Variational calculation of ground-state energy of positronium negative ions

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The ground-state energy of positronium negative ions, Ps^-, is calculated using double-basis-set Hylleraas functions in which four nonlinear parameters are used. The optimized result of $E=-0.524\,010\,140\,465\,7$ Ry obtained by using 744-term function represents the lowest variational energy for Ps^- in the literature to date to our knowledge. The wave function is then used to calculate the positron annihilation rate for Ps^-.

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Recently there has been considerable interest in precision calculations of the ground-state energy of positronium negative ions, Ps^-. A positronium negative ion is a three-body atomic system interacting via Coulomb forces. Calculations on the ground-state (the only known bound state) energy has attracted considerable interest ever since the early work of Wheeler [1]. From the experimental side, positronium negative ions have been observed in the laboratory by Mills [2]. The observation opens up possibilities to study various properties of this purely leptonic system. For example, the positron-annihilation rate for Ps^- was determined in the laboratory [3], and was found to be in good agreement with the theoretical decay rates [4,5]. Progress has been made to try to improve the measurement of the annihilation rate in the laboratory [6].

From the theoretical side, there has been a long history of theoretical investigations of ground-state energy of Ps^-. For earlier developments of theoretical calculations readers are referred to reviews on studies of this system [7–9]. The latest investigations include variational calculations using Hylleraas functions [10] and exponential variational functions [11,12], and a nonvariational calculation using hyperspherical harmonic functions [13]. The most accurate value for the ground-state energy in the literature was obtained by using 900-term variable exponential functions [12]. The error estimate of the ground-state energy is about 10^{-12} Ry [11]. This compares with the error of about 10^{-10} Ry when a 946-term Hylleraas function was used [10]. Such a difference in accuracy raises an interesting theoretical question about whether the use of Hylleraas functions would be capable of producing ground-state energy with an accuracy within errors of less than 10^{-12} Ry. In order to improve calculations using Hylleraas functions, we have to understand the shortcomings of employing the traditionally used single-basis expansion set. By using one set of nonlinear parameters, the wave function is forced to be well represented in one region in the configurational space. Apparently if we are interested in an extremely precise value of the ground-state energy, the wave function must be accurately represented in all regions, including the highly correlated inner region and the outer asymptotic region. From the computational aspect, the use of a single-basis set of Hylleraas functions may also have the well-known ill-conditioned numerical difficulties. When the basis set is sufficiently large, any additional terms may behave in the numerical sense linearly dependent of previously used terms. This would create numerical singularity in the process of solving eigenvalue problems.

In a related development of precision calculations of helium energy levels [14,15], double-basis sets of Hylleraas functions were used. By using two distinctive sets of nonlinear parameters, the wave function in the inner and outer asymptotic regions were well represented. Drake was able to obtain extremely accurate energy levels of helium atoms [16]. The estimated errors of energy levels in helium were found to improve by about a factor of 1000 when double-basis-set functions were used, as compared with the use of the usual single-basis sets. Furthermore, the use of double-basis sets would diminish the ill-conditioned numerical difficulties in using Hylleraas functions. Since the two basis sets divide the wave function into two well-separated configurational spaces, they are hence numerically independent of each other.

In the present calculation double-basis sets of Hylleraas functions with four nonlinear parameters are used to calculate the ground-state energy of Ps^-. Up to 744 terms are used. The use of optimized wave functions enables us to obtain the lowest variational energy of Ps^- to date. The wave functions are also used to calculate the positron annihilation rate as well as expectation values of various interparticle distances.

The Hamiltonian of the positronium negative ion is

$$H=-\frac{1}{m_1}\nabla_1^2-\frac{1}{m_2}\nabla_2^2-\frac{1}{m_p}\nabla_p^2+\frac{2q_1q_p}{r_{1p}}+\frac{2q_2q_p}{r_{2p}}+\frac{2q_1q_2}{r_{12}}\,, \tag{1}$$

where 1, 2, and p denote the electrons 1, 2, and positron, respectively; m_i and q_i are the mass and charge, respectively, for particle i; and r_{ij} represents the distance between particles i and j. Atomic units are used in this work, with energy expressed in rydbergs. Hylleraas-type wave functions of the form

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$$\Psi=\sum_{\substack{l\geq m\geq 0\\ k\geq 0}} C_{klm}\exp(-\alpha_1 r_{1p}-\beta_1 r_{2p})r_{12}^k(r_{1p}^l r_{2p}^m+r_{1p}^m r_{2p}^l)$$
$$+\sum_{\substack{l\geq m\geq 0\\ k\geq 0}} D_{klm}\exp(-\alpha_2 r_{1p}-\beta_2 r_{2p})r_{12}^k$$
$$\times(r_{1p}^l r_{2p}^m+r_{1p}^m r_{2p}^l) \quad (2)$$

are employed to represent the system, where $(k+l+m)\leq\omega$, with k, l, m, and ω being positive integers or zero.

One of the experimentally interesting parameters is the annihilation rate Γ given in units of ns^{-1},

$$\Gamma=2\pi\alpha^4\left[\frac{c}{a_0}\right]\left[1-\alpha\left[\frac{17}{\pi}-\frac{19\pi}{12}\right]\right]\frac{\langle\Psi|\delta(r_1-r_p)|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$
$$=100.617\,480\,9\langle\delta_{1p}\rangle\ . \quad (3)$$

In Eq. (3), the correction term proportional to α is due to the triplet lifetime [17] and the leading radiative correction to the singlet lifetime [18]. Absent in Eq. (3) are bound-state and relativistic effects, which have not yet been calculated.

The qualities of the wave functions can be tested by calculating the electron-positron and electron-electron cusp values. For a system interacting through Coulomb forces, $H\Psi/\Psi=E$ has a constant value for exact wave function Ψ. However, if Ψ is inexact, $H\Psi/\Psi$ is singular when $r_{ij}\to 0$ [19]. In order to have the singularities cancelled [20], the terms involving r_{ij}^{-1} in Eq. (1) would satisfy the following condition:

$$\left[\frac{2}{r_{ij}}\right]\left[-\left[\frac{1}{m_i}+\frac{1}{m_j}\right]\frac{\partial}{\partial r_{ij}}+q_i q_j\right]|\Psi\rangle=0\ . \quad (4)$$

This leads to the cusp condition

$$\left[-\frac{\partial}{\partial r_{ij}}+\mu_{ij}q_i q_j\right]|\Psi\rangle=0\ . \quad (5)$$

We multiply by $\langle\Psi|$ and let $r_{ij}\to 0$, and taking the average over the coordinates that do not involve r_{ij}, we obtain the integral form of the cusp condition between particles i and j [21,22]:

$$\left\langle\Psi\left|\delta(r_{ij})\frac{\partial}{\partial r_{ij}}\right|\Psi\right\rangle[\langle\Psi|\delta(r_{ij})|\Psi\rangle]^{-1}=q_i q_j\mu_{ij}\equiv\nu_{ij}\ , \quad (6)$$

where μ_{ij} is the reduced mass for particles i and j. The exact values for ν_{12} and ν_{1p} are $+0.5$ and -0.5, respectively. The present calculations have been performed using quadrupole-precision arithmetic (about 30 digits) on an IBM 3090.

Table I shows the convergence behavior for the ground-state energy of Ps^- when different expansion lengths for the wave functions are used. The nonlinear parameters are optimized for a given N. The optimized nonlinear parameters α_1 and β_1 for the first basis set are found to have nearly constant values of 0.5 and 0.3, respectively, throughout all the expansion sets used in Table I. It is seen that this basis set represents the outer asymptotic region of the wave function. The second expansion sets are found to have much larger optimized nonlinear parameters. The values of α_2 and β_2 are found nearly equal to each other, and they increase from about 0.84 to 1.5 as ω is increased from $\omega=9$ to 14. The second basis set hence represents the highly correlated inner part of the wave function. It is evident that the two optimized sets of basis do represent different regions of the wave function in the configurational space, and the computational difficulties due to the ill-conditioned aspect of using Hylleraas functions are also reduced.

The results shown in Table I also indicate that convergence is quite fast. The optimized 406-term function already produces the ground-state energy value that is lower than that obtained in Ref. [10] in which a single-basis 946-term Hylleraas function was used. Also, the present optimized 616-term function is capable of producing a result which is lower than that in Refs. [11] and

TABLE I. Convergence behavior for the ground-state energy of Ps^-. The nonlinear parameters are optimized for a given N. The digits inside the parentheses in E_{ext} represent the uncertainty of the last digits quoted.

N	ω	α_1	β_1	α_2	β_2	E (Ry)
						Present calculation
250	9	0.490	0.292	0.84	0.83	−0.524 010 140 201 76
322	10	0.499	0.298	0.927	0.93	−0.524 010 140 403 81
406	11	0.501	0.298	1.096	1.10	−0.524 010 140 452 77
504	12	0.503	0.298	1.295	1.295	−0.524 010 140 462 70
616	13	0.502	0.298	1.38	1.38	−0.524 010 140 465 14
744	14	0.503	0.298	1.505	1.505	−0.524 010 140 465 71
E_{ext}						−0.524 010 140 465 88(17)
						Other calculations
						−0.524 010 116[a]
						−0.524 010 140 464[b]
						−0.524 010 140 41[c]

[a]References [13].
[b]References [11,12].
[c]Reference [10].

TABLE II. Expectation values of various functions involving interparticle distances.

Ref.	$\langle\delta(r_{1p})\rangle$	ν_{1p}	$\langle r_{1p}\rangle$	$\langle r_{1p}^2\rangle$	$\langle r_{1p}^{-1}\rangle$	$\langle(r_{1p}r_{2p})^{-1}\rangle$
Present calculation[a]	0.020 733 198 0	−0.500 000 20	5.489 633 252	48.418 937 2	0.339 821 023 06	0.090 935 346 528 9
[10][b]	0.020 733 302 3	−0.500 02	5.489 631 88	48.418 842 7	0.339 821 03	0.090 935 35
[11][c]	0.020 733 190	−0.499 997 08	5.489 633 2525	48.418 937 227	0.339 821 023 05	0.090 935 346 42
[13][d]	0.020 733 02	−0.5	5.488 81	48.390	0.339 827 8	
	$\langle\delta(r_{12})\rangle$	ν_{12}	$\langle r_{12}\rangle$	$\langle r_{12}^2\rangle$	$\langle r_{12}^{-1}\rangle$	$\langle(r_{12}r_{1p})^{-1}\rangle$
Present calculation[a]	1.709 971 5[−4][e]	0.499 977 3	8.548 580 655	93.178 633 80	0.155 631 905 653	0.060 697 690 295
[10][b]	1.710 105[−4]	0.499 68	8.548 577 94	93.178 445 6	0.155 631 91	0.060 697 69
[11][c]	1.709 985 0[−4]	0.499 929 3	8.548 580 655	93.178 633 849	0.155 631 905 65	0.060 697 690 32
[13][d]	1.710 131[−4]		8.546 99	93.121	0.155 643 6	

[a]744-term Hylleraas function, double-basis set.
[b]Ho [10], 946-term Hylleraas functions, single-basis set.
[c]Frolov [11], 800-term exponential variational expansion.
[d]Krivec *et al.* [13], 225 hyperspherical functions.
[e]Results shown in this column $A\,[-B]$ implies $A\times10^{-B}$.

[12], in which up to 900-term exponential variational functions were used. It seems that the explicit optimization of the four nonlinear parameters used in the present calculation has an advantage over the use of exponential variational functions in which the nonlinear parameters have been generated randomly. Our present result obtained using the optimized 744-term function represents the lowest variational ground-state energy of Ps^- to date, to our knowledge. In Table I we also show the extrapolated energy value obtained by using the formula [23]

$$E_{\rm ext}=E_1+\frac{(E_1-E_0)(E_2-E_1)}{2E_1-E_0-E_2}\ , \tag{7}$$

where E_0, E_1, and E_2, are the energy eigenvalues obtained by using the 504- ($\omega=12$), 616- ($\omega=13$), and 744- ($\omega=14$) term wave functions, respectively. We obtain the extrapolated energy as

$$E_{\rm ext}=-0.524\,010\,140\,465\,88\ \text{Ry}\ .$$

In comparing with the 744-term result, we estimate that the uncertainty in our calculation is within 1.7×10^{-13} Ry. A comparison of the ground-state energy of Ps^- with other recent calculations is shown in Table I. Earlier results can be found in Ref. [10].

Once the energy-minimized wave functions are obtained, they are used to calculate $\langle\delta_{1p}\rangle$ and then the positron annihilation rate Γ, by using Eq. (3). We obtain a value of 0.020 733 198 0 for $\langle\delta_{1p}\rangle$ by using the 744-term wave function. Results are shown in Table II. This compares with Frolov's value of 0.020 733 190 [11]. Our positron annihilation rate is determined as $2.086\,122\,2\pm5\times10^{-7}$. The uncertainty is estimated by calculating the results using the 504-, 616-, and the 744-term wave functions. Frolov [11] has obtained a value of 2.086 121, and Krivec, Haftel, and Mandelzweig [13] have determined a rate of 2.08610±0.000 06 using a nonvariational approach. We summarize the recent calculations of the positron annihilation rate in Table III. Earlier calculations can be found in Ref. [10].

To test the quality of our wave functions, we have also calculated the positron-electron and electron-electron cusp values. Results for ν_{1p} and ν_{12} are shown in Table II. For the 744-term wave function we obtain $\nu_{1p}=-0.500\,000\,20$ and $\nu_{12}=0.499\,977\,3$. These values are compared with the exact values of −0.5 and 0.5, respectively. Our best cusp values lie slightly closer to the exact ones than those of Frolov [11], who obtained −0.499 997 08 and 0.499 929 3 for ν_{1p} and ν_{12}, respectively. Our good results for cusp values in the integral form indicate that our 744-term wave function is quite accurate in the overall configurational space.

In this work we also use the optimized wave functions to calculate expectation values of various functions involving interparticle distances. The results involving r_{1p} and r_{12} are shown in Table II. Comparisons with recent calculations are also shown in Table II. In general, our results agree very well with those of Frolov [11]. Earlier calculations of the expectation values of interparticle distances can be found in Ref. [10].

TABLE III. Positron annihilation rate in Ps^- calculated by using Eq. (3).

Author	Γ (nsec^{-1})	ν_{1p}
Ho [10] (946-term Hylleraas function)	2.086 13	−0.500 02
Frolov [11] 800-term exponential variational expansion	2.086 121	−0.499 997 08
Krivec *et al.* [13] 225 hyperspherical functions	2.086 10 ±0.000 06	−0.5
Ho (present calculation) 744-term Hylleraas functions, double-basis set	2.086 122 2 $\pm5\times10^{-7}$	−0.500 000 20
Mills [3] experiment	2.09±0.09	

In summary, we have carried out an elaborate calculation of ground-state energy of positronium ions. By using double-basis four-parameter Hylleraas functions with up to 744 terms, we have obtained the lowest ground-state energy to date. The optimized wave functions are then used to evaluate the positron annihilation rate as well as expectation values of various functions involving inter-particle distances. It is hoped that these results will motivate further experimental activities to improve the measurement of the positron annihilation rate, which in turn will provide a stringent test on further theoretical investigations of the corrections due to bound-state and relativistic effects.

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