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 $^{2,4}S^o$ symmetries with the two electrons in a spin-triplet state. The binding energy against dissociation into the H($2p$) + Ps($2p$) channel was 7.03×10^{-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 1.514×10^{-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 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 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 rates 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 $^2S^o$ 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 ($L_{\rm c.m.}$), 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., $\Pi = (-1)^{L_{\rm spectator}+L_{\rm c.m.}+L_{\rm rel}}$. It is 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 $^2S^o$ 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.

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 $^2S^o$ 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 $H^-(2p^2\,{}^3P^e)$ + e^+ chan-

nel with a threshold energy of $-0.125\,355$ hartree [16,17]. The stability of the $H^-(2p^2\,^3P^e)$ 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 indicates a large energy advantage associated with binding the positron to the negative ion.

The present calculations were performed with the configuration interaction (CI) approach [18–20] with a nonrelativistic Hamiltonian and assuming an infinitely massive nucleus. 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,

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

$$\min(\ell_1, \ell_2) \leq L_{\text{int}}, \tag{2}$$

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

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 [18–20]. The orbital basis sets for the positron and electrons were identical.

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 [19]. The resulting Hamiltonian matrix was diagonalized with the Davidson algorithm [21], 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 $J \geq 9$. A major technical problem afflicting CI calculations of positron-atom interactions is the slow convergence of the energy with J [10,20]. 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 [20,22–25], viz.

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 and the binding energy is $\varepsilon = -(\langle E\rangle + 0.1875)$. 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 results of the $J \to \infty$ energy extrapolations at $J = 10$ are also given.

J	n	N_{CI}	$\langle E\rangle_J$	$\langle\varepsilon\rangle_J$
1	20	4200	−0.167 558 18	−0.019 941 82
2	40	16 400	−0.179 384 58	−0.008 115 42
3	60	45 000	−0.183 273 91	−0.004 226 09
4	80	85 000	−0.185 105 16	−0.002 394 84
5	100	129 200	−0.186 126 84	−0.001 373 16
6	120	177 200	−0.186 752 37	−0.000 747 63
7	140	225 200	−0.187 158 97	−0.000 341 03
8	160	273 200	−0.187 435 69	−0.000 064 31
9	180	321 200	−0.187 630 74	0.000 130 74
10	200	369 200	−0.187 771 74	0.000 271 74
			$\langle E\rangle_\infty$	$\langle\varepsilon\rangle_\infty$
1-term Eq. (4)			−0.188 004 01	0.000 504 01
2-term Eq. (4)			−0.188 114 61	0.000 614 61
3-term Eq. (4)			−0.188 171 96	0.000 671 96
4-term Eq. (4)			−0.188 202 78	0.000 702 78

$$\Delta E_J \approx \frac{A_E}{(J+\frac{1}{2})^6} + \frac{B_E}{(J+\frac{1}{2})^7} + \frac{C_E}{(J+\frac{1}{2})^8} + \frac{D_E}{(J+\frac{1}{2})^9} \cdots. \tag{4}$$

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 [26].

The $J \to \infty$ limit has been determined by fitting sets of $\langle E\rangle_J$ values to asymptotic series with either 1, 2, 3, or 4 terms. The coefficients, A_E, B_E, C_E, and D_E for the four-term expansion are determined at a particular J from 5 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 asymptotic series analysis to helium has resulted in CI calculations reproducing the ground state energy to an accuracy of $\approx 10^{-8}$ hartree [24,25].

Figure 1 shows the estimates of $\langle E\rangle_\infty$ as a function of J. A quick visual examination suggests that the three-term and four-term extrapolations are converging to a common energy 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 listed in Table I), 7.03×10^{-4} hartree, is from the four-term extrapolation at $J = 10$.

Having 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 $np^2\,^3P^e$ negative ion bound states [27] that can act as a parent state to bind the

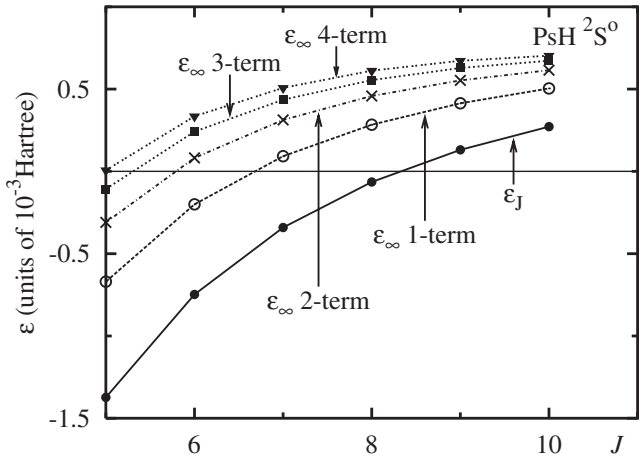

FIG. 1. The binding energy, $\varepsilon = -(\langle E\rangle + 0.1875)$, of the $^{2,4}S^o$ state of PsH as a function of J. The directly calculated energy is shown as the solid line while the $J \to \infty$ limits using Eq. (4) with 1, 2, 3, or 4 terms are shown as the dashed lines. The H($2p$) + Ps($2p$)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

positron. The treatment of such systems requires the use of a frozen core approximation. The details of this approximation have been discussed in detail elsewhere [18–20], 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 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 [19,28].

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 $-0.188\,854\,91$ and $-0.111\,562\,87$ hartree. The experimental binding energies are $-0.188\,858$ and $-0.111\,547$ hartree, respectively [29]. Electronic stability requires a total three-body energy of $-0.174\,062\,87$ hartree. The energy of the $^3P^e$ excited state of Na^- is -0.11382 hartree; i.e., the Na($3p$) has an electron affinity of 0.00226 hartree with respect to attaching an electron to the $^3P^e$ state. This is reasonably close to the original value of Norcross, 0.00228 hartree [27].

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 three-body energy (relative to the Na^+ core) as a function of J. The binding energy ε_J is defined as $\varepsilon_J = -(\langle E\rangle + 0.174\,062\,87)$. The positron complex is more tightly bound than for PsH and becomes electronically stable when $J > 5$.

Figure 2 shows the variation of ε_∞ as a function of J. Once again the three- and four-term extrapolations seem to

TABLE II. The energy of the $^{2,4}S^o$ state of NaPs as a function of J. The threshold for binding is $-0.174\,062\,87$ hartree. The column n_- gives the total number of occupied electron orbitals, n_+ gives the number of positron orbitals, while $N_{\rm CI}$ gives the total number of configurations. The results of the $J \to \infty$ energy extrapolations at $J = 10$ are also given.

J	n_-	n_+	$N_{\rm CI}$	$\langle E\rangle_J$	ε_J
1	21	20	4620	−0.153 785 69	−0.020 277 18
2	41	40	17 220	−0.166 142 55	−0.007 920 32
3	61	60	46 220	−0.170 332 51	−0.003 730 35
4	81	80	86 620	−0.172 316 00	−0.001 746 87
5	101	100	131 220	−0.173 417 63	−0.000 645 23
6	121	120	179 620	−0.174 086 61	0.000 023 75
7	141	140	228 020	−0.174 516 58	0.000 453 71
8	161	160	276 420	−0.174 805 52	0.000 742 66
9	181	180	324 820	−0.175 006 36	0.000 943 49
10	201	200	373 200	−0.175 149 72	0.001 086 85
				$\langle E\rangle_\infty$	ε_∞
1-term Eq. (4)				−0.175 385 87	0.001 323 00
2-term Eq. (4)				−0.175 493 81	0.001 430 94
3-term Eq. (4)				−0.175 547 87	0.001 485 00
3-term Eq. (4)				−0.175 576 63	0.001 513 76

be converging to a common energy which is somewhat larger than the best explicit calculation. The four-term value of ε_∞ determined at $J = 10$ was 0.001514 hartree. This is probably 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 annihilation rate of $\Gamma_{\rm core} \approx 1.5 \times 10^5\ {\rm s}^{-1}$ is small because the positron cannot occupy a $\ell = 0$ orbital.

The PsH and NaPs $^{2,4}S^o$ complexes are stable against autoionization, and only decay slowly by positron annihi-

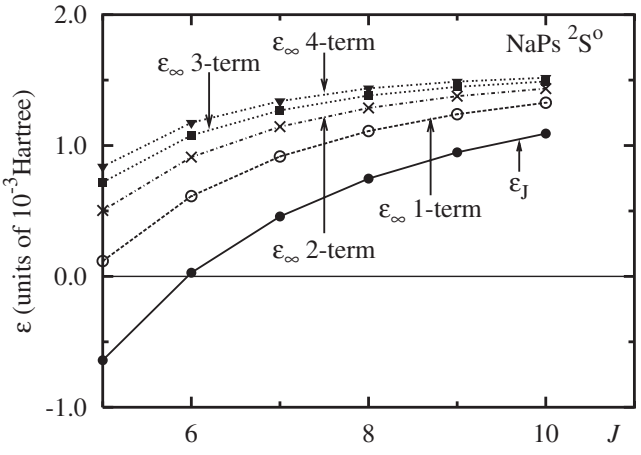

FIG. 2. The binding energy (in units of hartree) of the $^{2,4}S^o$ state of NaPs as a function of J. The directly calculated binding energy is shown as the solid line while the $J \to \infty$ limits using Eq. (4) are shown as the dashed lines. The Na($3p$) + Ps($2p$) threshold is shown as the horizontal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

lation. However, there are other possible decay modes. Both these 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, a $^{2,4}P^e$ state could also decay by autoionization. Because of 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 $^{2,4}S^o$ symmetry that are bound. The K^-, Rb^-, and Cs^- ions have all been predicted to have $np^2\,^3P^e$ bound states [27]. So the existence of a stable $^{2,4}S^o$ positronic complex would seem to be highly likely.

It is unlikely that any of these complexes will be isolated in the laboratory in near future. The formation of positronic compounds is known to be notoriously difficult [30]. Further, the $^3P^e$ ion states [16,17,27,31] that could serve as suitable parents have never been identified in the laboratory.

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 $^1S^o$ 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 $Ps^-\,^3P^e$ ion is known to be stable for certain m_{e^+}/m_{e^-} mass ratios [35,36]. In circumstances where the mass ratios make the $^3P^e$ state of the charged exciton, (e^-, e^-, h), stable, it could be expected that a biexciton state of $^{1,3,5}S^o$ symmetry would be electronically stable.

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[1] J. A. Wheeler, Ann. N.Y. Acad. Sci. **48**, 219 (1946).
[2] E. A. Hylleraas and A. Ore, Phys. Rev. **71**, 493 (1947).
[3] A. Ore, Phys. Rev. **83**, 665 (1951).
[4] D. B. Kinghorn and R. D. Poshusta, Phys. Rev. A **47**, 3671 (1993).
[5] K. Varga, J. Usukura, and Y. Suzuki, Phys. Rev. Lett. **80**, 1876 (1998).
[6] J. Usukura and Y. Suzuki, Nucl. Instrum. Methods Phys. Res., Sect. B **171**, 67 (2000).
[7] K. Varga, Phys. Rev. Lett. **83**, 5471 (1999).
[8] G. G. Ryzhikh and J. Mitroy, J. Phys. B **30**, 5545 (1997).
[9] K. Strasburger and H. Chojnacki, J. Chem. Phys. **108**, 3218 (1998).
[10] J. Mitroy, M. W. J. Bromley, and G. G. Ryzhikh, J. Phys. B **35**, R81 (2002).
[11] R. J. Drachman, Phys. Rev. A **19**, 1900 (1979).
[12] J. Di Rienzi and R. J. Drachman, Phys. Rev. A **66**, 054702 (2002).
[13] Z. C. Yan and Y. K. Ho, J. Phys. B **36**, 4417 (2003).
[14] A. I. Alekseev, Zh. Eksp. Teor. Fiz. **34**, 1195 (1958) [Sov. Phys. JETP **7**, 826 (1958)].
[15] A. I. Alekseev, Zh. Eksp. Teor. Fiz. **36**, 1839 (1959) [Sov. Phys. JETP **9**, 1312 (1959)].
[16] G. W. F. Drake, Phys. Rev. Lett. **24**, 126 (1970).
[17] M. Bylicki and E. Bednarz, Phys. Rev. A **67**, 022503 (2003).
[18] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **65**, 012505 (2001).
[19] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **65**, 062505 (2002).
[20] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **73**, 052712 (2006).
[21] A. Stathopolous and C. Froese Fischer, Comput. Phys. Commun. **79**, 268 (1994).
[22] C. Schwartz, Phys. Rev. **126**, 1015 (1962).
[23] R. N. Hill, J. Chem. Phys. **83**, 1173 (1985).
[24] M. W. J. Bromley and J. Mitroy, Int. J. Quantum Chem. **107**, 1150 (2007).
[25] S. Salomonson and P. Oster, Phys. Rev. A **40**, 5559 (1989).
[26] W. Kutzelnigg and J. D. Morgan III, J. Chem. Phys. **96**, 4484 (1992).
[27] D. W. Norcross, Phys. Rev. Lett. **32**, 192 (1974).
[28] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **68**, 052714 (2003).
[29] NIST Atomic Spectra Database Version 3.0 (2005), http://physics.nist.gov/cgi-bin/AtData/main_asd.
[30] M. Charlton and J. W. Humberston, *Positron Physics* (Cambridge University Press, Cambridge, England, 2001).
[31] E. Holoien, Phys. Norv. **1**, 53 (1961).
[32] Y. Suzuki and J. Usukura, Nucl. Instrum. Methods Phys. Res., Sect. B **171**, 67 (2000).
[33] C. G. Bao and T. Y. Shi, Phys. Rev. A **67**, 042505 (2003).
[34] J. Usukura, Y. Suzuki, and K. Varga, Phys. Rev. B **59**, 5652 (1999).
[35] A. P. Mills, Jr., Phys. Rev. A **24**, 3242 (1981).
[36] A. K. Bhatia and R. J. Drachman, Phys. Rev. A **28**, 2523 (1983).