and 25 LTOs for $\ell=0, 1$, and 2, respectively were used for the $L=0$ partial wave. The value of L_{max} was 18 and the number of LTOs was 15 for orbitals with $\ell\geq 3$. A total of 40, 33, and 40 positron LTOs for $\ell=0, 1$, and 2, respectively, were used for the p -wave calculation. The value of L_{max} was 15 and the number of LTOs was 15 for the orbitals with $\ell\geq 3$. The smaller value of L_{max} used for the p -wave calculations was the consequence of the larger dimensionality of the linear equation system. The outer limit of the integration range was $625a_0$ for both the s and p waves.

The $L=0$ phase shifts for positron-Cu scattering plotted in Fig. 3 include a correction due to the $L_{max}\rightarrow\infty$ extrapolation. The extrapolation correction was not large, being 0.01–0.02 rad for most of the energies depicted in Fig. 3. In most cases the extrapolation correction amounted to less than 5% in the phase shifts. Also shown in this figure are the DW phase shifts using the model of Mitroy and Ivanov [12]. The agreement between the two sets of phase shifts is quite reasonable. Part of the difference between the distorted wave (DW) and CI-Kohn phase shifts arises from the fact that the DW phase shifts were tuned using a e^+ Cu binding energy (0.005 597 hartree) [8,49] that was slightly different from the binding energy (0.005 12 hartree) obtained from the current CI basis [8].

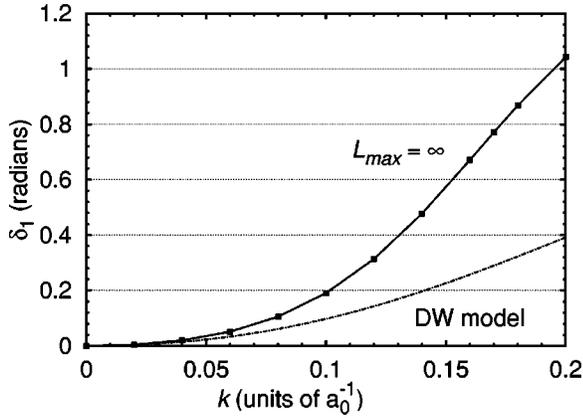


FIG. 4. The p -wave phase shift δ_1 as a function of k (in a_0^{-1}) for positron scattering from copper. Included are the phase shifts with the $L_{max} \rightarrow \infty$ correction and the DW phase shifts of Mitroy and Ivanov [12].

The $L=1$ phase shifts are plotted in Fig. 4. The $L_{max} \rightarrow \infty$ correction resulted in a 2–12% increase in the phase shift with the relative contribution of the extrapolation being larger at the higher momenta. The present CI-Kohn phase shifts are substantially larger than the DW phase shifts of Ref. [12]. The rapid increase of the phase shift to $k = 0.2a_0^{-1}$ signifies that the e^+ -Cu system is on the verge of forming a p -wave shape resonance. This point is discussed in more detail later.

The calculation of $Z_{\text{eff}}^{(0)}$ is complicated by two competing trends that affect the convergence pattern as L_{max} increases [8]. First, as the scattering length decreases with increasing L_{max} , there is a tendency for $Z_{\text{eff}}^{(0)}$ to decrease as a consequence of the normalization conditions that relate the wave function in the interaction region to the asymptotic wave function. Then there is the tendency for the electron pileup in the vicinity of the positron to be better represented as L_{max} increases. This second effect generally leads to $Z_{\text{eff}}^{(0)}$ increasing with increasing L_{max} . Taken in conjunction, these two effects make a direct extrapolation of $Z_{\text{eff}}^{(0)}$ to the $L_{max} \rightarrow \infty$ limit somewhat problematic.

The tendency for $Z_{\text{eff}}^{(0)}$ to reflect changes in the phase shift was incorporated into the extrapolation procedure used to get to the $L_{max} \rightarrow \infty$ limit. First, $Z_{\text{eff}}^{(0)}/[\sin(\delta)/k]$ was tabulated as a function of L_{max} . The $L_{max} \rightarrow \infty$ limit of $Z_{\text{eff}}^{(0)}/[\sin(\delta)/k]$ was then determined by assuming the successive increment scale as a power law. Finally, the limiting value of $Z_{\text{eff}}^{(0)}$ is determined by multiplying by the $L_{max} \rightarrow \infty$ limit of $[\sin(\delta)/k]$. This procedure is effectively the same as that previously used to determine $Z_{\text{eff}}^{(0)}$ at threshold [8].

Figure 5 depicts the present calculation of $Z_{\text{eff}}^{(0)}(k)$ for s -wave scattering. About 20–30% of the total contribution to $Z_{\text{eff}}^{(0)}$ came from the extrapolation procedure. Also shown on Fig. 5 is the energy dependence of $Z_{\text{eff}}^{(0)}(k)$ given by the semiempirical DW calculation [12]. The DW calculation gives a value at threshold, 96.4, that is, about 25% larger than the CI-Kohn value of 72.9. Close to 10% of that difference is due to a different treatment of core annihilation by the distorted wave calculation (the DW used an enhancement

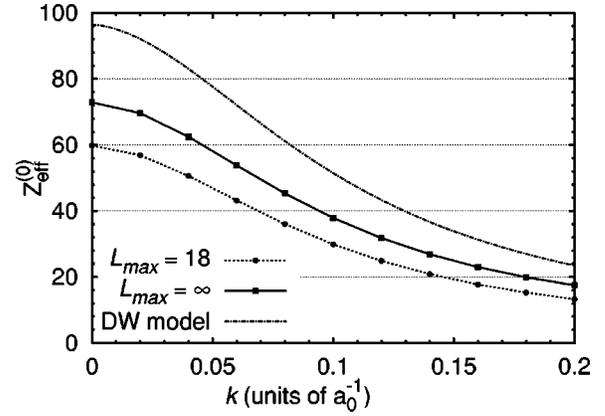


FIG. 5. The annihilation parameter $Z_{\text{eff}}^{(0)}(k)$ is plotted as a function of k for s -wave e^+ -Cu scattering. First, for the explicit $L_{max} = 18$ series, second, for the $L_{max} = 19 \rightarrow \infty$ extrapolated series, and finally, using the DW model of Mitroy and Ivanov [12].

factor for core annihilation). Another 5% is due to the fact that the DW calculation was tuned to a binding energy slightly different than that given by the present Hamiltonian. When this is taken into account, the agreement between the DW and CI-Kohn $Z_{\text{eff}}^{(0)}(k)$ is very satisfactory.

The calculation of $Z_{\text{eff}}^{(1)}$ was complicated by a rather slow convergence with L_{max} . As was the case for hydrogen, the convergence of $Z_{\text{eff}}^{(1)}$ with L_{max} was slower than the convergence of $Z_{\text{eff}}^{(0)}$. For example, at $k = 0.1a_0^{-1}$, $Z_{\text{eff}}^{(1)}$ was 16.96 for the $L_{max} = 15$ calculation. Application of the extrapolation procedure resulted in a value of 45.9, i.e., about 2.7 times larger. The derived exponent $p_Z = 1.45$ of the extrapolation is significantly smaller than the expected value of 2. Some estimate of the uncertainty associated with the extrapolation can be determined by arbitrarily setting p_Z to 2. When this is done the extrapolation increases $Z_{\text{eff}}^{(1)}$ by a factor of 1.85 to 31.4. The application of the simple power law algorithm given by Eqs. (23)–(25) results in some uncertainty in the $Z_{\text{eff}}^{(1)}$ $L_{max} \rightarrow \infty$ contribution, since a value of $L_{max} = 15$ is not large enough to ensure that the higher increments to $Z_{\text{eff}}^{(1)}$ can be given precisely by the power law formulas. We estimate that it would be necessary to extend the calculation to $L_{max} = 20$ to ensure that at least 50% of the true value of $Z_{\text{eff}}^{(1)}$ was obtained by explicit calculation. Due to the dimensionality of the linear equations (dimension = 9823×9823) it was not possible to extend the calculation to include orbitals with larger angular momentum.

The extrapolated $Z_{\text{eff}}^{(1)}$ shown in Fig. 6 was estimated by simply multiplying the extrapolation correction (i.e., $Z_{\text{eff}}^{(1)(\infty)} - Z_{\text{eff}}^{(1)(L_{max}=15)}$) by 0.85. The actual decision to multiply by 0.85 was based on examinations of convergence patterns of the annihilation rate for positronic atoms and scattering systems [8,50,51]. In every system examined the exponent p_Z or p_Γ asymptotes to 2 from below with increasing L_{max} . Therefore, there is a tendency for the extrapolation using Eqs. (23)–(25) to overestimate the size of the correction. It is reasonable to ascribe an uncertainty of about 15% to the extrapolation correction and so Fig. 6 shows a band of values for $Z_{\text{eff}}^{(1)}$. The total Z_{eff} (Fig. 7) obtained by summing the s -

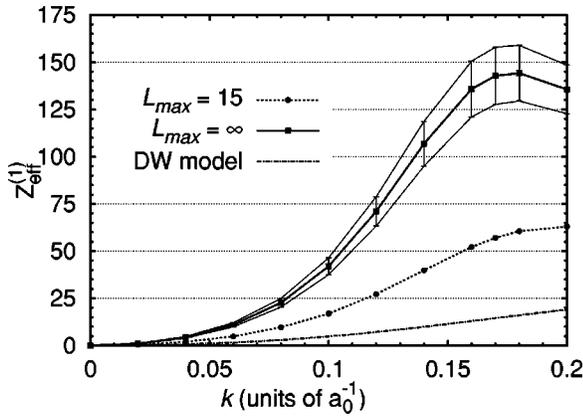


FIG. 6. The annihilation parameter $Z_{\text{eff}}^{(1)}(k)$ is plotted as a function of k for p -wave e^+ -Cu scattering. The lowest curve was computed using the DW model of Mitroy and Ivanov [12]. The second lowest curve gives the CI-Kohn calculation with $L_{\text{max}}=15$. The top curves include the $L_{\text{max}}=16 \rightarrow \infty$ correction and allow for a 15% uncertainty in the magnitude of the correction.

and p -wave contributions also includes this band of uncertainty. A more complicated extrapolation procedure could have been devised, but it was decided to follow the precepts of Occam's razor, *Entities should not be multiplied unnecessarily*, and use the simplest possible method capable of giving a reasonable estimate of the correction.

The largest value attained by $Z_{\text{eff}}^{(1)}(k)$ in the interval occurred at $k=0.18a_0^{-1}$ and it was about 160. Figure 6 shows that the CI-Kohn calculation of $Z_{\text{eff}}^{(1)}(k)$ gives much larger values than that given by the DW calculation. This result can be explained by reference to Fig. 4 where the CI-Kohn phase shift is seen to be much larger than the DW phase shift. This indicates that the effective potential for the positron in the CI-Kohn calculation is actually more attractive than the distorted wave potential. A more attractive potential nature leads to an increased positron charge density in the vicinity

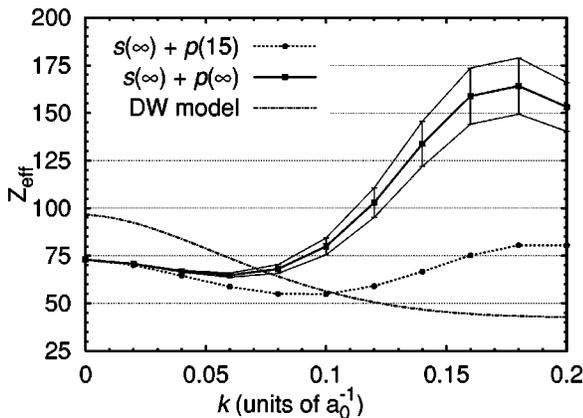


FIG. 7. The annihilation parameter $Z_{\text{eff}}(k)$ is plotted as a function of k for e^+ -Cu scattering. The lowest curve was computed using the DW model of Mitroy and Ivanov [12]. The second lowest curve gives the CI-Kohn calculation with $L_{\text{max}}=15$. The top curves include the $L_{\text{max}}=16 \rightarrow \infty$ correction and allow for a 15% uncertainty in the magnitude of the correction.

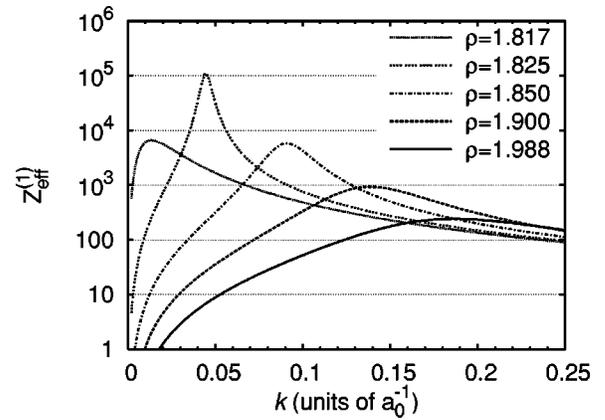


FIG. 8. The DW annihilation parameter $Z_{\text{eff}}^{(1)}(k)$ is plotted for a series of ρ values as a function of k for e^+ -Cu scattering. The calculation with $\rho=1.988a_0$ was tuned to give the CI-Kohn p -wave phase shift at $k=0.1a_0^{-1}$. The $\rho=1.817a_0$ potential supports a bound state with a binding energy of 9.2×10^{-5} hartree. The momentum at which the $Z_{\text{eff}}^{(1)}(k)$ maximum occurs shifts closer to threshold as ρ decreases.

of the atom and a larger $Z_{\text{eff}}^{(1)}$. The DW model potential, retaining G_v and G_c unchanged, was revised so that the p -wave phase shift at $k=0.1a_0^{-1}$ was equal to the CI-Kohn phase shift. When this was done, the value of $Z_{\text{eff}}^{(1)}$ increased to 52 at $k=0.1a_0^{-1}$ and to 230 at $k=0.2a_0^{-1}$ (see the $\rho=1.988a_0$ curve of Fig. 8).

With $Z_{\text{eff}}^{(1)}$ being so large, the obvious question is whether the $L=2$ partial wave will also make a significant contribution to $Z_{\text{eff}}(k)$. An explicit calculation has not been done, but the DW calculation does provide guidance. At $k=0.2a_0^{-1}$, the DW calculation gave $Z_{\text{eff}}^{(2)}=0.31$. Although the p -wave parameter $Z_{\text{eff}}^{(1)}$ was sensitive to the details of the model potential, $Z_{\text{eff}}^{(2)}$ hardly changed as the cutoff parameter was altered. Therefore, it can be safely concluded that $Z_{\text{eff}}(k)$ has only a small contribution from the higher partial waves when $k < 0.2a_0^{-1}$. Figure 7 shows the summed contribution from the $L=0$ and $L=1$ partial waves. The notable feature here is the tendency for $Z_{\text{eff}}(k)$ to increase as the momentum increases from $k=0.05a_0^{-1}$.

V. SPECULATIONS ABOUT SHAPE RESONANCES

It has been shown in Fig. 4 that the p -wave phase shift is a precursor to a shape resonance. A series of DW calculations with slightly different potential parameters have been performed in order to exhibit the impact that a shape resonance will have on $Z_{\text{eff}}(k)$. The value ρ has been decreased in a series of increments, thereby increasing the attraction of the positron to the atom. Figure 8 shows that the resonance becomes increasingly pronounced and closer to threshold as the net attraction gets stronger. The peak value of $Z_{\text{eff}}^{(1)}$ for the sharpest resonance with a resonance energy of about 0.001 hartree was 110 000.

The large enhancements of $Z_{\text{eff}}^{(1)}(k)$ in the vicinity of the resonance energy provide another mechanism that can result in very large values of $Z_{\text{eff}}(k)$. The large annihilation rates

seen in traditional positron annihilation experiments have been the subject of much interest ever since the first experiments yielding large values of $Z_{\text{eff}}(k)$ [52–56]. It has been postulated that there are two different mechanisms for positron annihilation; these are (1) direct annihilation and (2) resonant annihilation. Direct annihilation describes the annihilation of the positron with the target electrons and the direct annihilation rate was strongly correlated with the size of the elastic cross section [33,56,57]. Resonant annihilation was mainly important for large molecules with closely spaced vibrational levels. In resonant annihilation, the positron is trapped in a Feshbach resonance associated with a vibrationally excited state. The resonant annihilation process was deemed to be the mechanism responsible for the large annihilation rates seen for some molecules [33,57,58].

It has been shown that there is a natural upper limit for Z_{eff} for thermal positrons annihilating in a gas by direct annihilation. Even though $Z_{\text{eff}}^{(0)}(k)$ can get arbitrarily large as the scattering length increases, the thermally averaged annihilation rate $\langle Z_{\text{eff}} \rangle_T$ has an upper bound because the energy region over which $Z_{\text{eff}}^{(0)}(k)$ is large decreases as the scattering length increases [12,33,57]. Values between 200 and 1300 have been suggested as the maximum possible $\langle Z_{\text{eff}} \rangle_T$ for the systems that annihilate by the direct annihilation mechanism [33,57,12].

The thermally averaged $\langle Z_{\text{eff}}^{(1)} \rangle_T$ has been determined for each of the curves in Fig. 8 at a hypothetical positron temperature of 300 K. The values obtained were 25, 55, 800, and 19 000 for the $\rho=1.988$, 1.90, 1.85, and $1.825a_0$ curves, respectively. The very large value of 19 000 occurs because the position of the resonance peak at $k \approx 0.044a_0^{-1}$ is close to the mean energy of a positron swarm at a temperature of 300 K. This is an order of magnitude larger than the maximum possible $\langle Z_{\text{eff}} \rangle_T$ one can get from the direct annihilation mechanism due to s -wave scattering.

We therefore assert that there exists a third mechanism that can lead to large values of the positron annihilation parameter $Z_{\text{eff}}(k)$. The presence of a shape resonance at low energies can easily result in Z_{eff} , achieving 100 000 at the resonance peak. Even when the impact of thermal averaging is taken into consideration, a value of $\langle Z_{\text{eff}} \rangle_T$ exceeding 10 000 is possible provided the resonance energy is positioned close to the mean thermal energy. The two assumptions underpinning this prediction are that (1) the positron-atom (or molecule) potential is sufficiently attractive to support a shape resonance and (2) that short-range electron-positron correlations act to enhance the coalescence matrix element. Both of these assumptions are eminently reasonable. The ability of positrons to form bound states with many atoms and molecules [32] is certainly supportive of assumption (1). The copper atom with a positron binding energy of 0.005 60 hartree is just on the threshold of forming a shape resonance. One would expect that a system, such as magnesium, with a larger positron binding energy of about 0.016 hartree [14,51] would therefore be quite likely to exhibit a p -wave shape resonance.

Short-range electron-positron correlations are known to increase the annihilation rate of all known electron-positron

systems [12,33,59] and so one expects G_v to be larger than unity. Even if G_v was decreased to $G_v=4$ (roughly equal to the value adopted for Kr [12]), the size of $\langle Z_{\text{eff}} \rangle_T$ resulting from a shape resonance could still exceed 1000 by a comfortable margin.

Impact of weakly bound state on $Z_{\text{eff}}^{(1)}$

The curve with $\rho=1.817a_0$ in Fig. 8 is for a potential that just supports a p -wave bound state with a binding energy of 9.25×10^{-5} hartree. The annihilation parameter shows a rapid increase with k near threshold with a peak value of 6600 achieved at $k=0.013a_0^{-1}$. When the thermal average is done at 300 K one gets $\langle Z_{\text{eff}}^{(1)}(k) \rangle_T=2300$. A potential that supports a bound state with a larger binding energy gives $Z_{\text{eff}}^{(1)}(k)$, which rises more slowly at threshold while achieving a peak value, which is smaller. As the state becomes more weakly bound, the rise of $Z_{\text{eff}}^{(1)}(k)$ from threshold becomes sharper and the peak value becomes larger.

At the moment there is no hard evidence to support the contention that the polarization potential between a positron and an atom is sufficiently strong to support a p -wave bound state. Although Gribakin and King [60] reported evidence of a p -wave bound state in their calculations of e^+ -Mg scattering, this prediction should not be taken seriously since their method of calculation does overestimate the strength of the positron-atom interaction [14,51]. The $\rho=1.817a_0$ curve shown in Fig. 8 gives a good idea of what can be expected when the potential supports a weak p -wave bound state, the uncertainty is about whether such a bound state can exist.

VI. CONCLUSIONS

It has been shown that the application of the Kohn variational method to positron-hydrogen scattering with a short-range basis consisting of electron and positron functions centered only on the nucleus can result in phase shifts that are comparable in accuracy to those of the best previous calculations [2,9,15–19]. Convergent close-coupling calculations containing roughly the same physics as the present CI-Kohn calculations have been reported previously [7], but these calculations did not compute the annihilation parameter. The much slower convergence of the annihilation parameter leads to greater uncertainties in the values of Z_{eff} , but even here one can expect the results to have a precision of better than 5%.

The K -matrix form of the Kohn-variational method was used without the appearance of any noticeable singularities. The singularity problem was eliminated for all practical purposes by choosing to represent the positron wave function with a L^2 basis that can be enlarged systematically. Furthermore, the large size of the L^2 basis meant that the computed phase shifts were not very sensitive to the exponent used to generate the LTOs for a given ℓ . Thus, the calculations at different energies all used the same short-range LTO basis.

Comparison of the CI-Kohn phase shift and Z_{eff} with the DW results indicates that a simple central potential model can do a reasonable job of reproducing the results of a more sophisticated calculation provided the adjustable parameters

can be tuned correctly. One complication of the DW model is the need to tune the polarization potential separately for s - and p -wave scattering.

One notable feature of the Z_{eff} calculations is the apparently slower convergence for p -wave scattering. This can be explained by consideration of the nature of the contact matrix element. The main contributions to the matrix element come from the region of space where the electron and positron charge distributions overlap. The presence of the additional centrifugal barrier in the interaction Hamiltonian means the electron and positron charge distributions are pushed further away from the nucleus. Therefore, the formation of a virtual Ps cluster will occur further away from the nucleus and will result in a more slowly convergent annihilation matrix element. This of course has disturbing implications for calculations of the higher partial waves. As the importance of the centrifugal barrier increases with increasing L , one can expect the calculation of $Z_{\text{eff}}^{(L)}$ to converge increasingly slowly with L_{max} .

The CI-Kohn calculations indicate that the effective positron-atom potential that can support an s -wave bound state will most likely result in an attractive potential well for p -wave scattering. The present CI-Kohn calculation is on the

verge of supporting a shape resonance in the p -wave. The existence of a p wave shape resonance could lead to quite prominent enhancements in $Z_{\text{eff}}^{(1)}(k)$ if the resonance energy is close to threshold. Although copper is not an easy atom to create for a beam experiment, the present results have implications for atoms such as Zn, Cd, and Mg. The group IIB atoms, Zn and Cd, have positron binding energies roughly comparable in size to Cu, and therefore one can expect them to have elastic cross sections, and $Z_{\text{eff}}(k)$ roughly similar to that of Cu. The magnesium system with its much larger positron binding energy can be expected to have a shape resonance with better definition. The present results certainly increase the desirability of performing elastic scattering or annihilation experiments on group II and IIB atoms of the periodic table.

ACKNOWLEDGMENTS

A number of IT support staff, Jean-Claude Nou, Corey Hoffman, Mark Bradbury, Pavel Stulik, and Roy Pidgeon assisted this work by maintaining the author's GNU/Linux workstations and by giving access to additional workstations.

-
- [1] J. Mitroy, Aust. J. Phys. **46**, 751 (1993).
 - [2] J. Mitroy, Aust. J. Phys. **48**, 646 (1995).
 - [3] A.A. Kernoghan, M.T. McAlinden, and H.R.J. Walters, J. Phys. B **28**, 1079 (1995).
 - [4] M.T. McAlinden, A.A. Kernoghan, and H.R.J. Walters, J. Phys. B **29**, 555 (1996).
 - [5] G.G. Ryzhikh and J. Mitroy, J. Phys. B **30**, 5545 (1997).
 - [6] K. Higgins, P.G. Burke, and H.R.J. Walters, J. Phys. B **23**, 1345 (1990).
 - [7] I. Bray and A.T. Stelbovics, Phys. Rev. A **48**, 4787 (1993).
 - [8] M.W.J. Bromley and J. Mitroy, Phys. Rev. A **66**, 062504 (2002).
 - [9] A.K. Bhatia, A. Temkin, R.J. Drachman, and H. Eiserike, Phys. Rev. A **3**, 1328 (1971).
 - [10] P. Van Reeth and J.W. Humberston, J. Phys. B **32**, 3651 (1999).
 - [11] J.W. Humberston, J. Phys. B **6**, L305 (1973).
 - [12] J. Mitroy and I.A. Ivanov, Phys. Rev. A **65**, 042705 (2002).
 - [13] M.W.J. Bromley and J. Mitroy, Phys. Rev. A **65**, 062506 (2002).
 - [14] J. Mitroy and G.G. Ryzhikh, J. Phys. B **34**, 2001 (2001).
 - [15] A.K. Bhatia, A. Temkin, and H. Eiserike, Phys. Rev. A **9**, 219 (1974).
 - [16] A.K. Bhatia, R.J. Drachman, and A. Temkin, Phys. Rev. A **9**, 223 (1974).
 - [17] A.K. Bhatia, R.J. Drachman, and A. Temkin, Phys. Rev. A **16**, 1719 (1977).
 - [18] G.G. Ryzhikh and J. Mitroy, J. Phys. B **33**, 2229 (2000).
 - [19] Y.R. Kuang and T.T. Gien, Phys. Rev. A **55**, 256 (1997).
 - [20] J. Mitroy, Aust. J. Phys. **52**, 973 (1999).
 - [21] T. Koga, H. Tatewaki, and A.J. Thakkar, Phys. Rev. A **47**, 4510 (1993).
 - [22] W.R. Johnson, D. Kolb, and K. Huang, At. Data Nucl. Data Tables **28**, 333 (1983).
 - [23] W. Kohn, Phys. Rev. **71**, 902 (1947).
 - [24] J. Callaway, Phys. Rep. **45**, 89 (1978).
 - [25] R.K. Nesbet, *Variational Methods in Electron-atom Scattering Theory* (Plenum, New York, 1980).
 - [26] P.G. Burke and C.J. Joachain, *Theory of Electron-atom Collisions. Part 1: Potential Scattering* (Plenum, New York, 1995).
 - [27] T. Kato, Phys. Rev. **80**, 475 (1950).
 - [28] S.I. Rubinow, Phys. Rev. **98**, 183 (1955).
 - [29] E.A.G. Armour and J.W. Humberston, Phys. Rep. **204**, 165 (1991).
 - [30] P.A. Fraser, Adv. At. Mol. Phys. **4**, 63 (1968).
 - [31] R.P. McEachran, D.L. Morgan, A.G. Ryman, and A.D. Stauffer, J. Phys. B **10**, 663 (1977).
 - [32] J. Mitroy, M.W.J. Bromley, and G.G. Ryzhikh, J. Phys. B **35**, R81 (2002).
 - [33] V.A. Dzuba, V.V. Flambaum, G.F. Gribakin, and W.A. King, J. Phys. B **29**, 3151 (1996).
 - [34] G. Gribakin and J. Ludlow, J. Phys. B **65**, 339 (2002).
 - [35] C. Schwartz, Ann. Phys. (N.Y.) **16**, 36 (1961).
 - [36] W.H. Miller and B.M.D.D. Jansen op de Haar, J. Chem. Phys. **86**, 6213 (1987).
 - [37] C.W. McCurdy, T.N. Rescigno, and B.I. Schneider, Phys. Rev. A **36**, 2061 (1987).
 - [38] T.N. Rescigno, B.H. Lengsfeld, and C.W. McCurdy, in *Modern Electronic Structure Theory*, edited by D.R. Yarkony (World Scientific, Singapore, 1995), Vol. 2, Chap. 9, pp. 501–588.
 - [39] J. Nuttall, Ann. Phys. (N.Y.) **52**, 428 (1969).
 - [40] K.R. Brownstein and W.A. McKinley, Phys. Rev. **170**, 1255 (1968).

- [41] R.D. Woods and D.S. Saxon, *Phys. Rev.* **95**, 577 (1954).
[42] R.R. Lucchese, *Phys. Rev. A* **40**, 6879 (1989).
[43] P.G. Burke, K.A. Berrington, and C.V. Sukumar, *J. Phys. B* **14**, 289 (1981).
[44] D.H. Oza and J. Callaway, *Phys. Rev. A* **27**, 2840 (1983).
[45] D.H. Oza, *Phys. Rev. A* **30**, 1101 (1984).
[46] I. Bray and A.T. Stelbovics, *Phys. Rev. Lett.* **69**, 53 (1992).
[47] G. Liu and T.T. Gien, *Phys. Rev. A* **46**, 3918 (1992).
[48] S.K. Houston and R.J. Drachman, *Phys. Rev. A* **3**, 1335 (1971).
[49] G. Ryzhikh and J. Mitroy, *J. Phys. B* **31**, 4459 (1998).
[50] M.W.J. Bromley and J. Mitroy, *Phys. Rev. A* **65**, 012505 (2002).
[51] M.W.J. Bromley and J. Mitroy, *Phys. Rev. A* **65**, 062505 (2002).
[52] D.A.L. Paul and L. Saint-Pierre, *Phys. Rev. Lett.* **11**, 493 (1963).
[53] V.I. Goldanskii and Y.S. Sayasov, *Phys. Lett.* **13**, 300 (1964).
[54] M. Charlton, *Rep. Prog. Phys.* **48**, 737 (1985).
[55] T.J. Murphy and C.M. Surko, *Phys. Rev. Lett.* **67**, 2954 (1991).
[56] V.A. Dzuba, V.V. Flambaum, W.A. King, B.N. Miller, and O.P. Sushkov, *Phys. Scr.* **46**, 248 (1993).
[57] G.F. Gribakin, *Phys. Rev. A* **61**, 022720 (2000).
[58] S.J. Gilbert, L.D. Barnes, J.P. Sullivan, and C.M. Surko, *Phys. Rev. Lett.* **88**, 043201 (2002).
[59] M.J. Puska and R.M. Nieminen, *Rev. Mod. Phys.* **66**, 841 (1994).
[60] G.F. Gribakin and W.A. King, *Can. J. Phys.* **74**, 449 (1996).