Energy and expectation values of the PsH system.

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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 PsH\(^{\infty}\) energy was -0.789196740 hartree which is the lowest variational energy to date. The 2\(\gamma\) annihilation rate for PsH\(^{\infty}\) was 2.47178 \(\times\) 10\(^{15}\) s\(^{-1}\).

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 \cite{1}, a variety of methods have been applied to determine its structure. These include variational calculations with Hylleraas type basis sets \cite{2, 3, 4, 5}, variational calculations with explicitly correlated gaussians (ECGs) \cite{6, 7, 8, 9}, quantum Monte Carlo methods \cite{10, 11, 12, 13, 14} and most recently the configuration interaction method \cite{15, 16, 17, 18}. The lowest variational energy for PsH\(^{\infty}\) prior to the present article was that of Yan and Ho \cite{4}. Their largest calculation gave an energy of -0.7891967051 hartree. Bubin and Adamowicz used a 3200 dimension ECG basis to give an energy of -0.788870707 hartree for PsH\(^{1}\) \cite{19}.

In this work, the stochastic variational method (SVM) is used to construct a wave function with a lower energy than the value estimated by Yan and Ho as the variational limit (e.g. -0.7891967147(42) hartree). It is worth noting that the energy of the largest calculation, namely -0.789196740 hartree, is lower than the previous best energy of Yan and Ho \cite{4}, namely -0.7891967051 hartree. Yan and Ho examined the convergence pattern associated with their sequence of increasingly larger calculations and estimated that the true energy was actually 9.6(4.2) \(\times\) 10\(^{-9}\) hartree lower (e.g. -0.7891967147(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 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 non-linear 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 \cite{20}. This problem is probably more widespread than just the PsH calculation of Yan and Ho. It could occur whenever one extrapolates a sequence of energies while using a family of basis functions that are characterized by a parameter which has been subjected to a non-linear optimization.

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, \(\Gamma\) varied most as the basis dimension was increased. But, the increase in \(\Gamma\) 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 \ref{table1}. They are compared with the

\begin{align}
\Gamma &= 4\pi r_e^2 c \langle \Psi | \sum_i O_{ip}^S \delta(r_i - r_p) | \Psi \rangle \\
&= 1.009394 \times 10^{11} \sum_i \langle \delta(r_i - r_p) \rangle_S .
\end{align}

The sum is over the electron coordinates, the \(\delta\)-function expectation is evaluated in \(a_0^3\), and \(\Gamma\) 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 \ref{table1} 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 1.98x\(10^{-7}\) hartree. This is a substantial improvement over the previous best energy of Yan and Ho \cite{4}, namely -0.7891967051 hartree. Yan and Ho examined the convergence pattern associated with their sequence of increasingly larger calculations and estimated that the true energy was actually 9.6(4.2) \(\times\) 10\(^{-9}\) hartree lower (e.g. -0.7891967147(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 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 non-linear 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 \cite{20}. This problem is probably more widespread than just the PsH calculation of Yan and Ho. It could occur whenever one extrapolates a sequence of energies while using a family of basis functions that are characterized by a parameter which has been subjected to a non-linear optimization.

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A comprehensive set of the best set of expectation values are listed in Table \ref{table1}. They are compared with the
results of another, but completely independent, large basis SVM calculation [5]. The expectation value for the virial theorem \((V)/(T)\) provides an estimate of the wave function accuracy and the deviation of \((V)/(T)\) from -2 was only \(7.3 \times 10^{-8}\) hartree.

The energies of the different mass variants of PsH were computed by rediagonalizing the Hamiltonian with the same basis but with \(m_{H_1}\) set to 1836.1527 \(m_e\), \(m_{H_2}\) set to 3670.483 \(m_e\) and \(m_{H_3}\) set to 5496.899 \(m_e\). The energies of PsH, PsH\(_2\) and PsH\(_3\) were \(-0.788870618\) hartree, \(-0.789033556\) hartree and \(-0.789087767\) hartree respectively. The energy of the 3200 ECG wave function of Bubin and Adamowicz [19] for PsH\(_3\) was \(-0.788870707\) hartree, which is \(1.0 \times 10^{-7}\) hartree below the present energy. To summarize, a close to converged binding energy is

| \(N\) | \(\langle r_{H+e} \rangle\) | \(\langle r_{H+e}^2 \rangle\) | \(\langle 1/r_{e-e} \rangle\) | \(\langle r_{e-e} \rangle\) | \(\langle \delta(e^- - e^-) \rangle\) | \(\langle \delta(H^+ - e^+) \rangle\) | \(\Gamma\) | \((V)/(T) + 2\) | \(E\) |
|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|------|-----------------|------|
| 750  | 3.661596        | 7.812895        | 0.3705556       | 3.480249        | 4.39845 \times 10^{-3} | 1.63863 \times 10^{-3} | 2.46852 | 5.51 \times 10^{-7} | -0.789195993 |
| 900  | 3.661613        | 7.812961        | 0.3705544       | 3.480263        | 4.39321 \times 10^{-3} | 1.63635 \times 10^{-3} | 2.46879 | 7.96 \times 10^{-7} | -0.789196542  |
| 1200 | 3.661621        | 7.813024        | 0.3705550       | 3.480270        | 4.38188 \times 10^{-3} | 1.63153 \times 10^{-3} | 2.47129 | 2.21 \times 10^{-7} | -0.789196673  |
| 1500 | 3.661624        | 7.813040        | 0.3705549       | 3.480271        | 4.37628 \times 10^{-3} | 1.62850 \times 10^{-3} | 2.47134 | 1.30 \times 10^{-7} | -0.789196718  |
| 1800 | 3.661624        | 7.813046        | 0.3705549       | 3.480272        | 4.37639 \times 10^{-3} | 1.62828 \times 10^{-3} | 2.47178 | 7.3 \times 10^{-8}  | -0.789196740  |

Hylleraas \(N = 5741\) [4, 5] 2.47258  -0.789196705
Hylleraas \(N \rightarrow \infty\) extrapolation [4, 5] 2.47264(2)  -0.789196715(5)

reported for the PsH\(_\infty\) ground state. The present energy is \(2.5 \times 10^{-8}\) 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 inter-particle cusp conditions) will have a tendency to underestimate the electron-positron coalescence matrix element. Table II shows a consistent increase in \(\Gamma\) as the size of the calculation is increased.

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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    |
| $\langle V \rangle / \langle T \rangle + 2$ | $7.3 \times 10^{-8}$ | $6 \times 10^{-7}$ |
| $E$      | -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 |
| $\langle \delta(e^- - e^-) \rangle$ | $1.62828 \times 10^{-3}$ | $1.63857 \times 10^{-3}$ |
| $\langle \delta(e^- - e^-) \rangle$ | $4.37639 \times 10^{-2}$ | $4.3867 \times 10^{-3}$ |
| $\langle \delta(e^+ - e^-) \rangle$ | 0.0244877 | 0.024461 |
| $\Gamma$ | 2.47178 | 2.46909 |