Relativistic effects in positronium hydride

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Relativistic effects in the ground-state energy of positronium hydride up to orders $O(\alpha^4 mc^2)$ and $O((\mu/M)\alpha^4 mc^2)$ are calculated using fully correlated basis sets in Hylleraas coordinates. The resulting binding energy against the dissociation into a positronium and a hydrogen is 1.064 041 68(27) eV. The two-photon annihilation rate is also calculated and the result is 2.472 208(20) nsec^{-1}. [S1050-2947(99)03812-3]

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I. INTRODUCTION

Positronium hydride (PsH) is an exotic atom which consists of a positronium and a hydrogen. The stability of the ground state of PsH was established by the pioneer work of Ore [1]. Since then, there has been much theoretical work towards more precise calculations for the ground-state energy [2]. This four-body system provides a unique testing ground for computational methods which must include not only electron-electron correlations, but also electron-positron correlations. This is because any Hartree-Fock-type calculations would fail to predict the existence of bound states against the dissociation into a positronium and a hydrogen. The existence of such a bound state of PsH was reported experimentally by Pareja *et al.* [3] in a condensed-matter phase. The first convincing evidence for the formation of PsH in vacuum was recently obtained by Schrader *et al.* [4] from collisions between positrons and methane. The measured binding energy of 1.1 ± 0.2 eV is in accord with most theoretical predictions. Since this experimental progress, there have been several theoretical works on the nonrelativistic ground-state energy [5–10]. In particular, recent advances [11] in high-precision variational calculations for three-electron atomic systems, using multiple basis sets in Hylleraas coordinates, now make it possible to study four-body positronic atoms, such as positronium hydride. The most accurate result of 5 parts in 10^9 in accuracy was recently obtained by Yan and Ho [12]. With such precise energy eigenvalues, we are now in a position to consider relativistic effects in PsH. The relativistic effects in PsH are more abundant than in electronic atoms, due to the existence of the electron-positron annihilation channel which does not present in electronic atoms. Although Bhatia and Drachman [13] have recently calculated some relativistic corrections to Ps^-, to the best of our knowledge there has been no complete evaluation on relativistic effects in any kinds of positronic atoms (except positronium). In this work we present high-precision calculations for the ground state of PsH, including all finite nuclear mass and lowest-order relativistic effects due to the Breit interaction.

II. FORMULATION

For the ground state of PsH, the leading relativistic corrections of $O(\alpha^2)$ a.u. can be evaluated from expectation values of the Breit operator [14,15]

$$H_{\rm rel}=B_1+B_2-\pi\alpha^2\sum_{i>j} q_i q_j\left(1+\frac{8}{3}\mathbf{s}_i\cdot\mathbf{s}_j\right)\delta(\mathbf{r}_{ij}) -\frac{1}{2}\pi Z\alpha^2\sum_{i=1}^{3} q_i\,\delta(\mathbf{r}_i)+\frac{m}{M}\tilde{\Delta}_2+H_{\rm ann}, \tag{1}$$

where m and M are the electron (positron) and nuclear masses, respectively, Z is the nuclear charge which is 1 for PsH, indices 1, 2, and 3 refer to electron, electron, and position coordinates, respectively, and $q_1=-1$, $q_2=-1$, and $q_3=1$. In Eq. (1),

$$B_1=-\frac{\alpha^2}{8}\sum_{i=1}^{3}\nabla_i^4, \tag{2}$$

$$B_2=\frac{\alpha^2}{2}\sum_{i>j}^{3} q_i q_j\left[\frac{1}{r_{ij}}\boldsymbol{\nabla}_i\cdot\boldsymbol{\nabla}_j+\frac{1}{r_{ij}^3}\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\boldsymbol{\nabla}_i)\boldsymbol{\nabla}_j\right], \tag{3}$$

$$\tilde{\Delta}_2=-\frac{Z\alpha^2}{2}\sum_{j=1}^{3} q_i\left[\frac{1}{r_j}\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}_j+\frac{1}{r_j^3}\mathbf{r}_j\cdot(\mathbf{r}_j\cdot\boldsymbol{\nabla})\boldsymbol{\nabla}_j\right], \tag{4}$$

with $\nabla=\Sigma_{i=1}^{3}\nabla_i$, and $H_{\rm ann}$ is the interaction due to the electron and positron annihilation channel [15], which has no analog in the theory of electronic atoms, and can be written in the form

$$H_{\rm ann}=\frac{\pi\alpha^2}{2}[(3+4\mathbf{s}_2\cdot\mathbf{s}_3)\delta(\mathbf{r}_{23})+(3+4\mathbf{s}_3\cdot\mathbf{s}_1)\delta(\mathbf{r}_{31})]. \tag{5}$$

Since the total spin function is

$$\chi=[\alpha(1)\beta(2)-\beta(1)\alpha(2)]\alpha(3), \tag{6}$$

the expectation values of $\mathbf{s}_1\cdot\mathbf{s}_2$, $\mathbf{s}_2\cdot\mathbf{s}_3$, and $\mathbf{s}_3\cdot\mathbf{s}_1$ are $-3/4$, 0, and 0, respectively, and $H_{\rm rel}$ can thus be simplified into

$$H_{\rm rel}=B_1+B_2+\pi\alpha^2\sum_{i>j}^{3}\delta(\mathbf{r}_{ij})-\frac{1}{2}\pi Z\alpha^2\sum_{i=1}^{3} q_i\,\delta(\mathbf{r}_i) +\frac{m}{M}\tilde{\Delta}_2+H_{\rm ann}, \tag{7}$$

TABLE I. Nonrelativistic ground-state energies for various isotopes of positronium hydride, in $2R_\infty$. PsH^∞ is for the case of infinite nuclear mass.

System	Energy
PsH^∞	−0.789 196 714 7(42)
PsH	−0.788 870 648(12)
	−0.788 8534 [a]
PsD	−0.789 033 546 1(50)
	−0.789 0163 [a]
PsT	−0.789 087 749 3(44)
	−0.789 070 5 [a]
Psμ	−0.786 316 31(90)
	−0.786 299 8 [a]

[a]Reference [6].

where $H_{\rm ann}=(3\pi\alpha^2/2)[\delta(\mathbf{r}_{23})+\delta(\mathbf{r}_{31})]$. Finite nuclear mass corrections of order $O((m/M)\alpha^2)$ a.u. come from the mass scaling of these terms, cross terms with a mass-polarization operator, and the relativistic recoil term $\tilde{\Delta}_2$ first derived by Stone [14].

III. CALCULATIONS AND RESULTS

The expectation values of these operators are evaluated from nonrelativistic wave functions in Hylleraas coordinates and solved variationally [12]. The Schrödinger Hamiltonian in scaled center of mass plus relative coordinates is

$$H_0=\sum_{i=1}^{3}\left(-\frac{1}{2}\nabla_i^2+\frac{Zq_i}{r_i}\right)+\sum_{i>j}^{3}\left(\frac{q_iq_j}{r_{ij}}-\frac{\mu}{M}\nabla_i\cdot\nabla_j\right), \quad (8)$$

in units of $2R_M$, where $R_M=(1-\mu/M)R_\infty$, and $\mu=mM/(m+M)$ is the electron reduced mass. The finite nuclear mass corrections can be extracted by comparing the results obtained from two calculations: one calculation includes the mass-polarization term $-(\mu/M)\Sigma_{i=1}^{3}\boldsymbol{\nabla}_i\cdot\boldsymbol{\nabla}_j$, the other excludes this term. For the nonrelativistic energy E_M, it is convenient to treat the mass-polarization term as a perturbation and express E_M in powers of μ/M up to $O((\mu/M)^2)$. The result is

$$E_M=-0.789\,196\,714\,7(42)-0.190\,088\,80(20)\,(\mu/M)-0.327(36)\,(\mu/M)^2, \quad (9)$$

in units of $2R_M$. Equation (9) can be used to calculate the ground-state energies for various hydrogen isotopes and the results are listed in Table I, together with a comparison with the Frolov and Smith results using same values of nuclear masses [6]. The uncalculated contribution of order $O((\mu/M)^3)$ and higher, which only affects the system Psμ at the one part in 10^7 level, is included as a part of uncertainties.

After obtaining the nonrelativistic wave functions, the next step is to evaluate the expectation values of Breit operators. Technical details about how to deal with singular integrals and how to accelerate very slowly converged resulting series can be found in Ref. [16]. Table II lists the convergence study of the matrix elements of the Breit operators as the size of basis increases progressively, and their extrapolated values. Table III presents all the contributions of orders $(\mu/M)^n$, $n=0,1,2$, α^2, and $(\mu/M)\alpha^2$ to the ground-state energy of PsH, as well as the determination of the binding energy against the dissociation into a positronium and a hydrogen. In the calculation of the dissociation threshold, we should emphasize that the ground-state energies of H and Ps must include relativistic and quantum electrodynamic (QED) corrections to a required precision, as calculated by Pachucki [17]. For example, the Lamb shift to the hydrogen $1\,^2S_{1/2}$ state is 1.242×10^{-6} a.u. which is in the same order of the α^2 contribution to the PsH ground-state energy. However, the hyperfine splitting of 2.16×10^{-7} a.u. in the hydrogen $1\,^2S_{1/2}$ state was not included. The resulting dissociation threshold is higher than the nonrelativistic value by an amount of 0.006 79 eV. In Table III we also compare our binding energy with the Frolov and Smith result [6], which contains only the finite nuclear mass correction to the nonrelativistic

TABLE II. Convergence of the expectation values of the Breit operators (in $2R_\infty$) for the ground state of PsH with infinite nuclear mass and $\alpha^{-1}=137.035\,989\,5(61)$. N is the size of basis set.

N	$B_1\times10^5$	$B_2\times10^6$	$\delta(\mathbf{r}_{31})$	$\sum_{i>j}^{3}\delta(\mathbf{r}_{ij})$	$-\sum_{i=1}^{3}q_i\delta(\mathbf{r}_i)$	$\tilde{\Delta}_2\times10^5$
50	−2.597 50	−6.651 1	0.021 883 76	0.048 813 71	0.345 867 571	−5.585 789 2
120	−2.626 10	−6.995 8	0.023 486 28	0.051 638 49	0.353 974 980	−5.638 706 6
256	−2.613 21	−7.105 1	0.024 067 51	0.052 636 66	0.352 486 875	−5.631 742 5
502	−2.608 70	−7.140 1	0.024 312 92	0.053 061 22	0.353 028 121	−5.634 127 6
918	−2.605 69	−7.152 8	0.024 438 02	0.053 273 08	0.353 137 710	−5.634 408 1
1589	−2.604 17	−7.155 9	0.024 484 46	0.053 354 48	0.353 067 676	−5.633 956 9
2625	−2.603 82	−7.154 1	0.024 491 22	0.053 359 71	0.353 064 315	−5.633 877 2
3501	−2.604 41		0.024 494 43	0.053 364 84	0.353 061 798	−5.633 860 3
4705			0.024 495 72	0.053 365 88	0.353 061 704	
∞	−2.604 10(30)	−7.153 0(20)	0.024 496 29(20)	0.053 365 60(30)	0.353 061 694(10)	−5.633 858 0(20)
[7]			0.024 415 8	0.053 258 2	0.353 346	
[10]			0.024 461 1	0.053 308 9	0.352 733 8	

TABLE III. Contributions to the ground-state energy of PsH and the determination of the binding energy (BE). Units are $2R_\infty$; otherwise stated. The conversion factor from $2R_\infty$ to eV is 27.211 396.

Contribution	Value
$(\mu/M)^0$	−0.789 196 714 7(42)
$(\mu/M)^1$	0.000 326 106 76(11)
$(\mu/M)^2$	−0.000 000 040(10)
α^2	0.000 005 266 3(36)
$(\mu/M)\,\alpha^2$	−0.000 000 018 0(50)
α^2 $(e^-e^+$ annihi.)	0.000 012 294 25(10)
$(\mu/M)\,\alpha^2$ $(e^-e^+$ annihi.)	−0.000 000 002 15(14)
Total	−0.788 853 107(10)
Energy H($1\,^2S_{1/2}$) [a]	−0.499 733 254
Energy Ps($1\,^1S_0$) [a]	−0.250 017 057
Dissociation threshold	−0.749 750 311
BE	0.039 102 796(10)
BE (eV) (theory)	1.064 041 68(27)
BE (eV) (theory) [b]	1.064 661
BE (eV) (experiment) [c]	1.1±0.2

[a]Reference [17].
[b]Reference [6].
[c]Reference [4].

energy. The accuracy of the experimental measurement of Schrader *et al.* [4] is not high enough to test our calculations.

It is also interesting to consider positron annihilation processes in PsH. The most important one is the two-photon annihilation, where the calculations for the rate of annihilation $\Gamma_{2\gamma}$ have received great attention in the past two decades [2,6–10]. $\Gamma_{2\gamma}$ can be expressed in the form [18]

$$\Gamma_{2\gamma}=n\pi\alpha^4 c a_0^{-1}\langle\delta(\mathbf{r}_{31})\rangle\ \mathrm{sec}^{-1}, \tag{10}$$

where n is the number of electrons, α is the fine-structure constant, c is the speed of light, and a_0 is the Bohr radius. Table IV shows the two-photon annihilation rates and comparison with other calculations. For PsH^∞, our calculation improves in computational accuracy the previous best result of Usukura *et al.* [10] by a factor of 20. For PsH, however, the improvement over the Frolov and Smith [6] result is a factor of 2000.

TABLE IV. The two-photon annihilation rates and comparison with other calculations, in nsec^{-1}.

Author	Reference	PsH^∞	PsH
Ho	[2]	2.459	
Frolov and Smith	[6]	2.4361	2.4357
Frolov and Smith	[7]	2.4567	
Strasburger and Chojnacki	[8]	2.443	
Ryzhikh *et al.*	[9]	2.4520	
Usukura *et al.*	[10]	2.4722	
This work		2.472 641(20)	2.472 208(20)

In summary, we have performed a high-precision calculation for the PsH binding energy, including the lowest-order relativistic corrections and the finite nuclear mass effects, using fully correlated basis sets in Hylleraas coordinates. The computational accuracy that we have achieved is about 0.2 ppm. The two-photon annihilation rate has also been calculated to a computational accuracy of 8 ppm. Our work may become a timely challenge to experimentalists. The next-order corrections not included here come from the lowest-order quantum electrodynamic (QED) terms of order $O(\alpha^3)$ a.u., which could contribute to the binding energy at the 10 ppm level. There has been no published work on this problem so far. The new feature of QED effects in PsH is the existence of a positronium annihilation channel that does not exist in electronic atoms. The rest of the derivation for the QED terms should be standard and could be done using nonrelativistic quantum electrodynamics [17,19,20].

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