Large-dimension configuration-interaction calculations of positron binding to the group-II atoms

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The configuration-interaction (CI) method is applied to the calculation of the structures of a number of positron binding systems, including \(e^+\)Be, \(e^+\)Mg, \(e^+\)Ca, and \(e^+\)Sr. These calculations were carried out in orbital spaces containing about 200 electron and 200 positron orbitals up to \(\ell = 12\). Despite the very large dimensions, the binding energy and annihilation rate converge slowly with \(\ell\), and the final values do contain an appreciable correction obtained by extrapolating the calculation to the \(\ell \rightarrow \infty\) limit. The binding energies were 0.00317 hartree for \(e^+\)Be, 0.0170 hartree for \(e^+\)Mg, 0.0189 hartree for \(e^+\)Ca, and 0.0131 hartree for \(e^+\)Sr.

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I. INTRODUCTION

The ability of positrons to bind to a number of atoms is now well established [1–3], and all of the group-II elements of the periodic table are expected to bind a positron [1,4]. There have been two sets of calculations that are consistent, in that they tend to predict the same binding energy and annihilation rate. The first set of calculations were those undertaken on \(e^+\)Be and \(e^+\)Mg [5–7] with the fixed core stochastic variational method (FCSVM) [1,6,8]. Some time later, configuration-interaction (CI) calculations were undertaken on \(e^+\)Be, \(e^+\)Mg, \(e^+\)Ca, and \(e^+\)Sr [9,10]. The calculations for \(e^+\)Be and \(e^+\)Mg agreed to within the respective computational uncertainties, which were roughly about 5%–10% for the binding energy.

One feature common to all the CI calculations is the slow convergence of the binding energy and the annihilation rate. The attractive electron-positron interaction leads to the formation of a Ps cluster (i.e., something akin to a positronium atom) in the outer valence region of the atom [1,6,11,12]. The accurate representation of a Ps cluster using only single particle orbitals centered on the nucleus requires the inclusion of orbitals with much higher angular momenta than a roughly equivalent electron-only calculation [11,13–15]. For example, the largest CI calculations on the group-II positronic atoms and PsH have typically involved single particles bases with eight radial function per angular momenta, \(\ell\), and inclusion of angular momenta up to \(L_{\text{max}} = 10\) [9,10,12]. Even with such large orbital basis sets, between 5% and 60% of the binding energy and some 30%–80% of the annihilation rate were obtained by extrapolating from \(L_{\text{max}} = 10\) to the \(L_{\text{max}} = \infty\) limit.

Since our initial CI calculations [9,10,16], advances in computer hardware mean larger dimension CI calculations are possible. In addition, program improvements have removed the chief memory bottleneck that previously constrained the size of the calculation. As a result, it is now appropriate to revisit the group-II atoms to obtain improved estimates of their positron binding energies and other expectation values. The calculations that we have performed have orbital spaces more than twice as large as those reported previously. The estimated CI binding energies for all systems have increased, and furthermore the uncertainties resulting from the partial wave extrapolation have decreased.

II. CALCULATION METHOD

The CI method as applied to atomic systems with two valence electrons and a positron has been discussed previously [9,10], and only a brief description is given here. All calculations were done in the fixed core approximation. The effective Hamiltonian for the system with \(N_v = 2\) valence electrons and a positron was

\[
H = -\frac{1}{2} \sum_{i=1}^{N_v} V_0^2 - \sum_{i=1}^{N_v} \frac{1}{2} V_i^2 - V_{\text{dir}}(r_0) + V_{p1}(r_0)
\]

\[+ \sum_{i=1}^{N_v} \left[ V_{\text{dir}}(r_i) + V_{\text{exc}}(r_i) + V_{p1}(r_i) \right] - \sum_{i=1}^{N_v} \frac{1}{2} \sum_{j=1}^{N_v} \frac{1}{i<j} \left[ V_{\text{dir}}(r_i) + V_{\text{exc}}(r_i) + V_{p1}(r_i) \right]
\]

\[+ \sum_{i=1}^{N_v} V_{p2}(r_i) + \sum_{i=1}^{N_v} V_{p2}(r_i, r_j).
\] (1)

The index 0 denotes the positron, while \(i\) and \(j\) denote the electrons. The direct potential \(V_{\text{dir}}\) represents the interaction with the electronic core, which was derived from a Hartree-Fock (HF) wave function of the neutral atom ground state. The exchange potential \(V_{\text{exc}}\) between the valence electrons and the HF core was computed without approximation.

The one-body and two-body polarization potentials \(V_{p1}\) and \(V_{p2}\) are semiempirical with the short-range cutoff parameters derived by fitting to the spectra of their singly ionized ions. All details of the core-polarization potentials including the polarizabilities, \(\alpha_q\), are given in [9,10]. Note that the functional form of the polarization potential, \(V_{p1}\), was set to be the same for the electrons and the positron.

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The positron atom wave function is a linear combination of states created by multiplying atomic states to single particle positron states with the usual Clebsch-Gordan coupling coefficients:

\[
|\psi;LS\rangle = \sum_{\ell_j} c_{\ell_j}(L,S_{\ell_j} m_{\ell_j}) |L\ell_m \rangle |S_{\ell_j} \rangle^{1/2} \Psi_{\ell_m}(r) \Phi_{\ell_j}(r_0).
\]

(2)

In this expression \(\Phi_{\ell_j}(r_0)\) is an antisymmetric atomic wave function with good \(L\) and \(S\) quantum numbers and \(\ell_j\) and \(m_j\) refer to the angular momentum quantum numbers of the positron single particle orbital, \(\phi_j(r_0)\). The single particle orbitals are written as a product of a radial function and a spherical harmonic:

\[
\phi(r) = P(r)Y_{lm}(\hat{r}).
\]

(3)

As the calculations were conducted in a fixed core model we used HF calculations of the neutral atom ground states to construct the core orbitals. These HF orbitals were computed with a program that can represent the radial wave functions as a linear combination of Slater type orbitals (STOs) [17].

A linear combination of STOs and Laguerre type orbitals (LTOs) was used to describe the radial dependence of electrons occupying orbitals with the same angular momentum as those in the ground state. Orbitals that did not have any core orbitals with the same angular momentum were represented by a LTO set with a common exponential parameter. The STOs give a good representation of the wave function in the interior region while the LTOs largely span the valence region. The LTO basis [9,10] has the property that the basis can be expanded toward completeness without introducing any linear independence problems.

The CI basis included all the possible \(L=0\) configurations that could be formed by letting the two electrons and positron populate the single particle orbitals subject to two selection rules,

\[
\max(\ell_0, \ell_1, \ell_2) \leq L_{\text{max}},
\]

(4)

\[
\min(\ell_1, \ell_2) \leq L_{\text{int}}.
\]

(5)

In these rules \(\ell_0\) is the positron orbital angular momentum, while \(\ell_1\) and \(\ell_2\) are the angular momenta of the electrons. A large value of \(L_{\text{max}}\) is necessary as the attractive electron-positron interaction causes a pileup of electron density in the vicinity of the positron. The \(L_{\text{int}}\) parameter was used to eliminate configurations involving the simultaneous excitation of both electrons into high \(\ell\) states. Calculations on PsH and \(e^+\text{Be}\) had shown that the choice of \(L_{\text{int}}=3\) could reduce the dimension of the CI basis by a factor of 2 while having an effect of about 1% upon the binding energy and annihilation rate [9]. The present set of calculations were all performed with \(L_{\text{int}}=4\).

Various expectation values were computed to provide information about the structure of these systems. The mean distance of the electron and positron from the nucleus are denoted by \(\langle r_e\rangle\) and \(\langle r_p\rangle\). The 2\(\gamma\) annihilation rate for annihilation with the core and valence electrons was computed with the usual expressions [18–20]. The 2\(\gamma\) rate for the core (\(\Gamma_c\)) and valence (\(\Gamma_v\)) electrons are tabulated separately.

**Extrapolation issues**

The feature that differentiates mixed electron-positron CI calculations from purely electron CI calculations is the slow convergence of the calculation with respect to \(L_{\text{max}}\), the maximum \(\ell\) of any electron or positron orbital included in the CI basis. Typically, a calculation is made to \(L_{\text{max}} \approx 10\) (or greater), with various extrapolation techniques used to estimate the \(L_{\text{max}} \rightarrow \infty\) correction. For any expectation value one can write formally

\[
\langle X \rangle_{L_{\text{max}}} = \sum_{L=0}^{L_{\text{max}}} \Delta X^L,
\]

(6)

where \(\Delta X^L\) is the increment to the observable that occurs when the maximum orbital angular momentum is increased from \(L-1\) to \(L\), e.g.,

\[
\Delta X^L = \langle X \rangle^L - \langle X \rangle^{L-1}.
\]

(7)

Hence one can write formally

\[
\langle X \rangle = \langle X \rangle^L_{\text{max}} + \sum_{L=L_{\text{max}}+1}^{\infty} \Delta X^L.
\]

(8)

However, it is quite easy to make substantial errors in estimating the \(L_{\text{max}} \rightarrow \infty\) correction [21–23]. There have been a number of investigations of the convergence of CI expansions for electronic and mixed electron-positron systems [1,22,24–31]. The reliability of the different methods to estimate the \(L_{\text{max}} \rightarrow \infty\) correction for the energy and annihilation rate has been assessed in detail elsewhere [22]. In this work, only the briefest description of the recommended methods are described.

The recent computational investigations of helium [31] and some positron-atom systems [22] suggest that usage of an inverse power series of the generic type

\[
\Delta X_{L_{\text{max}}}^\ell = \frac{B_X}{(L_{\text{max}} + \frac{3}{2})^p} + \frac{C_X}{(L_{\text{max}} + \frac{3}{2})^{p+1}} + \frac{D_X}{(L_{\text{max}} + \frac{3}{2})^{p+2}} + \cdots
\]

(9)

is the best way to determine the \(L_{\text{max}} \rightarrow \infty\) correction for the energy \(E\) and the \(2\gamma\) annihilation rate. A three term series with \(n=4\) is used for the energy. One needs four successive values of \(E^L\) to determine the coefficients \(B_X, C_X,\) and \(D_X\). Once the coefficients have been fixed, the inverse power series is summed to \(J_{\text{max}}=100\), after which the approximate result

\[
\sum_{L=2}^{J_{\text{max}}+1} \frac{1}{(L + \frac{3}{2})^p} \approx \frac{1}{(p-1)(J_{\text{max}} + 1)^{p-1}}
\]

(10)

is used [23].

The correction to \(\Gamma\) follows the same general procedure as the energy, but with two differences. The power in Eq. (9) is set to \(n=2\) and only 2-terms are retained in the series (requiring three successive values of \(\Gamma^L\)).

The usage of the inverse power series is the preferred approach when the asymptotic form for \(\Delta X^L\) has been estab-
lished by perturbation theory. For other operators it is best to use a single-term inverse power series with an indeterminate power, e.g.,

$$\Delta X^{L} = \frac{A}{(L + \frac{1}{2})^p}. \quad (11)$$

The factors $A$ and $p$ can be determined from the three largest calculations using

$$p = \ln \left( \frac{\Delta X^{L_{\text{max}}^{-1}}}{\Delta X^{L_{\text{max}}}} \right) / \ln \left( \frac{L_{\text{max}} + \frac{1}{2}}{L_{\text{max}} - \frac{1}{2}} \right), \quad (12)$$

and

$$A = \Delta X^{L_{\text{max}}} (L_{\text{max}} + \frac{1}{2})^p. \quad (13)$$

Once $p$ and $A$ are determined, the $L_{\text{max}} \to \infty$ correction can be included using the same procedure as adopted for the multiterm fits to the energy and annihilation. This method is used in determination of the $L_{\text{max}} \to \infty$ estimates of $\langle r_e \rangle$, $\langle r_p \rangle$, and $\Gamma_c$. However, the value of $p$ is computed for all operators since it is useful to know whether $p_r$ and $p_v$ are close to the expected values of 4 and 2, respectively. While the subdivision of the annihilation rate into core and valence components is convenient for physical interpretation, it was also done on mathematical grounds. The calculation of $\Gamma_c$ does not explicitly include correlations between the core electrons and the positron, and so the $\Delta \Gamma_c^{L_{\text{v}}} \Gamma_c^{L_{\text{v}}}$ increments converge faster than the $\Delta \Gamma_c^{L_{\text{c}}} \Gamma_c^{L_{\text{c}}}$ increments (i.e., $p_{\text{c}} > p_{\text{v}}$).

III. CALCULATION RESULTS

A. Improved FCSVM data for $e^+\text{Be}$ and $e^+\text{Mg}$

The FCSVM [1,6] has also been applied to determine the structures of $e^+\text{Be}$ and $e^+\text{Mg}$ [6,7]. The FCSVM expands the wave function as a linear combination of explicitly correlated Gaussians (ECGs), with the core orbitals taken from a HF calculation. One- and two-body polarization potentials are included while orthogonality of the active electrons with the core is enforced by the use of an orthogonalizing pseudopotential [1,6,32]. The FCSVM model Hamiltonians are very similar to those used in the CI calculations. But there are some small differences in detail that lead to the FCSVM Hamiltonian giving slightly different energies.

The best previous FCSVM wave function for $e^+\text{Be}$ [7] gave a binding energy, 0.003 147 hartree, and annihilation rate $0.420 \times 10^9 \text{ s}^{-1}$, that were close to convergence. Some extensive reoptimizations seeking to improve the quality of the wave function in the asymptotic region yielded only minor changes (of the order of 1%) in the ground state properties [33]. The binding energy and annihilation rate for the improved description of the $e^+\text{Be}$ ground state are tabulated in Tables I and II. These values should be converged to better than 1% with respect to further enlargement and optimization of the ECG basis.

The more complex core for Mg does slow the convergence of the energy and other properties of $e^+\text{Mg}$ considerably [1]. The best energy previously reported for this system was 0.016 096 hartree [33]. The current best wave function, which is constructed from a linear combination of 1200 ECGs gives a binding energy of 0.016 930 hartree and a valence annihilation rate of $1.0137 \times 10^9 \text{ s}^{-1}$. Other expectation values are listed in Table I. Examination of the convergence pattern during the series of basis set enlargements and optimizations suggests that the binding energy and annihilation rate are converged to between 2% and 5%.

The FCSVM binding energies do have a weak dependence on one parameter in the calculation since the orthogonalizing pseudopotential is actually a penalty function, viz.

$$\lambda \hat{P} = \sum_{i \in \text{core}} \lambda_{i} |\phi_i \rangle \langle \phi_i|, \quad (14)$$

that was added to the Hamiltonian. Choosing $\lambda$ to be large and positive means the energy minimization automatically acts to construct a wave function which has very small overlap with the core [6,32,34]. The FCSVM properties reported in Tables I and II were computed with $\lambda = 10^3$ hartree. The core overlap (i.e., the expectation value of $\hat{P}$) was $1.86 \times 10^{-11}$ for $e^+\text{Be}$ and $1.61 \times 10^{-10}$ for $e^+\text{Mg}$.

B. CI results for group-II atoms

Table I contains the results of the current series of calculations on the four positronic atoms. The size of the calculations for the four atoms was almost the same. The electron-electron angular momentum selector was set to $L_{\text{max}}=4$. For $\ell > 3$ at least 15 LTOs were included in the radial basis sets for the electron and positron orbitals. For $\ell \leq 2$ the dimension of the orbital basis sets were slightly larger than 15 and the basis sets for electrons occupying orbitals with the same angular momentum as those in the core were typically a mix of STOs (to describe the electron close to nucleus) and LTOs. The calculations used basis sets with $L_{\text{max}}<12$ had configuration spaces which were subsets of the $L_{\text{max}}=12$ and this expedited the computations since one list of radial matrix elements was initially generated for the $L_{\text{max}}=12$ basis and then reused for the smaller basis sets.

The secular equations that arose typically had dimensions of about 500 000 and the diagonalizations were performed with the Davidson algorithm using a modified version of the program of Stathopoulos and Froese-Fischer [35]. Convergence was not very quick and about 16 000 iterations were needed to achieve convergence in some cases. It was possible to speed up the diagonalization for $L_{\text{max}} < 12$. An edited eigenvector from the $L_{\text{max}}=12$ calculation was used as the
initial eigenvector estimate, and this often reduced the number of iterations required by 50%.

1. Results for $e^+\text{Be}$

The lowest energy dissociation channel is the $e^+\text{Be}$ channel, which has an energy of $-1.011\,811\,67$ hartree with respect to the doubly ionized frozen core. The agreement of the extrapolated CI binding energy of $\varepsilon=0.003\,169$ hartree with the FCSVM binding energy of $\varepsilon=0.003\,180$ is better than 1%. A similar level of agreement exists for the $\langle r_c \rangle$ and $\langle r_p \rangle$ expectation values.

The only expectation value for which 1% level of agreement does not occur is the annihilation rate and here the extrapolated CI value of $0.4110\times10^9$ s$^{-1}$ is only about 3.5% smaller than the FCSVM of $0.4267\times10^9$ s$^{-1}$. However, it is known that the convergence of the annihilation rate with respect to an increasing number of radial basis functions is slower than the convergence of the energy $[22,31]$. This

\begin{tabular}{|c|c|c|c|c|c|}
\hline
$L_{\text{max}}$ & $E$ & $\varepsilon$ & $\langle r_c \rangle$ & $\langle r_p \rangle$ & $\Gamma_c$ & $\Gamma_v$ \\
\hline
$10^9$ & $-1.0143769$ & (0.002533) & (2.639) & (10.746) & (0.001962) & (0.2411) \\
9 & $-1.01435756$ & 0.00254859 & 2.638877 & 10.874256 & 0.00193993 & 0.24026720 \\
10 & $-1.01448318$ & 0.00267151 & 2.6418168 & 10.699433 & 0.00198405 & 0.25651433 \\
11 & $-1.01457837$ & 0.00276670 & 2.6441227 & 10.574208 & 0.00201619 & 0.27004634 \\
12 & $-1.01465138$ & 0.00283971 & 2.6459282 & 10.482126 & 0.00204005 & 0.28140404 \\
$\approx$ & 3.1806 & 3.1806 & 2.9339 & 3.6871 & 3.5764 & 2.1006 \\
FCSVM & $-1.0151335$ & 0.003180 & 2.65673 & 10.09755 & 0.002144 & 0.410976 \\
$10^9$ & $-0.8473592$ & (0.0145092) & (3.382) & (7.101) & (0.010845) & (0.5429) \\
9 & $-0.84741494$ & 0.01450067 & 3.3831320 & 7.116532 & 0.01079647 & 0.54089010 \\
10 & $-0.84790548$ & 0.01499121 & 3.3936654 & 7.071950 & 0.01084944 & 0.57692369 \\
11 & $-0.84828090$ & 0.01536663 & 3.4026294 & 7.040929 & 0.01087921 & 0.60775407 \\
12 & $-0.84857204$ & 0.01565777 & 3.4093312 & 7.018703 & 0.01089568 & 0.63435278 \\
$\approx$ & 3.0496 & 3.0496 & 2.3690 & 3.9985 & 7.0953 & 1.7706 \\
FCSVM & $-0.849002$ & 0.016930 & 3.447 & 6.923 & 0.0112 & 0.1037 \\
$10^9$ & $-0.6986443$ & (0.0123578) & (4.456) & (6.848) & (0.01355) & (0.7335) \\
9 & $-0.69855551$ & 0.01226895 & 4.4602428 & 6.863740 & 0.01343426 & 0.72709017 \\
10 & $-0.69975764$ & 0.01347109 & 4.4873848 & 6.872414 & 0.01320307 & 0.78001274 \\
11 & $-0.70069553$ & 0.01440898 & 4.5110869 & 6.885039 & 0.01304512 & 0.82640757 \\
12 & $-0.70143637$ & 0.01514981 & 4.5315631 & 6.898804 & 0.01288316 & 0.86733542 \\
$\approx$ & 2.8286 & 2.8286 & 1.7546 & -1.0371 & 1.6361 & 1.5037 \\
FCSVM & $-0.7052160$ & 0.0189295 & 4.86076 & 6.923 & 0.009780 & 1.478148 \\
$10^9$ & $-0.6602186$ & (0.0048689) & (4.850) & (7.056) & (0.01487) & (0.7488) \\
9 & $-0.65997599$ & 0.00462598 & 4.8638673 & 7.100141 & 0.01464684 & 0.73239378 \\
10 & $-0.66146709$ & 0.00611708 & 4.8979559 & 7.123685 & 0.01432317 & 0.78845209 \\
11 & $-0.66263875$ & 0.00728874 & 4.9283728 & 7.150071 & 0.01403253 & 0.83908980 \\
12 & $-0.66357065$ & 0.00822064 & 4.9552753 & 7.176708 & 0.01377785 & 0.88177286 \\
$\approx$ & 2.7459 & 2.7459 & 1.4725 & -0.1134 & 1.5844 & 1.4934 \\
FCSVM & $-0.6684520$ & 0.0131020 & 5.65380 & 6.743 & 0.008456 & 1.552589 \\
\hline
\end{tabular}
TABLE II. Binding energies (in hartree) of positronic beryllium, magnesium, calcium, and strontium. Only the latest calculations of a given type by a particular group are listed in this table.

<table>
<thead>
<tr>
<th>Calculation</th>
<th>$e^+\text{Be}$</th>
<th>$e^+\text{Mg}$</th>
<th>$e^+\text{Ca}$</th>
<th>$e^+\text{Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI ($L_{\text{max}}=12$)</td>
<td>0.002840</td>
<td>0.015658</td>
<td>0.015150</td>
<td>0.008221</td>
</tr>
<tr>
<td>CI ($L_{\text{max}}\to\infty$)</td>
<td>0.003169</td>
<td>0.017040</td>
<td>0.018929</td>
<td>0.013102</td>
</tr>
<tr>
<td>CI ($L_{\text{max}}\to\infty$)</td>
<td>0.003187</td>
<td>0.017099</td>
<td>0.019122</td>
<td>0.013321</td>
</tr>
<tr>
<td>Previous-CI$^b$</td>
<td>0.003083</td>
<td>0.01615</td>
<td>0.01650</td>
<td>0.01005</td>
</tr>
<tr>
<td>FCSVM</td>
<td>0.003180</td>
<td>0.016930</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMC$^c$</td>
<td>0.0012(4)</td>
<td>0.0168(14)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SVM$^d$</td>
<td></td>
<td>0.001687</td>
<td>0.01650</td>
<td>0.01005</td>
</tr>
<tr>
<td>PO$^e$</td>
<td></td>
<td>0.00055</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PO$^f$</td>
<td></td>
<td>0.00459</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBPT$^g$</td>
<td></td>
<td>0.0362</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$The ($L_{\text{rat}}\to\infty$) correction is added to the CI ($L_{\text{max}}\to\infty$) energy.
$^b$Previous CI ($L_{\text{max}}\to\infty$) [9,10].
$^c$DMC, the statistical uncertainty in the last digit(s) is given in the brackets [38].
$^d$Fully $ab\text{ initio}$ SVM [6].
$^e$Polarized orbital calculation, dipole only [39].
$^f$Polarized orbital calculation [40].
$^g$Many body perturbation theory [41].

means that a CI type calculation has an inherent tendency to underestimate the annihilation rate. For example, a CI calculation on PsH of similar size to the present $e^+\text{Be}$ calculation underestimated the annihilation rate by 6% [22]. That the exponent of the power law decay, $p_{\Gamma} = 2.10$, is larger than the expected asymptotic value of $p=2.0$ is consistent with this idea. A better estimate of the annihilation rate can be obtained by simply forcing $C_{\Gamma}$ to be zero in Eq. (9) and thus using $\Delta L_{12}$ to fit $B_{\Gamma}$. When this is done the annihilation rate increases to $0.4178 \times 10^9$ s$^{-1}$.

2. Results for $e^+\text{Mg}$

The results of the calculations with $e^+\text{Mg}$ are listed in Table I. The lowest energy dissociation channel is to $e^+\text{Mg}$, which has an energy of $-0.832 \times 10^9$ hartree with respect to the doubly ionized Mg$^{2+}$ core.

The CI calculations, reported in Table I for $L_{\text{max}}=9$, 10, 11, and 12 are largely consistent with the FCSVM calculations. The largest explicit CI calculation gives a binding energy of $0.015658$ hartree. Extrapolation to the $L_{\text{max}}\to\infty$ limit adds about 10% to the binding energy, and the final estimate was $0.017040$ hartree. Despite the better than 1% agreement between the CI and FCSVM calculations, a further binding energy increase of about 1% to 2% would be conceivable if both calculations were taken to the variational limit.

The slow convergence of $\Gamma_{\nu}$ with $L_{\text{max}}$ is evident from Table I and the extrapolation correction contributes about 36% to the overall annihilation rate. The present $L_{\text{max}}\to\infty$ estimate can be expected to be too small by 5%–10%.

All the other expectation values listed in Table I lie within 1% to 2% of those of the FCSVM expectation values. As a general rule, inclusion of the $L_{\text{max}}\to\infty$ corrections generally improves the agreement between the CI and FCSVM calculations.

3. Results for $e^+\text{Ca}$

The results of the calculations with $e^+\text{Ca}$ are listed in Table I. Since neutral calcium has an ionization potential smaller than the energy of Ps ground state (the present model potential and electron orbital basis gives $-0.436 \times 10^9$ hartree for the Ca$^+$ energy and $-0.659 \times 10^9$ hartree for the neutral Ca energy), its lowest energy dissociation channel is the Ps+Ca$^+$ channel. The present model potential gives this channel an energy of $-0.686 \times 10^9$ hartree.

The energies listed in Table I indicate that $e^+\text{Ca}$ is the positron atom with the largest known binding energy, namely $a=0.018 \times 10^9$ hartree. The $L_{\text{max}}\to\infty$ correction contributes 20% of the binding energy. The partial wave series is more slowly convergent for $e^+\text{Ca}$ than for $e^+\text{Mg}$ [i.e., $p_E$ is smaller, and the coefficients $C_E$ and $D_E$ in Eq. (10) are larger]. This is expected since calcium has a smaller ionization potential, and so the electrons are located a greater distance away from the nucleus. This makes it easier for the positron to attract the electrons, and the stronger pileup of electron density around the positron further from the nucleus requires a longer partial wave expansion to represent correctly.

The slower convergence of the wave function with $L_{\text{max}}$ makes an even larger impact on the annihilation rate. Some 41% of the annihilation rate of $\Gamma_{\nu}=1.478 \times 10^9$ s$^{-1}$ comes from the $L_{\text{max}}\to\infty$ correction. As mentioned earlier for $e^+\text{Mg}$, it is likely that this value is slightly smaller than the true annihilation rate.

The extrapolation corrections for $\langle r_p \rangle$ and $\Gamma_{\nu}$ listed in Table I are unreliable. The $e^+\text{Ca}$ system, at large distances, consists of Ca$^{++}$+Ps. In other calculations of positron binding systems it has been noticed that systems that decay asymptotically into Ps+X do not have an $\langle r_p \rangle$ that changes monotonically with $L_{\text{max}}$ [9,16]. Initially, the positron becomes more tightly bound to the system as $L_{\text{max}}$ increases, resulting in a decrease in $\langle r_p \rangle$. However, $\langle r_p \rangle$ tends to increase at the largest values of $L_{\text{max}}$. The net result of all this is that $\Delta \langle r_p \rangle^L$ (and by implication $\Delta L^L$) approach their asymptotic forms very slowly. The best policy is simply not to give any credence to the extrapolation corrections for either of these operators for $e^+\text{Ca}$ (and $e^+\text{Sr}$). The small value of $p$ for $\Delta \langle r_p \rangle^L$ suggests that the reliability of the $L_{\text{max}}\to\infty$ correction may be degraded for this expectation value as well.

4. Results for $e^+\text{Sr}$

The results of the calculations for $e^+\text{Sr}$ are listed in Table I. Since neutral strontium has an ionization potential smaller than the energy of Ps ground state (the present model potential and electron orbital basis gives $-0.405 \times 10^9$ hartree for the Sr$^+$ energy and $-0.612 \times 911$ 01 hartree for the neutral Sr energy), its lowest energy dissociation channel is the Ps+Sr$^+$ channel, which has an energy of $-0.655 \times 10^9$ hartree. The small ionization potential of $0.207 \times 10^9$ hartree means that the structure of the $e^+\text{Sr}$ ground state will be dominated by a $\Psi(\text{Sr}^+)\Psi(\text{Ps})$ type configuration [1].
leads to slower convergence of the ground state with $L_{\text{max}}$ which is evident from Table I.

As expected, the binding energy of $e^+\text{Sr}$ is smaller than that of $e^+\text{Ca}$. Previous investigations have indicated that positron binding energies should be largest for atoms with ionization potentials closest to 0.250 hartree (the Ps binding energy) [4,36]. There is obviously some uncertainty in the precise determination of the binding energy due to the fact that $L_{\text{max}} \rightarrow \infty$ correction constitutes some 37% of the binding energy of 0.013 102 hartree. The net effect of errors due to the extrapolation correction are not expected to be excessive. Applying Eq. (9) with only the first two terms retained (i.e., $D_{E}=0$) results in a final energy 0.012 764 hartree, which is 3% smaller than the value of 0.013 102 Hartree. The present $e^+\text{Sr}$ binding energy is some 30% larger than the energy of the previous CI calculation listed in Table II [10].

The final estimate of the valence annihilation rate was 1.553 $\times 10^8$ s$^{-1}$ and some 43% of the annihilation rate comes from the $L_{\text{max}} \rightarrow \infty$ correction. This value of $\Gamma_v$ could easily be 10% smaller than the true annihilation rate. The explicitly calculated expectation values for $\langle r_p^2 \rangle$, $\langle r_p^4 \rangle$, and $\Gamma_v$ at $L_{\text{max}}=12$ should be preferred since the $L_{\text{max}} \rightarrow \infty$ corrections in these cases are likely to be unreliable.

### C. Three-body clustering

While the truncation of the basis to $L_{\text{int}}=4$ has little effect on the $e^+\text{Be}$ system, its effect is larger for the $e^+\text{Sr}$ system. The more loosely bound alkaline-earth-metal atoms have their electrons localized further away from the nucleus, and this makes it easier for the positron to form something like a Ps$^-$ cluster [4,37]. When this occurs, correlations of the positron with both electrons increase in strength, and the inclusion of configurations with $L_{\text{int}} > 4$ becomes more important.

The relative size of these neglected $L_{\text{int}} > 4$ configurations can be estimated using techniques similar to those adopted for the $L_{\text{max}} \rightarrow \infty$ corrections. Calculations for a succession of $L_{\text{int}}$ values were performed in earlier works [9,10]. The assumption is made that the binding energy and annihilation rate increments scale as $A/(L_{\text{int}}+4)^3$ (note, the power of 4 for the annihilation is used since $L_{\text{int}}$ only has a direct effect on electron-electron correlations). The difference between $L_{\text{int}}=2$ and $L_{\text{int}}=3$ is used to estimate $A$ and then Eq. (10) determines the $L_{\text{int}} \rightarrow \infty$ correction (in the case of $e^+\text{Be}$ calculations up to $L_{\text{int}}=10$ exist [9]).

Table II contains a summary of the final binding energies obtained from the present CI calculations, and earlier binding energies obtained alternate methods. As part of this table, energies with an additional $L_{\text{int}} \rightarrow \infty$ correction are also given. The size of the correction ranges from 1.8 $\times 10^{-5}$ hartree for $e^+\text{Be}$ to 21.9 $\times 10^{-5}$ hartree for $e^+\text{Sr}$. Even though these estimations of the correction are not rigorous, they indicate that the underestimate in the binding energy resulting from a truncation of the configuration space to $L_{\text{int}} < 4$ is most likely to be 2% or smaller.

A similar analysis could be done for the annihilation rate but previous results indicate that $\Gamma_v$ is less sensitive than $e$ to an increase in $L_{\text{int}}$ [9,10]. The net increases in $\Gamma_v$ for $e^+\text{Be}$, $e^+\text{Mg}$, $e^+\text{Ca}$, and $e^+\text{Sr}$ were 0.0011 $\times 10^8$ s$^{-1}$, 0.0030 $\times 10^8$ s$^{-1}$, 0.0039 $\times 10^8$ s$^{-1}$, and 0.0039 $\times 10^8$ s$^{-1}$, respectively. All of these extra contributions to $\Gamma_v$ correspond to changes of less than 0.5%.

### IV. SUMMARY AND CONCLUSIONS

The summary of binding energies, produced by the current methods and other completely different approaches presented in Table II shows that the only methods that consistently agree with each other are the CI and FCSVM calculations. Both these methods are variational in nature, both use realistic model potentials designed on very similar lines, and both have shown a tendency for the binding energies to slowly creep upwards as the calculation size is increased (refer to Refs. [1,6,10] for examples of earlier and slightly smaller binding energies). The PO and MBPT approaches do not give reliable binding energies.

The diffusion Monte Carlo method [38] gives an $e^+\text{Mg}$ binding energy of 0.0168±0.0014 hartree which is very close to the present energy. This calculation was fully ab initio and did not use the fixed core approximation. However, application of the same diffusion Monte Carlo method to $e^+\text{Be}$ gave a binding energy which is only half the size of the present value.

The present binding energies are all larger than those given previously [9,10] due to the usage of a radial basis which was almost twice the size of earlier calculations. In two cases, $e^+\text{Ca}$ and $e^+\text{Sr}$ the increase in binding energy exceeds 10%. The binding energies for $e^+\text{Be}$ and $e^+\text{Mg}$ are in agreement with those of FCSVM calculations to within their mutual uncertainties. Further enlargement of the basis could lead to the positron binding energies for Mg, Ca, and Sr increasing by a few percent.

Estimates of the annihilation rate have also been extracted from the CI wave functions. The present annihilation rates are certainly underestimates of the true annihilation rate. The annihilation rate converges very slowly with respect to the radial basis and similar sized calculations on PsH suggest that the present annihilation rates could easily be too small by at least 5% [22,31,42].

The speed at which the partial wave expansion converges with respect to $L_{\text{max}}$ is seen to decrease as the ionization energy of the parent atom decreases [1,10]. In addition, the importance of three-body clustering (i.e., convergence with respect to $L_{\text{int}}$) was seen to increase as the ionization energy of the parent atom decreased [4].

The main factor limiting the size of the calculations now is the time taken to perform the diagonalizations. Although the calculations were performed on a Linux/Myrinet-based cluster, the sheer number of iterations (16 000 in the worst case), used by the Davidson method, meant that it could take 30 days to perform a diagonalization using 24 CPUs. However, the main reason for adopting the Davidson method was the availability of a program that was easy to modify [35]. Usage of the more general Lanczos method [43] might lead to a quicker diagonalization and thus permit even larger calculations.
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