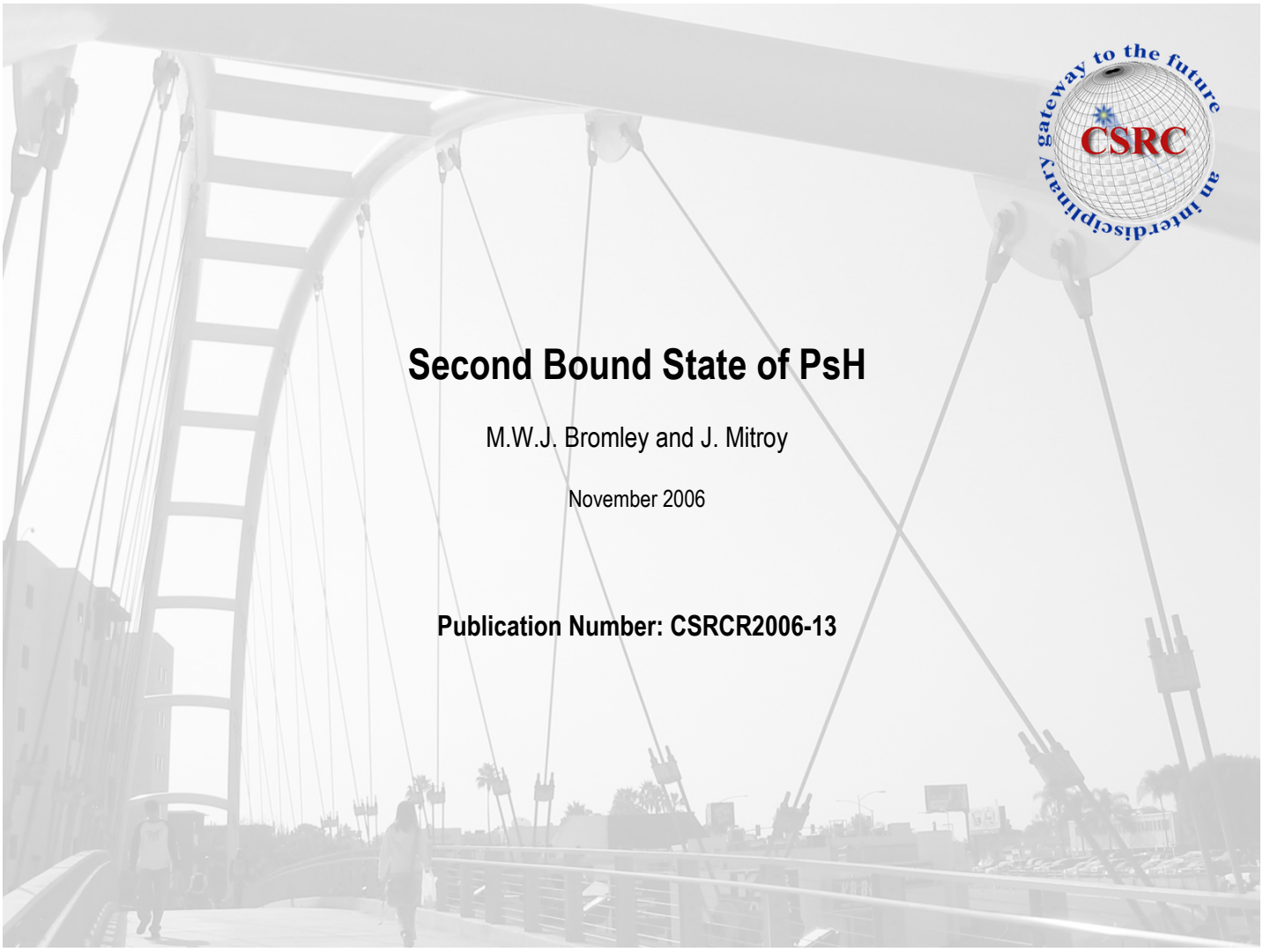

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Second bound state of PsH

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The existence of a second bound state of PsH that is electronically stable and also stable against positron annihilation by the normal 2γ and 3γ processes is demonstrated by explicit calculation. The state can be found in the ^{2,4}S$^{\rm o}$ symmetries with the two electrons in a spin triplet state. The binding energy against dissociation into the H($2p$) + Ps($2p$) channel was 6.06×10^{-4} Hartree. The dominant decay mode of the states will be radiative decay into a configuration that autoionizes or undergoes positron annihilation. The NaPs system of the same symmetry is also electronically stable with a binding energy of 1.553×10^{-3} Hartree with respect to the Na($3p$) + Ps($2p$) channel.

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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 [4–6], a compound that is best described as e^+PsH [7], and a (p^+, $4e^-$, $2e^+$) complex [7]. Additionally, a number of atoms have been identified as being capable of binding positronium and positrons [8–10]

A common feature of all these systems is that the positron annihilation process occurs by either a 2γ or 3γ process with rates of order 10^9 s^{-1} or 10^6 s^{-1} (for those systems for which an annihilation rate has been determined). In the present letter, we identify a new class of positronic compounds that are electronically stable, and in addition they have the unusual feature of decaying very slowly by 2γ or 3γ annihilation. Stable variants of PsH, and NaPs are identified and initial estimates of their binding energies are given. The existence of a new bound state of PsH is somewhat surprising given the amount of activity involved in identifying the resonant states of the Ps-H complex [11–13]. The new PsH and NaPs bound states are unnatural parity states with symmetry conditions that act to prevent positron annihilation and to also prevent decay into the the lowest energy dissociation products. These systems have the two electrons in a spin triplet state, a total orbital angular momentum of zero, and an odd parity, i.e. $L^\Pi = 0^-$. Positron annihilation by the 2γ or 3γ process is forbidden for such a state.

First consider the 2γ process (which occurs at a rate of 8×10^9 s^{-1} for the Ps ground state). For this process to occur, the annihilating electron-positron pair must be in a spin singlet state and the relative angular momentum must be zero. (The decay rate is not absolutely zero since the Ps($2p$) levels can undergo 2γ and 3γ annihilation at rate proportional to α^5 and α^6 respectively [14, 15]. The rates for the different Ps($2p$) levels have been calculated to be approximately 10^4 s^{-1} [14, 15].)

Now consider the electron-positron annihilation of a PsH state of ^{2}S$^{\rm o}$ symmetry. The relative angular momentum of the annihilating pair ($L_{\rm rel}$) must be zero. This means the total angular momentum of the state will come from the center-of-mass motion of the annihilating pair ($L_{\rm cm}$), and from the angular momentum of the spectator electron ($L_{\rm spectator}$). The total parity of the state is determined by the parity of the individual constituents, i.e. $\Pi = (-1)^{L_{\rm spectator}+L_{\rm cm}+L_{\rm rel}}$. It is simply not possible to form an odd parity state with a total angular momentum of zero if any one of the constituent angular momenta is zero. Consequently, a two electron/one positron state of ^{2}S$^{\rm o}$ 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 ^{2}S$^{\rm o}$ (or ^{4}S$^{\rm o}$) 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.

These L^Π conditions also act to prevent the dissociation of these four-body systems into combinations of the lower energy dissociation channels. Once again consider a ^{2}S$^{\rm o}$ state of PsH. Dissociation into Ps($1s$)+H($1s$) is forbidden since $\Pi = (-1)^L$ 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($2p$) (p-wave) with an energy of -0.1875 Hartree. Another possible decay would be into the H$^-$(2p^2 ^{3}P^e)+e^+ channel with a threshold energy of -0.125355 Hartree [16–18]. The stability of the H$^-$($2p^2$

^{3}P^e) bound state also suggests a mechanism for binding. One can think of the positron trapped into a $2p$ state of the H^- attractive potential well. 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 $H^-(2p^2\ ^3P^e)$ state is very diffuse, but this model does suggest that there is a large energy advantage associated with binding the positron to the negative ion.

All the calculations in the present paper were performed with a configuration interaction approach [19–21]. 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,

$$\max(\ell_0, \ell_1, \ell_2) \ \le \ J \ , \tag{1}$$

$$\min(\ell_1, \ell_2) \ \le \ L_{\rm int} \ , \tag{2}$$

$$(-1)^{(\ell_0+\ell_1+\ell_2)} \ = \ -1 \ . \tag{3}$$

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 [19–21]. The orbitals basis sets for the positron and electrons were identical.

TABLE I: The energy of the ^{2,4}S^o state of PsH as a function of J. 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 name) while N_{CI} gives the total number of configurations. The results of the $J \to \infty$ energy extrapolations at $J = 10$ are also given.

J	n	N_{CI}	$\langle E\rangle_J$
1	15	1800	−0.16755817
2	30	6975	−0.17938456
3	45	19125	−0.18327387
4	60	36000	−0.18510508
5	75	54675	−0.18612672
6	90	74925	−0.18675211
7	105	95175	−0.18715811
8	120	115425	−0.18743280
9	135	135675	−0.18762315
10	150	155925	−0.18775631
			$\langle E\rangle_\infty$
1-term eq.(4)			−0.18797567
2-term eq.(4)			−0.18806917
3-term eq.(4)			−0.18810659

The Hamiltonian was diagonalized in a basis constructed from a large number of single particle orbitals, including orbitals up to $\ell = 10$. There were 15 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 $L_{\rm int} = 3$ and gave a CI basis dimension of 155925. The parameter $L_{\rm int}$ does not have to be particularly large since it is mainly concerned with electron-electron correlations [20]. The resulting Hamiltonian matrix was diagonalized with the Davidson algorithm [22], and a total of 300 iterations were required for the largest calculation.

The energy of the PsH ^{2,4}S^o state as a function of J is given in Table I. The calculations only give an energy lower than the H($2p$) + Ps($2p$) threshold of -0.1875 Hartree for $J \ge 9$. A major technical problem afflicting CI calculations of positron-atom interactions is the slow convergence of the energy with J [10, 21]. 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 written as an inverse power series [21, 23–26], viz

$$\Delta E_J \approx \frac{A_E}{(J+\frac{1}{2})^6} + \frac{B_E}{(J+\frac{1}{2})^7} + \frac{C_E}{(J+\frac{1}{2})^8} + \dots \ . \tag{4}$$

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 [27].

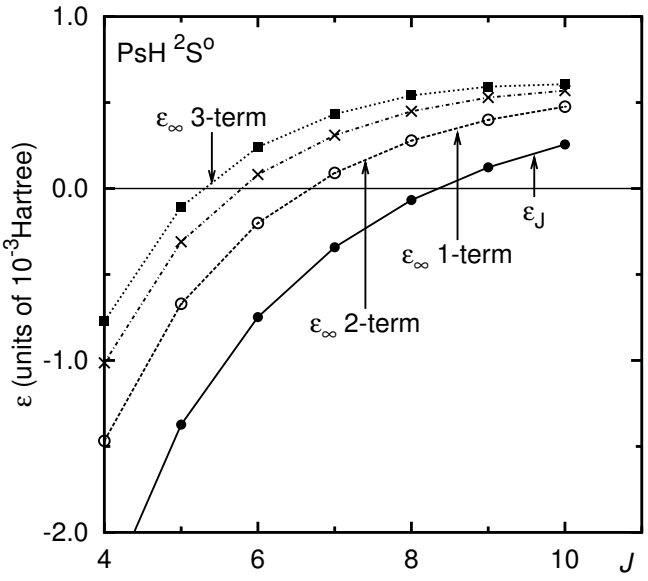

FIG. 1: The binding energy, $\varepsilon = -(\langle E\rangle + 0.1875)$, of the ^{2,4}S^e state of PsH as a function of J. The directly calculated energy is shown as the solid line while the $J \to \infty$ limits using eq. (4) with 1, 2 or 3 terms are shown as the dashed lines. The H($2p$) + Ps($2p$) dissociation threshold is shown as the horizontal solid line.

The $J \to \infty$ limit, has been determined by fitting sets of $\langle E\rangle_J$ values to asymptotic series with either 1, 2 or

3 terms. The coefficients, A_E, B_E and C_E for the 3-term expansion are determined at a particular J from 4 successive energies ($\langle E\rangle_{J-3}$, $\langle E\rangle_{J-2}$, $\langle E\rangle_{J-1}$ 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 asymptotic series analysis to helium has resulted in CI calculations reproducing the ground state energy to an accuracy of $\approx 10^{-8}$ Hartree [26, 28].

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 while the energy of the three-term extrapolation is close to stabilized at $J = 10$. The impact of the extrapolations is significant since they more than double the binding energy. The most precise estimate of the binding energy is the three-term extrapolation at $J = 10$, namely 6.06×10^{-4} Hartree (this is computed using the $\langle E\rangle_\infty$ in Table I).

TABLE II: The energy of the ^{2,4}S^o state of NaPs as a function of J. The threshold for binding is -0.17410932 Hartree. The column n_- gives the total number of occupied electron orbitals, n_+ gives the number of positron orbitals, while N_{CI} gives the total number of configurations. The results of the $J \to \infty$ energy extrapolations at $J = 10$ are also given.

J	n_-	n_+	N_{CI}	$\langle E\rangle_J$	ε_J
1	16	15	2040	−0.153740547	−0.02031794
2	31	30	7440	−0.166301513	−0.00775597
3	46	45	19815	−0.170503790	−0.00355470
4	61	60	36915	−0.172480804	−0.00157768
5	76	75	55815	−0.173572387	−0.00048610
6	91	90	76290	−0.174230717	0.00017223
7	106	105	96765	−0.174650110	0.00059162
8	121	120	117240	−0.174928718	0.00087023
9	136	135	137715	−0.175119526	0.00106104
10	151	150	158190	−0.175253262	0.00119477
				$\langle E\rangle_\infty$	ε_∞
1-term eq.(4)				−0.17547356	0.00141507
2-term eq.(4)				−0.17556808	0.00150960
3-term eq.(4)				−0.17561102	0.00155252

Having the established the stability of the ^{2,4}S^o state of PsH, it is natural to ask whether other systems with this symmetry are stable. The obvious candidates are the alkali atoms, since some of them have np^2 ^{3}P^e negative ion bound states [29] that can act as a parent state to bind the positron. The treatment of such systems requires the use of a frozen core approximation. The details of this approximation have been discussed in great detail elsewhere [19–21], 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 semi-empirical 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 [20, 30].

The system that was investigated was the ^{2,4}S^o state of NaPs. The energies of the $3s$ and $3p$ states in the model potential were -0.18885491 and -0.11156294 Hartree. The experimental binding energies are -0.188858 and -0.111547 Hartree respectively [31]. Electronic stability requires a total 3-body energy of -0.17405849 Hartree. The energy of the ^{3}P^e excited state of Na^- is -0.11342529 Hartree, i.e the Na($3p$) has an electron affinity of 0.001862 Hartree with respect to attaching an electron to the ^{3}P^e state. This is reasonably close to the original value of Norcross, 0.00228 Hartree [29].

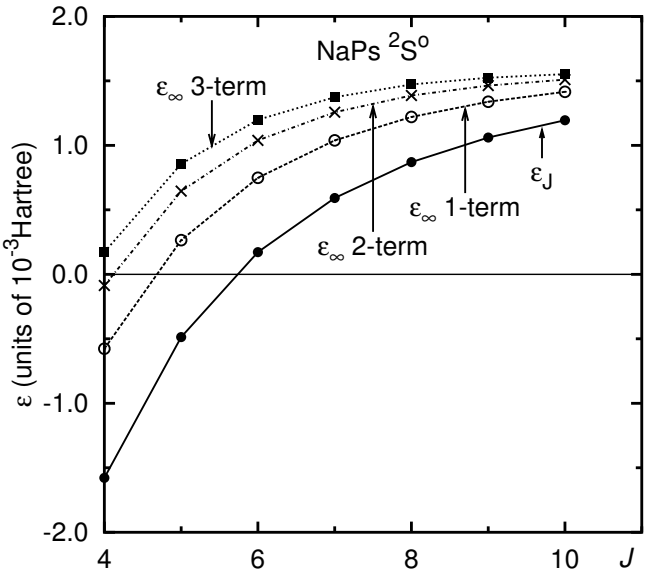

FIG. 2: The binding energy (in units of Hartree) of the ^{2,4}S^o state of NaPs as a function of J. The directly calculated binding energy is shown as the solid line while the $J \to \infty$ limits using eq. (4) with 1, 2 or 3 terms are shown as the dashed lines. The Na($3p$) + Ps($2p$) dissociation threshold is shown as the horizontal solid line. lines.

The calculations upon NaPs were very similar in scope and scale to those carried out upon PsH. About the only difference was that an extra $\ell = 1$ orbital was added to the electron basis. Table II gives the 3-body energy (relative to the Na^+ core) as a function of J. The binding energy ε_J is defined as $\varepsilon_J = -(\langle E\rangle + 0.17410932)$. The positron complex is more tightly bound than for PsH and becomes electronically stable when $J \geq 5$.

Figure 2 shows the variation of ε_∞ as a function of J. Once again the two and three term extrapolations seem to be converging to a common energy which is some-

what larger than the best explicit calculation. The 3-term value of ε_∞ determined at $J = 10$ was 0.001553 Hartree. This is probably the the best estimate of the binding energy of the complex. The positron can annihilate with the core electrons via the 2γ process since the symmetry considerations are irrelevant here. However, the annihilate rate of $\Gamma_{\rm core} = 1.66 \times 10^6$ s^{-1} is small because the positron cannot occupy a $\ell = 0$ orbital.

The PsH and NaPs ^{2,4}S$^{\rm o}$ complexes are stable against auto-ionizaton, and only decay slowly by positron annihilation. However there are other possible decay modes. Both these complexes can emit a photon, decaying to a state of ^{2,4}P$^{\rm e}$ 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, a ^{2,4}P$^{\rm e}$ state could also decay by auto-ionization. Due to their low binding energies, these systems can be expected to have a structure composed of an Ps($2p$) cluster loosely bound to an atomic X(np) excited state. The lifetime of these states can be expected to be comparable to the lifetime of the fragments against single photon decay, e.g. H($2p$) $\rightarrow$ H($1s$). So the overall lifetimes of the states can be expected to be of order 10^{-8} - 10^{-9} seconds.

It is possible that there are other positronic complexes of ^{2,4}S$^{\rm o}$ symmetry that are bound. The K^-, Rb^- and Cs^- ions have all been predicted to have np^2 ^{3}P$^{\rm e}$ bound states. So the existence of a stable ^{2,4}S$^{\rm o}$ positronic complex would seem to be highly likely. It would also be interesting to examine Li as this does not appear to have a bound ^{3}P$^{\rm e}$ negative ion [29].

Besides the alkali atoms, another physical system possibly admitting an unnatural parity bound state would be the di-positronium molecule. There have been two attempts to find such a bound state, they were unsuccessful or inconclusive [32, 33]. However, the investigation of Bao and Shi showed that a ^{1}S$^{\rm o}$ state was very close to being bound, even if it was not bound [33]. This raises the tantalizing possibility that a more exhaustive calculation might reveal the existence of a Ps_2 state that decayed very slowly by positron annihilation. Besides the Ps_2 molecule itself, there is the possible existence of a new biexciton excited state [34]. The parent Ps^- ^{3}P$^{\rm e}$ ion is known to be stable for certain m_{e^+}/m_{e^-} mass ratios [35, 36]. In circumstances where the mass ratios make the ^{3}P$^{\rm e}$ state of the charged exciton (e^-,e^-,h) state stable, it could be expected that a biexciton state of ^{1,3,5}S$^{\rm o}$ symmetry would be electronically stable.

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