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Positron and positronium interactions with Cu

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The configuration-interaction (CI) method is used to investigate the interactions of positrons and positronium with copper at low energies. The calculations were performed within the framework of the fixed-core approximation with semiempirical polarization potentials used to model dynamical interactions between the active particles and the $(1s\text{-}3d)$ core. Initially, calculations upon the e^+Li system were used to refine the numerical procedures and highlighted the extreme difficulties of using an orthodox CI calculation to describe the e^+ Li system. The positron binding energy of e^+Cu derived from a CI calculation which included electron and positron orbitals with $\ell \leqslant 18$ was 0.005 12 hartree while the spin-averaged annihilation rate was 0.507×10^9 s^{-1}. The configuration basis used for the bound-state calculation was also used as a part of the trial wave function for a Kohn variational calculation of positron-copper scattering. The positron-copper system has a scattering length of about $13.1a_0$ and the annihilation parameter $Z_{\rm eff}$ at threshold was 72.9. The dipole polarizability of the neutral copper ground state was computed and found to be $41.6a_0^3$. The structure of CuPs was also studied with the CI method and it was found to have a binding energy of 0.0143 hartree and an annihilation rate of $\sim 2\times 10^9$ s^{-1}.

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I. INTRODUCTION

The bound state of a positron and a neutral copper atom was shown to be stable with a binding energy of 0.005 518 hartree in an application of the fixed-core stochastic variational method (FCSVM) [1]. Subsequently, the configuration-interaction (CI) method was used to confirm the prediction of positron binding to copper [2]. The difficulties of representing a highly correlated electron-positron pair using single-particle orbitals centered on the nucleus means that CI calculations require an orbital basis containing terms with high angular momentum. The initial CI calculation used a large basis containing terms up to $\ell = 14$, but the radial basis was an *ad hoc* basis constructed from Slater-type orbitals (STOs). While this first CI calculation was able to confirm the stability of positronic copper, the resulting binding energy, 0.003 69 hartree was only about 65% of the FCSVM binding energy. A better CI calculation was performed by Dzuba *et al.* [3] who solved the Dirac equation in a finite range box of radius $30a_0$ while using a *B*-spline basis to represent the radial dependence of the wave function. The advantage of the *B*-spline basis was that the convergence of the energy with the number of basis functions could be studied systematically. Confining the system inside a box meant that the convergence of the energy with respect to the number of ℓ terms in the single-particle basis was accelerated. The final energy quoted by Dzuba *et al.*, 0.006 25 hartree, incorporated a correction to the energy which took the final size of the box into consideration.

In the present work, the CI method is used in conjunction with a model Hamiltonian derived from the Hartree-Fock core to determine the structure of e^+Cu. The radial dependence of the orbitals used to model the wave function of the active electron and the positron was described by a large basis of Laguerre-type orbitals. In this respect, the calculation is close to convergence. The angular basis included terms up to $\ell = 18$ and about 94% of the binding energy was obtained by explicit calculation. The convergence of the annihilation rate was somewhat slower with ℓ, but about 75% annihilation rate was obtained by explicit calculation. A subsidiary calculation was undertaken to determine the polarizability of the ground state of neutral copper, since the standard polarizability tabulation [4] gives two recommended values.

Calculations of positronic lithium (e^+Li) by the CI method were also done. This CI calculation was very exacting as positronic lithium consists of a very strongly correlated e^+-e^- pair located far from the nucleus. Positronic lithium is one of the best examples of a positron binding system that is *not suitable to treatment by the CI method* [5,6]. The calculation was undertaken purely and simply to determine what it would take to get an explicit prediction of positron binding to Li with the CI method, and to highlight the difficulties of performing CI calculations upon such systems. The program development necessary to handle the exacting e^+Li calculations had one useful byproduct. The numerics of the program had to be made very robust and consequently the CI calculations upon e^+Cu were straightforward by comparison.

The CI program used to perform the bound-state calculations was adapted to perform scattering calculations using the Kohn variational method. This was applied to positron scattering from copper, giving estimates of the scattering length and the annihilation parameter $Z_{\rm eff}$ for the $L = 0$ partial wave. The present calculation of $Z_{\rm eff}$ during a collision process is particularly timely as there has been renewed interest in understanding the dynamics of positron annihilation during collision processes [7–12].

Finally, the model Hamiltonian used for the positron-copper studies was also used in a CI calculation of the CuPs binding energy and annihilation rate. The neutral positro-

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nium (Ps) atom is known to bind to a number of one-electron atoms. Since the theoretical demonstration that positronium hydride (PsH) was bound in 1951 [13], a variety of computational methods have been used to study the structure of PsH with the result that its binding energy and annihilation rate are now known very precisely [14–16]. Positronium binding to three of the alkali atoms, Li [17], Na [17], and K [18] has also been established. The electronic stability of CuPs was established in a previous CI calculation [19], but this calculation was really an exploratory calculation and did not aim to achieve a converged estimate of the binding energy and annihilation rate. The present calculation gives a greatly improved description of the CuPs system.

II. DETAILS OF THE CALCULATION

The CI method, as applied to positron-atomic systems, has been discussed previously [19,20], so only a brief description is given here. All calculations were done in the fixed-core approximation. The model Hamiltonian for the system is

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

The direct potential (V_{dir}) represents the interaction with the core which was derived from the Hartree-Fock (HF) wave function of the neutral atom ground state. The Hartree-Fock wave functions were computed with the program described by Mitroy [21] and the basis set of Koga [22] was used. The exchange potential (V_{exc}) between the valence electron 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 has been adopted for both the positron and electron. In this work, $g_\ell^2(r)$ was defined to be

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

where ρ_l is an adjustable cutoff parameter. The two-body polarization potential (V_{p2}) [5] is defined as

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

The parameters of the core-polarization potential for Li^+ and Cu^+ are listed in Table I. The Li^+ core has a small polarizability ($0.1925a_0^3$) [23] which exerts only a minor influence on the behavior of the valence particles. The Cu^+ core polarizability is $5.36a_0^3$ [24].

TABLE I. Dipole polarizabilities (in a_0^3) and cutoff parameters (in a_0) of the Li^+ and Cu^+ core-polarization potentials. The value of ρ_{p2} gives the cutoff parameter used in $g_{\rho 2}^2(r)$.

System	α_d	ρ_0	ρ_1	ρ_2	ρ_3	$\rho_{>3}$; ρ_{p2}
Li^+	0.1925 [23]	1.40	1.40	1.40	1.40	1.40
Cu^+	5.36 [24]	1.9883	2.03	1.83	1.80	1.91

The positronic atom wave function was a linear combination of states created by coupling electron orbitals $\phi_j(\mathbf{r}_1)$ and positron orbitals $\phi_j(\mathbf{r}_0)$ with Clebsch-Gordan coupling coefficients,

$$|\Psi;LS\rangle=\sum_{i,j} c_{i,j}\langle \ell_i m_i \ell_j m_j|LM_L\rangle \times\left\langle \frac{1}{2}\mu_i\frac{1}{2}\mu_j\middle| SM_S\right\rangle \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_0). \quad (5)$$

The single-particle orbitals are written as a product of a radial function and a spherical harmonic,

$$\phi(\mathbf{r})=P(r)Y_{lm}(\hat{\mathbf{r}}). \quad (6)$$

The starting point for these calculations was a HF calculation for the ground states of the neutral atoms. These HF orbitals are written as a linear combination of STOs, [21,22] and, therefore, it was sensible to use a linear combination of STOs and Laguerre-types orbitals (LTOs) (see Ref. [20] for a definition of the LTOs) to describe the radial dependence of valence electrons occupying orbitals with the same angular momentum as those in the ground state. The STOs act to give a good representation of the wave function in the interior region while the LTOs describe the wave function further from the nucleus. The set of orbitals $\{\phi_i\}$ completely spanned the space defined by the raw STO and LTO basis functions since the total number of orbitals was equal in dimension to that of the combined STO + LTO basis. It should be emphasized that the mixed basis was only used for the $\ell=0$ electron orbitals of e^+Li, and the $\ell=0$, 1, and 2 electron orbitals of e^+Cu, all other symmetries used a pure LTO basis. As is usual with a Laguerre basis, the LTO functions used a common exponential parameter λ_α for a given ℓ [20]. A Gram-Schmidt orthogonalization of the orbital set was performed to ensure that all the electron and positron orbitals were orthonormal. The exponents for the LTOs were optimized manually. When $\ell\geqslant 4$ the exponents for the electron and positron orbitals were the same. This was expected since the dominant one-body term in the effective Hamiltonian is the $\ell(\ell+1)/(2r^2)$ operator.

The CI basis was constructed by populating all the possible $L=0$ configurations that could be formed by letting the electron and positron occupy the orbitals subject to the selection rule,

$$\max(\ell_0,\ell_1)\leqslant L_{max}. \quad (7)$$

In this expression ℓ_0 is the positron angular momentum and ℓ_1 is the electron angular momentum. The CI basis can thus be characterized by the L_{max} parameter. A large value of L_{max} is necessary as the attractive electron-positron interaction causes a pileup of electron density in the vicinity of the positron.

Various expectation values were computed to provide information about the structures of these systems. The mean distances of the electron and positron from the nucleus are denoted by $\langle r_e \rangle$ and $\langle r_p \rangle$, respectively, while $\langle r_{ep}^2 \rangle$ denotes the mean-square distance between the valence electron and the positron. The 2γ annihilation rate for annihilation with the core (Γ_c) and valence (Γ_v) electrons were computed with the usual expressions [14,20,25,26].

The $L_{max} \rightarrow \infty$ limits were estimated with a simple extrapolation technique. Making the assumption that the successive increments X_L to any expectation value $\langle X \rangle$ scale as $1/L^p$ for sufficiently large L, one can write

$$\langle X \rangle = \lim_{L_{max} \rightarrow \infty} \left(\sum_{L=0}^{L_{max}} X_L + \Delta \sum_{L=L_{max}+1}^{\infty} \frac{1}{L^p} \right). \tag{8}$$

The power series is easy to evaluate since the coefficient Δ and p are trivially determined from two successive values of X_L [20], e.g.,

$$\Delta = X_{L_{max}} (L_{max})^p, \tag{9}$$

$$\left(\frac{L_{max}}{L_{max}-1} \right)^p = \frac{X_{L_{max}-1}}{X_{L_{max}}}. \tag{10}$$

There is a degree of uncertainty attached to the extrapolation since the asymptotic form in L_{max} (i.e., p) is not known for many operators. Recently, Gribakin and Ludlow [27] showed that $p=4$ and $p=2$, when the energy and annihilation increments were computed using second-order perturbation theory. However, as will be seen, the asymptotic region for p_E is not reached for L_{max} as large as 18 in the case of e^+Cu or even 30 in the case of e^+Li.

III. REVISION OF THE FCSVM ENERGY FOR e^+Cu

The short-range part of the core-polarization potential, i.e., $g(r)$ in Eq. (3) is approximated by a linear combination of Gaussians in FCSVM calculations. The set of Gaussians originally used in Ref. [1] has been replaced by an improved set which more faithfully reproduces the exponential cutoff, $g(r)$, over the radial range of interest.

Repeating the FCSVM calculation with the improved core polarization gave a binding energy of 0.005 597 hartree. The spin-averaged rate for annihilation with the valence electron was 0.544×10^9 s^{-1} while the core annihilation rate was $0.033\,94 \times 10^9$ s^{-1}. The mean distance of the positron from the nucleus was $8.662a_0$, while the mean distance of the electron was $3.578a_0$. The mean electron-positron distance was $7.724a_0$.

The revised FCSVM binding energy for neutral copper was 0.282 931 hartree, while the electron affinity was 0.034 267 hartree.

TABLE II. Theoretical and experimental energy levels (in hartree) of some of the low-lying states of Cu. The energies are given relative to the energy of the Cu^+ core. The column V_s gives the energies when only static terms are included in the core potential, while V_{s+pol} adds the polarization potential to the model Hamiltonian. The experimental energies for the spin-orbit doublets are statistical averages. The second last row gives the oscillator strength for the resonant transition while the last row gives the dipole polarizability (in a_0^3) of the $4s$ ground state (note, the contribution to α_d from the core is included).

Level	V_s	V_{s+pol}	Experiment [50,51]
$4s$	−0.238 480 6	−0.283 942 3	−0.283 939
$4p$	−0.124 904 9	−0.144 038 4	−0.144 056
$5s$	−0.080 704 7	−0.086 265 4	−0.087 392
$5p$	−0.054 838 9	−0.058 843 1	−0.058 933
$4d$	−0.055 174 7	−0.056 402 4	−0.056 399
$6s$	−0.040 876 1	−0.042 688 5	−0.043 143
$5d$	−0.030 920 9	−0.031 484 1	−0.031 564
$4f$	−0.031 253 9	−0.031 356 4	−0.031 391
$f_{4s \rightarrow 4p}$	0.9619	0.7064	
α_d	75.68	41.65	

IV. CALCULATION RESULTS

A. Tests of the model potentials

1. Lithium

The model Hamiltonian for Li is almost exactly the same as the model potential used for earlier FCSVM calculations [5,6]. The accuracy with which this model describes the structure of Li and Li^- has been discussed in these previous works [5,6].

2. The structure of neutral Cu

The ability of the underlying potential to give a good description of neutral copper is of course crucial in describing the interaction of the positron with these atoms. Table II gives a comparison of the existing model potential and experimental binding energies for Cu. Inclusion of the core-polarization potentials dramatically improves the agreement of the fixed-core Hamiltonian with experiment (for work using similar core Hamiltonians refer to Refs. [28–32]).

The dipole polarizability was computed by evaluating the oscillator strength sum rule. The value obtained, $41.6a_0^3$ (Table II), can be used to help resolve the existing uncertainty over the dipole polarizability of Cu. The tabulation of Ref. [4] gives values of $41.1a_0^3$ [33] and $49.3a_0^3$ [34]. An assessment of the accuracy of the polarizability was done by examining the oscillator strength for the resonant $4s \rightarrow 4p$ collision. The present oscillator strength of 0.702 is in reasonable agreement with the experimental value of 0.659 ± 0.006 [35]. The experimental oscillator strength was derived from the lifetime with a small correction due to an alternate decay path. The Cu $3d^{10}4p\ ^2P^o$ level can decay to the $3d^{10}4s\ ^2S^e$ ground state or the $3d^9 4s^2\ ^2D^e$ metastable state. The experimental lifetimes for the $3d^{10}4p\ ^2P^o$ level [35] were converted to oscillator strengths using the oscilla-

TABLE III. The energy and electron affinity (EA) of the Cu^- ion as a function of L_{int}. Energies are in hartree relative to the energy of the Cu^+ core. The N_{CI} column denotes the number of configurations. The V_{p2} potential was rescaled by a factor of 0.7 for one of the CI calculations. The index L_{int} is equal to $\max(\ell_1,\ell_2)$.

Model	L_{int}	$N_{CI}(^1S^e)$	$E(4s^2\ ^1S^e)$	EA
Calculations without core polarization				
CI (this work)	10	1627	−0.265 196	0.026 715
FCSVM [1]			−0.265 154	0.026 693
Relativistic CI [3]			−0.264 24	0.025 94
Calculations with core polarization				
CI (this work)	0	253	−0.304 767	0.020 825
CI (this work)	1	463	−0.316 021	0.032 079
CI (this work)	2	634	−0.317 019	0.033 077
CI (this work)	3	787	−0.317 266	0.033 324
CI (this work)	10	1627	−0.317 398	0.033 456
CI (with $0.7\times V_{p2}$)	10	1627	−0.322 003	0.038 061
FCSVM (this work)			−0.317 198	0.034 267
Relativistic CI: *ab initio* core polarization [3]			−0.318 02	0.041 30
relativistic CI: Rescaled core polarization [3]			−0.328 69	0.044 75
Experiment [37,51]			−0.329 354	0.045 41

tor strengths for the $3d^{10}4p\ ^2P^o \rightarrow 3d^9 4s^2\ ^2D^e$ transition state quoted in Ref. [36]. The corrections were of the order of about 1–2%. Since the present calculation is in reasonable agreement with the experimental oscillator strength, we recommend that the polarizability of Doolen, $41.1a_0^3$ [33], given in Ref. [4] should be adopted as the preferred value.

Although no explicit calculations upon Ag have been done, the present calculations also have implications for the dipole polarizability of Ag. Once again, there are two recommended values [4], they are $48.4a_0^3$ [33] and $57.8a_0^3$ [34]. The good agreement obtained with the result by Doolen [33] for Cu suggests that $48.4a_0^3$ should be adopted as the preferred polarizability for Ag.

The earlier FCSVM calculations upon e^+Cu used a model potential that was very similar to the present model potential with the major difference being the form of the cutoff parameter in the polarization potentials. The FCSVM calculation used a single value of $\rho = 2.0a_0$, irrespective of the angular momentum state of the valence particles. The dipole polarizability of neutral copper in this potential was $42.5a_0^3$.

The *ab initio* many body perturbation theory (MBPT) core-polarization potential of Dzuba *et al.* [3] underestimates the strength of the core-polarization potential. Therefore, the core-polarization potentials for individual ℓ values were rescaled to bring the binding energies into agreement with experiment. Dzuba *et al* adopted the following scaling factors, 1.18 for $\ell = 0$, 1.42 for $\ell = 1$, and 1.8 for $\ell = 2$.

3. The electron affinity of Cu

The results of a series of calculations for the Cu^- ground state with successively larger basis sets are listed in Table III. The basis used to calculate the electron affinity (EA) was the same as the electron orbital basis used for the e^+ Cu calculations. The present EA of 0.033 46 hartree is marginally smaller than the FCSVM electron affinity of 0.034 267 hartree and about 25% smaller than the CI-MBPT EA of Dzuba *et al.*, 0.0447 hartree. The experimental EA is 0.045 41 hartree [37].

The different way these calculations treat core polarization can explain a major part of the difference in the EA. The FCSVM and CI calculations define the short-range cut off factor empirically, and use it in the one- and two-body polarization potentials. Usage of an ℓ-dependent cutoff parameter in the CI calculations only results in a minor change to the EA.

Dzuba *et al.* [3] appear to treat one- and two-body polarization potentials differently. As mentioned earlier, they scale their ℓ-dependent core-polarization potential by multiplying factors to obtain agreement with experiment. However, they do not appear to multiply the two-body polarization potential by any sort of equivalent factor (no explicit statement about this is made in Ref. [3], but later calculations upon Ag^- and Au^- by the same group [38] state no scaling is done to the two-body potential). Therefore their one- and two-body polarization potentials could be inconsistent in the asymptotic region. The *a priori* justification for usage of a polarization potential that is rescaled for just one part of the core-polarization potential is uncertain. The effect of the two-body polarization potential is to decrease the EA. So although CI-MBPT gives an electron affinity in agreement with experiment, this has been obtained by the expedient of deciding to strengthen only that part of the core-polarization potential that increases the electron affinity. The electron affinity obtained by Dzuba *et al* when they used their purely *ab initio* core-polarization potential was 0.4130 hartree, about 10% smaller than experiment.

The procedure of Dzuba *et al.* was mimicked by weakening the strength of the two-body part of the core-polarization

TABLE IV. Results of CI calculations for e^+Li for orbital bases with a given L_{max}. $E(e^+\mathrm{Li})$ is given relative to the energy of the Li^+ core. The total number of electron and positron orbitals are denoted by N_e and N_p, respectively. The mean electron-nucleus distance $\langle r_e\rangle$, the mean positron-nucleus distance $\langle r_p\rangle$, and the mean square electron-positron distance $\langle r_{ep}^2\rangle$ are given in a_0 and a_0^2. The Γ_v and Γ_c columns give the valence and core annihilation rates, respectively (in 10^9 s^{-1}). The results in the row ∞ are from an $L_{max}\rightarrow\infty$ extrapolation while p gives the exponent used in Eq. (8) to make that extrapolation.

L_{max}	N_e	N_p	N_{CI}	$E(e^+\mathrm{Li})$	$\langle r_e\rangle$	$\langle r_p\rangle$	$\langle r_{ep}^2\rangle$	Γ_c	Γ_v
0	17	16	272	−0.191 624 66	3.831 43	15.5651	283.93	0.000 197	0.001 10
1	32	31	497	−0.199 830 84	3.951 47	10.6469	120.69	0.001 904	0.030 97
2	47	46	722	−0.210 150 81	4.156 97	7.908 11	60.564	0.004 019	0.124 75
3	62	61	947	−0.219 123 72	4.371 59	7.078 09	40.211	0.004 714	0.234 92
4	77	76	1172	−0.225 903 48	4.575 64	6.806 73	32.104	0.004 728	0.338 16
5	92	91	1397	−0.230 936 08	4.766 34	6.728 74	27.950	0.004 521	0.429 97
10	167	166	2522	−0.243 023 09	5.538 93	6.985 41	21.195	0.003 399	0.746 26
15	242	241	3647	−0.247 097 54	6.073 63	7.344 36	19.389	0.002 813	0.923 44
20	317	316	4772	−0.248 834 27	6.420 48	7.605 25	18.606	0.002 517	1.033 85
25	392	391	5897	−0.249 670 85	6.630 32	7.769 38	18.215	0.002 362	1.107 25
27	422	421	6347	−0.249 878 28	6.687 85	7.815 01	18.115	0.002 322	1.129 71
28	437	436	6572	−0.249 964 16	6.712 38	7.834 54	18.074	0.002 305	1.139 79
29	452	451	6797	−0.250 040 24	6.734 48	7.852 18	18.037	0.002 290	1.149 19
30	467	466	7022	−0.250 107 82	6.754 41	7.868 11	18.004	0.002 277	1.157 96
p				3.50	3.05	3.00	3.31	2.04	
∞				−0.250 886	7.036	8.100	17.61	0.002 11	1.404
FCSVM [6]				−0.252 477	9.108	9.966	16.24	0.001 58	1.741

potential by multiplying it by a scaling factor of 0.70. When this was done, the EA increased to 0.038 06 hartree. Thus about half of the difference between the calculated EA and experiment can be recovered by weakening the strength of the two-body potential. The remainder of the difference can probably be attributed to effects not taken into account by the present calculation. They are relativistic effects, inclusion of other polarities of the polarization potential, and other dynamical effects due to the weak binding of electrons in the $3d^{10}$ core.

B. e^+Li results

The results of a series of successively larger calculations using the LTO basis sets are reported in Table IV. All energies are given relative to the energy of the Li^+ ground state which is adopted as the zero-energy position. The largest calculation included angular terms up to $L_{max}=30$ had a minimum of 15 LTOs per spherical harmonic, and had a total of 7022 configurations. This calculation gave an energy of −0.250 107 8 hartree. Despite the inclusion of a large number of single-particle orbitals, the condition for binding is only just satisfied by 0.000 107 8 hartree. The exponents of the LTOs for each ℓ are not particularly well optimized. An optimization of the exponents was done when $L_{max}=20$. However, during the course of these calculations it had been noticed that the optimal values of the LTO exponents for a given ℓ generally changed as L_{max} was increased. Thus, the binding energy of 0.000 107 8 hartree is not believed to represent the variational limit for $L_{max}=30$.

The FCSVM calculations suggested that the e^+Li system consisted of a deformed Ps atom orbiting the Li^+ core [5]. The tendency for the CI wave function to increasingly resemble Ps orbiting a Li^+ core as L_{max} increased is noticeable in the trend for $\langle r_{ep}^2\rangle$ to decrease as L_{max} increases (this expectation is $12.0a_0^2$ for the Ps ground state). The other notable feature about Table IV is the very slow convergence with L_{max}. Building up the wave function for a Ps cluster located at approximately $10a_0$ from the nucleus requires a very large partial-wave expansion. The slow but steady buildup of the Ps cluster was also seen in the gradual increase in the annihilation rate.

The slow convergence of the wave function is also apparent in the partial-wave decomposition given in Table VI. The percentage of the valence wave function comprising orbitals with $\ell=J$ is defined as

$$d_J=\int d^3r_0 d^3r_1 \left|\sum_{i,j} c_{i,j}\delta_{J\ell_i}\delta_{J\ell_j}\langle \ell_i m_i \ell_j m_i|LM_L\rangle \times\langle S_i M_{S_i}\frac{1}{2}\mu_j|SM_S\rangle\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_0)\right|^2. \quad (11)$$

Only 32.7% and 30.2% of the CI wave function comes from the $J=0$ and $J=1$ partial waves. A projection of the FCSVM wave function for e^+-Li gave 25.1% and 25.9% of the wave function in these partial waves [5]. The difference between these percentages was expected since the CI wave function is not converged with respect to further increase of L_{max}.

The behavior of the mean positron radius $\langle r_p\rangle$ is not monotonic. Initially, the positron drifts into the atom as L_{max} is increased. Then, after achieving a minimum value, the

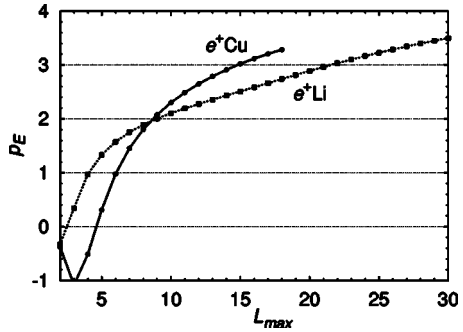

FIG. 1. The exponent relating two separate energy increments using Eq. (10) as a function of L_{max} for e^+Li, and e^+Cu. The analysis of Gribakin and Ludlow [27] suggests a limiting value of 4 as $L_{max}\rightarrow\infty$.

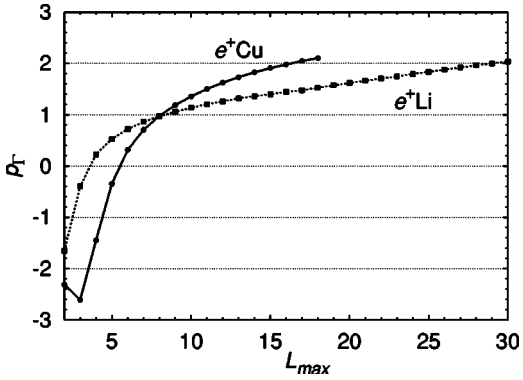

FIG. 2. The exponent relating two separate annihilation rate increments using Eq. (10) as a function of L_{max} for e^+Li, and e^+Cu. The analysis of Gribakin and Ludlow [27] suggests a limiting value of 2 as $L_{max}\rightarrow\infty$.

positron starts to drift away from the atom. This outward drift is accompanied by an outward drift in the mean radius of the electron $\langle r_e\rangle$.

Figure 1 shows values of p_E computed from Eq. (10) as a function of L. It is noticeable that energy increments for e^+-Li do not agree with the expected analytic form [27], namely, $p_E=4$, even when $L_{max}=30$. Although it is possible that the energy is not absolutely stable with respect to further increase in the radial basis, one intuitively expects that a better radial basis would lead to slightly smaller values of p_E at larger values of ℓ and this would further enlarge the discrepancy with the Gribakin and Ludlow estimate. The behavior of p_Γ as a function of L_{max} is shown in Fig. 2. The value of p_Γ increases steadily as a function of L_{max} and is slightly larger than 2 at $L_{max}=30$. It is not clear whether the tendency for p_Γ to overshoot the expected value of 2 [27] is due to a radial basis that is not quite converged or whether it is an intrinsic property of the CI method.

The extrapolations to the $L_{max}\rightarrow\infty$ limit using Eq. (8) are only included in Table IV for completeness. Given that the variational optimization of the radial basis is uncertain, the $L_{max}\rightarrow\infty$ limits should be regarded as indicative rather than as a serious estimate of the binding energy and annihilation rate.

C. The structure of e^+Cu

The properties of e^+Cu, as given by the current CI calculation, are summarized in Table V. The system has a binding energy of 0.005 12 hartree, which is slightly smaller than the binding energies given by the FCSVM and CI-MBPT calculations. The explicit calculation gives about 95% of the binding energy with the remainder coming from the $L_{max}=19\rightarrow\infty$ extrapolation.

The present energy should be relatively close to converged. The $L_{max}=18$ binding energy changed by about 0.000 03 hartree when the number of radial functions for $\ell\geqslant 4$ was changed from 14 to 15. The present binding energy is 10% smaller than the FCSVM binding energy of 0.005 597 hartree and about 20% smaller than the CI-MBPT binding energy of 0.006 25 hartree.

TABLE V. Results of CI calculations for e^+Cu for orbital bases with a given L_{max}. The binding energy of the positron with respect to the Cu ground state, $\varepsilon=|E(e^+\mathrm{Cu})|-0.283\,942\,2$. The organization of the rest of the table is the same as Table VI.

L_{max}	N_e	N_p	N_{CI}	$E(e^+\mathrm{Cu})$	ε	$\langle r_e\rangle$	$\langle r_p\rangle$	Γ_c	Γ_v
0	22	20	440	−0.282 741 1	−0.001 201 1	3.035 44	32.3568	0.000 358	0.000 145
1	42	39	820	−0.283 089 2	−0.000 852 9	3.042 90	28.3245	0.001 575	0.001 813
2	60	57	1144	−0.283 542 4	−0.000 399 7	3.064 49	23.2177	0.005 027	0.010 09
3	77	74	1433	−0.284 244 2	0.000 302 1	3.111 90	17.6973	0.011 368	0.033 98
4	92	89	1658	−0.285 057 2	0.001 115 0	3.172 26	14.1170	0.017 663	0.070 19
5	107	104	1883	−0.285 816 1	0.001 873 9	3.229 62	12.2071	0.022 227	0.109 32
10	182	179	3008	−0.287 914 7	0.003 972 6	3.404 95	9.693 48	0.030 100	0.255 74
15	257	254	4133	−0.288 563 6	0.004 621 4	3.472 49	9.281 66	0.031 460	0.329 17
16	272	269	4358	−0.288 629 3	0.004 687 1	3.480 06	9.245 52	0.031 571	0.338 85
17	287	284	4583	−0.288 683 4	0.004 741 2	3.486 42	9.216 47	0.031 659	0.347 41
18	302	299	4808	−0.288 728 2	0.004 786 0	3.491 80	9.192 86	0.031 729	0.354 99
p				3.29		2.96	3.63	3.95	2.10
∞				−0.289 060	0.005 117	3.539	9.043	0.0321	0.4744
FCSVM revision of Ref. [1]					−0.005 597	3.578	8.663	0.0339	0.544
CI-MBPT [3]					−0.00 625				

Figure 1 and Table V show the convergence of successive increments to the binding energy as a function of L_{max}. Once again, the convergence of the incremental contributions to the expected asymptotic form with $p_E=4$ is slow. It is probable that the successive increments to ε only achieve the asymptotic form when the binding energy is already converged for all practical purposes. In a previous work on the alkaline-earth elements [39], the fact that the energy increments had not reached their asymptotic form meant that a more involved approach to the extrapolation correction was warranted. The extra complexity is hardly needed here since only 5% of the binding energy comes from the extrapolation.

The energy difference between the FCSVM and CI calculation is mainly due to the different core-polarization potentials. As mentioned earlier, the polarizability of the Cu ground state computed with the FCSVM core-polarization potential was $42.5a_0^3$, which is slightly larger than the polarizability when computed with the CI model potential of $41.7a_0^3$. Therefore, the slightly smaller e^+Cu binding energy could be a consequence of a model atom with a slightly smaller dipole polarizability. This has been checked by repeating the CI calculations with $\rho_\ell=2.0a_0$ for all ℓ (this is equivalent to the core-polarization potential used for the FCSVM calculation). When this was done, the $L_{max}=\infty$ binding energy increased to 0.005 47 hartree, the remaining discrepancy with the FCSVM binding energy of 0.005 597 hartree can probably be attributed to the radial basis.

The differences with the CI-MBPT binding energy of 0.006 25 hartree [3] are also likely to be the consequence of two different core interactions. As mentioned earlier, the CI MBPT core-polarization potential was scaled by multiplying the one-body potential by scaling factors between 1.18 and 1.80. Since a corresponding scaling factor was not applied to the two-body potential, it is likely that strength of their V_{p2} potential is too small. Since the two-body e^+-e^- core-polarization potential generally decreases the positron binding energy it is not surprising that the CI-MBPT binding energy is larger than the other predictions of the binding energy. It should also be noted that the CI-MBPT calculation was a relativistic calculation [3].

The energies from these three different model Hamiltonians give an indication of the uncertainty in the positron binding energy. The small differences in the binding energies further strengthen the evidence for the stability of e^+Cu. One of the largest areas of uncertainty is the specification of the core-polarization potential acting on the positron. It is quite likely that the present calculation, with a polarization potential tuned to the electron-core interaction, underestimates the strength of this potential. Comparisons of the scattering lengths of He, Ne, and Ar for electron and positron scattering [12] suggest that the positron core-polarization potential is stronger than the electron core-polarization potential. The sensitivity of the calculation to the positron core-polarization potential can easily be estimated by repeating the calculation with a different set of cutoff parameters. The one-body parameters for $V_{p1}(r_0)$, ρ_ℓ, were all reduced by $0.20a_0$ and the two-body parameter ρ_{p2} was reduced by $0.10a_0$. When this was done the $L_{max}=\infty$ binding energy was 0.005 23 hartree. A reduction in ρ_ℓ by $0.20a_0$ does represent a substantial increase in the strength of $V_{p1}(r_0)$, but it only results in a 2% increase in the size of the binding energy. Similarly, the correlation-polarization potential used in the CI-MBPT calculation probably underestimates the strength of this potential since the strong electron-positron correlations are difficult to represent in an orthodox MBPT expansion [7,17].

TABLE VI. The partial-wave decomposition of the e^+Cu and e^+Li ground state expressed as a percentage (i.e., $d_J\times100$). For reasons of brevity some values of d_J have been omitted. The partial-wave decomposition of the e^+Li FCSVM wave function was taken from Ref. [5] while that for e^+Cu was computed from the wave function described in Sec. III.

	e^+Cu		e^+Li	
J	CI	FCSVM	CI	FCSVM
0	84.825 31	82.7838	32.733 29	25.0850
1	9.692 706	10.7793	30.164 26	25.9023
2	3.090 622	3.5271	16.070 55	16.2376
3	1.275 410	1.5042	8.859 242	10.4985
4	0.556 028	0.6762	4.948 303	6.8839
5	0.261 822		2.821 204	
6	0.131 264		1.647 775	
10	0.013 355		0.245 440	
15	0.001 564		0.036 501	
18	0.000 536		0.014 045	
20			0.007 905	
25			0.002 209	
30			0.000 723	

The breakdown of the e^+Cu wave functions listed in Table VI shows that the high ℓ terms comprise a significant part of the wave function. The $J=0$ and $J=1$ terms comprise 84.9% and 9.67% of the CI wave function. These are reasonably close to the percentages obtained from the projections of the FCSVM wave function listed in Table VI.

The $L_{max}=18$ annihilation rate, Γ_v was only 0.355×10^9 s^{-1}. Upon extrapolation with $p_\Gamma=2.10$ a value of 0.474×10^9 s^{-1} is obtained. This is about 20% smaller than the FCSVM annihilation rate. Only a small part of this difference can be attributed to the different binding energies of these two models. It has been shown [11,12] that the ratio $\Gamma^2/\varepsilon\approx6.4\times10^{19}$ s^{-2} hartree^{-1} for positronic atoms with a parent ionization potential greater than 6.80 eV. Positronic atoms with a smaller binding energy have a longer exponential tail which means the positron is less likely to annihilate with the valence electrons. Therefore a calculation that has a binding energy that is 10% smaller will generally give an annihilation rate which is 5% smaller. We suspect that the bulk of the difference with the FCSVM annihilation is related to the radial basis. It has been noted during the course of these calculations that the annihilation rate was more sensitive to the inclusion of additional orbitals than was the binding energy. The value of p_Γ is larger than the asymptotic value of 2 suggested by the analysis of Gribakin and Ludlow [27]. This could be an indication that further optimization of the radial basis is desirable.

V. SCATTERING OF POSITRONS FROM Cu

The annihilation rate during a collision with an atom or molecule is characterized by the $Z_{\rm eff}$ parameter, which can be interpreted as the number of electrons available for annihilation during a collision. In the simplest model of annihilation, namely, the plane-wave Born approximation, $Z_{\rm eff}$ is equal to the number of electrons in the atom or molecule [40]. This is sometimes called the Dirac rate.

One of the salient features of the early annihilation experiments was that the measured $Z_{\rm eff}$ was much larger than the Dirac rate [41]. At that time the suggestion was made that positrons forming bound states with the gas molecules were somehow responsible for the large rates [41–43]. As time evolved, further research resulted in experiments yielding ever larger values of $Z_{\rm eff}$, for example, heptane with 58 electrons has a $Z_{\rm eff}$ of 242 000 [44]. The details of how the bound states actually increased $Z_{\rm eff}$ were somewhat vague until a model was advanced in which $Z_{\rm eff}$ was proportional to the density of vibrational levels [7,10].

The tendency to associate bound states with large values of $Z_{\rm eff}$ immediately raises the question of whether the converse is true. Is the threshold $Z_{\rm eff}$ always large when the scattering system supports a bound state? An initial answer to the question can be determined by applying effective range theory to the problem [12]. The real part of the scattering length A is given by

$$A=\frac{1}{\sqrt{2|\varepsilon|}}, \tag{12}$$

while at zero energy $Z_{\rm eff}$ becomes

$$Z_{\rm eff}(k=0)=4.40153\times 10^{-11}\frac{\Gamma}{\sqrt{|\varepsilon|^3}}. \tag{13}$$

In these equations, ε is the binding energy expressed in hartree while the annihilation rate is given in s^{-1}. A similar equation has been derived by Gribakin [11] using a different technique. It is worth noting that similar techniques have been long used in nucleus physics to relate the binding energy and lifetimes of hadronic atoms to the determination of the low-energy elastic and absorption cross sections [45–47].

The application of effective range theory to e^+Cu using the FCSVM energy and annihilation rate gave a scattering length of $9.45a_0$ and a threshold $Z_{\rm eff}$ of 60.8 [12]. Usage of the CI binding energy and annihilation rate would give similar values for the scattering length and $Z_{\rm eff}$ which do not need to be given here.

More refined estimates of the threshold $Z_{\rm eff}$ and scattering length have been determined by tuning a model potential to the properties of the e^+Cu ground state, and then using that model potential in a solution of the Schrödinger equation [12]. This gave a scattering length of $11.8a_0$ and a threshold $Z_{\rm eff}$ was 96.4. These two calculations, with their broadly consistent results, gave an indication that the existence of an e^+ atom bound state did not necessarily imply a large threshold $Z_{\rm eff}$.

However, an explicit solution of the Schrödinger equation is also desirable to give an absolute demonstration that the e^+-Cu scattering system has only a moderately large $Z_{\rm eff}$. In this section, the results of a Kohn variational calculation reporting the scattering length and threshold $Z_{\rm eff}$ for the $L=0$ partial wave are given.

Application of the Kohn variational method

The Schrödinger equation was solved at zero energy by converting the CI program to handle a Kohn variational calculation. This involved adding two additional basis functions to the calculation. These functions were

$$\phi_s=\psi_{4s}(\mathbf{r}_1)r_0, \tag{14}$$

$$\phi_c=\psi_{4s}(\mathbf{r}_1)[1-\exp(-\beta r_0)]A, \tag{15}$$

where $\psi_{4s}(\mathbf{r}_1)$ is the wave function of the Cu ground state and A is the scattering length. The $[1-\exp(-\beta r_0)]$ factor is used to make ϕ_c go to zero as $r_0\rightarrow 0$. The factor β was set to 2.0 for the present calculations. The scattering lengths and $Z_{\rm eff}$ were insensitive to the precise value chosen for β.

The trial wave function had the form

$$|\Psi;LS\rangle=\phi_s+\phi_c+\sum_{i,j}c_{i,j}\langle \ell_i m_i \ell_j m_j|LM_L\rangle \times\left\langle \frac{1}{2}\mu_i\frac{1}{2}\mu_j\middle|SM_S\right\rangle \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_0). \tag{16}$$

The short-range functions were almost the same as the basis used in the calculation of the e^+Cu ground state. Some extra positron orbitals for the $\ell=0,1$, and 2 partial waves were added to better describe the positron at large distances from the nucleus were added to the basis. A total of 50 $\ell=1$ LTOs were used for the positron wave function since it is the $\ell=1$ LTOs that represent the relaxation of the positron in the field of the dipole polarization potential. The radial integrals were performed to a maximum radius of $625a_0$. It is believed the scattering length is converged to better than 5% with respect to further enlargements of the radial basis.

The annihilation parameter $Z_{\rm eff}$ is calculated from the scattering wave function by the identity [8,40,48],

$$Z_{\rm eff}=4N_e\int d^3r_0 d^3r_1,\ldots,d^3r_{N_e} \times|\hat{O}^s\Psi(\mathbf{r}_0;\mathbf{r}_1,\ldots,\mathbf{r}_{N_e})|^2\delta(\mathbf{r}_0-\mathbf{r}_1), \tag{17}$$

where $\Psi(\mathbf{r}_0;\mathbf{r}_1,\ldots,\mathbf{r}_{N_e})$ is the total wave function of the system and $\hat{O}^s$ is a spin-projection operator that only allows annihilation to occur in the 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., $Z_{\rm eff}=N_e$.

The details of the annihilation rate calculation were checked by performing calculations upon the e^+-H system. The value of $Z_{\rm eff}$ for the $J=0$ partial wave at $k=0.5a_0^{-1}$ in the three-state H($1s$, $2s$, $2p$) close-coupling approximation,

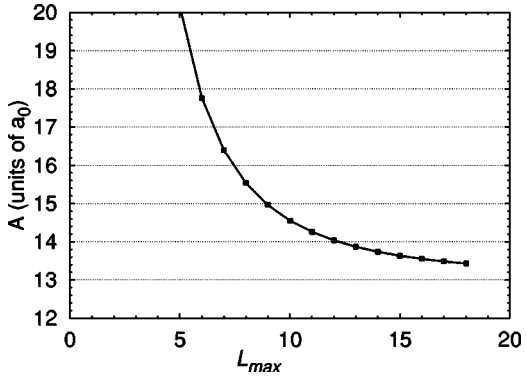

FIG. 3. The scattering length (in a_0) for e^+-Cu scattering as a function of L_{max}.

namely, 0.4465, is in agreement with that previously determined in a momentum-space *T*-matrix calculation [8], namely, 0.4464. The contributions to $Z_{\rm eff}$ from the valence and core electrons were computed separately and denoted as $Z^c_{\rm eff}$ and $Z^v_{\rm eff}$.

The scattering length for e^+-Cu scattering is shown in Fig. 3 as a function of L_{max}. The scattering length changes sign at $L_{max}=3$ since this is the minimum L_{max} for positron binding. The scattering length decreases monotonically for $L_{max}>3$ and was $A=13.43\ a_0$ at $L_{max}=18$. The power-series extrapolation gives $p_A=3.55$ and a final scattering length of $13.07a_0$ which is about 10% larger than the model potential scattering length of $11.8a_0$ [12]. (Note, the model potential analysis [12] was tuned to the FCSVM energy of 0.005 597 hartree. This accounts for 5% of the discrepancy between the model potential and Kohn scattering lengths.)

Figures 4 and 5 show that the variation of $Z^v_{\rm eff}$ versus L_{max} and the variation of the incremental contribution, $\Delta Z^v_{\rm eff}$ versus L_{max}, are not monotonic. The annihilation parameter reaches a maximum near $L_{max}=3$, decreases steadily until $L_{max}=10$, and then starts to increase for $L_{max}>12$. This behavior is caused by two opposing trends. First, theoretical analyses have shown that the threshold $Z^v_{\rm eff}$ should be proportional to A^2 for large values of the scattering length [10,12]. Therefore, $Z^v_{\rm eff}$ should decrease as L_{max} increases. The tendency for $Z^v_{\rm eff}$ to decrease as L_{max} increases from

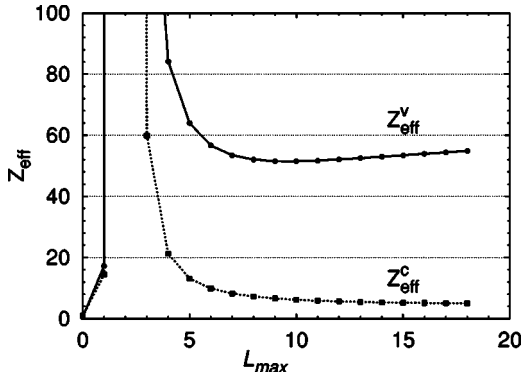

FIG. 4. The threshold $Z^v_{\rm eff}$ (solid line) and $Z^c_{\rm eff}$ (dashed line) for *s*-wave e^+-Cu scattering as a function of L_{max}. At $L_{max}=2$ the annihilation parameter $Z^v_{\rm eff}$ was 10 000.

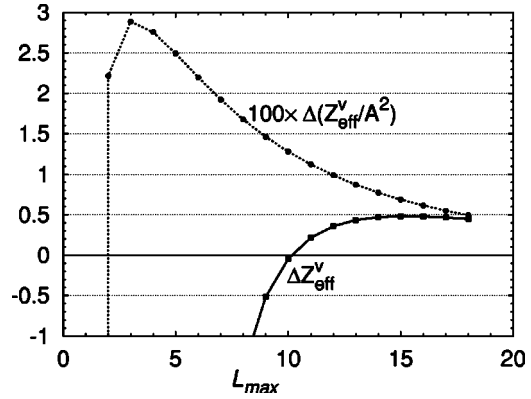

FIG. 5. The incremental contributions to the annihilation parameter $\Delta Z^v_{\rm eff}$ (solid line) for *s*-wave e^+-Cu scattering as a function of L_{max}. Also shown are incremental contributions to the ratio $Z^v_{\rm eff}/A^2$.

$3\rightarrow10$ is essentially a consequence of the normalization of the asymptotic wave function. The increase in $Z^v_{\rm eff}$ for $L_{max}>12$ occurs because the inclusion of orbitals with increasingly larger ℓ into the calculation permits a better localization of the positron close to the electron. However, the incremental changes to $Z^v_{\rm eff}$ for successive values of $L_{max}>12$ show clearly that $Z^v_{\rm eff}$ is nowhere near its asymptotic form at $L_{max}=18$.

These two effects mean that a simple extrapolation of $Z^v_{\rm eff}$ is fraught with uncertainty. For example, at $L_{max}=18$, one obtains $Z^v_{\rm eff}=54.84$. Performing the extrapolation with $p_Z=0.69$ gave 140.7. Such a large contribution to $Z^v_{\rm eff}$ from the $L_{max}=19\rightarrow\infty$ terms is simply an artifact of the extrapolation procedure.

Taking the view that the difficulties with $Z^v_{\rm eff}$ are due to simultaneous variation of A with L_{max} suggests that the ratio, $Z^v_{\rm eff}/A^2$ would be more amenable to analysis. Figure 5 shows that incremental changes to $Z^v_{\rm eff}/A^2$ for successive L_{max} exhibit a steady and regular decrease as L_{max} increases. Although this is not shown, the behavior of $Z^v_{\rm eff}/A^2$ is a smoothly increasing function for increasing L_{max}. Therefore, the $L_{max}=19\rightarrow\infty$ contribution was determined by first extrapolating $Z^v_{\rm eff}/A^2$ to ∞. Then $\langle Z^v_{\rm eff}/A^2\rangle_\infty$ was multiplied by the extrapolated scattering length of $13.07a_0$ to give 68.28 for the $L_{max}=\infty$ limit of $Z^v_{\rm eff}$.

The behavior of $Z^c_{\rm eff}$ with L_{max} shown in Fig. 4 was relatively smooth at large L_{max} and showed a tendency to decrease as L_{max} decreased. At $L_{max}=18$, $Z^c_{\rm eff}$ was 4.99. Performing an extrapolation with $p_Z=3.57$ yielded a final value of 4.63 for $Z^c_{\rm eff}$.

Combining the core and valence $Z_{\rm eff}$ yields a value of 59.84 at $L_{max}=18$. The extrapolation to the $L_{max}=\infty$ limit gave $Z_{\rm eff}=72.91$ which should be regarded our best estimate of the threshold annihilation parameter.

The present calculation shows unequivocally that $Z_{\rm eff}$ for a metal vapor does not have to be very large. Analysis of a large number of annihilation experiments for noble gases and molecules with single bonds has resulted in the semiempirical formula [9,49],

TABLE VII. Results of CI calculations for CuPs with $L_{int}=3$ for increasing L_{max}. The total number of electron and positron orbitals are denoted by N_e and N_p, respectively. The three-body energy of the CuPs (in hartree) relative to the energy of the Cu^+ core is denoted by E(CuPs), while ε gives the binding energy against dissociation into Cu + Ps. The mean electron-nucleus distance $\langle r_e \rangle$, and positron-nucleus distance $\langle r_p \rangle$, are given in a_0. The valence 2γ annihilation rate (Γ_v) and core annihilation rate (Γ_c) are given in 10^9 s^{-1}. The results in the row ∞ are from an $L_{max}\rightarrow\infty$ extrapolation and the exponents used in making the extrapolation are in the row labeled *p*.

L_{max}	N_e	N_p	N_{CI}	E(CuPs)	ε	$\langle r_e \rangle$	$\langle r_p \rangle$	Γ_c	Γ_v
0	15	12	1440	−0.439 805 5	−0.094 135 7	3.494 39	5.369 08	0.165 79	0.102 24
1	28	23	4677	−0.482 342 6	−0.051 598 6	3.549 79	5.046 20	0.173 99	0.224 65
2	40	32	10 470	−0.505 641 9	−0.028 299 3	3.614 46	4.936 44	0.171 02	0.372 72
3	48	40	16 194	−0.520 004 7	−0.013 936 5	3.673 95	4.920 97	0.163 99	0.527 87
4	56	48	22 578	−0.528 668 1	−0.005 273 1	3.730 59	4.953 70	0.155 52	0.661 99
5	64	56	29 106	−0.534 216 9	0.000 275 7	3.779 65	5.000 79	0.148 16	0.774 68
6	72	64	35 858	−0.537 939 2	0.003 998 0	3.821 04	5.049 24	0.142 19	0.868 84
7	80	72	42 834	−0.540 519 3	0.006 578 0	3.855 46	5.093 96	0.137 46	0.947 73
8	88	80	49 810	−0.542 353 6	0.008 412 4	3.883 74	5.133 11	0.133 75	1.014 17
9	96	88	56 786	−0.543 686 8	0.009 745 6	3.906 74	5.166 23	0.130 85	1.070 59
10	104	96	63 762	−0.544 673 4	0.010 732 2	3.925 28	5.193 65	0.128 57	1.118 88
p				2.86	2.86	2.04	1.79	2.33	1.48
∞				−0.549 52	0.015 58	4.093	5.521	0.113	2.028

$$\ln(Z_{\rm eff}) \approx B|I-E_{Ps}|^{-1}+A, \tag{18}$$

where $B\approx 44$ and $A\approx -1$ (the atomic ionization potential I, and Ps binding energy E_{Ps} are given in eV). Using Eq. (18) as a guide, there have been speculations that metal vapors such as Zn and Cd, and by implication Cu, could have threshold $Z_{\rm eff}$ of order 10^6 [9]. The earlier model potential and effective range estimates [12] had suggested that such large values of $Z_{\rm eff}$ were very unlikely. The present Kohn variational calculation completely excludes the possibility.

VI. THE STRUCTURE OF CuPs

In the present section, the CI method is used to determine the structure and binding energy of CuPs. The CuPs system is relatively amenable to treatment by the CI method as the Ps cluster was localized relatively close to the nucleus. Generally the closer the Ps cluster is to the nucleus, the more quickly convergent the wave function is with L_{max}.

Technical details

All details of the effective Hamiltonian (apart from the additional valence electron) are exactly as that used earlier. The atomic wave function is taken to be a linear combination of states created by coupling antisymmetric atomic states to single-particle positron states; viz,

$$|\Psi;LS\rangle = \sum_{i,j} c_{i,j}\langle L_i M_i \ell_j m_j | L M_L\rangle \times \left\langle S_i M_{S_i} \frac{1}{2}\mu_j \middle| S M_S \right\rangle \Phi_i(\text{atom};L_iS_i)\phi_j(\mathbf{r}_0). \tag{19}$$

The CI basis consisted of all the possible $L=0$ configurations that could be formed by letting the two electrons and positron populate all the single-particle orbitals with two restrictions. Suppose ℓ_1 and ℓ_2 are the orbital angular momenta of the two electrons in a given CI basis function, then the rules

$$\max(\ell_1,\ell_2,\ell_0) \leqslant L_{max}, \tag{20}$$

$$\min(\ell_1,\ell_2) \leqslant L_{int}, \tag{21}$$

define the basis. The selection rule involving L_{int} is used to reduce the dimension of the CI basis without compromising the accuracy of the wave function. A previous study of PsH showed the choice $L_{int}=3$ could halve the dimension of the resulting secular equations with less than a 1% change in the binding energy [20].

The condition for binding is that the energy of the CuPs state be lower than the energy of the Ps(1s) + Cu(4s) dissociation channel. The binding energy for a particular basis is thus defined as $\varepsilon = |E(\text{CuPs})| - (0.283\,941\,2 + 0.250)$ and binding occurs when ε is positive. [Note, the Cu(4s) energy of 0.283 941 2 hartree is slightly different from that given in Table I due to a smaller LTO basis for the $\ell=0$ electron.] Table VII gives energies and expectation values for a series of calculations with increasing L_{max}. The number of Laguerre orbitals of a particular type are also listed in the table. The largest calculation included single-particle orbitals up to $L_{max}=10$ and this calculation included 63 762 configurations. The exponents of the orthogonal Laguerre orbitals were optimized manually.

The $L_{max}=10$ estimate of the binding energy was 0.010 732 hartree. Using the $L_{max}=8,9$, and 10 calculations to extrapolate to ∞ gave a binding energy of 0.015 58 hartree. The correction to the binding energy was almost 50%. With such a large correction, some estimate of the uncertainty in the correction is desirable and the procedure

TABLE VIII. Results of CI calculations for CuPs for orbital bases with a given L_{int} with a fixed $L_{max}=10$ ($N_e=104$ and $N_p=96$ for all calculations). The organization of the table is the same as Table VII.

L_{int}	N_{CI}	E(CuPs)	ε	$\langle r_e \rangle$	$\langle r_p \rangle$	Γ_c	Γ_v
0	12 885	−0.538 214 7	0.004 273 5	3.982 10	5.284 50	0.122 93	1.105 19
1	30 344	−0.542 509 3	0.008 568 1	3.945 80	5.230 42	0.126 12	1.111 03
2	49 886	−0.544 085 0	0.010 143 8	3.930 86	5.204 67	0.127 83	1.115 49
3	63 762	−0.544 673 4	0.010 732 2	3.925 28	5.193 65	0.128 57	1.118 88

adopted in Ref. [39] was used to make an estimate of the uncertainty. The exponent p_E was 2.86, somewhat smaller than the expected value of $p_E=4$. Since the exponent p_E increases with increaseing L_{max}, an estimate of the minimum binding energy can be made by simply using $p_E=4$ in Eq. (8). This gave a binding energy of 0.013 56 hartree. Choosing an intermediate value, $p_E=3.43$, gave a binding energy of 0.014 33 hartree. The $p_E=3.43$ extrapolation probably gives the most reasonable estimate of the $L_{max}\rightarrow\infty$ binding energy.

Table VIII reports a sequence of calculations for $L_{int}=0,1,2$, and 3 with L_{max} set to 10. These calculations retained all the electron and positron orbitals of the $L_{max}=10$ basis. One notable feature of Table VIII is that CuPs is stable for all values of L_{int}. Most of the expectation values hardly changed as L_{int} increased from 0 to 3. The exception was the binding energy ε, which doubled in size as L_{int} increased from 0 to 3. However, the convergence pattern suggests that ε is converged to better than 5% with respect to further enlargement of L_{int}. Other quantities would appear to be converged at the 1% level with respect to a further increase in L_{int}.

The explicitly calculated annihilation rate (Γ_v) at $L_{max}=10$, 1.12×10^9 s^{-1} is only about half of the extrapolated annihilation rate of 2.03×10^9 s^{-1}. The value of p_Γ derived from the $L_{max}=8,9$, and 10 calculations was 1.48. Choosing $p_\Gamma=2$ gave $\Gamma_v=1.576\times10^9$ s^{-1} while an intermediate p_Γ of 1.74 gave $\Gamma_v=1.735\times10^9$ s^{-1}. The annihilation rates for PsH [14], LiPs [17], and NaPs [17] suggest that the CuPs annihilation rate should be slightly greater than 2.0×10^9 s^{-1}. The present annihilation rate is consistent with this idea when the uncertainties relating to the convergence of the CI wave function are taken into consideration.

VII. CONCLUSIONS

The CI method has been used to compute the binding energies and annihilation rates for e^+Li and e^+Cu. The calculations upon e^+Li dramatically reveal the difficulties associated with performing a CI calculation upon a system that can be regarded as a Ps cluster orbiting a residual ion core at large distances from the nucleus.

The calculations upon the e^+Cu ground state complement the previous calculations for this system [1,3]. Variations in the details of the core-polarization potential contribute to three different binding energies ranging from 0.0051 to 0.0062 hartree. It is clear that the specification of the core-polarization potential represents the largest source of uncertainty in understanding the positron-copper interaction. The extent to which the core-polarization potential is also compensating for relativistic shifts in the energy also requires clarification.

The Kohn variational calculations for e^+-Cu scattering gave $13.07a_0$ for the scattering length and 72.91 for the threshold $Z_{\rm eff}$. These calculations were not performed in the expectation that they would motivate an experimental investigation. Due to its high melting temperature and the existence of a low-lying metastable state, a gas of neutral copper atoms in the ground state is rather hard to make. Instead, these calculations were performed to improve understanding about the dynamics of the positron annihilation process. The present calculations demonstrate in a convincing manner that atoms that have an ionization potential not much larger than 6.80 eV, and which can bind a positron do not necessarily have a very large $Z_{\rm eff}$ at threshold.

The CI method has been used to compute the binding energies and other expectation values for CuPs. The present best estimate of the binding energy, 0.0143 hartree, is about four times as large as that reported previously [19].

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