# Comment on the Ground State of Positronium Hydride

S. K. Houston
*Department of Applied Mathematics and Computing Science, University of Sheffield, Sheffield S10 2TN, England*
and
Richard J. Drachman
*Theoretical Studies Branch, Goddard Space Flight Center, Greenbelt, Maryland* 20771
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A new, more accurate calculation of the ground-state wave function of positronium hydride has been carried out. The method is variational and is similar to that reported by Lebeda and Schrader. The "molecule" is found to be stable against separation into positronium and hydrogen by at least 0.672 eV, an increase of 2% above the best previous value. The mean lifetime against two-photon annihilation is 0.407 nsec, as obtained from the energy-minimizing wave function. The "cusp value" of $-0.477$ is close to the exact value $-\frac{1}{2}$, giving an indication of the quality of the trial function.

Two recent papers[1,2] have put the description of the ground-state properties of the positronium hydride "molecule" (PsH) on a good quantitative footing. In particular, the first of these[1] used a fairly realistic trial function to obtain a binding energy against dissociation into positronium and hydrogen of 0.0484 Ry. Since we had completed a calculation[3] of the very similar $s$-wave positron-helium scattering wave function, it seemed worthwhile to adapt our method to the problem of PsH.

The PsH system consists of a proton fixed at the origin of coordinates, two electrons ($\vec{r}_1$ and $\vec{r}_2$), and a positron ($\vec{x}$). The nonrelativistic Hamiltonian is

$$H=-\nabla_x^2-\nabla_1^2-\nabla_2^2+2\left(\frac{1}{x}-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{r_{12}}-\frac{1}{\rho_1}-\frac{1}{\rho_2}\right), \tag{1}$$

where $r_{12}\equiv|\vec{r}_1-\vec{r}_2|$, $\rho_i\equiv|\vec{x}-\vec{r}_i|$, lengths are in units of $a_0$, and energies in rydbergs. Using a trial function $\Psi(\vec{r}_1,\vec{r}_2,\vec{x})$ one first calculates the ground-state energy

$$E_0=\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle \tag{2}$$

and the dissociation energy $E_d=\frac{3}{2}-E_0$. Various other properties of the ground state may also be evaluated. These are (a) the two-photon annihilation rate in nsec$^{-1}$:

$$\lambda=\frac{100.9\,\langle\Psi|\delta(\vec{r}_1-\vec{x})|\Psi\rangle}{\langle\Psi|\Psi\rangle}\ ; \tag{3}$$

(b) the cusp value, emphasized by Schrader:

$$\nu=\frac{\langle\Psi|\delta(\vec{r}_1-\vec{x})(\partial/\partial\rho_1)|\Psi\rangle}{\langle\Psi|\delta(\vec{r}_1-\vec{x})|\Psi\rangle}. \tag{4}$$

This quantity probes the accuracy of the trial function near the point of coalescence between positron and electron, and should equal $-\frac{1}{2}$.

(c) The probability $P_n$ of finding the residual hydrogen atom in state $n$ following annihilation of PsH:

$$P_n=\frac{\int d\vec{x}\,|\int d\vec{r}\,\phi_n^*(r)\,\Psi(\vec{r},\vec{x},\vec{x})|^2}{\langle\Psi|\delta(\vec{r}_1-\vec{x})|\Psi\rangle}. \tag{5}$$

The trial functions we used were of the following form:

$$\Psi=\sum_{l,m,n} C_{lmn}\,e^{-\alpha x}\,x^l(e^{-\beta r_1}r_1^m\rho_1^n+e^{-\beta r_2}r_2^m\rho_2^n)\,\phi(r_1r_2). \tag{6}$$

Two different forms for $\phi$ were tested:

$$\phi_c=e^{-z(r_1+r_2)},\qquad \phi_0=e^{-(z_1r_1+z_2r_2)}+e^{-(z_2r_1+z_1r_2)} \tag{7}$$

(these are referred to as "closed-shell" and "open-shell" functions by analogy with the standard two-electron–atom terminology; we are not implying that the ground state of $H^2$ is the dominant configuration in PsH). Only five of the six coordinates expressing the general form of the $s$-wave function are included; we omitted the variable $r_{12}$ so that all integrals could be performed analytically. (In Ref. 1 the coordinate $x$ was omitted instead.) In Tables I and II we present results for the two functions. The nonlinear parameters are approximately optimized during the variational energy calculation, and the conventional reporting values of $N$ are chosen to show the convergence rates.

The closed-shell results in Table I are worse

TABLE I. Convergence, for the closed-shell wave function, of various properties of PsH. The nonlinear parameters are $\alpha=0.5279$, $\beta=-0.3760$, $z=1.032$.

| $N$ | 20 | 35 | 56 | Previous work |
|---|---|---|---|---|
| $E_d$ | 0.04102 | 0.04612 | 0.04761 | 0.0484[a] |
| $\lambda$ (nsec)$^{-1}$ | 2.148 | 2.322 | 2.390 | 2.095[a] |
| $t$ (nsec) $=1/\lambda$ | 0.466 | 0.431 | 0.418 | 0.477 |
| $P_{1s}$ | 0.9852 | 0.9865 | 0.9869 | 0.9770[b] |
| $P_{2s}$ | 0.0017 | 0.0015 | 0.0014 | 0.0030[b] |
| $P_{3s}$ | 0.00035 | 0.00014 | 0.00018 | 0.0003[b] |
| $P_{2p}$ | 0.0035 | 0.0033 | 0.0032 | 0.0084[b] |
| $P_{3p}$ | 0.00054 | 0.00046 | 0.00046 | 0.0013[b] |
| $\nu$ | $-0.4092$ | $-0.4511$ | $-0.4718$ | $-0.4070$[a] |

[a]Reference 1. [b]Reference 2.

TABLE II. Convergence, for the open-shell wave function, of various properties of PsH. The nonlinear parameters are $\alpha = 0.56$, $\beta = -0.1917$, $z_1 = 0.7054$, $z_2 = 1.163$.

| $N$ | 10 | 20 | 35 | 56 | $\infty$ |
|---|---|---|---|---|---|
| $E_d$ | 0.02674 | 0.04398 | 0.04836 | 0.04943 | 0.0497 |
| $\lambda$ (nsec)$^{-1}$ | 1.825 | 2.229 | 2.3963 | 2.459 | 2.496 |
| $t$ (nsec) $= 1/\lambda$ | 0.548 | 0.449 | 0.417 | 0.407 | 0.401 |
| $\nu$ | −0.3428 | −0.4225 | −0.4596 | −0.4766 | −0.491 |

than those reported previously[1] as far as the energy is concerned. Nevertheless, the cusp value $\nu$ seems better; perhaps the annihilation rate is also. The values of $P_n$ are qualitatively in agreement with the corrected values of Ref. 2, which used a very simple trial function.

The open-shell results in Table II give an improvement in the dissociation energy of 2% for the 56-term function, as well as a good value for $\nu$. (With this type of trial function the evaluation of $P_n$ would be rather time consuming, and we did not carry it out; we do not expect the results to differ too much from those in Table I.) The extrapolated values represent estimates based only on the limited type of trial function used here. Further work using more general functional forms is presently under way.[4]

[1]C. F. Lebeda and D. M. Schrader, Phys. Rev. 178, 24 (1969).
[2]D. M. Schrader and T. Petersen, Phys. Rev. A 3, 61 (1971); 5, 1974 (1972).
[3]S. K. Houston and R. J. Drachman, Phys. Rev. A 3, 1335 (1971).
[4]D. M. Schrader (private communication).

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# High-Temperature Quantum Corrections to the Second Virial Coefficient for a Hard-Core-Plus-Attractive-Well-Potential Model

José J. D'Arruda
*Department of Physics, University of Wisconsin Center, Richland Center, Wisconsin* 53581
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High-temperature asymptotic expansions of $B_{\rm dir}$ for a hard-core–plus–attractive-well potential are calculated using a method developed by Hill and reformulated by D'Arruda and Hill. To lowest order, we find the first quantum correction from the well to be independent of the shape of the well and to depend only on the value of the potential at the core.

## I. GENERAL FORMULATION

We begin with the formulation of Boyd, Larsen, and Kilpatrick[1] and write the second virial coefficient $B$ in the form

$$B = B_{\rm dir} + B_{\rm exch} , \tag{1}$$

where

$$B_{\rm dir} = \sqrt{2}\, N\lambda^3 \int d\vec{\mathbf{r}}[2^{-3/2}\lambda^{-3} - G(\vec{\mathbf{r}}, \vec{\mathbf{r}}; \beta)] \tag{2}$$

and

$$B_{\rm exch} = \mp \sqrt{2}\, N\lambda^3 (2S+1)^{-1} \int d\vec{\mathbf{r}} G(\vec{\mathbf{r}}, -\vec{\mathbf{r}}; \beta) . \tag{3}$$

The minus (upper) sign in $B_{\rm exch}$ is associated with Bose statistics and the plus sign with Fermi statistics. Here $S$ is the spin, $\lambda = (2\pi\hbar\beta/m)^{1/2}$ is the thermal de Broglie wavelength, and $\beta = (kT)^{-1}$.

Since it has already been shown that the repulsive core present in realistic two-body potentials and in hard spheres leads to a rapid suppression of the exchange piece at high temperature, we shall focus our efforts only on $B_{\rm dir}$. Qualitatively, the exchange piece is nontrivial only if the particles are allowed to come closer to each other than the thermal wavelength. If this is not possible because of the presence of the repulsive forces, the exchange is negligible. $G$ is the thermal Green's function for the relative motion:

$$G(\vec{\mathbf{r}}', \vec{\mathbf{r}}; \beta) = \langle \vec{\mathbf{r}}' \,|\, e^{-\beta H_r} \,|\, \vec{\mathbf{r}} \rangle , \tag{4}$$

where

$$H_r = -\left(\frac{\hbar^2}{m}\right)\nabla^2 + V(r) \tag{5}$$

is the Hamiltonian for the relative motion of a pair of particles of mass $m$.

Following the general procedure as given in earlier work,[2,3] we may write

$$B_d = -\sqrt{2}\, N\lambda^3 \Delta , \tag{6}$$

$$\Delta = \sum_{l=0}^{\infty} (2l+1)\left((2\pi i)^{-1}\int_{W_0 - i\infty}^{W_0 + i\infty} e^{\beta W} f^l(W)\, dW\right) , \tag{7}$$

where the integration contour in the complex $W$ plane lies to the right of all singularities and where