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Positronic complexes with unnatural parity

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The structure of the unnatural parity states of PsH, LiPs, NaPs, and KPs are investigated with the configuration interaction and stochastic variational methods. The binding energies (in hartree) are found to be 8.17 $\times 10^{-4}$, 4.42 $\times 10^{-4}$, 15.14 $\times 10^{-4}$, and 21.80 $\times 10^{-4}$, respectively. These states are constructed by first coupling the two electrons into a configuration which is predominantly ${}^3P^e$, and then adding a p-wave positron. All the active particles are in states in which the relative angular momentum between any pair of particles is at least $L=1$. The LiPs state is Borromean since there are no three-body bound subsystems (of the correct symmetry) of the (Li$^+$, e^-, e^-, e^+) particles that make up the system. The dominant decay mode of these states will be radiative decay into a configuration that autoionizes or undergoes positron annihilation.

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I. INTRODUCTION

The stability of a bound state composed of two electrons and a positron, the positronium negative ion, was first demonstrated in a seminal calculation by Wheeler [1]. Shortly after this calculation, the four-body systems, PsH and Ps$_2$ were shown to be stable [2,3]. Since that time, only a few other electronically stable states have been discovered that can be formed from combinations of p^+, e^-, and e^+. These are additional bound states of Ps$_2$ [4–7], a compound that is best described as e^+PsH [8], and a (p^+, $4e^-$, $2e^+$) complex [8]. Additionally, a number of atoms have been identified as being capable of binding positronium and positrons [9–11].

Just recently, a new class of positronic compounds that are electronically stable was identified [12]. The new PsH and NaPs bound states were unnatural parity states with symmetry conditions that act to prevent decay into the lowest energy dissociation products. An unnatural parity state is a state with parity equal to $\Pi=(-1)^{L+1}$, where L is the orbital angular momentum of the state. These PsH and NaPs systems have the two valence electrons in a spin-triplet state, a total orbital angular momentum of zero, and an odd parity, i.e., $L^\Pi=0^-$. In addition, these states had the unusual feature of decaying very slowly by 2γ or 3γ annihilation.

In this paper, more details about the $L^\Pi=0^-$ negative parity states of PsH and NaPs are given. Negative parity states of LiPs and KPs are also identified as being electronically stable. The LiPs state has the additional distinction of being a Borromean state [13–16] since the (Li$^+$, e^-, e^-, e^+) system has no stable three-body state that can act as a parent for the four-body ${}^{2,4}S^o$ state. We have adopted the definition of Richard: *A bound state is Borromean if there is no path to build it via a series of stable states by adding the constituents one by one* [13].

It should be noted that there are analogs of these states in the alkaline-earth metal sequence. Configuration interaction (CI) approaches have been used to demonstrate the stability of the Be$^-$, Mg$^-$, Ca$^-$, and Sr$^-$ np^3 ${}^4S^o$ states [17,18]. However, the issue of whether an electron can be attached to the ${}^3P^e$ state of H$^-$ into an ${}^4S^o$ state of H^{2-} has been the subject of some controversy. A complex rotation method was applied to a large basis CI wave function and a shape resonanace lying about 1.4 eV above the ${}^3P^e$ threshold was predicted [19]. However, this was contradicted by a much more sophisticated hyperspherical calculation that exhibited no sign of a resonance [20].

II. THEORETICAL OVERVIEW

A. Symmetry conditions for binding

The stability of these systems lies in the symmetry relations between the pairs of particles that make up the system. The discussion of these conditions will be addressed specifically to PsH, but these conditions, with some small modifications, will also apply to the other systems addressed in this paper.

The electronic stability of PsH can be motivated by consideration of the H$^-$($2p^2$ ${}^3P^e$) bound state [21–23]. This state has an energy of −0.125 355 45 hartree [23] and is electronically stable due to symmetry conditions. It cannot decay into the H($1s$)+e^- channel since the $\ell=1$ partial wave of the electron automatically results in a state of negative parity. The $L^\Pi=0^-$ state of PsH is formed when the positron is trapped into a $2p$ state of the H$^-$ attractive potential well. The possible decay modes are constrained by the symmetry conditions. Dissociation into Ps($1s$)+H($1s$) is forbidden since

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$\Pi=(-1)^L$, where L is the orbital angular momentum between the Ps(1s) and H(1s) fragments. Similarly, dissociation into Ps(ns)+H($n\ell$) or Ps($n\ell$)+H(ns) does not occur since it is not possible to construct an $L^\Pi=0^-$ state if one of the angular momentum is zero. The lowest energy dissociation channel would be into Ps(2p)+H(2p) (with the two fragments in a p-wave) with an energy threshold of −0.1875 hartree. Another possible decay would be into the $\mathrm{H}^-(2p^2\,{}^3P^e)+e^+$ channel but the threshold energy here is −0.125 355 45 hartree [23].

It is easy to see that there is potentially a large energy advantage associated with binding the positron to the negative ion. If the H^- state is regarded as a point particle with an internal energy of ≈−0.125 hartree, then a positron in the 2p state will lower the total energy to −0.250 hartree. In actuality the $\mathrm{H}^-(2p^2\,{}^3P^e)$ state is diffuse [22], but the advantage of attaching the positron to the negative ion is clear.

B. Symmetry conditions for annihilation

The dominant electron-positron annihilation processes are the 2γ and 3γ processes. The 2γ annihilation rate for bound systems is proportional to the probability of finding an electron and a positron at the same position in a spin-singlet state according to

$$\Gamma = 4\pi r_e^2 c\langle\Psi|\sum_i O_{ip}^S\delta(\mathbf{r}_i-\mathbf{r}_p)|\Psi\rangle$$

$$= 2.018\,788\times10^{11}\sum_i\langle\delta(\mathbf{r}_i-\mathbf{r}_p)\rangle_S \qquad (1)$$

[24–26], where the sum is over the electron coordinates, the δ-function expectation is evaluated in a_0^3, and Γ is given numerically in s^{-1}. The operator O_{ip}^S is a spin projection operator to select spin-singlet states for the i,p electron-positron pairs in the wave function Ψ which is antisymmetrized in the electron coordinates. The rate constant for the Ps ground state is about $8\times10^9\ \mathrm{s}^{-1}$. Equation (1) involves a contact interaction which means that the relative angular momentum of the annihilating pair (L_{rel}) must be zero [24]. However, electron-positron annihilation is possible even when the relative angular momentum of the annihilating pair is greater than zero. For example the Ps(2p) levels can undergo 2γ annihilation at rates proportional to α^5 and α^6, respectively [27,28]. The rates for the different Ps(2p) levels have been calculated to be approximately $10^4\ \mathrm{s}^{-1}$ [27,28]. Similarly, the 3γ process, which happens when the annihilating pair are in a spin-triplet state, can also occur at a rate proportional to α^6 when the pair have a relative angular momentum of 1. The discussions below about the symmetry conditions for positron annihilation concern the fast 2γ and 3γ processes for pairs in relative s states.

Consider the electron-positron annihilation of a PsH state of ${}^2S^o$ symmetry. The relative angular momentum of the annihilating pair (L_{rel}) must be zero. This means the total angular momentum of the state will come from the center-of-mass motion of the annihilating pair ($L_{\mathrm{c.m.}}$), and from the angular momentum of the spectator electron ($L_{\mathrm{spectator}}$). The total parity of the state is determined by the parity of the individual constituents, i.e., $\Pi=(-1)^{L_{\mathrm{spectator}}+L_{\mathrm{c.m.}}+L_{\mathrm{rel}}}$. It is simply not possible to form an odd parity state with a total angular momentum of zero if any one of the angular momenta is zero. Consequently, a two electron–one positron state of ${}^2S^o$ symmetry cannot decay by the fast 2γ process.

These arguments also apply to the 3γ annihilation process. The 3γ process occurs for electron-positron pairs in a spin-triplet state with a relative angular momentum of zero. Once again, it is simply impossible to form a state of ${}^2S^o$ (or ${}^4S^o$) symmetry if the relative angular momentum of the annihilating pair is zero. So it is reasonable to conclude that the lowest order 3γ decay is not possible from a ${}^{2,4}S^o$ state.

III. CALCULATION METHODS

A. Configuration interaction method

A majority of the calculations in the present paper were performed with a configuration interaction approach [29–31]. The CI basis was constructed by letting the two electrons (particles 1 and 2) and the positron (particle 0) form all the possible total angular momentum $L_T=0$ configurations, with the two electrons in a spin-triplet state, subject to the selection rules,

$$\max(\ell_0,\ell_1,\ell_2)\le J, \qquad (2)$$

$$\min(\ell_1,\ell_2)\le L_{\mathrm{int}}, \qquad (3)$$

$$(-1)^{(\ell_0+\ell_1+\ell_2)}=-1. \qquad (4)$$

In these rules ℓ_0, ℓ_1, and ℓ_2 are respectively the orbital angular momenta of the positron and the two electrons. We define $\langle E\rangle_J$ to be the energy of the calculation with a maximum orbital angular momentum of J. The single particle orbitals were Laguerre type orbitals (LTOs) with a common exponent chosen for all the orbitals of a common ℓ [29–31]. The orbital basis sets for the positron and electrons were identical.

A major technical problem afflicting CI calculations of positron-atom interactions is the slow convergence of the energy with J [10,31]. The $J\to\infty$ energy, $\langle E\rangle_\infty$, is determined by the use of an asymptotic analysis. The successive increments, $\Delta E_J=\langle E\rangle_J-\langle E\rangle_{J-1}$, to the energy can be written as an inverse power series [31–35], viz.

$$\Delta E_J\approx\frac{A_E}{\left(J+\frac{1}{2}\right)^6}+\frac{B_E}{\left(J+\frac{1}{2}\right)^7}+\frac{C_E}{\left(J+\frac{1}{2}\right)^8}+\frac{D_E}{\left(J+\frac{1}{2}\right)^9}+\cdots. \qquad (5)$$

The first term in the series starts with a power of 6 since all the possible couplings of any two of the particles result in unnatural parity states [36].

The $J\to\infty$ limit, has been determined by fitting sets of $\langle E\rangle_J$ values to asymptotic series with either one, two, three, or four terms. The coefficients, A_E, B_E, C_E, and D_E, for the four-term expansion are determined at a particular J from five successive energies ($\langle E\rangle_{J-4}$, $\langle E\rangle_{J-3}$, $\langle E\rangle_{J-2}$, $\langle E\rangle_{J-1}$ and

$\langle E\rangle_J$). Once the coefficients have been determined it is easy to sum the series to ∞ and obtain the variational limit. Application of an asymptotic series analysis to helium has resulted in CI calculations reproducing the ground state energy to an accuracy of $\approx 10^{-8}$ hartree [35,37].

The treatment of the alkali metals Li, Na, and K requires the use of a frozen core approximation. The details of this approximation have been discussed in great detail elsewhere [29–31], so only the briefest description is given here. The model Hamiltonian is initially based on a Hartree-Fock (HF) wave function for the neutral atom ground state. The core orbitals are then frozen. The direct part of the core potential is attractive for electrons and repulsive for the positron. The impact of the direct and exchange part of the HF core interactions on the active particles are computed without approximation. One- and two-body semiempirical polarization potentials are then added to the potential. The adjustable parameters of the core-polarization potential are defined by reference to the spectrum of neutral atom [30,38].

B. Stochastic variational method (SVM)

In the stochastic variational approach an explicitly correlated Gaussian (ECG) is constructed by placing the particles (electrons and positrons) into Gaussian single particle orbitals

$$r_i^l Y_{lm}(\hat{r}_i)\exp\{-\beta_i r_i^2\} = \mathcal{Y}_{lm}(\mathbf{r}_i)\exp(-\beta_i r_i^2), \tag{6}$$

and using an

$$\exp[-\alpha_{ij}(\mathbf{r}_i-\mathbf{r}_j)^2], \tag{7}$$

Gaussian correlation function between the ith and jth particles. The N-particle trial function is then

$$\Psi_{LS}(\mathbf{r}) = \mathcal{A}\Bigg\{ [[[\mathcal{Y}_{l_1}\mathcal{Y}_{l_2}]_{l_{12}}\mathcal{Y}_{l_3}]\ldots]_{LM_L}\chi_{SM_S} \times\prod_{i=1}^{N}\exp(-\beta_i r_i^2)\prod_{i<j}\exp\,[-\alpha_{ij}(\mathbf{r}_j-\mathbf{r}_i)^2\}]\Bigg\}, \tag{8}$$

where $\mathcal{A}$ is an antisymmetrizer and χ_{SM_S} is the spin function of the particles. The nonlinear variational parameters β_i and α_{ij} are selected by an iterative trial and error procedure. Full details are given in Refs. [39,40]. The orbital angular momentum quantum numbers l_i are restricted to occupy the lowest possible values consistent with the overall symmetry of the state. The spherical part of the ECG basis functions effectively allows the internal angular momentum to be distributed between the different parts of the systems. Accordingly, Eq. (8) implicitly includes all possible internal symmetries that can make a contribution to the energy. This has been verified with test calculations.

IV. RESULTS OF CALCULATIONS

A. $A^-(np^2\,{}^3P^e)$ states

Table I gives the energies of the various parent states of the APs systems (where A stands for H, Li, Na, K). These are relevant to the determination of the energy thresholds. The energies for the $A^-(np^2\,{}^3P^e)$ states were taken from CI calculations which used an exact subset of the basis used for the calculations upon the APs system. The energy for the $\mathrm{H}^-(np^2\,{}^3P^e)$ state was taken from a large CI-Hylleraas calculation [23] that was converged to eleven significant digits. The results of an SVM calculation of this state are detailed in Table II.

TABLE I. The energies of various parent states relevant to the structure and energy threshold for the APs unnatural parity states. The polarizability only allows for $np\rightarrow kd$ excitations since $np\rightarrow ks$ excitations cannot occur in the ${}^3P^e$ channel. The energy for the $\mathrm{H}^-(np^2\,{}^3P^e)$ state was taken from Bylicki and Bednarz [23], while those for the alkali metal systems were from the present CI calculations.

	$A(np)$	$A(np^2\,{}^3P^e)$	$A(np)$+Ps$(2p)$	α_d (a_0^3)
H	−0.12500	−0.12535545	−0.1875	173.3
Li	−0.13023850	Unbound	−0.19273850	142.7
Na	−0.11156287	−0.11382478	−0.17406287	302.0
K	−0.10018265	−0.10450418	−0.16268271	557.6

The dipole polarizabilities listed in Table I show an interesting correlation between the polarizability of the $A(np)$ state and the electron affinity in the $A^-(np^2\,{}^3P^e)$ channel. The larger the polarizability, the larger the binding energy. The Li$(2p)$ level has the smallest polarizability and is the one

TABLE II. Properties of the $\mathrm{H}^-({}^3P^e)$, $\mathrm{PsH}({}^{2,4}S^o)$ and $\mathrm{LiPs}({}^{2,4}S^o)$ ground states. Data are given assuming an infinite nuclear mass (n). All quantities are given in atomic units. The magnitude of the binding energy against dissociation into the lowest energy fragmentation channels is given by ε while T_+ and T_- represent the positron and electron kinetic energy operators.

Property	PsH	H^-	LiPs
N	400	400	1000
$\langle V\rangle/\langle T\rangle+2$	5.1×10^{-8}	4.4×10^{-9}	5.6×10^{-5}
E	−0.188317	−0.12535545	−7.472871
ε	0.000817	0.00035545	0.000215
$\langle T_-\rangle$	0.156579554	0.125355451	
$\langle T_+\rangle$	0.031737544		
$\langle r_{ne^-}\rangle$	8.867	11.657619	4.3177
$\langle r_{ne^+}\rangle$	14.243		12.991
$\langle r_{e^-e^-}\rangle$	14.001	19.58289	7.6429
$\langle r_{e^+e^-}\rangle$	12.722		12.531
$\langle 1/r_{ne^-}\rangle$	0.174397	0.160521	1.4358
$\langle 1/r_{ne^+}\rangle$	0.084716		0.089443
$\langle 1/r_{e^-e^-}\rangle$	0.089023	0.0700331	0.40130
$\langle 1/r_{e^+e^-}\rangle$	0.101789		0.096298
$\langle r_{ne^-}^2\rangle$	121.185	271.2046	45.959
$\langle r_{ne^+}^2\rangle$	247.910		192.691
$\langle r_{e^-e^-}^2\rangle$	245.959	556.893	92.533
$\langle r_{e^+e^-}^2\rangle$	202.204		182.800

TABLE III. The energy of the $^{2,4}S^o$ state of PsH as a function of J and with $L_{\text{int}}=3$. The threshold for binding is −0.1875 hartree. The column n gives the total number of occupied electron orbitals (the number of positron orbitals was the same) while N_{CI} gives the total number of configurations. The radial expectation values for the electron, $\langle r_e\rangle$, and the positron, $\langle r_p\rangle$ are given in a_0. The results of the $J\to\infty$ extrapolations using Eq. (5) at $J=10$ are given.

J	n	N_{CI}	$\langle E\rangle_J$	ε	$\langle r_e\rangle$	$\langle r_p\rangle$
1	20	4200	−0.16755818	−0.01994182	7.08076	13.10807
2	40	16400	−0.17938458	−0.00811542	6.95155	11.88797
3	60	45000	−0.18327391	−0.00422609	7.08870	11.66425
4	80	85000	−0.18510516	−0.00239484	7.23884	11.70642
5	100	129200	−0.18612684	−0.00137316	7.37821	11.82951
6	120	177200	−0.18675237	−0.00074763	7.50464	11.97767
7	140	225200	−0.18715897	−0.00034103	7.61882	12.13043
8	160	273200	−0.18743569	−0.00006431	7.72208	12.27939
9	180	321200	−0.18763074	0.00013074	7.81562	12.42101
10	200	369200	−0.18777213	0.00027213	7.90047	12.55387
			$J\to\infty$ extrapolations			
1-term Eq. (5)			−0.18800504	0.00050504	8.04024	12.77272
2-term Eq. (5)			−0.18811689	0.00061689	8.14930	12.95211
3-term Eq. (5)			−0.18817637	0.00067637	8.23457	13.09609
4-term Eq. (5)			−0.18821031	0.00071031	8.30116	13.21039

atom that is unable to support a negative ion in the $^3P^e$ channel.

This behavior is reminiscent of the electron affinity systematics of the alkaline-earth metals in the $^2P^o$ channel. The ground states of Be and Mg do not have an electron affinity while those of Ca, Sr, and Ba have electron affinities that become larger as the atom, and its polarizability, become larger [41]. The critical polarizability for the alkali metal sequence is somewhere between 142 and $173a_0^3$. The polarizability of calcium, which just binds an electron with an electron affinity of $\approx 7\times10^{-4}$ hartree [42–44], is about $160a_0^3$ [38,45].

B. PsH

1. Configuration interaction method

The Hamiltonian was diagonalized in a basis constructed from a large number of single particle orbitals, including orbitals up to $\ell=10$. There were 20 radial basis functions for each ℓ. Note, the symmetry of the state prevented the electrons or positrons from occupying $\ell=0$ orbitals. The largest calculation was performed with $J=10$ and $L_{\text{int}}=3$ and gave a CI basis dimension of 369 200. The parameter L_{int} does not have to be particularly large since it is mainly concerned with electron-electron correlations [30]. The resulting Hamiltonian matrix was diagonalized with the Davidson algorithm [46], and a total of 300 iterations were required for the largest calculation. The present calculation is very slightly different from that reported in [12]. One of the $\ell=10$ Laguerre functions in [12] was input with the incorrect n. The inclusion of the correct Laguerre function resulted in the final binding energy reported in [12] changing by about 1%.

The energy of the PsH $^{2,4}S^o$ state as a function of J is given in Table III. The calculations only give an energy lower than the H(2p)+Ps(2p) threshold of −0.1875 hartree for $J\geqslant 9$. Figure 1 shows the estimates of $\langle E\rangle_\infty$ as a function of J. A quick visual examination suggests that the extrapolations are converging to a common energy which attests to the reliability of the extrapolations in J. The impact of the extrapolations is significant since they more than double the binding energy. The best CI estimate of the binding energy is the four-term extrapolation at $J=10$ listed in Table III, namely 7.10×10^{-4} hartree. The main area where improve-

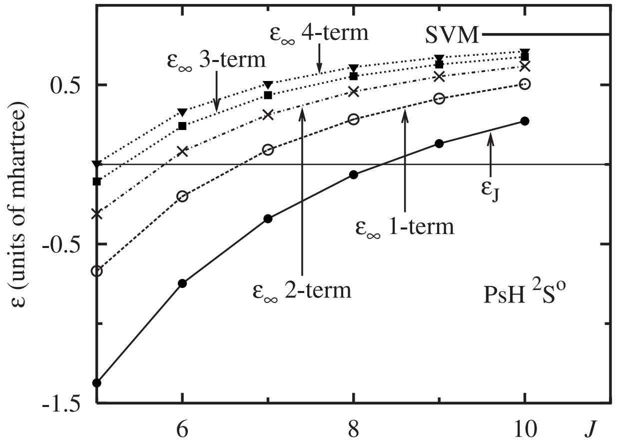

FIG. 1. The binding energy, $\varepsilon=-(\langle E\rangle+0.1875)$, of the $^{2,4}S^o$ state of PsH as a function of J. The directly calculated energy is shown as the solid line while the $J\to\infty$ limits using Eq. (5) with one, two, three, or four terms are shown as the dashed lines. The binding energy of the SVM wave function is also shown. The H(2p)+Ps(2p) dissociation threshold is shown as the horizontal solid line.

ment could be made is in the dimension of the radial basis. A precursor to the present CI calculation with 15 LTOs gave an extrapolated binding energy of 6.06×10^{-4} hartree.

The extrapolations of the other expectation values in Table III were done using Eq. (5). It should be noted that there is no formal justification for the use of Eq. (5) for expectation values other than the energy, so there is an additional degree of uncertainty for these extrapolations. In practice, this extra uncertainty is not that significant since the finite dimension of the radial basis represents a larger source of error.

2. Stochastic variational method

For the PsH calculation, the two electrons have been placed in $\ell_1=\ell_2=1$ orbitals and coupled to an $L=1$ state with a total spin of $S=1$. The positron is then placed into an $\ell_0=1$ orbital and the whole composite is coupled to $L=0$. The largest calculation had a total of 400 ECGs. A summary of the energy and other expectation values is given in Table II.

The energy of the best SVM wave function was $-0.188\,317$, yielding a binding energy of 8.17×10^{-4} hartree. The deviation of the wave function from the exact virial theorem expectation, $(\langle V\rangle/\langle T\rangle+2)$, was 5.1×10^{-8}. A many body system interacting by purely coulombic interactions is known to satisfy $(\langle V\rangle/\langle T\rangle=-2)$ [39]. The SVM binding energy is just over 10% larger than the CI energy and should be closer to the variational limit.

One interesting aspect of the $^4S^o$ state is that it is more tightly bound than its $\mathrm{H}(2p^2)$ parent. Its binding energy is more that twice as large as the $\mathrm{H}(2p^2)$ binding energy of 3.55×10^{-4} hartree [23]. It is also more compact. The mean electron distance from the nucleus of $\langle r_e\rangle=8.86a_0$ is smaller than that for $\mathrm{H}(2p^2)$, namely $\langle r_e\rangle=11.66a_0$. In short, the addition of the positron has resulted in a complex that has a larger binding energy than its three-body parent.

The SVM radial expectation for the positron, $\langle r_p\rangle$ was $14.24a_0$, somewhat larger than the extrapolated CI value of $13.67a_0$. In the CI calculation the positron is localized closer to the nucleus even though the CI wave function is less tightly bound. This is a purely computational limitation, due to the nature of LTO basis which is relatively compact. Improving the radial expectation for the CI wave function would require an increase in the number of radial functions per ℓ.

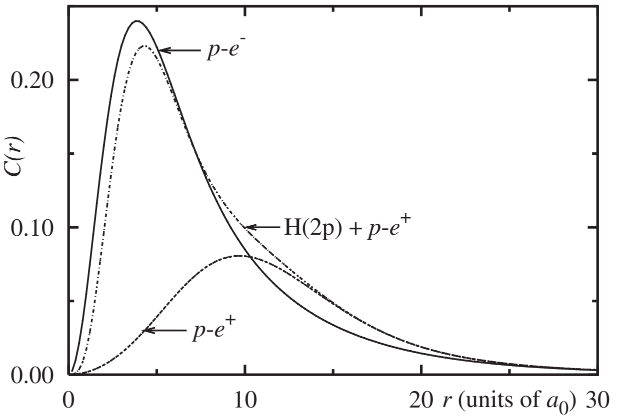

FIG. 2. The correlation functions for the (p,e^-) and (p,e^+) particles of PsH. Also shown is a correlation function obtained by adding the (p,e^+) correlation function to the (p,e^-) correlation function of the $\mathrm{H}(2p)$ state.

The interparticle correlation function, $C(r)$, is defined as the probability of finding any pair of particles a certain distance apart. The correlation functions shown in Figs. 2 and 3 are consistent with a structure consisting of a $\mathrm{Ps}(2p)$ complex weakly bound to the $\mathrm{H}(2p)$ state. Consider an idealized structure consisting of a product wave function of the form $\Psi=\Phi(\mathrm{Ps}[2p])\Phi(\mathrm{H}[2p])\Phi_{\mathrm{Ps}}(R)$, where $\Phi_{\mathrm{Ps}}(R)$ is the wave function describing the motion of the $\mathrm{Ps}(2p)$ center of mass. The (p,e^-) and (p,e^+) correlation functions arising from the $\mathrm{Ps}(2p)$ cluster should be the same. Therefore, adding the (p,e^+) correlation function to the (p,e^-) $C(r)$ of $\mathrm{H}(2p)$ state should give a correlation function that is the same as the actual (p,e^-) correlation Fig. 2 shows a strong degree of resemblance between the actual (p,e^-) correlation function and that obtained from a $\Phi(\mathrm{Ps}[2p])\Phi(\mathrm{H}[2p])\Phi_{\mathrm{Ps}}(R)$. Similarly, adding the (e^-,e^-) correlation function to the (e^+,e^-) $C(r)$ of $\mathrm{Ps}(2p)$ state should give a correlation function that is the same as the actual (e^-,e^-) correlation function. Once again, the two curves shown in Fig. 3 show a degree of similarity.

The energies of the finite mass variants of PsH have also been determined. The energies of $\mathrm{Ps}^1\mathrm{H}$, $\mathrm{Ps}^2\mathrm{H}$, and $\mathrm{Ps}^3\mathrm{H}$ are $-0.188\,239\,8$, $-0.188\,278\,4$, and $-0.188\,291\,3$ hartree, respectively. The binding energies are 8.078×10^{-4}, 8.124×10^{-4}, and 8.140×10^{-4} hartree, respectively.

C. LiPs

The $^2S^o$ state of LiPs is a very unusual state in that it is a Borromean state [13–16]. This is because all the possible three-body parent states, namely the $^3P^e$ states of Li^-, $e^+\mathrm{Li}$, and Ps^-, are themselves unstable.

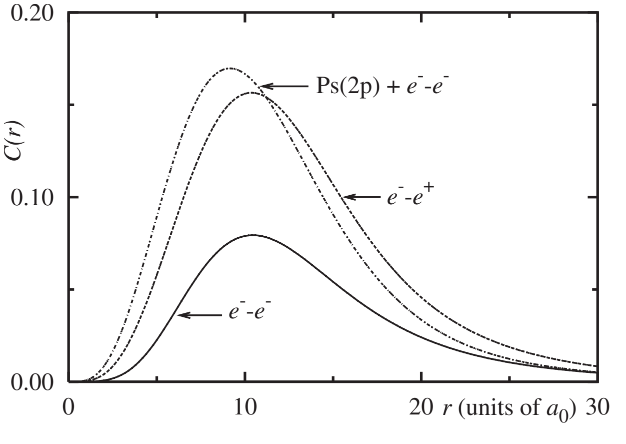

FIG. 3. The correlation functions for the (e^-,e^-) and (e^-,e^+) particles of PsH. Also shown is a correlation function obtained by adding the (e^-,e^-) correlation function to the (e^-,e^+) correlation function of the $\mathrm{Ps}(2p)$ state.

TABLE IV. Results of CI calculations for the $^1S^o$ state of LiPs for a series of J, with fixed $L_{\mathrm{int}}=3$. The three-body energy of the system, relative to the energy of the Li^+ core, is denoted by E (in hartree). The threshold for binding is −0.192 238 50 hartree, and ε gives the binding energy (in hartree) against dissociation into Ps($2p$)+Li($2p$). The core annihilation rate in units of s^{-1} is given in the Γ_c column. The numbers in square brackets indicate powers of 10. Other aspects of the table design are identical to those of Table III.

J	n	N_{CI}	E	ε	$\langle r_e \rangle$	$\langle r_p \rangle$	Γ_c
1	20	4200	−0.17291946	−0.01981904	6.86606	12.84274	4.5441[4]
2	40	16400	−0.18449498	−0.00824351	6.75226	11.69309	6.5727[4]
3	60	45000	−0.18828973	−0.00444877	6.89326	11.50143	6.5611[4]
4	80	85000	−0.19007657	−0.00266192	7.04675	11.56062	6.1767[4]
5	100	129200	−0.19107655	−0.00166195	7.18989	11.69580	5.7955[4]
6	120	177200	−0.19169133	−0.00104717	7.32070	11.85451	5.4761[4]
7	140	225200	−0.19209300	−0.00064550	7.43986	12.01755	5.2173[4]
8	160	273200	−0.19236789	−0.00037061	7.54860	12.17700	5.0080[4]
9	180	321200	−0.19256282	−0.00017568	7.64806	12.32954	4.8376[4]
10	200	369200	−0.19270505	−0.00003345	7.73914	12.47367	4.6972[4]
11	220	417200	−0.19281127	0.00007278	7.82273	12.60906	4.5806[4]
			$J\to\infty$ extrapolations				
1-term Eq. (5)			−0.19300706	0.000268567	7.97681	12.85861	4.3656[4]
2-term Eq. (5)			−0.19310120	0.000362688	8.09858	13.06361	4.2226[4]
3-term Eq. (5)			−0.19315143	0.000412934	8.19533	13.23002	4.1331[4]
4-term Eq. (5)			−0.19318032	0.000441825	8.27254	13.36466	4.0698[4]

The Ps^- ion has been thoroughly investigated and does not possess a stable $^3P^e$ state [47,48].

Similarly, the Li^- ion is believed not to have a stable $^3P^e$ state [49,50]. We have also performed some very large CI calculations upon the Li^- ion and these calculations gave no indication of a bound state in the $^3P^e$ symmetry.

Finally, the e^+Li system is also not stable in the $^3P^e$ channel. Once again a very large CI calculation has been performed and once again there was no indication of a bound state. Further, some calculations of e^+-Li scattering in the $^3P^e$ channel also gave no sign of a bound state. The polarizabilities given in Table I also indicate that it should be easier to bind a positron to the H($2p$) state than the Li($2p$). The SVM was also used to check whether the e^+H state is stable in the $^3P^e$ channel, and once again there was no indication of a bound state.

The calculations upon LiPs were very similar in scope and scale to those carried out upon PsH although the calculations were taken to $J=11$ in order to have an explicit calculation that gave binding. The sequence of CI energies and other expectation values as a function of J are given in Table IV. The binding energy ε_J is defined as $\varepsilon_J=-(\langle E\rangle+0.192\,738\,50)$.

Figure 4 depicts the binding energy and extrapolations as a function of J. Only for the $J=11$ basis has $\langle\varepsilon\rangle_J$ crossed the threshold for binding.

The most reliable estimates of the energy is that given after the four-term extrapolation is used to determine the $J\to\infty$ limit of the binding energy. The different curves in Fig. 4 tend to be closer together as the number of terms in the extrapolation increase. The binding energy of 4.42×10^{-4} hartree is just over half that of the PsH state.

The positron can annihilate with the core electrons via the 2γ process since the symmetry considerations are irrelevant here. However, the annihilation rate of $\Gamma_{\mathrm{core}}\approx4\times10^4\ \mathrm{s}^{-1}$ is small because the positron cannot occupy a $\ell=0$ orbital.

The mean positron-nucleus distance of $\langle r_p\rangle=13.5a_0$ for the CI wave function was almost the same as the CI wave function estimate for PsH despite the smaller binding energy. Part of the reason for this lies in the LTO basis sets which were almost identical for the two atoms. The finite range of the LTO basis could be acting to artificially confine the positron. However, it must be remembered that the asymptotic

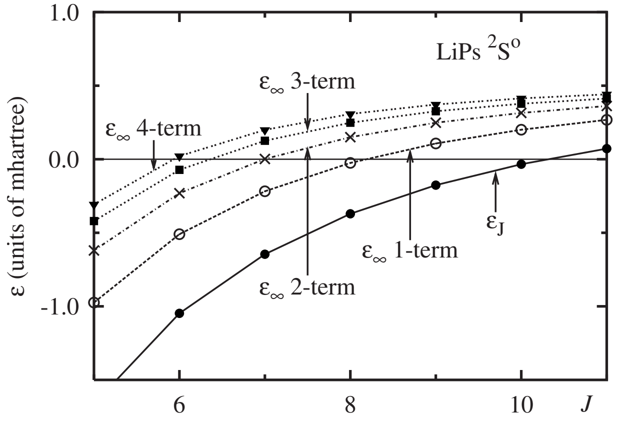

FIG. 4. The binding energy of the $^{2,4}S^o$ state of LiPs as a function of J. The directly calculated binding energy is shown as the solid line while the $J\to\infty$ limits using Eq. (5) are shown as the dashed lines. The Li($2p$)+Ps($2p$) dissociation threshold is shown as the horizontal solid line.

TABLE V. The energy of the $^{2,4}S^o$ state of NaPs as a function of J. Energies are given relative to that of the Na$^+$ core while the threshold for binding is −0.174 062 87 hartree. The column n_- gives the total number of occupied electron orbitals, while n_+ gives the number of positron orbitals. Other aspects of the table design are identical to those of Table IV.

J	n_-	n_+	N_{CI}	E	ε	$\langle r_e\rangle$	$\langle r_p\rangle$	Γ_c
1	21	20	4620	−0.15378569	−0.02027718	7.74287	13.88608	1.4441[5]
2	41	40	17220	−0.16614255	−0.00792032	7.58513	12.48950	2.2339[5]
3	61	60	46220	−0.17033251	−0.00373035	7.71039	12.16854	2.2948[5]
4	81	80	86620	−0.17231600	−0.00174687	7.85240	12.16161	2.1849[5]
5	101	100	131220	−0.17341763	−0.00064523	7.98365	12.25289	2.0625[5]
6	121	120	179620	−0.17408661	0.00002375	8.10085	12.37548	1.9577[5]
7	141	140	228020	−0.17451658	0.00045371	8.20440	12.50450	1.8733[5]
8	161	160	276420	−0.17480552	0.00074266	8.29583	12.62983	1.8060[5]
9	181	180	324820	−0.17500636	0.00094349	8.37645	12.74713	1.7523[5]
10	201	200	373220	−0.17514972	0.00108685	8.44734	12.85449	1.7093[5]
				$J\to\infty$ extrapolations				
1-term Eq. (5)				−0.17538587	0.00132300	8.56412	13.03133	1.63839[5]
2-term Eq. (5)				−0.17549381	0.00143094	8.65082	13.17118	1.59424[5]
3-term Eq. (5)				−0.17554787	0.00148500	8.71500	13.27807	1.56638[5]
4-term Eq. (5)				−0.17557663	0.00151376	8.76225	13.35833	1.54841[5]

Ps(2p) cluster will also be confined by the $L=1$ centrifugal barrier.

2. The stochastic variational method

For the SVM, in the LiPs case, the first two electrons are placed in the $\ell_1=\ell_2=0$ orbits and their spins are coupled to zero, the next two electrons are in the $\ell_3=\ell_4=1$ orbits (with the total angular momentum coupled to 1) and their spins are coupled to 1. Finally, the positron is placed in an $\ell_0=1$ orbit and the total orbital angular momentum is coupled to 1.

The threshold for binding is the Li(2p) ($E=-7.410\,156\,5$ hartree [51]) plus the Ps(2p) energy. So the energy threshold for an absolute variational proof of binding is at −7.472 656 5 hartree. The energy and expectation values of the SVM LiPs wave functions are listed in Table II. The best variational energy was −7.472 871 hartree, equivalent to a binding energy of 2.15×10^{-4} hartree. The energy optimization was not fully completed and the binding energy of the CI calculation is probably more reliable. The primary purpose of the SVM calculation was to give an absolute proof that the unnatural parity state of LiPs was electronically stable.

D. NaPs

The calculations upon NaPs were very similar in scope and scale to those carried out upon LiPs. About the only difference was that an extra $\ell=1$ orbital was added to the electron basis.

The energies of the Na(3s) and Na(3p) states in the model potential were −0.188 854 91 and −0.111 562 87 hartree. The experimental binding energies are −0.188 858 and −0.111 547 hartree, respectively [52]. Electronic stability requires a total three-body energy of −0.174 062 87 hartree and the binding energy ε_J is defined as $\varepsilon_J=-(\langle E\rangle+0.174\,062\,87)$. The energy of the $^3P^e$ excited state of Na$^-$ is −0.113 425 29 hartree, i.e., the Na(3p) has an electron affinity of 0.002 262 hartree with respect to attaching an electron to the $^3P^e$ state. This is reasonably close to the original value of Norcross, 0.002 28 hartree [49].

Table V gives the energies and radial expectation values as a function of J while Fig. 5 shows the variation of ε_∞ as a function of J. Once again the three- and four-term extrapolations seem to be converging to a common energy. In this case the $J\to\infty$ correction increases the binding energy by about 40% from 10.87×10^{-4} hartree to 15.14×10^{-4} hartree. The binding energy of the NaPs unnatural parity state is about twice as large as that of PsH.

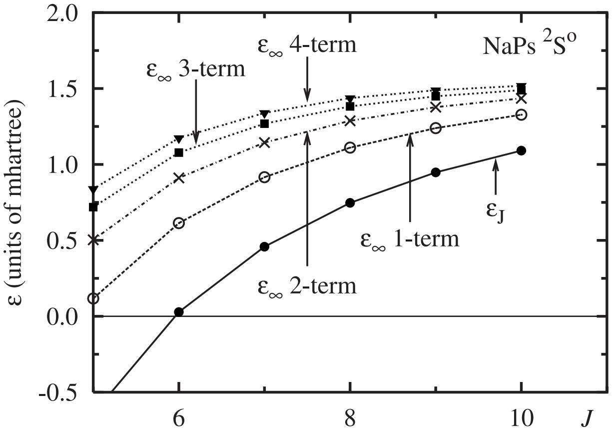

FIG. 5. The binding energy of the $^{2,4}S^o$ state of NaPs as a function of J. The directly calculated binding energy is shown as the solid line while the $J\to\infty$ limits using Eq. (5) with one, two, or three terms are shown as the dashed lines. The Na(3p)+Ps(2p) dissociation threshold is shown as the horizontal solid line.

TABLE VI. The energy of the $^{2,4}S^o$ states of KPs as a function of J. The threshold for binding is −0.162 682 65 hartree and the energies are given relative to that of the K$^+$ core. Other aspects of the table design are identical to those of Table V.

J	n_-	n_+	N_{CI}	E	ε	$\langle r_e \rangle$	$\langle r_p \rangle$	Γ_c
1	21	20	4620	−0.14168301	−0.02099965	8.49503	14.71924	3.4488[5]
2	41	40	17220	−0.15457885	−0.00810380	8.29108	13.13410	5.4508[5]
3	61	60	46220	−0.15914469	−0.00353796	8.39896	12.70578	5.7120[5]
4	81	80	86620	−0.16132591	−0.00135675	8.53370	12.64979	5.4824[5]
5	101	100	131220	−0.16253700	−0.00014566	8.66023	12.71399	5.1917[5]
6	121	120	179620	−0.16326995	0.00058729	8.77291	12.81839	4.9358[5]
7	141	140	228020	−0.16373804	0.00105538	8.87154	12.93315	4.7280[5]
8	161	160	276420	−0.16405038	0.00136772	8.95749	13.04566	4.5629[5]
9	181	180	324820	−0.16426580	0.00158314	9.03227	13.15085	4.4319[5]
10	201	200	373220	−0.16441830	0.00173564	9.09676	13.24589	4.3282[5]
				$J \to \infty$ extrapolations				
1-term Eq. (5)				−0.16466950	0.00198684	9.20300	13.40245	4.1575[5]
2-term Eq. (5)				−0.16478114	0.00209848	9.27933	13.52387	4.0541[5]
3-term Eq. (5)				−0.16483516	0.00215250	9.33339	13.61318	3.9924[5]
4-term Eq. (5)				−0.16486273	0.00218008	9.37076	13.67636	3.9562[5]

The annihilation rate with the core electrons was $\Gamma_{\mathrm{core}} \approx 1.5 \times 10^5\ \mathrm{s}^{-1}$ is small. Although this is three times larger than Γ_{core} for LiPs, in absolute terms the annihilation rate is still small.

E. KPs

The calculations upon KPs were very similar in scope and scale to those carried out upon LiPs. About the only difference was that an extra $\ell = 1$ orbital was added to the electron basis.

The energies of the K($4s$) and K($4p$) states in the model potential were −0.159 520 and −0.100 182 65 hartree. The experimental binding energies are −0.159 516 and −0.100 176 hartree, respectively [52]. Electronic stability requires a total three-body energy of −0.162 682 65 hartree and the binding energy ε_J is defined as $\varepsilon_J = -(\langle E \rangle + 0.162\,682\,65)$. The energy of the $^3P^e$ excited state of K$^-$ is −0.104 498 hartree, i.e., the K($4p$) has an electron affinity of 0.004 322 hartree with respect to attaching an electron to the $^3P^e$ state. This is close to the original value of Norcross, 0.004 37 hartree [49].

Table VI gives the energies and radial expectation values as a function of J while Fig. 6 shows the variation of ε_∞ as a function of J. The three and four term extrapolations seem to be converging to a common energy. In this case the $J \to \infty$ corrections increase the binding energy by about 20% from 17.36×10^{-4} hartree to 21.80×10^{-4} hartree. The KPs system has the largest binding energy of all the systems considered in this paper.

V. SUMMARY

A number of PsX systems (X=H, Li, Na, and K) are seen to have electronically stable $^{2,4}S^o$ complexes that are stable against autoionization, and in addition these states only decay slowly by positron annihilation. All the particles in these effectively four-body complexes are in a relative P state with respect to each other. The most unusual of the systems is LiPs since the $^{2,4}S^o$ states are of Borromean type. The sequence of calculations suggest that there would also exist unnatural parity $^{2,4}S^o$ complexes of RbPs and CsPs and, most likely, they would have binding energies larger than KPs.

Due to their low binding energies, these systems can be expected to have a structure composed of a Ps($2p$) cluster loosely bound to an atomic $X(np)$ excited state. This has been confirmed by the correlation functions for PsH which were computed using the SVM.

Although these complexes are electronically stable and decay very slowly by electron-positron annihilation there are other decay processes that act to shorten the lifetime. These

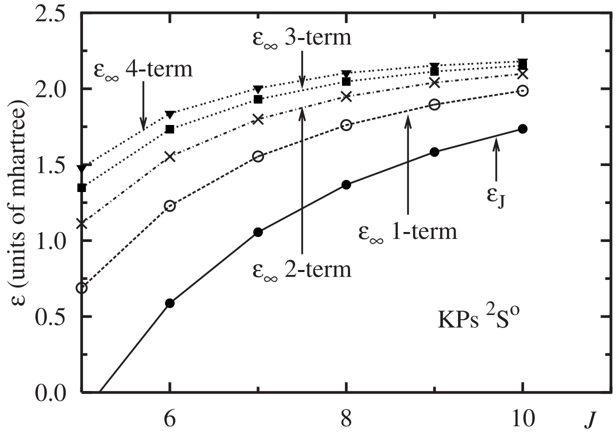

FIG. 6. The binding energy of the $^{2,4}S^o$ state of KPs as a function of J. The directly calculated binding energy is shown as the solid line while the $J \to \infty$ limits using Eq. (5) are shown as the dashed lines. The K($4p$)+Ps($2p$) dissociation threshold is at $\varepsilon = 0$.

complexes can emit a photon, decaying to a state of ${}^{2,4}P^e$ symmetry. For example, a Ps(np) fragment in the complex can emit a photon decaying to a Ps$(1s)$ type fragment. The Ps$(1s)$ fragment could then annihilate by the 2γ or 3γ process. In addition, the resulting ${}^{2,4}P^e$ state could also decay by autoionization. The lifetime of these states can be expected to be comparable to the lifetime of the fragments against single photon decay, e.g., $X(2p) \rightarrow X(1s)$. So the overall lifetimes of the states can be expected to be of order $10^{-8}-10^{-9}$ s.

It is unlikely that any of these complexes will be identified in the laboratory in the near future. The formation of positronic compounds is known to be notoriously difficult [53]. That these states are unnatural parity states compounds the difficulty since such states are not readily formed in normal collision systems. For example, the ${}^{3}P^e$ ion states [21–23,49] that could serve as suitable parents have never been identified in the laboratory.

Besides the PsH and APs systems, there are other related physical systems that could have unnatural parity bound states. For example, there is the possible existence of a new biexciton excited state [54]. While the Ps$^-$ ion might not have a stable ${}^{3}P^e$ state, it is known that the (M^+,e^-,e^-) ion is stable for $M^+/m_e < 0.4047$ and $M^+/m_e > 16.8$ [47,48]. It could be expected that a biexciton state, (e^-,e^-,h,h), with ${}^{1,3,5}S^o$ symmetry would be electronically stable when the mass ratios make the ${}^{3}P^e$ state of the charged exciton (e^-,e^-,h) stable. The system might also exhibit Borromean binding; there might be a bound biexciton state even though neither of the ${}^{3}P^e$ (e^-,e^-,h) or (e^-,h,h) states was stable.

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