Energy and expectation values of the PsH system

J. Mitroy
Faculty of Technology, Charles Darwin University, Darwin NT 0909, Australia
(Received 20 December 2005; published 5 May 2006)

Close to converged energies and expectation values for PsH are computed using a ground state wave function consisting of 1800 explicitly correlated gaussians. The best estimate of the $Ps^{\infty}H$ energy was −0.789 196 740 hartree which is the lowest variational energy to date. The 2γ annihilation rate for $Ps^{\infty}H$ was $2.471\,78\times10^{9}$ s^{-1}.

DOI: 10.1103/PhysRevA.73.054502 PACS number(s): 36.10.Dr, 31.15.Ar

The calculation of positronium hydride (PsH) represents one of the simplest possibilities for studying mixed electronic and positronic systems. Since its stability was first identified in 1951 by Ore [1], a variety of methods have been applied to determine its structure. These include variational calculations with Hylleraas type basis sets [2–5], variational calculations with explicitly correlated gaussians (ECGs) [6–9], quantum Monte Carlo methods [10–14], and most recently the configuration interaction method [15–18]. The lowest variational energy for $Ps^{\infty}H$ prior to the present paper was that of Yan and Ho [4]. Their largest calculation gave an energy of −0.789 196 705 1 hartree. Bubin and Adamowicz used a 3200 dimension ECG basis to give an energy of −0.788 870 707 hartree for $Ps^{1}H$ [19].

In this work, the stochastic variational method (SVM) is used to construct a wave function with a lower energy than the best wave function of Yan and Ho. Indeed, the best SVM energy of −0.789 196 740 hartree is even lower than the value estimated by Yan and Ho as the variational limit [e.g., −0.789 196 714 7(42) hartree].

The SVM used for this work has been described in a number of articles [20–22] and only the briefest description is given here. The SVM expands the wave function in a linear combination of ECGs. Such basis functions have Hamiltonian matrix elements that can be computed very quickly and the energy is optimized by performing a trial and error search over the exponential parameters that define the basis. The SVM has been used to solve a number of many-body problems in different areas of physics [20,22].

For the present set of calculations a basis containing 1800 ECGs was used for the final calculation. All the optimizations of the ECG basis were done with the H mass set to ∞. The annihilation rates given in Tables I and II are proportional to the probability of finding an electron and a positron at the same position in a spin singlet state according to

$$\Gamma = 4\pi r_e^2 c\langle\Psi|\sum_i O_{ip}^S \delta(\mathbf{r}_i-\mathbf{r}_p)|\Psi\rangle \tag{1}$$

$$=1.009\,394\times10^{11}\sum_i \langle\delta(\mathbf{r}_i-\mathbf{r}_p)\rangle_S, \tag{2}$$

[7,23,24]. 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 ip electron-positron pair.

Table I lists a number of expectation values obtained from a sequence of increasingly larger calculations. The net energy improvement when the basis was increased from 900 to 1800 ECGS, while being subjected to additional optimization, was 1.98×10^{-7} hartree. It is worth noting that the energy of the largest calculation, namely, −0.789 196 740 hartree, is lower than the previous best energy of Yan and Ho [4], namely, −0.789 196 705 1 hartree. Yan and Ho examined the convergence pattern associated with their sequence of

TABLE I. Behavior of some PsH expectation values for a sequence of ECG type variational calculations of increasing size. All quantities are given in atomic units with the exception of the 2γ annihilation rates which are in units of 10^9 s^{-1}. Some of the data for the earlier calculation [7] have not been published before, the data attributed to these calculations were computed using the same ECG basis.

N	$\langle r_{H^+e^+}\rangle$	$\langle r^2_{H^+e^-}\rangle$	$\langle 1/r_{e^-e^-}\rangle$	$\langle r_{e^+e^-}\rangle$	$\langle\delta(e^--e^-)\rangle$	$\langle\delta(H^+-e^+)\rangle$	Γ	$\langle V\rangle/\langle T\rangle+2$	E
750[a]	3.661596	7.812895	0.3705556	3.480249	4.39845×10^{-3}	1.63863×10^{-3}	2.46852	5.51×10^{-7}	−0.789195993
900	3.661613	7.812961	0.3705554	3.480263	4.39321×10^{-3}	1.63635×10^{-3}	2.46879	7.96×10^{-7}	−0.789196542
1200	3.661621	7.813024	0.3705550	3.480270	4.38188×10^{-3}	1.63153×10^{-3}	2.47129	2.21×10^{-7}	−0.789196673
1500	3.661624	7.813040	0.3705549	3.480271	4.37628×10^{-3}	1.62850×10^{-3}	2.47134	1.30×10^{-7}	−0.789196718
1800	3.661624	7.813046	0.3705549	3.480272	4.37639×10^{-3}	1.62828×10^{-3}	2.47178	7.3×10^{-8}	−0.789196740
Hylleraas $N=5741$[b]							2.47258		−0.789196705
Hylleraas $N\to\infty$ extrapolation[b]							2.47264(2)		−0.789196715(5)

[a]Reference [7].
[b]References [4,5].

 ©2006 The American Physical Society

TABLE II. Properties of the PsH ground state. Data are given for H assuming infinite mass. All quantities are given in atomic units with the exception of the annihilation rates which are in units of 10^9 s^{-1}. The positron and electron kinetic energy operators are written as T_+ and T_-.

Property	Present SVM	SVM [9]
N	1800	1600
$\langle V\rangle/\langle T\rangle+2$	7.3×10^{-8}	6×10^{-7}
E	−0.789196740	−0.789165554
$\langle T_-\rangle$	0.3261733	0.3261732
$\langle T_+\rangle$	0.1368503	0.1368501
$\langle r_{H^+e^-}\rangle$	2.311526	2.311525
$\langle r_{H^+e^+}\rangle$	3.661624	3.661622
$\langle r_{e^-e^-}\rangle$	3.574787	3.574783
$\langle r_{e^+e^-}\rangle$	3.480272	3.480271
$\langle 1/r_{H^+e^-}\rangle$	0.7297090	0.7297087
$\langle 1/r_{H^+e^+}\rangle$	0.3474618	0.3474618
$\langle 1/r_{e^-e^-}\rangle$	0.3705549	0.3705549
$\langle 1/r_{e^+e^-}\rangle$	0.4184961	0.4184960
$\langle r^2_{H^+e^-}\rangle$	7.813046	7.813015
$\langle r^2_{H^+e^+}\rangle$	16.25453	16.25448
$\langle r^2_{e^-e^-}\rangle$	15.87546	15.87538
$\langle r^2_{e^+e^-}\rangle$	15.58427	15.58423
$\langle 1/r^2_{H^+e^-}\rangle$	1.207067	1.207063
$\langle 1/r^2_{H^+e^+}\rangle$	0.1721631	0.1721637
$\langle 1/r^2_{e^-e^-}\rangle$	0.2139099	0.2139106
$\langle 1/r^2_{e^-e^+}\rangle$	0.3491440	0.3491428
$\langle\delta(H^+-e^-)\rangle$	0.177279	0.177186
$\langle\delta(H^+-e^+)\rangle$	1.62828×10^{-3}	1.63857×10^{-3}
$\langle\delta(e^--e^-)\rangle$	4.37639×10^{-2}	4.3867×10^{-3}
$\langle\delta(e^+-e^-)\rangle$	0.0244877	0.024461
Γ	2.47178	2.46909

increasingly larger calculations and estimated that the true energy was actually $9.6(4.2)\times10^{-9}$ hartree lower (e.g., −0.789 196 714 7(42) hartree). The present calculation indicates that the actual correction should have been more than three times as large as that estimated by Yan and Ho. Although the sign of size of energy correction is not large, it is apparent that the procedure used to determine the energy correction is faulty. In Hylleraas calculations one typically does some sort of nonlinear optimization to choose the exponential parameters that give the minimum energy. This has the unintended byproduct of distorting the convergence pattern of the energy and thus introducing large uncertainties in the extrapolation of the energy [25].

The coalescence matrix elements, $\langle\delta(e^--e^-)\rangle$ and $\langle\delta(H^+-e^+)\rangle$ were more sensitive to the increase in basis size than any other quantity. This sensitivity is due to the fact that the wave function amplitude between two repelling particles is expected to be small at their coalescence point and the ECG functional form is not the natural choice to describe the behavior of the relative wave function for two strongly repelling particles. With respect to the more physically interesting observables, the annihilation rate, Γ varied most as the basis dimension was increased. But, the increase in Γ was just larger than 0.1% when the basis was increased from 900 to 1800.

A comprehensive set of the best set of expectation values are listed in Table II. They are compared with the results of another, but completely independent, large basis SVM calculation [9]. The expectation value for the virial theorem $\langle V\rangle/\langle T\rangle$ provides an estimate of the wave function accuracy and the deviation of $\langle V\rangle/\langle T\rangle$ from −2 was only 7.3×10^{-8} hartree.

The energies of the different mass variants of PsH were computed by rediagonalizing the Hamiltonian with the same basis but with $m_{^1\mathrm{H}}$ set to $1836.1527m_e$, $m_{^2\mathrm{H}}$ set to $3670.483m_e$, and $m_{^3\mathrm{H}}$ set to $5496.899m_e$. The energies of Ps^1H, Ps^2H and Ps^3H were −0.788 870 618, −0.789 033 556 and −0.789 087 767 hartree respectively. The energy of the 3200 ECG wave function of Bubin and Adamowicz [19] for Ps^1H was −0.788 870 707 hartree, which is 1.0×10^{-7} hartree below the present energy.

To summarize, a close to converged binding energy is reported for the $Ps^\infty H$ ground state. The present energy is 2.5×10^{-8} hartree lower than the estimated variational limit of Yan and Ho. The procedure by Yan and Ho to estimate the variational limit probably tends to underestimate the size of the necessary energy correction.

Although the present energy is better than that of Yan and Ho, this does not necessarily mean that the present SVM annihilation rate is more accurate. Any basis of ECGs (which cannot satisfy the exact interparticle cusp conditions) will have a tendency to underestimate the electron-positron coalescence matrix element. Table I shows a consistent increase in Γ as the size of the calculation in increased.

This work was supported by a research grant from the Australian Research Council. The authors would like to thank S. Caple for access to additional computer facilities.

[1] A. Ore, Phys. Rev. **83**, 665 (1951).
[2] C. F. Lebeda and D. M. Schrader, Phys. Rev. **178**, 24 (1969).
[3] Y. K. Ho, Phys. Rev. A **34**, 609 (1986).
[4] Z. C. Yan and Y. K. Ho, Phys. Rev. A **59**, 2697 (1999a).
[5] Z. C. Yan and Y. K. Ho, Phys. Rev. A **60**, 5098 (1999b).
[6] K. Strasburger and H. Chojnacki, J. Chem. Phys. **108**, 3218 (1998).
[7] G. G. Ryzhikh and J. Mitroy, J. Phys. B **32**, 4051 (1999).
[8] A. M. Frolov and V. H. Smith, Jr., Phys. Rev. A **56**, 2417 (1997).

[9] J. Usukura, K. Varga, and Y. Suzuki, Phys. Rev. A **58**, 1918 (1998).
[10] D. Bressanini, M. Mella, and G. Morosi, J. Chem. Phys. **108**, 4756 (1998).
[11] D. Bressanini, M. Mella, and G. Morosi, Phys. Rev. A **57**, 1678 (1998).
[12] N. Jiang and D. M. Schrader, J. Chem. Phys. **109**, 9430 (1998).
[13] T. Yoshida and G. Miyako, Phys. Rev. A **54**, 4571 (1996).
[14] S. Chiesa, M. Mella, and G. Morosi, Phys. Rev. A **69**, 022701 (2004).
[15] J. Mitroy, M. W. J. Bromley, and G. G. Ryzhikh, *Positronic Atoms* (Kluwer Academic, The Netherlands, 2001), p. 199, in [26].
[16] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **65**, 012505 (2002).
[17] S. L. Saito, J. Chem. Phys. **118**, 1714 (2003).
[18] M. W. J. Bromley, J. Mitroy, and G. G. Ryzhikh, Nucl. Instrum. Methods Phys. Res. B **171**, 47 (2000).
[19] S. Bubin and L. Adamowicz, J. Chem. Phys. **120**, 6051 (2004).
[20] G. G. Ryzhikh, J. Mitroy, and K. Varga, J. Phys. B **31**, 3965 (1998).
[21] K. Varga and Y. Suzuki, Comput. Phys. Commun. **106**, 157 (1997).
[22] Y. Suzuki and K. Varga, *Approach to Quantum-Mechanical Few-Body Problems*, 172 (Springer, New York, 1998).
[23] C. Lee, Sov. Phys. JETP **6**, 281 (1958); [Sov. Phys. JETP **33**, 365 (1957)].
[24] S. M. Neamtan, G. Darewych, and G. Oczkowski, Phys. Rev. **126**, 193 (1962).
[25] J. Mitroy and M. W. J. Bromley (unpublished).
[26] C. M. Surko and F. A. Gianturco, eds., *New Directions in Antimatter Physics and Chemistry* (Kluwer Academic Publishers, The Netherlands, 2001).