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Ground state and *S*-wave autodissociating resonant states of positronium hydride

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The fully correlated calculations in Hylleraas coordinates for the nonrelativistic ground-state energy and the first three *S*-wave resonances of positronium hydride are reported. For the resonances, the positions and widths are determined using the method of complex-coordinate rotation. Our results significantly improve previous work. For example, the ground-state energy is about five parts in 10^9 in accuracy, the lowest variational upper bound reported to date. A comparison with other previous work is made. [S1050-2947(99)04204-3]

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I. INTRODUCTION

In this work, we present a calculation of ground-state energy and resonance parameters for the lowest three *S*-wave autodissociating resonant states of positronium hydride (PsH). PsH consists of a positronium atom and a hydrogen atom. Such a positronic four-body system was observed in the laboratory by Schrader *et al.* [1]. The calculation of the PsH ground-state energy is a unique testing ground for studying correlation effects among electrons and positron. This is because calculations within the Hartree-Fock approximation do not give a bound state against the dissociation into a positronium and a hydrogen atom. Early reviews for this subject can be found in Ref. [2]. Ho [3] calculated the ground-state energy in Hylleraas coordinates. Yoshida and Miyako [4] studied the ground-state energy using a quantum Monte Carlo (QMC) method. Frolov and Smith [5,6] calculated bound properties for PsH, its isotopes, and the Ps_2 molecule, using explicitly correlated Gaussian (ECG) functions and the James-Coolidge expansion. The ECG method was also used by Strasburger and Chojnacki [7] to study the PsH and PsLi^+ systems. Very recently, the stochastic variational method (SVM) was applied to the study of PsH and other positronic systems in Refs. [8] and [9] with high accuracy. In terms of our recent success of the application of Hylleraas coordinates to the studies of PsH resonances [10,11], here we reexamine the PsH ground-state energy for the purpose of achieving as high a precision as possible, which is essential for studying relativistic and QED effects in this system.

Resonances in positronium-hydrogen scattering are the result of a Rydberg series of a positron attaching to a negative hydrogen ion, H^- [12]. The lowest *S* state in this series lies below the Ps-H threshold, and becomes the ground state of PsH. The higher members of the Rydberg series that are located in the Ps-H continuum would become resonances in Ps-H scattering. *S*-wave resonances were investigated by using the method of complex-coordinate rotation [13–15]. *S*-wave triply excited autodissociating resonant states in PsH were also calculated [16]. Drachman [12] used an optical potential to calculate *S*-, *P*-, and *D*-wave resonance energies in Ps-H scattering. Recently, we reported calculations of *P*- and *D*-wave autodissociating resonances in PsH by using the method of complex-coordinate rotation and employing Hylleraas functions [10,11]. Campbell *et al.* [17] reported energies and widths for *S*-, *P*-, and *D*-wave resonances in Ps-H scattering using a 22-state (coupled-pseudostate) approximation. Because of the continuous theoretical interest and the recent experimental interest in PsH, here we report a calculation of the three lowest *S*-wave resonances in Ps-H scattering. Using the method of complex-coordinate rotation [18] and extensive Hylleraas-type wave functions, we report both the resonance positions and widths for such states. A comparison is made for the resonance energies and widths with other results in the literatures.

II. WAVE FUNCTIONS

The Hamiltonium for the PsH system with infinite nuclear mass is (in atomic units)

$$H=T+V, \tag{1}$$

with

$$T=-\frac{1}{2}(\nabla_1^2+\nabla_2^2+\nabla_3^2) \tag{2}$$

and

$$V=-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{r_3}+\frac{1}{r_{12}}-\frac{1}{r_{23}}-\frac{1}{r_{13}}, \tag{3}$$

where indices 1, 2, and 3 refer to electron, electron, and positron coordinates, respectively. The wave function can be expanded according to

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\sum_{i=1}^{N} a_i\psi_i(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\pm(1\leftrightarrow 2), \tag{4}$$

where Ψ_i is a general term in the basis set, which has the form

$$r_1^{j_1}r_2^{j_2}r_3^{j_3}r_{12}^{j_{12}}r_{23}^{j_{23}}r_{31}^{j_{31}}e^{-\alpha r_1-\beta r_2-\gamma r_3}Y_{(l_1l_2)l_{12},l}^{LM}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) \tag{5}$$

with

TABLE I. Nonrelativistic ground-state energy of positronium hydride, in $2R_\infty$.

Ω	No. of terms	$E(\Omega)$	$E(\Omega)-E(\Omega-1)$	$R(\Omega)$
3	50	−0.786 172 022 2		
4	120	−0.788 500 266 0	−0.002 328 243 7	
5	256	−0.789 037 398 3	−0.000 537 132 3	4.33
6	502	−0.789 158 895 6	−0.000 121 497 3	4.42
7	918	−0.789 187 922 3	−0.000 029 026 7	4.19
8	1589	−0.789 194 876 8	−0.000 006 954 5	4.17
9	2625	−0.789 196 380 9	−0.000 001 504 1	4.62
10	3501	−0.789 196 607 6	−0.000 000 226 7	6.64
11	4705	−0.789 196 679 9	−0.000 000 072 4	3.13
12	5741	−0.789 196 705 1	−0.000 000 025 2	2.87
Extrapolation		−0.789 196 714 7(42)		

$$Y^{LM}_{(l_1l_2)l_{12},l_3}=\sum_{m_i}\langle l_1m_1;l_2m_2|l_1l_2;l_{12}m_{12}\rangle\langle l_{12}m_{12};l_3m_3|l_{12}l_3;LM\rangle Y_{l_1m_1}(\hat{\mathbf{r}}_1)Y_{l_2m_2}(\hat{\mathbf{r}}_2)Y_{l_3m_3}(\hat{\mathbf{r}}_3), \tag{6}$$

which is a vector-coupled product of spherical harmonics required for the three electrons to form a state of total angular momentum L. For S symmetry, $l_i=0$ and $L=0$. For the ground state, the basis set is divided into five blocks, according to correlations among the two electrons and one positron as follows [19]:

Sector 1: all j_{12}, $j_{23}=0$, $j_{31}=0$,

Sector 2: all j_{12}, $j_{23}=0$, $j_{31}\neq 0$,

Sector 3: all j_{12}, $j_{23}\neq 0$, $j_{31}=0$,

Sector 4: $j_{12}=0$, $j_{23}\neq 0$, $j_{31}\neq 0$,

Sector 5: $j_{12}\neq 0$, $j_{23}\neq 0$, $j_{31}\neq 0$.

Each block has its own nonlinear parameters α_i, β_i, and γ_i, and is assigned an integer Ω_i, where $i=1,\ldots,5$, according to

$$\{\Omega_1,\Omega_2,\Omega_3,\Omega_4,\Omega_5\}=\{\Omega,\Omega,\Omega,(\Omega,9)_{\min},(\Omega,9)_{\min}\},$$

where $(a,b)_{\min}$ denotes min(a,b). All terms in Eq. (5) are included such that

$$j_1+j_2+j_3+j_{12}+j_{23}+j_{31}\leqslant\Omega_i. \tag{7}$$

However, terms which may potentially cause near linear dependences are excluded. For example, if $l_1=l_2$ and $\alpha\approx\beta$, then terms with $j_1>j_2$ are omitted, as well as terms with $j_1=j_2$ when $j_{23}>j_{31}$. The general methods for evaluating three-body integrals in Hylleraas coordinates can be found in Ref. [20].

III. CALCULATIONS AND RESULTS

A. Ground-state energy

In the calculations of the ground-state energy, the nonlinear parameters are optimized by analytically calculating the derivatives [21]

$$\frac{\partial E}{\partial\alpha}=2\left\langle\Psi|H|\frac{\partial\Psi}{\partial\alpha}\right\rangle-2E\left\langle\Psi\left|\frac{\partial\Psi}{\partial\alpha}\right.\right\rangle, \tag{8}$$

TABLE II. Comparison with other calculations for the nonrelativistic ground-state energy of positronium hydride, in $2R_\infty$.

Author (Year)	Method	Ref.	Energy
Ho (1986)	Hylleraas	[3]	−0.788 945
Yoshida and Miyako (1996)	QMC	[4]	−0.7891(20)
Frolov and Smith (1997)	ECG	[5]	−0.789 179 4
Frolov and Smith (1997)	James-Coolidge	[6]	−0.789 136 9
Strasburger and Chojnacki (1998)	ECG	[7]	−0.789 185
Ryzhikh, Mitroy, and Varga (1998)	SVM	[8]	−0.789 194 4
Usukura, Varga, and Suzuki (1998)	SVM	[9]	−0.789 196 553 6
This work	Hylleraas		−0.789 196 714 7(42)

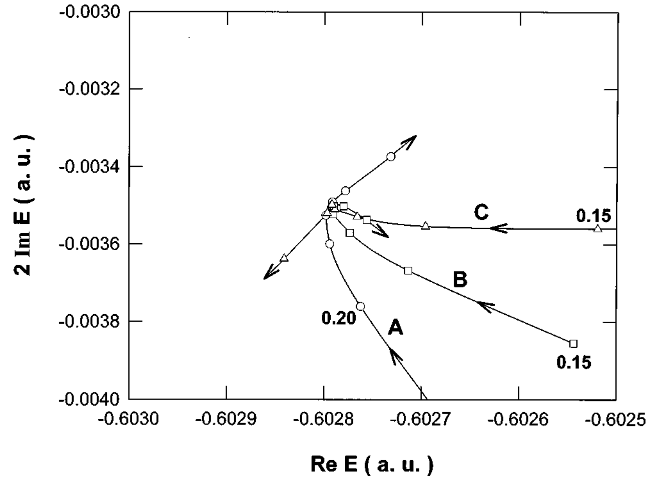

FIG. 1. Complex eigenvalue for the lowest *S*-wave resonance in Ps-H scattering, obtained by using different values of rotational angle θ. Shown next to the selected poles are the values of θ in radians. Poles are calculated with $\Delta\theta = 0.05$ rad, with the arrows indicating the direction of increasing θ.

where α represents any nonlinear parameters, and the normalization $\langle\Psi|\Psi\rangle = 1$ is assumed. Newton's method is applied to locate the zeros of the first derivatives. Provided that the initial α_i, β_i, and γ_i are chosen close to a minimum, the procedure converges in a few iterations.

Table I lists the results for the nonrelativistic ground-state energy, together with a detailed account of the convergence process as the size of the basis set is enlarged. The ratio $R(\Omega)$ is defined by

$$R(\Omega) = \frac{E(\Omega-1) - E(\Omega-2)}{E(\Omega) - E(\Omega-1)}. \tag{9}$$

It can be seen that the convergence is quite smooth. The extrapolated value was obtained using the procedure described in Ref. [19]. A comparison with selected recent calculations is contained in Table II. The accuracy we have achieved is about five parts in 10^9, which is a factor of 50 improvement over the best result of Ref. [9].

B. *S*-wave resonances

For calculations of the *S*-wave autodissociating resonant states, we use the method of complex-coordinate rotation [18]. The radial coordinates are transformed by

$$r_{ij} \rightarrow r_{ij} e^{i\theta}, \tag{10}$$

where r_{ij} is the radial distance between the charged particles i and j.

The transformed Hamiltonian can be written as

$$H(\theta) = T e^{-2i\theta} + V e^{-i\theta}, \tag{11}$$

where T and V are those given in Eqs. (2) and (3), respectively. Complex eigenvalues are obtained by diagonalizing the transformed Hamiltonian, and the complex resonance energy is given by

$$E_{\text{res}} = E_r - i\Gamma/2, \tag{12}$$

TABLE III. Complex resonance eigenvalue for the lowest *S*-wave resonance $S(1)$, obtained by using different series of basis sets with $\theta = 0.35$.

Ω	N	γ	E_r (a.u.)	Γ (a.u.)
7	918	0.35	−0.602 855	0.003 294
8	1589	0.35	−0.602 821	0.003 452
9	2625	0.30	−0.602 792	0.003 498
9	2625	0.35	−0.602 793	0.003 499
9	2625	0.40	−0.602 790	0.003 502
9	2625	0.45	−0.602 792	0.003 491

where E_r is the resonance position, and Γ the resonance width. In the wave functions described in Eq. (5), we choose the nonlinear parameters $\alpha = \beta = 0.9$, and let γ have values ranging from 0.30 to 0.45. The nonlinear parameter γ can also be considered as a variational parameter to determine the stabilized complex resonance eigenvalues.

Figure 1 shows the θ dependence (rotational paths) of the resonance parameters for the lowest *S*-wave resonance. Set *A* is from $\Omega = 9$, with $\gamma = 0.45$ and $N = 2625$; set *B* is from $\Omega = 9$, with $\gamma = 0.40$; and set *C* is from $\Omega = 9$, with $\gamma = 0.35$. The results shown in Fig. 1 show the typical "stabilization" behavior for a complex resonance eigenvalue. All of the rotational paths "meet" and "converge" near the resonance pole in the complex-energy plane. From Fig. 1, the complex eigenvalue exhibits the most slowing down, i.e., $\partial|E|/\partial\theta \approx$ minimum, on *B* near $\theta = 0.35$. Table III shows results when different values of γ are used with θ and N being fixed at 0.35 rad and 2625 terms, respectively. This indicates that the optimized resonance eigenvalue with respect to the change of γ, i.e., $\partial|E|/\partial\gamma \approx$ (minimum), occurs at about $\gamma = 0.40$, when values of θ and N are fixed. In fact, at such values of θ and N, γ has a large range of values from 0.30 to 0.45, such that the complex eigenvalue is stabilized. The final resonance energy E_r and the width Γ for the lowest *S*-wave autodissociating resonance state are determined as

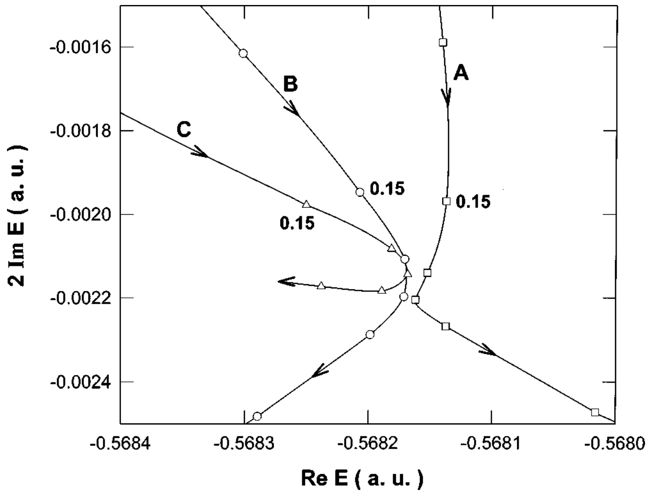

FIG. 2. Complex eigenvalue for the second lowest *S*-wave resonance in Ps-H scattering obtained by using different values of rotational angle θ. Shown next to the selected poles are the values of θ in radians. Poles are calculated with $\Delta\theta = 0.05$ rad, with the arrows indicating the direction of increasing θ.

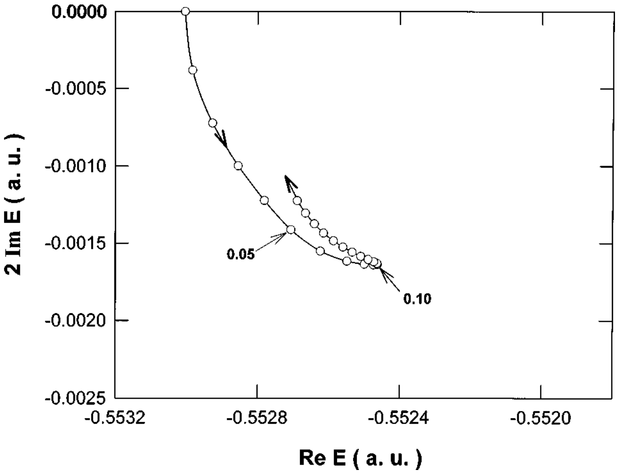

FIG. 3. Complex eigenvalue for the third lowest *S*-wave resonance in Ps-H scattering obtained by using different values of rotational angle θ. The curve is for $\gamma = 0.30$ and $N = 2625$. Shown next to the selected poles are the values of θ in radians. Poles are calculated with $\Delta\theta = 0.01$ rad, with the arrow indicating the direction of increasing θ.

$-0.602\,79 \pm 0.000\,02$ and $0.003\,50 \pm 0.000\,04$ a.u., respectively. Table III also contains the convergence study as the size of the basis set is enlarged. We estimate that when the basis set reaches to $\Omega = 7$ ($N = 918$), the uncertainties for the resonance parameters are $\pm 1.0 \times 10^{-4}$ and $\pm 2 \times 10^{-4}$ a.u., for E_r and Γ, respectively. For $\Omega = 8$ ($N = 1589$), the uncertainties for E_r and Γ are reduced to 5×10^{-5} and 1×10^{-4} a.u., respectively. When Ω is increased to 9 ($N = 2625$), the estimated uncertainties for the final results are determined as $\pm 2 \times 10^{-5}$ and 4×10^{-5} a.u. for E_r and Γ, respectively.

Figure 2 shows the θ dependence (rotational paths) of the resonance parameters for the second *S*-wave resonance state $S(2)$. Set *A* is from $\Omega = 9$, with $\gamma = 0.40$ and $N = 2625$ terms; set *B* is from $\Omega = 9$, with $\gamma = 0.35$; and set *C* is from $\Omega = 9$, with $\gamma = 0.30$. The results shown in Fig. 2 show the rotational paths ''meet'' and ''converge'' near the resonance pole in the complex-energy plane. From Fig. 2, the complex eigenvalue exhibits the most slowing down, i.e., $\partial|E|/\partial\theta \approx$ (minimum), on *C* near $\theta = 0.25$. The final resonance E_r and the width Γ for the second *S*-wave autodissociating resonance state are determined as -0.56817 ± 0.00005 and 0.00215 ± 0.00010 a.u., respectively.

Figure 3 shows the θ dependence for the third lowest *S*-wave resonance state $S(3)$ in Ps-H scattering. The optimized γ for this state is $\gamma = 0.30$ with $N = 2625$ terms. The rotational path that shows the most slowing down $\partial|E|/\partial\theta \approx$ (minimum) occurs around $\theta = 0.10$ rad. With the use of other basis set, i.e., $\gamma = 0.28$, and with other expansion lengths, we estimate the resonance energy E_r and width Γ for this state as -0.55245 ± 0.00020 and 0.0016 ± 0.0004 a.u., respectively. For practical purposes, we have not extended calculations beyond the use of $N = 2625$ terms. It should be also mentioned that this state lies above the $\mathrm{H}(1S) + \mathrm{Ps}(N = 2)$ threshold (with threshold energy of -0.5625 a.u.). The multichannel aspect of this state leads to the more difficult nature for calculations of such a state, and the subsequent larger estimated uncertainties for its resonance parameters.

IV. DISCUSSIONS AND SUMMARY

Table IV shows a comparison of the energies and widths for the *S*-wave resonances in Ps-H scattering, expressed in eV, with other calculations in the literature. The resonance energy is measured from the Ps-H threshold of -0.75 a.u., and a conversion factor of 1 a.u. $= 27.2116$ eV is used. In Table IV, the notations for different Rydberg states are those of Drachman [12]. In other words, the lowest resonance $S(1)$ is denoted as the $2S$ state in Drachman's notation. Similarly, the $S(2)$ and $S(3)$ resonances are called the $3S$ and $4S$ states, respectively. In Table IV, we also show Drachman's *S*-wave results that include the Feshbach shifts for comparison. It is seen that by including the coupling with the Ps-H continuum, the optical potential QHQ (eigenvalues of the closed space part of the Hamiltonian) results are shifted downward (negative shifts) to come closer to the complex-rotation results. The lowest $1S$ state has a large negative shift. The eigenvalue for the $1S$ state, obtained from the optical potential result, is 1.078 eV [12] above the Ps-H threshold. By including the interaction with continuum, the eigenvalue is shifted downward to lie below the threshold and to become the bound state of PsH. The magnitude of the shift decreases with increasing *n*. For example, the $2S$ state has a smaller shift, and that for the $3S$ state even smaller.

TABLE IV. Comparisons for resonance energies (relative to the Ps-H threshold) and widths (second entry inside the parentheses) for Ps-H scattering (in eV).

		Complex rotation		Optical potential Drachman [12]		
Resonance	State	Present results	Others	QHQ	QHQ +shfit	22-State approximation; Campbell *et al.* [17]
$S(1)$	$2S$	4.0058±0.0005	4.014±0.014[a]	4.076	4.0190	4.55
		(0.0952±0.0011)	(0.075±0.027)		(0.0303)	(0.084)
$S(2)$	$3S$	4.9479±0.0014	4.946[b]	5.010	4.996	
		(0.0585±0.0027)			(0.017)	
$S(3)$	$4S$	5.3757±0.0054	5.389[b]	5.410		
		(0.0435±0.011)				

[a] Reference [14].

[b] Reference [15].

When we compare our present complex-rotation results with those of Drachman's QHQ values, it is seen that the negative shifts for the $2S$, $3S$, and $4S$ states are 0.0702, 0.0621, and 0.0343 eV, respectively. Also from Table IV, it is seen that our present complex-rotation energy for the $2S$ state lies higher than that of the recent 22-state approximation [17]. The difference is about 0.54 eV. It is interesting to note that in Ref. [17], their PsH ground-state energy, obtained by using the 22-state approximation, lies higher than the variational calculation (Ref. [3] and the present calculation) with Hylleraas functions by about 0.43 eV.

In summary, we have carried out an investigation of S-wave resonances in Ps-H scattering. By using extensive Hylleraas functions, and with the use of the complex-rotation method, we have calculated the resonance parameters (both E_r and Γ) for the lowest three S-wave resonances. Our results are useful references for future work. It is hoped that they would stimulate experimental works to observe resonances in positronium-hydrogen scattering. Furthermore, we have also presented a calculation for the ground-state energy of PsH. Although there are no high-precision measurements reported so far for the PsH ground-state energy, with further advances in experiment, it would be very interesting to calculate lowest-order relativistic and QED corrections to the ground-state energy, together with finite nuclear mass corrections, up to orders $O(\mu/M)$, $O((\mu/M)^2)$, $O(\alpha^2)$, $O(\alpha^2\mu/M)$, $O(\alpha^3)$, and $O(\alpha^3\mu/M)$ a.u., where μ is the electron reduced mass, m the electron mass, M the nuclear mass, and α the fine-structure constant.

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