

## Configuration-interaction calculations of PsH and $e^+Be$

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The configuration-interaction (CI) method is applied to the study of the positronium-hydride (PsH) and positronic-beryllium ( $e^+Be$ ) systems. The binding energy and other properties are slowly convergent with respect to the angular momentum of the orbitals used to construct the CI basis states. The largest calculations recover 94% and 80% of the binding energy against dissociation when compared with existing calculations of PsH and  $e^+Be$ . Extrapolating using CI convergence trends improves these results to 99% and 98%, respectively. Convergence is not so good for the electron-positron annihilation rates, but the extrapolated annihilation rates were within 10% of the best calculations. Two different schemes have been used to construct the CI basis, and it is found that it is possible to discard roughly half the CI basis with almost no degradation in the binding energy and the annihilation rate. These investigations demonstrate the feasibility of using single particle orbitals centred on the nucleus to represent positronic systems with two valence electrons.

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### I. INTRODUCTION

The existence of positron and positronium atomic bound states has over recent years become increasingly well established, and remains one of the more interesting problems within the field of positron atomic physics [1,2].

Since the theoretical demonstration that positronium hydride was bound in 1951 [3], a variety of computational methods have been used to study positron ( $e^+$ ) and positronium (Ps) binding to atoms with varying degrees of success. So far, the two most successful approaches have been the stochastic variational method (SVM) [4,5] and the quantum Monte Carlo methods [6,7]. These methods owe their success to the fact that the interactions between pairs of particles are treated on an equal footing. This makes them particularly suitable for treating positron binding systems with their strong electron-positron correlations [4]. However, for various reasons, it is increasingly tedious to apply the SVM and its fixed-core variant [8] to heavier systems. For example, calculations upon  $e^+Zn$  [9] and KPs [10] each took almost one year of computer time, and even then the binding energies and annihilation rates were far from converged. Therefore, we decided to study the application of the configuration-interaction (CI) method to positron binding atomic states in order to determine whether it would make these heavier systems more accessible to investigation.

Although the CI method is one of the most commonly used methods in the calculation of atomic structures, it has not been applied to positronic systems on a large scale. The first CI calculation upon positronium hydride (PsH) did demonstrate the stability of the system, but only yielded 0.3% [11] of the three-body binding energy. This was improved to 35% by Strasburger and Chojnacki [12] and more recently to 85% [13] in a precursor to the present calculation. The main problem in applying the CI method to positron binding systems arises from the attractive electron-positron interaction that leads to the formation of a Ps cluster (i.e. something akin

to a positronium atom). The accurate representation of a Ps cluster using only single-particle orbitals centered on the nucleus requires the inclusion of terms with high angular momenta [14].

The first large-scale CI calculation upon a positronic atom was undertaken by Mitroy and Ryzhikh upon  $e^+Cu$  [14]. While this calculation was able to replicate an earlier prediction of positron binding, the binding energy was much smaller than the previous estimate computed with the fixed-core SVM (FCSVM) [15]. The CI basis was constructed with an *ad hoc* set of orbitals and it was clear that a converged binding energy would require a systematic approach to both the generation of single-particle orbitals and the CI basis. This was first achieved by Dzuba and coworkers [16,17] who used a *B*-spline basis for their converged CI calculations upon positronic copper and silver. An alternative approach was adopted by Bromley *et al.* [13,18] who used a mixed Slater and Laguerre-type orbital basis to investigate a variety of systems containing two valence electrons and a positron. While the basis can be increased systematically, the larger dimensionality associated with a system containing two electrons meant that these calculations gave energies far from convergence. Even so, the systems  $e^+Ca$ ,  $e^+Cd$ , and  $CuPs$  were all shown to be electrically stable [13,18].

In the present paper, the CI method is applied to the calculation of PsH and positronic-beryllium ( $e^+Be$ ) ground states. Since accurate binding energies and wave functions have been reported for both of these systems [8,19], they represent an ideal computational laboratory with which to study the suitability of the CI method. Another reason for investigating these systems is that they have completely different structures. The PsH system consists of a reasonably well-defined Ps atom bound to a H atom, somewhat similar to a light isotope of the  $H_2$  molecule [20]. Positronic beryllium, however, finds the positron orbiting a polarized neutral Be atom at a relatively large distance from the nucleus [8]. Although there are convergence difficulties associated with treating the Ps cluster, the present results indicate that it is possible to compute energies and annihilation rates that are close enough to convergence to be useful. The extrapolated

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binding energies are within 2% of the best previously computed values, while the annihilation rates are within 10% of the expected values.

## II. TECHNICAL DETAILS

The CI method is one of the standard approaches for computing atomic structures [21], so only a brief description is given here. The atomic wave function is taken to be a linear combination of states created by multiplying atomic states to single-particle positron states with the usual Clebsch-Gordan coupling coefficients,

$$|\Psi;LS\rangle = \sum_{i,j} c_{i,j} \langle L_i M_i l_j m_j | LM_L \rangle \times \left\langle S_i M_{S_i} \frac{1}{2} \mu_j \middle| S M_S \right\rangle \Phi_i^{\text{Atom}}(L_i S_i) \phi_j(\mathbf{r}_0). \quad (2.1)$$

In this expression  $\Phi_i^{\text{Atom}}(L_i S_i)$  is an antisymmetric atomic wave function with good  $L$  and  $S$  quantum numbers. The function  $\phi_j(\mathbf{r}_0)$  is a single-positron orbital. The single-particle orbitals that make up the total wave function are written as a product of a radial function and a spherical harmonic,

$$\phi(\mathbf{r}) = P(r) Y_{lm}(\hat{\mathbf{r}}). \quad (2.2)$$

The specific details of the calculation were slightly different for PsH and  $e^+ \text{Be}$ , so we will first describe the details of the PsH calculation, and then  $e^+ \text{Be}$ .

### A. Technical details for details for PsH

The Hamiltonian for the PsH atom consisting of  $N_e = 2$  electrons and a positron was

$$H = -\frac{1}{2} \nabla_0^2 + \sum_{i=1}^{N_e} -\frac{1}{2} \nabla_i^2 + \frac{1}{r_0} - \sum_{i=1}^{N_e} \frac{1}{r_i} + \sum_{i<j}^{N_e} \frac{1}{r_{ij}} - \sum_{i=1}^{N_e} \frac{1}{r_{i0}}. \quad (2.3)$$

In this expression, the  $\mathbf{r}_i$  refer to the electron coordinates while  $\mathbf{r}_0$  refers to the positron coordinate.

The single-particle orbital basis was constructed from an orthogonal Laguerre basis. The dimension of such a basis can be made arbitrarily large without any linear dependence problems arising. The Laguerre basis functions are defined by

$$\chi_\alpha(r) = N_\alpha r^{l+1} \exp(-\lambda_\alpha r) L_{n_\alpha - l - 1}^{(2l+2)}(2\lambda_\alpha r), \quad (2.4)$$

where the normalization constant is

$$N_\alpha = \sqrt{\frac{(2\lambda_\alpha)^{2l+3} (n_\alpha - l - 1)!}{(l + n_\alpha + 1)!}}. \quad (2.5)$$

The function  $L_{n_\alpha - l - 1}^{(2l+2)}(2\lambda_\alpha r)$  is an associated Laguerre polynomial that can be defined in terms of a confluent hypergeometric function [22] as

$$L_{n_\alpha - l - 1}^{(2l+2)}(2\lambda_\alpha r) = \frac{(n_\alpha + l + 1)!}{(n_\alpha - l - 1)! (2l + 2)!} \times M(-[n_\alpha - l - 1], 2l + 2, 2\lambda_\alpha r). \quad (2.6)$$

The Laguerre functions were not computed using the power-series expression for the confluent hypergeometric function. Rather, the recursion relation

$$(n + 1) L_{n+1}^\alpha(x) = (2n + \alpha + 1 - x) L_n^\alpha(x) \quad (2.7)$$

was used with  $L_0^{2l+2}(x)$  and  $L_1^{2l+2}(x)$  as starting values.

Besides its good linear dependence properties, the Laguerre basis has the advantage that the basis can be characterized by a single exponential parameter. This made it easy to optimize the PsH energy with respect to variations in the Laguerre basis.

Although a Laguerre basis does have the property that most of the matrix elements can be evaluated analytically, this was not done and all matrix elements were computed numerically using tabulations of the orbitals on a radial  $r$ -space grid. The details of the procedures used to evaluate the two-particle coulomb integrals may be found in the Appendix.

Two different approaches were used for the construction of the CI basis. In the first, all the possible  $L = 0$  configurations that could be formed by letting the two electrons and positron populate all the single-particle orbitals with  $l \leq L_{\text{max}}$  were included in the basis. The convergence of the binding energy and other system properties could then be studied as a function of  $L_{\text{max}}$ , thus permitting extrapolation to the  $L_{\text{max}} \rightarrow \infty$  limit.

The second approach used to construct the CI basis recognizes the fact that the electron-positron correlations are much stronger than the electron-electron correlations. It is the electron-positron correlations that largely mandate the inclusion of orbitals with large values of  $l$ . An additional parameter  $L_{\text{int}}$  was defined and used to restrict the size of the CI basis with a selection rule. Suppose  $l_1$  and  $l_2$  are the orbital angular momentum of the two electrons in a given CI basis function, then the rule

$$\min(l_1, l_2) \leq L_{\text{int}} \quad (2.8)$$

was used to reduce the size of the CI basis (note, a basis with  $L_{\text{int}} = L_{\text{max}}$  had no restrictions upon orbital occupancy). This rule can be motivated by writing the CI expansion in a close-coupling-type expansion, written heuristically as

$$|\Psi;LS\rangle = \sum_{im} c_{i,m} \phi_i^J(\mathbf{r}_1) [\phi_m^{Ps}(\mathbf{r}_2, \mathbf{r}_0)]_J = \sum_i c_{i,j} \phi_i^J(\mathbf{r}_1) \sum_{jk} [\phi_j(\mathbf{r}_2) \phi_k(\mathbf{r}_0)]_J. \quad (2.9)$$

One electron and positron are coupled to form a state with net angular momentum  $J$ , which is then coupled to the second electron (occupying a single-particle state with angular momentum  $J$ ). Suppose it is wished to include a state analogous to the Ps ground state with center of mass angular mo-

momentum zero coupled the rest of the system. Then the partial wave expansion of  $\phi^{Ps}(\mathbf{r}_0 - \mathbf{r}_2)$  would be written as  $\sum_{jk} [\phi_j(\mathbf{r}_2)\phi_k(\mathbf{r}_0)]_{j=0}$  with the net angular momentum of the coupled orbital product equal to zero. Thus, the  $L_{int}$  parameter is equivalent to the maximum orbital angular momentum of the Ps-type state (or H-type state) that would be included in a close-coupling expansion involving products of H-type and Ps-type states.

The secular equations that arise with three active particles typically have dimensions exceeding 10 000 and, therefore, the sparse matrix diagonalization was performed with an iterative algorithm. The program of Stathopoulos and Fischer [23], which uses the Davidson algorithm [24] was used to perform the diagonalizations. The largest calculations performed had dimensionalities of nearly 100 000. Typically 240 iterations were required to diagonalize the PsH Hamiltonian while about 800 iterations were required to diagonalize the  $e^+Be$  Hamiltonian.

Various expectation values were computed to provide information about the structure of the PsH ground state. The mean distance of the electron and positron from the nucleus are denoted by  $\langle r_e \rangle$  and  $\langle r_p \rangle$ . The mean of the square of the distance between the electron and positron,  $\langle r_{ep}^2 \rangle$ , was also computed.

The positronic atom will decay by electron-positron annihilation and the  $2\gamma$  annihilation rate is computed to give an estimate of the lifetime. (Note that the  $2\gamma$  rate also gives information about the tendency for the electron and positron to form a Ps cluster.) The annihilation rate for the  $2\gamma$  decay summed over all possible final states [25–27] is

$$\begin{aligned}
 \Gamma &= 4\pi c \alpha^4 a_0^2 N_e \langle \Psi(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}; \mathbf{r}_0) | \hat{O}_{N_e}^s \delta(\mathbf{r}_{N_e} - \mathbf{r}_0) | \\
 &\quad \times \Psi(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}; \mathbf{r}_0) \rangle \\
 &= 4\pi c \alpha^4 a_0^2 N_e \int d^3\tau | \hat{O}_{N_e}^s \Psi(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}; \mathbf{r}_{N_e}) |^2.
 \end{aligned} \quad (2.10)$$

The operator  $\hat{O}_{N_e}^s$  is a projection operator that selects spin-0 combinations of the  $N_e$  electron and the positron.

The  $L_{max} \rightarrow \infty$  limit was estimated using a simple extrapolation technique. Making the assumption that successive increments ( $X_L$ ) to any expectation value ( $\langle X \rangle$ ) scale as  $1/L^p$  for sufficiently large  $L$ , it is possible to write

$$\langle X \rangle = \lim_{L_{max} \rightarrow \infty} \left( \sum_{L=0}^{L_{max}} X_L + \Delta \sum_{L=L_{max}+1}^{\infty} \frac{1}{L^p} \right). \quad (2.11)$$

The power series is easy to evaluate, the coefficient  $\Delta$  is defined as

$$\Delta = X_{L_{max}} (L_{max})^p, \quad (2.12)$$

and the exponent  $p$  can be derived from

$$\left( \frac{L_{max}}{L_{max}-1} \right)^p = \frac{X_{L_{max}-1}}{X_{L_{max}}}. \quad (2.13)$$

There is a considerable degree of uncertainty attached to the extrapolation since the asymptotic form in  $L_{max}$  (i.e.,  $p$ ) is not known. However, the error in making the extrapolation can be kept to a reasonable size by making  $L_{max}$  as large as possible. Suppose 80% of the energy is given by explicit calculation, and also suppose that the error in the extrapolation correction (of the remaining contribution to the energy) is 20%, then the net error in the energy will be 4%. For PsH the net error in the extrapolated energy turned out to be about 1%. The annihilation rate is much more slowly convergent with  $L_{max}$  and here the error is 10%.

### B. Technical details for $e^+Be$

Many aspects of the calculation for  $e^+Be$  and PsH are the same, so only those aspects of the calculations that are different will be mentioned.

The calculations for  $e^+Be$  were done in a fixed-core approximation. The effective Hamiltonian for the system with  $N_e = 2$  valence electrons and a positron was

$$\begin{aligned}
 H &= -\frac{1}{2} \nabla_0^2 - \sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 + \sum_{i=1}^{N_e} [V_{dir}(\mathbf{r}_i) + V_{exc}(\mathbf{r}_i) + V_{p1}(\mathbf{r}_i)] \\
 &\quad - V_{dir}(\mathbf{r}_0) + V_{p1}(\mathbf{r}_0) + \sum_{i < j}^{N_e} \frac{1}{r_{ij}} - \sum_{i=1}^{N_e} \frac{1}{r_{i0}} - \sum_{i < j}^{N_e} V_{p2}(\mathbf{r}_i, \mathbf{r}_j) \\
 &\quad + \sum_{i=1}^{N_e} V_{p2}(\mathbf{r}_i, \mathbf{r}_0).
 \end{aligned} \quad (2.14)$$

For the  $e^+Be$  system, the direct potential  $V_{dir}$  represents the interaction with the  $1s^2 Be^{2+}$  core which is derived from a Hartree-Fock wave function and is the same for the electron and the positron (although opposite in sign). The exchange potential  $V_{exc}$  between the valence electrons and the Hartree-Fock core was also computed exactly.

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

$$V_{p1}(r) = -\frac{\alpha_d g^2(r)}{2r^4}. \quad (2.15)$$

The factor  $\alpha_d$  is the static dipole polarizability of the core and  $g^2(r)$  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 the electron. In this work,  $g^2(r)$  was defined to be

$$g^2(r) = 1 - \exp(-r^6/\rho^6), \quad (2.16)$$

where  $\rho$  is an adjustable cutoff parameter. The two-body polarization potential ( $V_{p2}$ ) is defined as

TABLE I. Results of CI calculations for PsH up to a given  $L_{max}$ . The total number of electron and positron orbitals are denoted by  $N_e$  and  $N_p$ , with the Laguerre-type orbital exponents in the  $\lambda$  column. The three-body energy of the PsH in Hartree system is denoted by  $E_{\text{PsH}}$ , while  $\varepsilon$  gives binding energy against dissociation into H + Ps. The mean electron-nucleus distance  $\langle r_e \rangle$ , the mean positron-nucleus distance  $\langle r_p \rangle$ , and the mean electron-positron distance  $\langle r_{ep}^2 \rangle$  are given in  $a_0$  and  $a_0^2$ . The spin-averaged  $2\gamma$  annihilation rate  $\Gamma$  is given in  $10^9 \text{ s}^{-1}$ . The results in the row  $\infty$  are from an  $L_{max} \rightarrow \infty$  extrapolation.

$L_{max}$	$N_e$	$N_p$	$\lambda$	$N_{conf}$	$E_{\text{PsH}}$	$\varepsilon$	$\langle r_e \rangle$	$\langle r_p \rangle$	$\langle r_{ep}^2 \rangle$	$\Gamma$
0	13	12	1.52	1092	-0.691 334 2	Unbound	2.118	3.866	24.51	0.3739
1	24	23	1.75	3457	-0.747 047 1	Unbound	2.085	3.501	17.17	0.7802
2	34	33	2.02	7837	-0.766 168 8	0.016 168 8	2.121	3.447	15.66	1.0752
3	43	42	2.12	13 660	-0.775 078 5	0.025 078 5	2.156	3.458	15.21	1.2820
4	51	50	2.25	20 836	-0.779 844 5	0.029 844 5	2.184	3.482	15.08	1.4306
5	59	58	2.40	29 900	-0.782 629 7	0.032 629 7	2.206	3.506	15.06	1.5414
6	67	66	2.60	41 620	-0.784 361 0	0.034 361 0	2.223	3.527	15.08	1.6265
7	75	74	2.85	56 044	-0.785 488 0	0.035 488 0	2.236	3.543	15.11	1.6937
8	83	82	3.05	73 956	-0.786 248 1	0.036 248 1	2.245	3.557	15.14	1.7475
9	91	90	3.25	95 324	-0.786 776 1	0.036 776 1	2.252	3.567	15.16	1.7913
$\infty$					-0.788 795 2	0.037 795 2	2.298	3.644	16.50	2.2792
SVM [27]					-0.789 196 1	0.039 196 1	2.311	3.662	15.58	2.4691

$$V_{p2}(\mathbf{r}_i, \mathbf{r}_j) = \frac{\alpha_d}{r_i^3 r_j^3} (\mathbf{r}_i \cdot \mathbf{r}_j) g(r_i) g(r_j). \quad (2.17)$$

The parameters of the core-polarization potential were the same as those used in an earlier FCSVM calculation [28]. The dipole polarizability,  $\alpha_d$  was set to  $0.0523a_0^3$  while  $\rho = 0.95a_0$ . It should be noted that the present polarization potential is not exactly the same as that used in the FCSVM calculation; in the FCSVM calculation the cutoff function  $g(r)$  was approximated by a linear combination of Gaussians. There was no need to make this additional approximation in the present work.

The starting point for the calculation was a Hartree-Fock calculation of the Be  $1s^2 2s^2$  ground state that defined the wave function for the  $\text{Be}^{2+}$  core. The Hartree-Fock 1s orbitals were expressed as a linear combination of Slater-type orbitals (STO), and therefore it was sensible to use a linear combination of STOs and Laguerre-type orbitals (LTO) to describe the radial dependence of the  $l=0$  electrons. The procedure used to define the electron orbitals was twofold. First, additional single-particle orbitals were added to the basis so that the set of orbitals completely spanned the space defined by the STO set. Then additional LTOs (with a common scaling parameter  $\lambda_\alpha$ ) were used to enlarge the orbital basis. It should be emphasized that the mixed basis was only used for the  $l=0$  electron orbitals, the  $l>0$  electron orbitals and all the positron orbitals used a pure Laguerre basis. A Gram-Schmidt orthogonalization of the entire orbital set was performed to ensure that all the electron and positron orbitals were orthonormal.

Another distinction between  $e^+ \text{Be}$  and PsH occurs in calculation of the annihilation rate. The  $2\gamma$  annihilations for the core and valence electrons were computed separately. The annihilation rate with the core electrons only is denoted  $\Gamma_c$ , while  $\Gamma$  is used to denote the net annihilation rate of the positron with all the electrons.

### III. RESULTS FOR PsH

The condition for binding is that the energy of the PsH state be lower than the energy of the  $\text{H}(1s) + \text{Ps}(1s)$  dissociation channel. The binding energy for a particular basis is thus defined as  $\varepsilon = (0.50 + 0.25) - E(\text{PsH})$  and binding occurs when  $\varepsilon$  is positive.

The formalism and numerics of the CI program were initially validated by reproducing the results of a previous CI calculation of PsH by Strasburger and Chojnacki [12]. Their best CI calculation gave a total energy of  $-0.763\,693\,86$  Hartree [29]. The present program with exactly the same Gaussian-type orbital basis was able to reproduce this energy to all significant figures. Being able to use a Gaussian, Slater, or a Laguerre basis (and even mix the types of basis functions) was a consequence of the decision to perform all integrations using numerical quadrature.

Table I gives energies and expectation values for a series of calculations on PsH with no restrictions upon orbital occupancy (i.e.,  $L_{int} = L_{max}$ ). The number of Laguerre orbitals of a particular type and their respective exponents are also listed in the table. The largest calculation included single-particle orbitals up to  $L_{max} = 9$ . The Laguerre exponents were optimized by hand, and it was found the best energy occurred when the electron and positron exponents were the same. That the electron and positron orbits should be the same for large values of  $l$  is understandable since the  $l(l+1)/(2r^2)$  centrifugal barrier dominates the nuclear attraction or repulsion for large  $l$ . (A slight improvement over the present calculation could be achieved by letting the electron and positron exponents for the  $l=0$  and  $l=1$  orbitals be slightly different, but this was not done.)

The most notable feature of Table I is the slow convergence of the binding energy and annihilation rate with  $L_{max}$ . Even though the largest calculation had a dimension of 95 324, only 93.8% of the binding energy was achieved (the latest estimates of the PsH binding energy [19] are expected

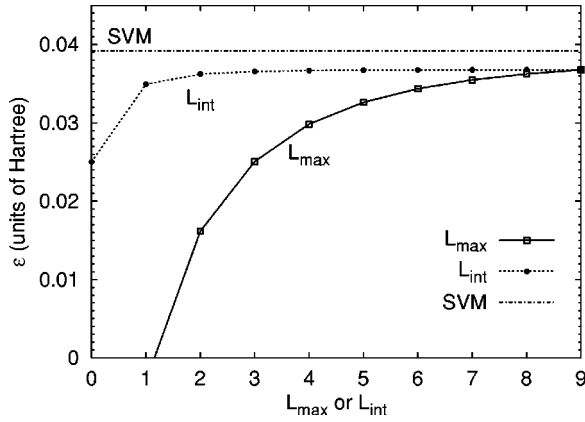


FIG. 1. PsH binding energy  $\varepsilon$  for a sequence of calculations with different values of  $L_{int}$  and  $L_{max}$ . The close to converged SVM energy is also shown for comparison purposes.

to be accurate to six significant digits). The convergence of the annihilation rate was even worse, with only 72.5% of the SVM annihilation rate [27] being achieved by the  $L_{max}=9$  calculation. The slow convergence of the PsH binding energy with  $L_{max}$ , and the even slower convergence of  $\Gamma$ , is consistent with previous CI calculations on this and other positron binding systems [13,14,16]. The slow convergence of  $\varepsilon$  and  $\Gamma$  with  $L_{max}$  is further illustrated in Figs. 1 and 2.

Equations (2.11) and (2.12) have been used to extrapolate the expectation values reported in Table I to the  $L_{max} \rightarrow \infty$  limit. The extrapolated binding energy is about 1% smaller than the expected value of 0.038 919 6 hartree while the annihilation rate is 10% smaller than the SVM annihilation rate. The extrapolated  $\langle r_e \rangle$  and  $\langle r_p \rangle$  are also quite reliable. The extrapolation of  $\langle r_{ep}^2 \rangle$  was not reliable. However, an inspection of the sequence of  $\langle r_{ep}^2 \rangle$  values in Table II suggests this expectation value has not yet reached its asymptotic region.

Table II shows the impact that configuration selection through use of the  $L_{int}$  parameter can have in restricting the size of the calculation without any major degradation in the quality of results. The data presented in Table II were computed with the same  $L_{max}=9$  single-particle orbital basis

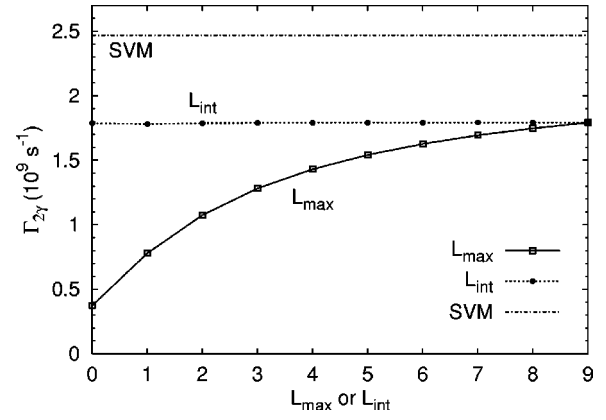


FIG. 2. PsH annihilation rate ( $\Gamma$  in units of  $10^9 \text{ s}^{-1}$ ) for a sequence of calculations with different values of  $L_{int}$  and  $L_{max}$ . The close to converged SVM annihilation rate is also shown for comparison purposes.

while  $L_{int}$  was increased in size from 0 to 9. The rapid convergence with respect to  $L_{int}$  is readily apparent in Fig. 1.

The most startling aspect of Table II is the stability of  $\Gamma$  for all values of  $L_{int}$  from 0 to 9. This is not entirely unexpected since the underlying idea behind the  $L_{int}$  selection procedure was to start with a calculation that gave the best possible description of a single electron-positron pair (within the constraints of the orbital basis). Even the  $L_{int}=0$  calculation will do a good job of representing the Ps cluster and describing its interaction with the rest of the system. Figure 2 also illustrates the tendency for  $\Gamma$  to be insensitive to the value of  $L_{int}$ .

Other properties of the system also show a degree of stability with respect to the variations in  $L_{int}$ . The mean positron distance  $\langle r_p \rangle$  decreases by 2% when  $L_{int}$  is increased from 0 to 1, but thereafter it changes by less than 0.5%. As expected, the energy shows a monotonic decrease as  $L_{int}$  increases and also shows a reasonably quick pattern of convergence. The energy of the  $L_{int}=2$  calculation is within 1.5% of the  $L_{int}=9$  energy even though it only includes 40% of the configurations.

The quick convergence for all properties with respect to

TABLE II. Results of a sequence of CI calculations with increasing  $L_{int}$  for the Ps-H system. The configurations were constructed from the full  $L_{max}=9$  orbital list. The organization of the table columns is the same as for Table I.

$L_{int}$	$N_{conf}$	$E_{PsH}$	$\varepsilon$	$\langle r_e \rangle$	$\langle r_p \rangle$	$\langle r_{ep}^2 \rangle$	$\Gamma$
0	10 010	-0.775 033 9	0.025 033 9	2.340	3.666	15.48	1.7864
1	23 276	-0.784 929 5	0.034 929 5	2.263	3.584	15.29	1.7811
2	37 926	-0.786 237 9	0.036 237 9	2.255	3.572	15.20	1.7869
3	51 660	-0.786 567 4	0.036 567 4	2.254	3.569	15.18	1.7893
4	63 492	-0.786 681 8	0.036 681 8	2.253	3.568	15.17	1.7903
5	73 788	-0.786 730 2	0.036 730 2	2.253	3.567	15.17	1.7910
6	82 548	-0.786 753 6	0.036 753 6	2.253	3.567	15.17	1.7911
7	89 196	-0.786 766 0	0.036 766 0	2.253	3.567	15.17	1.7912
8	93 668	-0.786 772 9	0.036 772 9	2.253	3.567	15.16	1.7913
9	95 324	-0.786 776 1	0.036 776 1	2.253	3.567	15.16	1.7913

$L_{int}$  suggests that the most efficient way to do a calculation is to pick a moderately sized value of  $L_{int}$ , say 2 or 3, then increase  $L_{max}$  systematically to the largest possible value. To further test this hypothesis, calculations were performed constraining  $L_{int}=3$ , and then increasing  $L_{max}$  systematically up to 9. This gave extrapolated binding energies and annihilation rates very close to the full  $L_{max}=L_{int}$  calculations. For example, the extrapolated binding energy was 0.038 58 hartree, less than 1% smaller than the extrapolated energy from the full CI expansion (0.038 79 hartree), while the extrapolated annihilation rate was  $2.280 \times 10^9 \text{ s}^{-1}$ , within 0.1% of the rate obtained from the full calculation.

#### Implications for PsH scattering calculations

One of the areas of recent activity in positron physics is in the scattering of positronium from atoms. In particular, there has been a lot of interest on the positronium-hydrogen scattering problem [30–33]. Accurate estimates of the PsH scattering lengths have only been obtained very recently [32] despite Ps-H being such an apparently simple scattering system. The determination of the scattering length was achieved by using a rather unorthodox modification of the SVM to scattering problems. The SVM technique is currently restricted in scope to the scattering length region and, therefore, a more general solution of the PsH scattering problem will probably be achieved with more traditional scattering techniques based upon the close-coupling (CC) ansatz.

The present calculations can give insight into the size of calculation required to obtain a converged solution with a close-coupling-type scattering wave function. For example, the ( $L_{int}=0$ ,  $L_{max}=9$ ) calculation achieved 68.4% of the ( $L_{int}=9$ ,  $L_{max}=9$ ) PsH binding energy. The  $L_{int}=0$  calculation would be roughly equivalent to a CC-type calculation with a basis written schematically as

$$|\Psi\rangle = \sum_i c_i H(ns) P_s(nl) F_l^{Ps}(R) + \sum_i c_i H(nl) P_s(ns) F_l^{Ps}(R), \quad (3.1)$$

where  $F_l^{Ps}(R)$  describes the motion of the Ps center of mass with orbital angular momentum  $l$ . The  $R$ -matrix calculation of Campbell *et al.* [31] using a wave function similar to this (their CC calculation restricted the hydrogen state to always be in its ground state) achieved 59.4% of the PsH binding energy. Given that the relative accuracy in the PsH binding energy scales in the same way as the threshold cross section, it is clear that further improvements in the present group of close-coupling calculations will need to be made before they are able to obtain more accurate cross sections. Using Table II as a rough guide, inclusion of H states with  $L=1$  will be required to achieve cross sections accurate at the 5% level, while H-type states with  $L=2$  will be needed to achieve accuracy at the 1–2% level.

#### IV. RESULTS FOR $e^+Be$

The  $e^+Be$  system consists of a positron weakly bound to a polarized beryllium atom. Since the ionization potential of

neutral Be is greater than 0.25 hartree (0.342 603 hartree [34]), the positron binding energy  $\varepsilon$  is calculated by the identity

$$\varepsilon = E(Be) - E(e^+Be), \quad (4.1)$$

where  $E(Be)$  is the two-electron binding energy of neutral beryllium.  $E(Be)$  for a given  $L_{max}$  was computed using a subset of the basis used for  $e^+Be$ , i.e., the positron orbitals are omitted and exactly the same set of electron orbitals are included. In effect, the  $\varepsilon$  should be regarded as the energy associated with the binding of a positron to a particular model of Be. There are, of course, some uncertainties associated with using a neutral Be binding energy that is not the lowest possible energy, but it will be seen that this procedure leads to a calculation scheme that probably gives the most sensible estimates of the positron binding energy.

Table III for  $e^+Be$  illustrates the convergence of the energy, annihilation rate, and other system properties as a function of  $L_{max}(=L_{int})$ . Table III for  $e^+Be$  is the analog of Table I for PsH. Table III does contain an additional column of results, the two electron energy of neutral Be, i.e.,  $E(Be)$  as a function of  $L_{max}$ , which is needed for determination of  $\varepsilon$  for each model Be atom. Once again, the binding energy and the annihilation rate converge slowly to their asymptotic values.

Somewhat surprisingly, the convergence of the binding energy and annihilation rate with  $L_{max}$  is slower for  $e^+Be$  than for PsH. At  $L_{max}=10$ , the CI calculation has recovered only 80% of the expected binding energy and about 60% of the annihilation rate. This occurs even though the mean radius for the positron, about  $10a_0$ , is well outside the Be charge cloud. A plausible explanation for this slow convergence in  $L_{max}$  is now advanced. One of the distinguishing features of all positron binding systems is the attractive electron-positron interaction that leads to the formation of a positronium cluster. This cluster can be expected to occur wherever the electron and positron charge clouds overlap. In the case of  $e^+Be$  this overlap will occur in the outer valence region, e.g., at a radius of about  $3-4a_0$ . So although the overlap of the positron and electron charge clouds is smaller in  $e^+Be$  than in PsH, the pile of the electron charge cloud around the positron is just as strong as in the region of overlap. Therefore, this localization of the electron charge cloud around the positron plays an important part in binding the positron to the atom, and probably contributes just as much to the strength of the annihilation rate in  $e^+Be$  as it does in PsH.

Another notable feature of Table III is the result that the positron does not bind to Be until  $L_{max}$  is equal to 3. This indicates that the dipole part of the polarization potential is not able to bind a positron to beryllium. This result has been noticed previously in beryllium [13] and it has been suggested that this is a general feature of positron binding systems [35].

The data in Table IV were computed for an orbital basis with  $L_{max}=10$  while the  $L_{int}$  parameter was increased in size from 0 to 10. This once again shows the importance of giving preferential treatment to electron-positron as opposed to

TABLE III. Results of CI calculations for  $e^+$ Be for orbital bases with given  $L_{max}$ . The total number of electron and positron orbitals are denoted by  $N_e$  and  $N_p$ , with the Laguerre-type orbital exponents in the  $\lambda$  column. The organization of the rest of the table is the same as Table I, except the column  $E_{Be}$  gives the two-body energy of the model neutral beryllium atom. The  $\Gamma$  column gives the total (= core + valence) annihilation rate (in  $10^9 \text{ s}^{-1}$ ) while  $\Gamma_c$  gives the annihilation rate (in  $10^9 \text{ s}^{-1}$ ) with the core electrons only. The results in the row  $\infty$  are from an  $L_{max} \rightarrow \infty$  extrapolation.

$L_{max}$	$N_e$	$N_p$	$\lambda_e$	$\lambda_p$	$N_{conf}$	$E_{e^+Be}$	$E_{Be}$	$\varepsilon$	$\langle r_e \rangle$	$\langle r_p \rangle$	$\Gamma_c$	$\Gamma$
0	9	12	1.22	0.45	540	-0.968 346 7	-0.969 928 9	Unbound	2.652	29.255	0.000 036	0.0002
1	18	21	1.45	0.90	1809	-1.009 907 6	-1.011 146 9	Unbound	2.573	26.527	0.000 092	0.0022
2	26	29	1.60	1.52	4113	-1.011 024 1	-1.011 632 6	Unbound	2.579	21.478	0.000 359	0.0163
3	34	37	1.75	1.75	7649	-1.011 869 7	-1.011 757 6	0.000 112	2.591	17.086	0.000 791	0.0491
4	42	45	2.00	2.00	13073	-1.012 598 6	-1.011 802 6	0.000 796	2.603	14.344	0.001 188	0.0904
5	50	53	2.20	2.20	20 481	-1.013 166 3	-1.011 822 3	0.001 344	2.614	12.827	0.001 470	0.1291
6	58	61	2.40	2.40	30 577	-1.013 583 8	-1.011 832 2	0.001 752	2.622	11.970	0.001 656	0.1617
7	66	69	2.65	2.65	43 393	-1.013 885 0	-1.011 837 6	0.002 047	2.629	11.452	0.001 780	0.1883
8	74	77	2.80	2.80	59 697	-1.014 102 4	-1.011 840 9	0.002 262	2.633	11.121	0.001 863	0.2097
9	82	85	2.95	2.95	79 457	-1.014 260 5	-1.011 842 8	0.002 418	2.637	10.898	0.001 921	0.2270
10	90	93	3.10	3.10	103 505	-1.014 376 9	-1.011 844 1	0.002 533	2.639	10.746	0.001 962	0.2411
$\infty$						-1.014 930 7	-1.011 847 7	0.003 083	2.653	10.244	0.002 112	0.3733
FCSVM [8]						-1.015 100	-1.011 953	0.003 147	2.654	9.842	0.002 22	0.418

the electron-electron correlations. Some interesting trends are apparent in the tabulation of the binding energy  $\varepsilon$  versus  $L_{int}$ . First, although there is a small downward creep in  $E(Be)$  and  $E(e^+Be)$  for  $L_{int} \geq 4$ ,  $\varepsilon$  hardly changes at all. The decrease in  $E(e^+Be)$  that occurs for  $L_{int} \geq 4$  arises mainly as a consequence of an improved description of the neutral Be atom, and is not the result of a stronger positron-atom attraction. Another noticeable feature is the excessively large positron binding energy for  $L_{int}=0$ . This arises because the  $L_{int}$  structure model of the neutral Be atom does not take into consideration the  $2s^2+2p^2$  configuration mixing that has a major influence on the structure of neutral beryllium. Restricting the basis to  $L_{int}=0$  means the positron interacts with a Be atom which is described by a wave function which is only marginally better than the Hartree-Fock wave function. Such wave functions are known to predict dipole polarizabilities  $\alpha_d$  that are too large. For example,  $\alpha_d$  for the neutral Be atom calculated within the restricted

Hartree-Fock formalism =  $45.62a_0^3$  [36], which decreased to  $37.29a_0^3$  [37] in a valence CI-type calculation with effective core polarization potentials. The use of a structure model that overestimates the polarizability leads to an excessively strong attractive interaction between the positron and the atom.

The other expectation values listed in Table IV also show a discontinuity between  $L_{int}=0$  and the other values of  $L_{int}$ . Calculations with  $L_{int} \geq 1$  show moderate variations in the expectation values that range from 5% to 15%. All of the expectation values are within 1% of their final values at  $L_{int}=3$ .

We have also verified that doing a series of  $L_{int}=3$  calculations for a succession of  $L_{max}$  values still leads to extrapolated binding energies and annihilation rates close to those of the full  $L_{int}=L_{max}$  calculations found in Table III. For example, the extrapolated binding energy of the  $L_{int}=3$  series of calculations was 0.003 052 (= -1.011 757 6

TABLE IV. Results of a sequence of CI calculations with increasing  $L_{int}$  for  $e^+Be$ . The configurations were constructed from the full  $L_{max}=10$  orbital list. The organization of the table columns is the same as Table II.

$L_{int}$	$N_{conf}$	$E_{e^+Be}$	$E_{Be}$	$\varepsilon$	$\langle r_e \rangle$	$\langle r_p \rangle$	$\Gamma_c$	$\Gamma$
0	6453	-0.982 739 9	-0.969 928 9	0.012 811 1	2.803	6.859	0.003 875	0.5508
1	17 217	-1.013 351 1	-1.011 146 9	0.002 042 3	2.636	11.207	0.001 812	0.2231
2	29 553	-1.014 073 4	-1.011 632 6	0.002 440 8	2.638	10.871	0.001 918	0.2356
3	43 201	-1.014 253 9	-1.011 757 6	0.002 496 3	2.639	10.796	0.001 944	0.2388
4	57 137	-1.014 318 3	-1.011 802 6	0.002 515 7	2.639	10.770	0.001 954	0.2400
5	69 825	-1.014 346 4	-1.011 822 3	0.002 524 1	2.639	10.758	0.001 958	0.2405
6	80 977	-1.014 360 4	-1.011 832 2	0.002 528 2	2.639	10.753	0.001 960	0.2408
7	90 081	-1.014 368 1	-1.011 837 6	0.002 530 5	2.639	10.749	0.001 961	0.2409
8	97 137	-1.014 372 6	-1.011 840 8	0.002 531 8	2.639	10.747	0.001 961	0.2410
9	101 633	-1.014 375 4	-1.011 842 9	0.002 532 5	2.639	10.746	0.001 962	0.2411
10	103 505	-1.014 376 9	-1.011 844 1	0.002 532 8	2.639	10.746	0.001 962	0.2411

+1.014 801 0) hartree, within 1% of the full CI result. The corresponding extrapolated  $L_{int}=3$  annihilation rate was  $0.037 19 \times 10^9 \text{ s}^{-1}$ , which was within 1% of that of the full CI calculation.

## V. SUMMARY AND FUTURE PERSPECTIVES

The configuration-interaction method has been used to compute the wave functions and energies for PsH and  $e^+\text{Be}$ . The calculation of positron binding for positronic beryllium also confirms the earlier prediction of binding by the SVM and FCSVM methods [4].

The present results give insight into the business of performing a CI calculation into positronic systems with more than one valence electron. It is clear that electron-positron correlations are difficult to treat with an orbital basis centered on the nucleus. A very large orbital basis, with quite large values of  $l$ , needs to be used to describe the electron-positron correlations with any degree of accuracy. Therefore, it is desirable that a larger part of the computational effort be devoted to the treatment of electron-positron as opposed to electron-electron correlations. This can be achieved by using the largest-possible single-orbital basis, whilst restricting the CI expansion to exclude those configurations that would have both electrons occupying orbitals with large values of  $l$ . Furthermore, the application of extrapolation corrections to the sequence of calculations can lead to estimates of the binding energy that are accurate at the level of 2% and annihilation rates that are accurate at the 10% level. Naturally, such large extrapolations must be used with caution.

The results of Tables II and IV suggest that choosing  $L_{int}=3$  will give results almost the same as a full CI calculation with no configuration selection. The inclusion of configurations involving the simultaneous excitations of both electrons to states with  $l>3$  is not needed for a description of the positronic atom or ion that is accurate at the 1–2% level. With these insights, it is planned to undertake a series of CI calculations to give improved descriptions of the structures of a number of positronic atoms, with  $e^+\text{Mg}$ ,  $e^+\text{Ca}$ ,  $e^+\text{Zn}$ ,  $e^+\text{Sr}$ ,  $e^+\text{Cd}$ , and CuPs being the obvious candidates for investigation.

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## APPENDIX

The necessity to include orbitals of relatively higher angular momentum meant that some technical difficulties that do not normally occur in ordinary atomic structure calculation had to be identified and overcome. Difficulties arose in the evaluation of the electron-electron and electron-positron coulomb interaction matrix element. The basic integral that has to be done is the Slater integral,

$$R^k(1,2,3,4) = \left\langle \psi_1(r_1) \psi_2(r_2) \left| \frac{r_{<}^k}{r_{>}^{k+1}} \right| \psi_3(r_1) \psi_4(r_4) \right\rangle, \quad (\text{A1})$$

where  $r_{<} = \min(r_1, r_2)$  and  $r_{>} = \max(r_1, r_2)$ . This integral can be written as

$$R^k(1,2,3,4) = \int_0^\infty \psi_2(r) \psi_4(r) \left[ \frac{Z^k(r)}{r^{k+1}} + r^{k+1} Y^k(r) \right] dr, \quad (\text{A2})$$

where

$$Z^k(r) = \int_0^r \psi_1(u) \psi_3(u) u^k du \quad (\text{A3})$$

and

$$Y^k(r) = \int_r^\infty \frac{\psi_1(u) \psi_3(u)}{u^{k+1}} du. \quad (\text{A4})$$

The running integral  $Y^k(r)$  is sometimes written as a subtraction, i.e.,

$$Y^k(r) = \int_0^\infty \frac{\psi_1(u) \psi_3(u)}{u^{k+1}} du - \int_0^r \frac{\psi_1(u) \psi_3(u)}{u^{k+1}} du \quad (\text{A5})$$

in order to have all integrations in the outward direction. However, this subtraction can lead to catastrophic errors for large values of  $k$ . This occurs because slightly different numerical procedures are used to evaluate the definite integral,  $\int_0^\infty [\psi_1(u) \psi_3(u) / u^{k+1}] du$  and the running integral  $\int_0^r [\psi_1(u) \psi_3(u) / u^{k+1}] du$  [38]. This means the value of the running integral for large  $r$  can be slightly different from the definite integral and that the limiting value of  $Y^k(r)$  as  $r$  goes to  $\infty$  is slightly different from zero. This can lead to large errors in the product  $r^k Y^k(r)$  when both  $r$  and  $k$  are large since a small error in  $Y^k(r)$  is multiplied by the  $r^k$  factor. The form Eq. (A4) for the evaluation of  $Y^k(r)$  is definitely preferred.

The actual integrations themselves were performed with Gaussian quadratures. The outer integration over the  $r \in [0, R_{max}]$  was done with a composite Gauss rule. Typically 512 points constructed from 32 segments were used in this integration. The inner integrations of Eqs. (A3) and (A4) to propagate  $Z^k(r_i)$  to  $Z^k(r_{i+1})$  (and similarly for  $Y^k$ ) were also done with a Gauss rule, typically a six-point rule was used. This algorithm was capable of generating Slater integrals with even high values of  $k$  too close to machine accuracy. For example, the  $k=48$  Slater integral with  $\psi_1 = \psi_2 = \psi_3 = \psi_4 = r^{25} \exp(-4r)$  was done as a test. Analytic evaluation gave  $R^{48} = 0.012 991 536 122 998 1$  while the Gaussian quadrature gave  $R^{48} = 0.012 991 536 122 998 2$ .



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