

Configuration-interaction calculations of positron binding to group-II elements

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The configuration-interaction (CI) method is applied to the study of positronic magnesium ($e^+\text{Mg}$), positronic calcium ($e^+\text{Ca}$), and positronic strontium ($e^+\text{Sr}$). The CI expansion was seen to converge slowly with respect to L_{max} , the maximum angular momentum of any orbital used to construct the CI basis. Despite doing explicit calculations with $L_{max}=10$, extrapolation corrections to the binding energies for the $L_{max}\rightarrow\infty$ limit were substantial in the case of $e^+\text{Ca}$ (25%) and $e^+\text{Sr}$ (50%). The extrapolated binding energies were 0.0162 hartree for $e^+\text{Mg}$, 0.0165 hartree for $e^+\text{Ca}$, and 0.0101 hartree for $e^+\text{Sr}$. The static-dipole polarizabilities for the neutral parent atoms were computed as a by-product, giving $71.7a_0^3$, $162a_0^3$, and $204a_0^3$ for Mg, Ca, and Sr, respectively.

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I. INTRODUCTION

In recent years, the ability of positrons to bind to alkaline-earth atoms, such as magnesium has become increasingly well established. Predictions of binding to magnesium have been made by the polarized orbital method [1,2] and a large many-body perturbation-theory (MBPT) [3,4] calculation confirmed this prediction. However, the uncertainties associated with both these methods meant that the predictions of binding were not universally accepted. More recently, the chemical stability of $e^+\text{Be}$ was established rigorously [5] with an *ab initio* calculation using the stochastic variation method (SVM) [5–8] that gave a binding energy lower than the best variational calculation of neutral Be [5,9]. However, the best description of the structure of $e^+\text{Be}$ was made using the fixed core SVM (FCSVM) [10]. In the FCSVM, the electrons are separated into valence and core electrons with the core electrons only acting to define the field in which the valence electrons and the positron establish the bound state. The FCSVM has also predicted positron binding to magnesium [5,10]. The FCSVM calculations are not fully *ab initio*, and therefore do not give a rigorous demonstration of binding. However, it has been found that the stability of $e^+\text{Mg}$ largely depends on the nature of the interaction between the valence electrons and the positron. The core potential can be varied quite markedly without affecting the existence of the bound state [11]. The FCSVM calculations have been widely accepted as giving convincing evidence for the stability of $e^+\text{Mg}$.

One problem with the FCSVM is that the presence of the core slows down the calculations dramatically, and furthermore makes the calculation more susceptible to round-off error. The most recent FCSVM binding energy for $e^+\text{Mg}$ of 0.015 612 hartree was estimated to lie about 10%–15% below the true binding energy (note, positron binding energies are reported as positive numbers throughout this paper). The FCSVM energy is only about half of the MBPT binding

energy, namely, 0.0362 hartree. Although it would seem unlikely, the possibility does exist that the FCSVM wave function is poorly converged and is, therefore, underestimating the true binding energy. While it would be desirable to perform a larger FCSVM calculation for positronic magnesium, the existing calculations probably represent the best calculation that can be performed without an improvement in the FCSVM algorithm or in the computing hardware.

The difficulties in applying the FCSVM to heavier systems have meant that the configuration-interaction (CI) method [12–16] is an increasingly attractive method to apply to positron binding systems. 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 [13,17,18]. However, the convergence problems associated with the CI method do not become significantly more severe as the number of orbitals in the core gets larger. A recent calculation upon PsH and $e^+\text{Be}$ [16] was able to achieve binding energies and annihilation rates that were in reasonable agreement with high-precision SVM and FCSVM calculations.

In this work, the CI method is applied to the calculation of the ground-state wave functions of $e^+\text{Mg}$, $e^+\text{Ca}$, and $e^+\text{Sr}$. The calculations upon $e^+\text{Mg}$ are consistent with the results of the FCSVM calculation. The calculations upon $e^+\text{Ca}$ represent a major improvement over an initial calculation of the $e^+\text{Ca}$ ground state [19] since the present orbital basis is almost twice as large. The calculation upon $e^+\text{Sr}$ gives very convincing evidence that $e^+\text{Sr}$ is electronically stable.

II. DETAILS OF THE CALCULATION

The CI method as applied to atomic systems with two valence electrons and a positron has been discussed previously [12], so only a brief description is given here. All calculations were done in the fixed core approximation. The effective Hamiltonian for the system with $N_e=2$ valence electrons and a positron was

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TABLE I. Dipole polarizabilities (in a_0^3) and cutoff parameters (in a_0) of the Mg^{2+} , Ca^{2+} , and Sr^{2+} core-polarization potentials.

System	α_d	ρ_0	ρ_1	ρ_2	ρ_3	$\rho_{>3}; \rho_{p2}$
Mg^{2+}	0.4814 [34]	1.1795	1.302	1.442	1.52	1.361
Ca^{2+}	3.16 [34]	1.6516	1.6594	1.9324	1.77	1.77
Sr^{2+}	5.813 [35]	1.755	2.0174	2.714	2.402	2.2221

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

The direct potential (V_{dir}) represents the interaction with the electron core which was derived from a Hartree-Fock (HF) wave function of the neutral atom ground state. The direct part of the core potential is attractive for electrons and repulsive for the positron. The exchange potential (V_{exc}) between the valence electrons and the HF core was computed without approximation.

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

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

The factor α_d is the static-dipole polarizability of the core and $g_l^2(r)$ 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 electrons. In this work, $g_l^2(r)$ was defined to be

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

where ρ_l is an adjustable cutoff parameter. The two-body polarization potential (V_{p2}) 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 all systems are listed in Table I. Table II gives a comparison of the experimental binding energies for the positive ions Mg^+ , Sr^+ , and Ca^+ . The values of ρ_l were tuned by minimizing the differences between the model potential and experimental energies. The values of ρ_l for $l > 3$ and for use in the two-body potential were taken as the arithmetic mean of ρ_0 , ρ_1 , ρ_2 , and ρ_3 . The inclusion of the core polarization potential improves the level of agreement between theory and experiment by about an order of magnitude (for work using

TABLE II. Theoretical and experimental energy levels (in hartree) of some of the low-lying states of the Mg^+ , Ca^+ , and Sr^+ ions. The energies are given relative to the energy of the X^{2+} core where $X = \text{Mg}, \text{Ca},$ or Sr . 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 core potential. The experimental energies for the spin-orbit doublets are statistical averages. The last row for each ion is the dipole polarizability (in a_0^3) of the ns ground state (the polarizability includes the contribution from the core).

Level	V_s	V_{s+pol}	Experiment [36]
Mg⁺			
3s	-0.541 873	-0.552 536	-0.552 536
3p	-0.384 391	-0.389 737	-0.389 736
4s	-0.231 799	-0.234 323	-0.234 481
3d	-0.224 952	-0.226 804	-0.226 801
4p	-0.183 477	-0.185 014	-0.185 114
5s	-0.128 674	-0.129 667	-0.129 751
4d	-0.126 548	-0.127 373	-0.127 381
4f	-0.125 011	-0.125 154	-0.125 153
α_d	38.49	35.01	
Ca⁺			
4s	-0.416 329	-0.436 287	-0.436 278
3d	-0.337 583	-0.373 858	-0.373 917
4p	-0.309 831	-0.320 844	-0.320 820
5s	-0.193 124	-0.198 293	-0.198 588
4d	-0.169 972	-0.175 133	-0.177 246
5p	-0.156 676	-0.160 060	-0.160 230
4f	-0.125 190	-0.126 189	-0.126 188
α_d	96.33	75.48	
Sr⁺			
5s	-0.379 713	-0.405 350	-0.405 350
4d	-0.318 148	-0.338 261	-0.338 262
5p	-0.283 046	-0.294 861	-0.294 861
6s	-0.180 622	-0.187 421	-0.187 846
5d	-0.158 103	-0.161 239	-0.162 323
6p	-0.146 470	-0.150 153	-0.150 369
4f	-0.125 579	-0.127 451	-0.127 451
α_d	127.47	90.14	

similar core Hamiltonians refer to [20–22]). The dipole polarizabilities of these ions are also reported in Table II. The dipole polarizabilities were computed by evaluating the oscillator strength sum rule

$$\alpha_d = \sum_j f_{ij} / (E_i - E_j)^2 \quad (5)$$

for all the states arising from the diagonalization of the Hamiltonian in a large L^2 basis. The oscillator strengths were computed with a modified dipole operator as in [22].

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

$$\begin{aligned}
 |\Psi; LS\rangle = & \sum_{i,j} c_{i,j} \langle L_i M_i l_j m_j | L M_L \rangle \\
 & \times \left\langle S_i M_{S_i} \frac{1}{2} \mu_j \middle| S M_S \right\rangle \Phi_i(\text{Atom}; L_i S_i) \phi_j(\mathbf{r}_0).
 \end{aligned} \tag{6}$$

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:

$$\phi(\mathbf{r}) = P(r) Y_{lm}(\hat{\mathbf{r}}). \tag{7}$$

The starting point for the calculation was the HF calculation for the ground state of the neutral atoms. These HF orbitals are written 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 (LTOs) to describe the radial dependence of electrons occupying orbitals with the same angular momentum as those in the ground state. The STOs give a good representation of the wave function in the interior region while the LTOs were used in the valence region.

First, 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, λ_α for given l) were used to enlarge the orbital basis. A Gram-Schmidt orthogonalization of the orbital set was performed to ensure that all the electron and positron orbitals were orthonormal. It should be emphasized that the mixed basis was only used for the $l=0, 1$, and 2 electron orbitals; all the other electron orbitals and positron orbitals used a pure Laguerre basis. The Laguerre basis has the advantage that it can be characterized by the exponential parameter. This made it easier to optimize the energy with respect to variations of the Laguerre basis.

The criteria used to generate the CI basis takes into account the different considerations that apply to the treatment of electron-electron and electron-positron correlations. In the first instance, the strong electron-positron correlations and the tendency for the electron and positron to coalesce into something resembling positronium mandates the use of an orbital basis with large values of l . However, an accurate treatment of electron-electron correlations does not require the simultaneous excitation of both electrons into orbitals with large l [16].

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;

$$\max(l_0, l_1, l_2) \leq L_{max}, \tag{8}$$

$$\min(l_1, l_2) \leq L_{int}. \tag{9}$$

In these rules l_0 is the positron orbital angular momentum, while l_1 and l_2 are the angular momenta of the electrons. 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. The L_{int} parameter was used to eliminate configurations involving the simultaneous excitation of both electrons into high l states. Calculations on PsH and e^+ Be showed that the choice $L_{int}=3$ could reduce the dimension of the CI basis by a factor of 2 while having a less than 1% effect upon the binding energy and annihilation rate [16]. The present set of calculations were performed with $L_{int}=3$ although calculations with smaller values of L_{int} were also done to give some indication of the convergence of the binding energy with L_{int} .

The secular equations that arose typically had dimensions exceeding 10 000 and therefore the diagonalizations were performed with the Davidson algorithm using a modified version of the program of Stathopolous and Froese-Fischer [23].

Various expectation values were computed to provide information about the structure of these systems. The mean distances of the electron and positron from the nucleus are denoted by $\langle r_e \rangle$ and $\langle r_p \rangle$. The 2γ annihilation rate for annihilation with the core and valence electrons was computed with the usual expressions [24–26]. The 2γ rate for the core (Γ_c) and valence (Γ_v) electrons were computed separately.

Initially, the $L_{max} \rightarrow \infty$ limits were estimated using 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

$$\langle X \rangle = \lim_{L_{max} \rightarrow \infty} \left(\sum_{L=0}^{L_{max}} X_L + \Delta \sum_{L=L_{max}+1}^{\infty} \frac{1}{L^p} \right). \tag{10}$$

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

$$\Delta = X_{L_{max}} (L_{max})^p, \tag{11}$$

and the exponent p can be derived from

$$\left(\frac{L_{max}}{L_{max}-1} \right)^p = \frac{X_{L_{max}-1}}{X_{L_{max}}}. \tag{12}$$

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 $p_E=4$ and $p_r=2$, when the energy and annihilation increments were computed using second order perturbation theory. Irrespective of the uncertainties in p , the errors in making the extrapolation were kept to a reasonable size by making $L_{max}=10$ for the largest calculation.

III. CALCULATION RESULTS

A. Tests of the model potentials for neutral atoms

An initial test of the underlying model potential is provided by the calculation of the energies of the ground and lowest-lying $nsnp \ ^1P^o$ excited states, the oscillator strength

TABLE III. Energy levels (in hartree), oscillator strengths for the resonant transition, and dipole polarizabilities (in a_0^3) for Mg, Ca, and Sr. The energy of the ground state and the lowest $^1P^o$ excited state (relative to the energy of the X^{2+} core) for CI basis sets with $L_{int} = 0, 1, 2, 3,$ and 10 . The number of configurations is given in the columns N_{CI} . The experimental energies are taken from [36] and [37]. The experimental oscillator strengths are taken from various sources with the uncertainty in the last digit(s) given in brackets. The polarizabilities, α_d in a_0^3 include the contribution from the core polarization.

L_{int}	$N_{CI}(^1S^e)$	$E(^1S^e)$	$N_{CI}(^1P^o)$	$E(^1P^o)$	ΔE	f_{if}	α_d
Mg							
0	120	-0.803 702 6	210	-0.654 141 8	0.149 560 9	1.899	98.417
1	225	-0.831 604 2	336	-0.672 784 5	0.158 819 7	1.685	70.232
2	270	-0.832 664 5	408	-0.673 528 4	0.159 136 1	1.724	71.542
3	306	-0.832 850 0	472	-0.673 691 9	0.159 158 2	1.728	71.639
10	558	-0.832 965 4	856	-0.673 804 0	0.159 161 4	1.729	71.687
FCSVM [10]		-0.832 07 2					
Experiment		-0.833 53 0		-0.673 824	0.159 705	1.80(5) [38] 1.75(9) [40]	75.0(35) [39]
Rel. CI with core excitations [41]					0.160 766	1.709	
Rel. CI-MBPT [28]		-0.833 556		-0.674 226	0.159 330	1.725	
CI + pol [34]							70.7
Ca							
0	120	-0.637 192 2	165	-0.527 056 7	0.110 135 5	2.245	203.31
1	186	-0.657 614 2	275	-0.552 823 4	0.104 790 8	1.625	157.30
2	241	-0.659 477 6	355	-0.553 131 6	0.106 346 0	1.734	161.67
3	277	-0.659 620 7	419	-0.553 189 1	0.106 431 6	1.737	161.73
10	529	-0.659 705 2	803	-0.553 233 4	0.106 471 9	1.739	161.76
Experiment		-0.660 930		-0.553 56 9	0.107 361	1.766(10) [42] 1.74(06) [38]	169(17) [43]
CI model pot [44]		-0.661 057		-0.553 847	0.107 210	1.745	
Rel. CI-MBPT [28]		-0.661 274		-0.553 498	0.107 776	1.732	
CI + pol [34]							156.0
Sr							
0	136	-0.593 465 7	192	-0.491 229 2	0.102 236 5	2.348	245.94
1	214	-0.610 323 4	336	-0.514 803 1	0.095 520 3	1.706	199.31
2	292	-0.612 792 0	480	-0.515 148 7	0.097 643 3	1.842	204.29
3	370	-0.612 943 4	576	-0.515 199 9	0.097 743 5	1.845	204.31
10	622	-0.613 026 6	960	-0.515 238 5	0.097 788 1	1.847	204.30
Experiment		-0.614 60 2		-0.515 73 6	0.098 866	1.81(8) [45] 1.92(6) [47]	186(15) [46]
Rel. CI-MBPT [28]		-0.614 40 9		-0.515 901	0.098 508	1.831	
CI + pol [48]					0.09614	1.81	

(using the length form of the matrix element) connecting these two states, and the dipole polarizability of the ground state. The oscillator strengths were computed with a modified dipole operator as in [22]. These calculations were done using an electron basis that was exactly the same as used for the e^+ atom calculations and the results are listed in Table III.

The energies reported in Table III are the energies of the two valence electrons and the energy zero is the system with both electrons removed. Comparison with the experimental energies indicates that the model potential energies are accurate at the 0.1%–0.2% level. The current CI method has one advantage over the FCSVM. The FCSVM is restricted to using a common ρ to describe the polarization potential, whereas there is no problem in using different ρ_i in CI calculations. This is the main reason why the FCSVM binding

energy for Mg does not agree as well with experiment as the present CI binding energy.

The oscillator strengths for the resonant $ns^2 \rightarrow nsnp$ transition give another test of the accuracy of the underlying model potentials and the orbital basis for the electrons. First, there is hardly any difference between the $L_{int} = 3$ and $L_{int} = 10$ calculations when it comes to representing the neutral atom ground state. At the present time the most sophisticated treatments of the oscillator strengths for the alkaline-earth atoms use a relativistic CI approach to treat the correlations of the two valence electrons while core polarization is treated using MBPT [28]. The present oscillator strengths agree with those of Porsev *et al.* [28] at the 1% level of accuracy. There is also reasonable agreement with some experimental determinations of the oscillator strengths.

TABLE IV. Binding energies (in hartree) of positronic magnesium, calcium, and strontium. Only the latest calculations of a given type by a particular group are listed in this table. The origin of the extrapolated energies is discussed in Sec. III F.

System	Present CI Explicit	Present CI Extrapolated	FCSVM	Other
$e^+ \text{Mg}$	0.014 509	0.016 15	0.015 612 [10]	0.0362, ^a 0.000 55 ^b 0.0168(14), ^c 0.004 59 ^d
$e^+ \text{Ca}$	0.012 358	0.016 50		0.008 099 ^e
$e^+ \text{Sr}$	0.004 869	0.010 05		

^aMBPT calculation [4].

^bPolarized orbital calculation, dipole only [1].

^cDMC, the statistical uncertainty in the last digit(s) is given in the brackets [30].

^dPolarized orbital calculation [2].

^eEarlier CI calculation with smaller basis [19].

B. Dipole polarizabilities

The dipole polarizabilities of the systems provide another very appropriate test of the accuracy of the structure model since the positron binds to the atom largely as a result of the polarization interaction between the neutral atom and the positron (in the case of $e^+ \text{Ca}$ and $e^+ \text{Sr}$ it is better to think of the polarization interaction between Ps and a residual positive ion). Since the dominant term in the polarization potential is the dipole term, it is worthwhile to determine whether the structure models correctly predict the dipole polarizabilities. The dipole polarizabilities were computed by diagonalizing the Schrödinger equation for states of $^1S^e$ and $^1P^o$ symmetries and then evaluating the sum rule, Eq. (5). The validity of the method has been verified on hydrogen and helium where test calculations have given results accurate to four digits. The present estimates of the polarizabilities are very close to those obtained in other high quality calculations and also agree with the available experimental data within experimental error.

Better estimates of α_d can be obtained by using the oscillator strengths of Porsev *et al.* to give a better estimate of the first and largest term (about 95% of the total) in the oscillator strength sum rule. When this is done, the estimates of the dipole polarizability are $71.4a_0^3$ for Mg, $158.6a_0^3$ for Ca, and $198.5a_0^3$ for Sr.

To summarize, tests on the structure of neutral Mg, Ca, and Sr reveal that the underlying core Hamiltonian and structure model for the valence electrons give a description of these atoms, which is accurate and generally give binding energies and oscillator strengths within 1% of state-of-the-art calculations.

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

There had been a number of predictions of positron binding to magnesium and the binding energies of these other calculations as well as the best estimates from the calculations described in the present paper are summarized in Table IV. The first polarized orbital (PO) calculation [1] only included the dipole component of the polarization potential. More recently, an improved version of the PO method [2] including higher multipoles and MBPT [3,4] were applied to

$e^+ \text{Mg}$ system. The energy from the PO calculation, 0.004 59 hartree, was derived from the scattering length using the identity $\varepsilon \approx 1/(2A^2)$. The MBPT calculation gave a binding energy of 0.0362 hartree [3,4], which is twice as large as the energy (0.015 612 hartree) given by the FCSVM calculation. The difference between the FCSVM and MBPT calculations warrants scrutiny since they both involve large-scale calculations to treat electron-electron and electron-positron correlations. Mitroy and Ryzhikh [10] suggested that the MBPT calculation overestimates the strength of the polarization-correlation potential energy due to the inclusion of two distinctly different manifolds of states in the MBPT expansion.

However, the FCSVM calculation only gave a lower bound to the binding energy. Since this calculation relies on a stochastic search, there was no guarantee that the calculation might not severely underestimate the binding energy (although visual examination of the convergence pattern suggested that the FCSVM energy was within 10%–15% of the variational limit). An independent calculation of the $e^+ \text{Mg}$ binding energy needed to be made to ultimately resolve the discrepancy between the MBPT and FCSVM binding energies.

The CI calculations, reported in Table V as a function of L_{max} and in Table VI as a function of L_{int} are largely consistent with the FCSVM calculations. The largest explicit calculation gives a binding energy of 0.014 51 hartree. Extrapolation to the $L_{max} \rightarrow \infty$ limit using Eqs. (10)–(12) gives 0.016 76 hartree for the binding energy. Only about 15% of the binding energy is obtained by extrapolation and so even if the correction was in error by 20% it would not significantly increase the uncertainty in the final binding energy. Since the exponents of the LTOs were optimized to give the lowest possible energy, and since there are at least 8 LTOs for every l value, the enlargement of the dimension of the LTO would not have much impact on the binding energy. One salient feature of the calculation is that the positron is already bound at $L_{max} = 2$. CI calculations of other $e^+ \text{X}$ systems have not established binding until $L_{max} \geq 3$ [13–15, 19, 29]. The tabulation of the binding energy in Table VI gives evidence that the binding energy is stable against further enlargement of L_{int} . There was only a 1% change in the

TABLE V. Results of CI calculations for e^+Mg for orbital bases with $L_{int}=3$ and for a series of L_{max} . The total number of electron and positron orbitals are denoted by N_e and N_p . The three-body energy of the e^+Mg ground-state (in hartree) system, relative to the energy of the Mg^{2+} core is denoted by $E(e^+Mg)$, while $\varepsilon=|E(e^+Mg)|-|E(Mg)|$, gives the binding energy against dissociation into e^+Mg . The mean electron-nucleus distance $\langle r_e \rangle$, and the mean positron-nucleus distance $\langle r_p \rangle$, are given in a_0 . The column $E(Mg)$ gives the two-body energy of neutral magnesium in the appropriate orbital basis. The Γ_v and Γ_c columns give the valence and core annihilation rates (in 10^9 sec^{-1}). The results in the row ∞ are from the $L_{max} \rightarrow \infty$ extrapolation using Eqs. (10)–(12) while p gives the exponents used for the extrapolations.

L_{max}	N_e	N_p	N_{CI}	$E(e^+Mg)$	$E(Mg)$	ε	$\langle r_e \rangle$	$\langle r_p \rangle$	Γ_c	Γ_v
0	15	12	1440	-0.800 980 1	-0.803 702 6	-0.002 722 6	3.210 96	23.037 16	0.000 249 9	0.000 407
1	29	21	4590	-0.829 962 5	-0.831 604 2	-0.001 641 7	3.171 08	19.416 51	0.000 690 0	0.005 74
2	38	29	8544	-0.833 867 7	-0.832 664 5	0.001 203 2	3.197 91	12.646 38	0.003 567	0.053 07
3	46	37	133 52	-0.837 610 3	-0.832 850 0	0.004 760 2	3.240 29	9.422 72	0.006 820	0.141 65
4	54	45	189 92	-0.840 597 0	-0.832 850 0	0.007 747 0	3.277 43	8.255 55	0.008 700	0.230 91
5	62	53	250 08	-0.842 789 3	-0.832 850 0	0.009 939 2	3.307 01	7.737 64	0.009 686	0.308 64
6	70	61	313 12	-0.844 362 7	-0.832 850 0	0.011 512 7	3.330 26	7.465 84	0.010 216	0.374 01
7	78	69	378 40	-0.845 493 0	-0.832 850 0	0.012 643 0	3.348 42	7.307 73	0.010 512	0.428 41
8	86	77	443 68	-0.846 311 9	-0.832 850 0	0.013 461 9	3.362 58	7.209 22	0.0106 82	0.473 62
9	94	85	508 96	-0.846 912 7	-0.832 850 0	0.014 062 7	3.373 62	7.144 68	0.010 784	0.511 30
10	102	93	574 24	-0.847 359 2	-0.832 850 0	0.014 509 2	3.382 25	7.100 69	0.010 846	0.542 87
p				2.82		2.82	2.34	3.64	4.64	1.68
∞				-0.849 606		0.016 756	3.4425	6.9547	0.010 99	0.9804
FCSVM [10]				-0.847 684	-0.832 072	0.0156	3.437	7.018	0.0121	0.955

binding energy when L_{int} was increased from 2 to 3.

One interesting feature of Table VI is the result that the binding energy for the $L_{int}=0$ calculation was roughly twice as large as the energies of the $L_{int}=1, 2, 3$ calculations. A similar result occurred for positronic beryllium [16]. The reason for this derives from the mechanism for binding. Positronic beryllium and, to a lesser extent positronic magnesium consist of a positron bound to the system by the polarization of the parent atom and in both cases the positron is predominantly found outside the electron charge distribution of the parent atom. The $L_{int}=0$ polarizabilities for both Be and Mg are too large, leading to an anomalously large positron binding energy.

The subdivision of the annihilation rate into core and valence components in Table V reveals that these two components have completely different behavior with L_{max} . The calculation of Γ_c does not explicitly include correlations between the core electrons and the positron. The annihilation rate is calculated simply as the overlap between the positron and core electron densities. Since the mean positron radius $\langle r_p \rangle$ decreases as L_{max} increases, it is not surprising that Γ_c increases as L_{max} increases. The $L_{max}=10$ value of the Γ_c should be close to converged. The behavior of Γ_v with L_{max}

is completely different. It converges very slowly, and the extrapolation correction adds about 80% to the annihilation rate. With such a large correction the obvious question is whether the extrapolation is reliable? A more detailed discussion of extrapolation issues is postponed to a later section.

The overall comparison between the present extrapolated expectation values and the earlier FCSVM calculation suggests that the two calculations agree when the uncertainties associated with both calculations are taken into consideration. The results are also compatible with a recently reported quantum Monte Carlo (QMC) calculation with a binding energy of 0.0168 ± 0.0014 hartree [30]. The QMC calculation was fully *ab initio* and did not use the fixed core approximation. Taken in conjunction, these three results suggest a binding energy in the vicinity of 0.016 hartree and provide conclusive evidence that the existing MBPT calculations [3,4] overestimate the positron binding energy.

D. Results for e^+Ca

The ionization potential of calcium is less than the binding energy of Ps, namely 0.250 hartree. Therefore, the lowest energy dissociation channel is $Ca^+ + Ps$. The initial predic-

TABLE VI. Results of CI calculations for e^+Mg for the complete orbital basis (i.e., $L_{max}=10$, $N_e=102$, and $N_p=93$) for a series of L_{int} values. The organization of the table is the same as Table V. The additional column reports α_d for Mg in a_0^3 (the contribution from the core is included).

L_{int}	N_{CI}	$E(e^+Mg)$	$E(Mg)$	ε	α_d	$\langle r_e \rangle$	$\langle r_p \rangle$	Γ_c	Γ_v
0	12 090	-0.830 383 0	-0.803 702 6	0.026 680	98.417	3.521 40	6.453 77	0.012 430	0.697 87
1	297 72	-0.845 489 1	-0.831 604 2	0.013 885	70.232	3.388 28	7.186 75	0.010 441	0.530 97
2	437 76	-0.847 026 2	-0.832 664 5	0.014 362	71.542	3.382 75	7.121 58	0.010 751	0.539 08
3	574 24	-0.847 359 2	-0.832 850 0	0.014 509	71.639	3.382 25	7.100 69	0.010 846	0.542 87

TABLE VII. Results of CI calculations for e^+Ca for orbital bases with different L_{max} ($L_{int}=3$). The total number of electron and positron orbitals are denoted by N_e and N_p . The three-body energy of the e^+Ca ground-state (in hartree) system, relative to the energy of the Ca^{2+} core is denoted by $E(e^+Ca)$, while ε gives binding energy (in hartree) against dissociation into $Ps+Ca^+$ (the threshold for binding is -0.6862865 hartree). The mean electron-nucleus distance $\langle r_e \rangle$, and the mean positron-nucleus distance $\langle r_p \rangle$, are given in a_0 . The Γ_v and Γ_c annihilation rates are in units of 10^9 sec^{-1} . The results in the row ∞ are from the $L_{max} \rightarrow \infty$ extrapolation while p gives the exponents used for the extrapolations.

L_{max}	N_e	N_p	N_{CI}	$E(e^+Ca)$	ε	$\langle r_e \rangle$	$\langle r_p \rangle$	Γ_c	Γ_v
0	15	12	1440	-0.629 680 1	-0.056 606 5	4.065 55	15.087 67	0.001 507	0.001 754
1	26	21	3717	-0.654 922 7	-0.031 363 8	4.072 31	12.453 14	0.002 813	0.015 892
2	36	29	7535	-0.666 544 5	-0.019 742 1	4.119 95	9.069 10	0.008 024	0.090 071
3	44	37	12159	-0.675 894 2	-0.010 392 3	4.187 78	7.735 57	0.011 811	0.200 433
4	52	45	17623	-0.682 914 1	-0.003 372 4	4.248 54	7.234 77	0.013 436	0.310 805
5	60	53	23447	-0.687 952 0	0.001 665 5	4.300 62	7.020 92	0.013 981	0.409 795
6	68	61	29559	-0.691 568 8	0.005 282 3	4.344 53	6.922 15	0.014 075	0.495 772
7	76	69	35895	-0.694 194 0	0.007 907 5	4.381 29	6.877 51	0.013 983	0.569 390
8	84	77	42231	-0.696 122 8	0.009 836 3	4.411 47	6.856 72	0.013 843	0.632 608
9	92	85	48567	-0.697 559 8	0.011 273 3	4.436 22	6.848 42	0.013 695	0.686 919
10	100	93	54903	-0.698 644 3	0.012 357 8	4.456 46	6.847 77	0.013 552	0.733 532
p				2.67	2.67	1.91	24.24	0.33	1.45
∞				-0.704 617	0.018 331	4.6679	6.8477	-0.059 63	1.6504

tion of positron binding was made by a precursor to the present calculation [19]. In this calculation, the number of LTOs was much smaller and L_{max} was 8 rather than 10 as in the present calculation.

The energies listed in Table VII indicate that e^+Ca is one of the most tightly bound positronic atoms with a binding energy comparable in magnitude to e^+Mg . The partial wave series is more slowly convergent for e^+Ca than for e^+Mg . This is expected since calcium has a smaller ionization potential and thus it is easier for the positron to attract the electron. The stronger pileup of electron density around the positron requires a longer partial-wave expansion to represent correctly.

The extrapolation of the binding energy yields a 50% correction to the binding energy. Figure 1 shows the energy

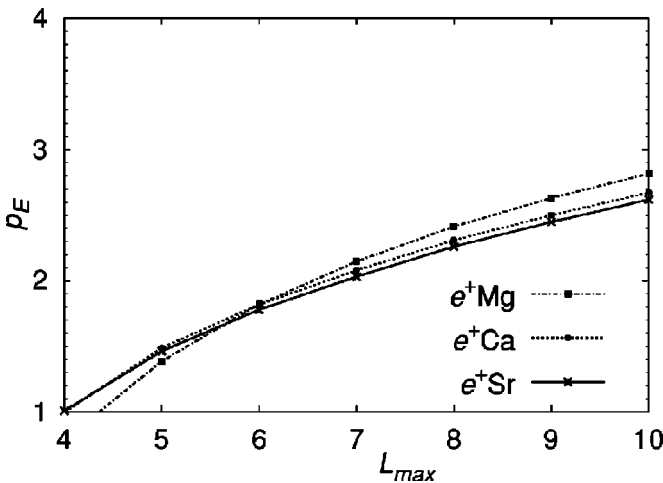


FIG. 1. The exponent relating two separate energy increments using Eq. (12) as a function of L_{max} for e^+Mg , e^+Ca , and e^+Sr . The analysis of Gribakin and Ludlow [27] suggests a limiting value of 4 as $L_{max} \rightarrow \infty$.

exponents derived from the $(L_{max}-2, L_{max}-1, L_{max})$ calculations for $L_{max}=6, 7, 8, 9$, and 10. It is evident that p is not constant and that it increases as L_{max} increases. Given this variation in p , it is likely that the extrapolation using $p=2.67$ overstates the contribution from $l > L_{max}$. The uncertainties associated with the extrapolation are discussed in more detail later.

Table VII also shows that the annihilation rate for e^+Ca is larger than that of e^+Mg . Previous research has shown that the annihilation rate generally increases as the ionization potential of the parent atom decreases [31,32]. As mentioned earlier, there is the stronger pileup of the electron density in the vicinity of the positron when the ionization potential is small.

The sequence of L_{int} calculations for e^+Ca listed in Table VIII show a different convergence pattern than for e^+Mg . The binding energy for $L_{int}=0$ is not abnormally larger than the $L_{int}=3$ binding energy. Positronic calcium is best described as Ps bound to Ca^+ . Therefore, the fact that the dipole polarizability is overestimated does not result in an anomalously large binding energy.

The extrapolation corrections for $\langle r_p \rangle$ and Γ_c listed in Table VII are obviously not reliable. The e^+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_{max} [15,16]. Initially, the positron becomes more tightly bound to the system as L_{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_{max} . The net result of all this is that $\langle r_p \rangle$ (and by implication Γ_c) approach their asymptotic forms very slowly. The variations in $\langle r_p \rangle$ and Γ_c are relatively small and the best policy is to simply not to give any credence to the extrapolation for either of these operators for e^+Ca and e^+Sr .

TABLE VIII. Results of CI calculations for e^+Ca and e^+Sr for the full orbital basis (i.e., $L_{max}=10$) with a series of L_{int} values. The organization of the table is the same as Table VII. The additional column reports α_d in a_0^3 (the contributions from the core are included).

L_{int}	N_{CI}	$E(e^+X)$	ε	α_d	$\langle r_e \rangle$	$\langle r_p \rangle$	Γ_c	Γ_v
e^+Ca								
0	118 05	-0.689 110 05	0.002 823 5	203.31	4.569 76	6.822 18	0.013 113	0.774 55
1	255 55	-0.696 004 24	0.009 717 7	157.31	4.483 75	6.905 07	0.013 032	0.726 98
2	412 55	-0.698 162 00	0.011 875 5	161.67	4.459 02	6.865 73	0.013 417	0.728 59
3	549 03	-0.698 644 33	0.012 357 8	161.73	4.456 46	6.847 77	0.013 552	0.733 53
e^+Sr								
0	143 68	-0.652 233 3	-0.003 116 5	245.94	4.947 19	7.096 36	0.014 127	0.765 95
1	313 96	-0.657 420 5	0.002 070 8	199.31	4.883 72	7.113 83	0.014 297	0.743 37
2	524 08	-0.659 671 3	0.004 321 5	204.29	4.853 82	7.075 76	0.014 708	0.743 78
3	742 84	-0.660 218 6	0.004 868 9	204.31	4.850 10	7.056 29	0.014 867	0.748 75

E. Results for e^+Sr

The strontium atom has an ionization potential of 0.209 25 hartree, smaller than that of magnesium and calcium. Therefore, the changes that occurred when going from e^+Mg to e^+Ca are also evident, but even more marked when going from e^+Mg to e^+Sr . The wave function and binding energy can be expected to converge even more slowly with L_{max} and the annihilation rate should be larger than that of e^+Ca . Both of these features can be seen in Table IX. The binding energy increases by about 30% when L_{max} is increased from 9 to 10 and the annihilation rate is larger than that of e^+Ca .

There is obviously some uncertainty in the precise determination of the binding energy due to the large contribution from the extrapolation correction. However the e^+Sr binding energy is clearly smaller than that of e^+Ca . This is consistent with a previous analysis that investigated positron binding to a model alkali atom [32]. The binding energy of the model e^+ alkali system decreased as the ionization energy of the parent atom decreased (provided the binding energy was less than 0.250 hartree).

A close to converged calculation of e^+Sr would entail a considerably larger calculation. An $L_{max}=14$ calculation would probably be needed to give an estimate of the binding energy accurate at the 5% level. Table VIII also suggests it might be worthwhile to increase L_{int} from 3 to 4. The mean electron radius of the HF ground state for neutral Sr is $4.63a_0$ [33]. The relatively large distance of the electrons from the nucleus may mean it is easier for the positron to form something like a Ps^- cluster, in which case correlations of the positron with *both* electrons might be more important than they are for e^+Be .

F. Extrapolation issues

The binding energies for e^+Ca , e^+Sr and the annihilation rates for e^+Mg , e^+Ca , and e^+Sr are all subject to quite large extrapolation corrections raising questions about their overall reliability. Fortunately, the analysis of Gribakin and Ludlow [27] can be utilized to assess the accuracy and, furthermore help devise an improved scheme. Gribakin and Ludlow suggested that the asymptotic form for the energy increments was $p_E=4$ while the annihilation rate was described by $p_\Gamma=2$.

TABLE IX. Results of CI calculations for e^+Sr for orbital bases with a given L_{max} . The extrapolations for $\langle r_p \rangle$ and Γ_c are unreliable. The threshold for binding is -0.655 349 8 hartree and organization of the table is the same as Table VII.

L_{max}	N_e	N_p	N_{CI}	$E(e^+Sr)$	ε	$\langle r_e \rangle$	$\langle r_p \rangle$	Γ_c	Γ_v
0	16	12	1632	-0.582 171 8	-0.073 177 9	4.379 04	12.862 46	0.003 830	0.003 218
1	28	23	4680	-0.606 689 2	-0.048 660 6	4.419 95	10.967 30	0.004 959	0.020 77
2	40	33	106 80	-0.621 592 1	-0.033 757 6	4.470 36	8.734 91	0.010 178	0.092 61
3	52	41	192 60	-0.632 774 7	-0.022 575 1	4.544 09	7.729 02	0.013 970	0.198 83
4	60	49	270 04	-0.641 144 0	-0.014 205 8	4.611 29	7.323 03	0.015 515	0.308 14
5	68	57	347 48	-0.647 183 5	-0.008 166 3	4.669 76	7.151 42	0.015 913	0.408 44
6	76	65	425 40	-0.651 550 3	-0.003 799 4	4.719 79	7.078 48	0.015 847	0.496 99
7	84	73	504 76	-0.654 743 7	-0.000 606 1	4.761 92	7.050 64	0.015 618	0.574 14
8	92	81	584 12	-0.657 105 1	0.001 755 4	4.797 08	7.044 37	0.015 350	0.640 84
9	100	89	663 48	-0.658 875 2	0.003 525 5	4.826 17	7.048 12	0.015 094	0.698 61
10	108	97	742 84	-0.660 218 6	0.004 868 9	4.850 10	7.056 29	0.014 867	0.748 75
p				2.62	2.62	1.86	-7.40	1.14	1.35
∞				-0.667 878	0.012 528	5.1146	∞	0.006 520	1.9436

TABLE X. Sensitivity of the energy and valence annihilation rate to the use of different exponents in the power series extrapolation. The exponents for energy are in the column p_E and the exponents for the annihilation rate in p_Γ .

Exponent p_E	E	Exponent p_Γ	Γ_v
$e^+\text{Mg}$			
2.82	0.016 756	1.68	0.980 38
3.41	0.016 151	1.84	0.899 05
4.00	0.015 789	2.00	0.841 75
$e^+\text{Ca}$			
2.67	0.018 331	1.45	1.650 42
3.33	0.016 500	1.72	1.344 08
4.00	0.015 467	2.00	1.174 82
$e^+\text{Sr}$			
2.62	0.012 528	1.35	1.943 61
3.31	0.010 050	1.67	1.451 31
4.00	0.008 720	2.00	1.223 42

It is evident from Fig. 1 that p_E increases for all systems as L_{max} increases. An extrapolation with $p_E=4$ would therefore tend to underestimate the magnitude of the extrapolation correction. Since the extrapolation with p_E derived from last three energy increments will tend to overestimate the extrapolation correction, it is clear that upper and lower bounds can be placed on the extrapolation correction. An additional calculation with p_E chosen halfway between 4 and the $L_{max}=10$ exponent was also done. This probably gives a more reliable estimate of the binding energy than either of the other estimates. The binding energies for all systems, using these three methods of determining p_E are given in Table X. The variations in the binding energy are 6% for $e^+\text{Mg}$, 20% for $e^+\text{Ca}$ and about 40% for $e^+\text{Sr}$. The actual uncertainty in the correction is about the same for all 3 systems, the smaller overall uncertainty for $e^+\text{Mg}$ occurs because the actual magnitude of the correction, when compared with the rest of the binding energy is much smaller.

The variations in the different estimates of the annihilation rate are larger than the binding energy, but they are not excessively large considering that only about 50% of the annihilation rate comes from the explicit calculation. The actual difference between the value of p derived from comparison of the increments to the annihilation rate, and the asymptotic value, $p_\Gamma=2$ given by Gribakin and Ludlow [27] are 0.32 for $e^+\text{Mg}$, 0.55 for $e^+\text{Ca}$, and 0.65 $e^+\text{Sr}$. The annihilation rates for the middle value of p_Γ are taken as the preferred estimate giving total annihilation rates of $0.91 \times 10^9 \text{ sec}^{-1}$ for $e^+\text{Mg}$, $1.36 \times 10^9 \text{ sec}^{-1}$ for $e^+\text{Ca}$, and $1.47 \times 10^9 \text{ sec}^{-1}$ for $e^+\text{Sr}$.

IV. SUMMARY

The CI method has been used to compute the wave functions and energies for $e^+\text{Mg}$, $e^+\text{Ca}$, and $e^+\text{Sr}$. The computed binding energy for positronic magnesium is consistent with a previous FCSVM calculation and a quantum Monte Carlo calculation. It would be reasonable to say that there is a consensus that the binding energy for $e^+\text{Mg}$ is about 0.016

hartree. The present best estimate of the binding energy is 0.0162 hartree with an overall uncertainty due to extrapolation of about $\pm 4\%$. The improved calculation for $e^+\text{Ca}$ shows a binding energy comparable in size to that of $e^+\text{Mg}$. The present best estimate of the $e^+\text{Ca}$ binding energy is about 0.0165 hartree with an uncertainty due to extrapolation of about $\pm 10\%$. The $e^+\text{Sr}$ binding energy of 0.0101 hartree has an associated uncertainty of about $\pm 20\%$. Even though the L_{max} correction more than doubles the binding energy in the case of $e^+\text{Sr}$, the error bounds are not ridiculously large.

While the present calculations are usefully accurate, it would be desirable to reduce the uncertainties associated with the extrapolations by performing even larger calculations. The main problem with doing larger calculations is that an orbital basis with 100 single-electron and 100 single-positron orbitals results in a very large number of electron-electron and electron-positron $1/r_{12}$ Coulomb integrals. These are currently stored in random access memory (RAM) and even a modest increase in the size of the calculation would result in a list of Coulomb integrals and orbital indices that took more than 1 Gbyte to store. Segmenting the Coulomb integral list would probably lead to calculations that could use an orbital list at least 50% larger than the present series of calculations.

Although an explicit calculation has not been done, the present binding energies for $e^+\text{Ca}$ and $e^+\text{Sr}$ give very strong evidence that positronic barium would also be stable. An analysis of positron binding to a model alkali atom showed that binding was expected for atoms with an ionization potential larger than 0.1767 hartree [32]. The ionization energy of barium is 0.1915 hartree, which exceeds this threshold. However, barium with two valence electrons is obviously not an alkali atom and this might affect the critical threshold. Fortunately, positronic calcium and strontium can provide guidance about how the model alkali atom analysis relates to systems with two valence electrons. Calcium has an ionization potential of 0.224 65 hartree and $e^+\text{Ca}$ has a binding energy of 0.016 55 hartree. Strontium has an ionization potential of 0.209 25 hartree and $e^+\text{Sr}$ has a binding energy of 0.010 05 hartree. The model alkali atoms with the same ionization energies had e^+ alkali bound states with binding energies of 0.010 49 and 0.004 64 hartree, respectively. Since the binding energies for $e^+\text{Ca}$ and $e^+\text{Sr}$ exceed the binding energies of the equivalent e^+ alkali system, it therefore seems reasonable to conclude that barium, with an ionization potential larger than the critical model alkali threshold of 0.1767 hartree, will also bind a positron. As barium has an ionization potential of 0.1915 hartree, it would be expected that the binding energy of $e^+\text{Ba}$ would converge very slowly with L_{max} . Since formal binding for $e^+\text{Sr}$ was only established at $L_{max}=8$, one should anticipate going beyond $L_{max}=10$ for $e^+\text{Ba}$.

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