# Hartree-Fock calculations for the positronium negative ion Ps⁻

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## Abstract

The total energy and several properties of the ground state of the positronium negative ion Ps⁻, obtained using the Hartree-Fock calculations, are presented. Calculations were performed using the restricted Hartree-Fock (RHF) and the spin extended Hartree-Fock (SEHF) methods. The total energies obtained from the RHF and the SEHF calculations are –0.24396487 hartree and –0.25691975 hartree, respectively. The RHF energy is higher than the ground state energy of the positronium (–0.25 hartree). The RHF method provides qualitatively incorrect ground state energy for the Ps⁻. As for the electron-positron pair annihilation rate, the RHF and the SEHF calculations yield $1.4582933 \times 10^{9} s^{-1}$ and $1.8975601 \times 10^{9} s^{-1}$, respectively. Compared with the electron-positron pair annihilation rate calculated by Frolov [Phys. Rev. A**60**, 2834 (1999)], the respective values are 69.9% and 91.0% of Frolov's value.

## 1. INTRODUCTION

The positronium Ps is the bound state of one electron and one positron. Ps forms the positronium negative ion Ps⁻ by capturing one electron. Ps⁻ was experimentally detected by Mills in an experiment is 1981.[1] Mills also measured the electron-positron pair annihilation rate, which is $(2.09 \pm 0.09) \times 10^{9} s^{-1}$.[2]

Quantum mechanical calculations for Ps⁻ have been carried out using methods with explicitly correlated functions (ECFs) because Ps⁻ is a three-body system. The ECF methods can provide highly accurate results. Hyllerass calculations were performed by Bhatia and Drachman[3] and Ho[4-6]. Krivec et al. calculated using the hyperspherical method.[7] Frolov used the variational methods with explicitly correlated exponential functions and obtained highly accurate results.[8-11] Varga et al. calculated using the stochastic variational method.[12] As far as we known, the most accurate energy

and properties were obtained by Frolov[11]. The electron-positron pair annihilation rates given from those calculations are in good agreement with the experimental value[2].

Until now, the Hartree-Fock (HF) and configuration interaction (CI) methods have not been employed for quantum mechanical calculations of Ps⁻. The HF and CI methods which are based on orbitals are standard methods for quantum mechanical calculations of atomic systems. Therefore, it is interesting to evaluate the ability of the HF and CI methods for Ps⁻. The electron-positron correlation effects are very important for the quantum mechanical calculations of electronic systems with positrons. Although the HF method is a simple one, it is possible to perfectly include electron-positron correlation effects in the calculations of Ps⁻. Hence, the HF calculation for Ps⁻ is very interesting. In this work, we performed the HF calculations for the ground state of Ps⁻, and by doing so, evaluated the ability of the HF method.

There are several variants of the HF method. In this work, we used the restricted HF (RHF) and the spin extended HF (SEHF) methods. The RHF method constrains to have the same spatial function for electrons with $\alpha$ and $\beta$ spins. The SEHF method treats spin symmetry adapted wave functions which have different spatial functions for electrons with $\alpha$ and $\beta$ spins. The SEHF method was introduced by Löwdin[13] and was developed by Goddard[14] and Kaldor[15]. The SEHF method has the advantage of including the electron-electron radial correlation effect.

The electron orbitals centered on the positron are expanded with some basis functions. The basis function used for the present calculations is the $B$-spline set. The $B$-splines of order $K$, $\{B_{i,K}(r)\}$, are piecewise polynomials of degree $K-1$ on a knot sequence in a cavity of radius $R$.[16,17] The advantage of $B$-splines is that they are very flexible and are relatively free from computational linear dependence. Hence, the errors caused by incompleteness of the basis function are very small.

Section 2 formulates the theoretical method. Section 3 gives computational details for RHF and SEHF wave functions. Section 4 compares our results with the values obtained by the accurate calculation. This section also includes perspectives for future studies of Ps⁻.

## 2. THEORETICAL ASPECTS

The total Hamiltonian of Ps⁻ in atomic unit is written as

$$H_{\text{total}} = -\frac{1}{2}\nabla_0^2 - \frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - r_{01}^{-1} - r_{02}^{-1} + r_{12}^{-1}, \tag{1}$$

where the positron refers to 0, and the electrons refer to 1 and 2. We introduce the center-of-mass coordinate $\boldsymbol{R}$ and the relative coordinates $\boldsymbol{r}_{01}$ and $\boldsymbol{r}_{02}$ as follows:

$$\mathbf{R} = \frac{1}{3}(\mathbf{r}_0 + \mathbf{r}_1 + \mathbf{r}_2) \tag{2}$$

$$\mathbf{r}_{01} = -\mathbf{r}_0 + \mathbf{r}_1 \tag{3}$$

$$\mathbf{r}_{02} = -\mathbf{r}_0 + \mathbf{r}_2 . \tag{4}$$

By separating the center-of-mass motion from $H_{\text{total}}$, the Hamiltonian for the relative motion is obtained:

$$H = -\nabla_1^2 - \nabla_2^2 - \nabla_1 \cdot \nabla_2 - r_1^{-1} - r_2^{-1} + r_{12}^{-1} . \tag{5}$$

The index 0 is omitted from Eq.(5) because the positron is fixed on the origin of the relative coordinate. The third term of Eq.(5) is the mass polarization term.

The HF wave function of Ps⁻ is

$$\Psi = [A(\mathbf{r}_1)B(\mathbf{r}_2) + (-1)^S B(\mathbf{r}_1)A(\mathbf{r}_2)]\Theta_M^S , \tag{6}$$

where $A$ and $B$ are orbitals of electrons, and $\Theta_M^S$ is the spin eigenfunction for two-electron systems. The orbital of electrons is the product of the radial orbital and the spherical harmonics: $A = a(r)Y_{l_A}^{m_A}(\theta, \varphi)$ and $B = b(r)Y_{l_B}^{m_B}(\theta, \varphi)$. Because $a$ and $b$ are functions of $r$, the HF method can include the electron-positron correlation effects perfectly. In case of $A = B$ and $A \neq B$, Eq.(6) is the RHF and the SEHF wave function, respectively. Accordingly, the SEHF method can include the electron-electron radial correlation effect. The electron radial functions $a$ and $b$ are expanded with basis functions $\phi_i$:

$$a = \sum_i C_i^a \phi_i \tag{7}$$

and

$$b = \sum_i C_i^b \phi_i . \tag{8}$$

The coefficients $C_i^a$ and $C_i^b$ are variationally determined. A set of equations for these coefficients is derived by minimizing the functional

$$\mathcal{L} = E - \lambda_a(\langle a|a \rangle - 1) - \lambda_b(\langle b|b \rangle - 1) \tag{9}$$

with respect to $a$ and $b$. Here, $\lambda_a$ and $\lambda_b$ are Lagrange multipliers, and $E$ is the total energy

$$E = \frac{\langle \Psi|H|\Psi \rangle}{\langle \Psi|\Psi \rangle} . \tag{10}$$

By setting the first variation in $\mathcal{L}$ equal to zero, the following equations are obtained:

$$\sum_j \langle \phi_i b | H - E | \phi_j b + (-1)^S b \phi_j \rangle C_j^a = \epsilon_a \sum_j \langle \phi_i | \phi_j \rangle C_j^a \tag{11}$$

and

$$\sum_j \langle a\phi_i | H - E | a\phi_j + (-1)^S \phi_j a \rangle C_j^b = \epsilon_b \sum_j \langle \phi_i | \phi_j \rangle C_j^b , \tag{12}$$

where $\epsilon_a$ and $\epsilon_b$ are new Lagrange multipliers. Eqs.(11) and (12) must be solved by the self-consistent field procedure.

The mass polarization operator in Eq.(5) can be written as

$$\boldsymbol{\nabla}_1 \cdot \boldsymbol{\nabla}_2 = \frac{1}{2} (\boldsymbol{\nabla}_{1+} \cdot \boldsymbol{\nabla}_{2-} + \boldsymbol{\nabla}_{1-} \cdot \boldsymbol{\nabla}_{2+}) + \frac{\partial}{\partial z_1} \cdot \frac{\partial}{\partial z_2} \tag{13}$$

with

$$\boldsymbol{\nabla}_\pm = \frac{\partial}{\partial x} \pm i \frac{\partial}{\partial y} , \tag{14}$$

where $i = \sqrt{-1}$ . In the spherical coordinate, these operators are rewritten as

$$\boldsymbol{\nabla}_\pm = \sqrt{\frac{8\pi}{3}} Y_1^{\pm 1} \left( \mp \frac{\partial}{\partial r} + l_z \right) + \sqrt{\frac{4\pi}{3}} r^{-1} Y_1^0 l_\pm \tag{15}$$

and

$$\frac{\partial}{\partial z} = \sqrt{\frac{4\pi}{3}} Y_1^0 \frac{\partial}{\partial r} - \sqrt{\frac{2\pi}{3}} r^{-1} (Y_1^{-1} l_+ - Y_1^1 l_-) , \tag{16}$$

where $l_+$ and $l_-$ are angular momentum ladder operators. Acting operators (15) and (16) on an atomic orbital $a(r)Y_l^m(\theta, \varphi)$, the following formulas can be obtained:

$$\boldsymbol{\nabla}_\pm a(r)Y_l^m(\theta, \varphi) = \pm \sqrt{\frac{(l \pm m + 1)(l \pm m + 2)}{(2l + 1)(2l + 3)}} \left( \frac{da}{dr} - l r^{-1} a \right) Y_{l+1}^{m\pm 1}$$

$$\mp \sqrt{\frac{(l \mp m - 1)(l \mp m)}{(2l - 1)(2l + 1)}} \left( \frac{da}{dr} + (l + 1)r^{-1}a \right) Y_{l-1}^{m\pm 1} \tag{17}$$

and

$$\frac{\partial}{\partial z} a(r)Y_l^m(\theta, \varphi) = \sqrt{\frac{(l - m + 1)(l + m + 1)}{(2l + 1)(2l + 3)}} \left( \frac{da}{dr} - l r^{-1} a \right) Y_{l+1}^m$$

$$+ \sqrt{\frac{(l - m)(l + m)}{(2l - 1)(2l + 1)}} \left( \frac{da}{dr} + (l + 1)r^{-1}a \right) Y_{l-1}^m . \tag{18}$$

In this work, matrix elements for the mass polarization vanish because HF wave functions of Ps⁻ are constructed with only *s*-orbitals.

## 3. COMPUTATIONAL ASPECTS

The ground state of Ps⁻ is ${}^1$S, and hence our wavefunction becomes

$$\Psi = \frac{1}{4\pi}\,[a(r_1)b(r_2) + b(r_1)a(r_2)]\Theta_0^0 \tag{19}$$

with

$$\Theta_0^0 = \frac{1}{\sqrt{2}}\,[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\;. \tag{20}$$

Electron radial orbitals of the RHF and SEHF wave functions are expanded with *B*-spline sets which consist of *N*-term *K*th-order *B*-splines on a knot sequence defined on an interval $[0, R]$. The exponential knot sequence was used with endpoints of *K*-fold multiplicity. Because the first and last terms of the *B*-splines with *K*-fold multiplicity are nonzero at $r = 0$ and $r = R$, respectively, the *N*-term *B*-spline set was constructed omitting them, in order to satisfy the boundary conditions. The parameters *N* and *K* of the *B*-spline sets were $N = 100$ and $K = 9$. The knot sequences were constructed of the initial interval $R_1 = 10^{-4}$ and $R = 90, 100, 110, 120,$ and $130$ au.

Eqs.(11) and (12) are solved by the self-consistent field procedure. Accordingly, it is important to prepare appropriate initial orbitals. We first calculated the total energy using single exponential functions $e^{-\zeta r}$, and obtained nonlinear parameters $\zeta$ which minimize the total energy. We then obtained coefficients of *B*-spline expansions which reconstructed the optimized $e^{-\zeta r}$ by solving the following equation:

$$\left(-\frac{1}{2\mu}\frac{d^2}{dr^2} - \frac{\zeta}{\mu}r^{-1}\right)\sum_i C_i B_{i,K}(r) = \epsilon \sum_i C_i B_{i,K}(r) \tag{21}$$

where $\mu$ is the reduced mass of the electron and the positron, i.e. $\mu = 0.5$. We employed coefficients obtained from Eq.(21) as the initial coefficients $C_i^a$ and $C_i^a$ to calculate Eqs.(11) and (12) self-consistently.

We calculated the averaged inter-particle distances $\langle r_1\rangle$ and $\langle r_{12}\rangle$, the virial ratio $\eta$, the electron-positron cusp $\nu_{\mathrm{ep}}$, and the electron-positron pair annihilation rate $\Gamma$ by using RHF and SEHF wave functions. The virial ratio $\eta$ is defined as

$$\eta = -\frac{\langle V\rangle}{\langle T\rangle}\;, \tag{22}$$

where $\langle V \rangle$ and $\langle T \rangle$ are the expectation values of the potential and kinetic energy, respectively. The exact virial ratio is 2. The electron-positron cusp $\nu_{ep}$ is calculated by

$$\nu_{ep} = -\frac{1}{2} \frac{d \log \rho(r)}{dr} \Bigg|_{r=0} , \tag{23}$$

where $\rho$ is the spherical averaged electron density. The exact $\nu_{ep}$ value is $\frac{1}{2}$. The electron-positron pair annihilation rate is

$$\Gamma = 2\pi\alpha^4 \frac{c}{a_0} \left[ 1 - \alpha\left(\frac{17}{\pi} - \frac{19\pi}{12}\right) \right] \frac{\langle \Psi | \delta(\boldsymbol{r}_1) | \Psi \rangle}{\langle \Psi | \Psi \rangle} , \tag{24}$$

where $\delta$ is Dirac's delta function, $\alpha$ is the fine structure constant, $c$ is the speed of light, and $a_0$ is the Bohr radius. Eq.(24) includes the triplet lifetime[18] and a radiative correction for the singlet lifetime[19].

## 4. RESULTS AND DISCUSSION

For the ground state of Ps⁻, we performed both the RHF and SEHF calculations. The total energy and several expectation values were calculated by using the obtained wave functions. We obtained 8-digit results from all calculations.

First, let us compare the results given by the RHF and SEHF methods. Table 1 shows the total energy and the electron-positron annihilation rate of the ground state of Ps⁻. The total energy obtained from the RHF calculation is higher than that of Ps. The RHF method results in a qualitatively incorrect total energy for Ps⁻. On the contrary, the SEHF method gives the total energy which is lower than that of Ps. That is the reason why the electron-electron radial correlation effect is introduced. The electron-positron pair annihilation rate is also improved by introducing the electron-electron radial correlation effect. Therefore, it is important for Ps⁻ to include the electron-electron correlation effects as well as the electron-positron correlation effects.

Table 1.  Total energy ($E$) and electron-positron pair annihilation rate ($\Gamma$) of Ps⁻.

|  | $-E$ (hartree) | $\Gamma$ ($10^9 \text{s}^{-1}$) |
|---|---|---|
| RHF | 0.24396487 | 1.4582933 |
| SEHF | 0.25691975 | 1.8975601 |

The RHF and SEHF calculations were carried out by using $B$-spline sets with $R$ = 90, 100, 110, 120, and 130. The total energy and the expectation values obtained from RHF calculations are independent of $R$ within a range of $R$ under consideration. SEHF calculations yield the results which

depend on values of $R$. Table 2. summarizes the total energy, the virial ratio, the averaged inter-particle distances $\langle r_1 \rangle$ and $\langle r_{12} \rangle$, the electron-positron cusp value, and the electron-positron pair annihilation rate given by SEHF calculations for each value of $R$. The total energy for $R = 110, 120$, and 130 is the lowest value. The virial ratios for $R = 120$ and 130 exhibit 8-digit accuracy. Hence, the $B$-spline set with $R < 110$ is unsuitable for Ps⁻ calculations. This shows that Ps⁻ is a very defuse system. The electron-positron cusp value given by the $B$-spline set with $R = 120$ is in agreement to 8-digits of the exact value. Consequently, the 100-term $B$-spline set with $R = 120$ is suitable for the SEHF calculation of Ps⁻.

Table 2. Total energy ($E$), virial ratio ($\eta$), averaged inter-distances ($\langle r_1 \rangle$ and $\langle r_{12} \rangle$), electron-positron cusp value ($v_{ep}$), and electron-positron pair annihilation rate ($\Gamma$) given by SEHF calculations for each value of $R$.

| $R$ (au) | 90 | 100 | 110 | 120 | 130 |
|---|---|---|---|---|---|
| $-E$ (hartree) | 0.25691973 | 0.25691974 | 0.25691975 | 0.25691975 | 0.25691975 |
| $\eta$ | 1.9999992 | 1.9999999 | 2.0000000 | 2.0000000 | 2.0000000 |
| $\langle r_1 \rangle$ (au) | 6.2352184 | 6.2353969 | 6.2354380 | 6.2354473 | 6.2354493 |
| $\langle r_{12} \rangle$ (au) | 10.053512 | 10.053864 | 10.053946 | 10.053964 | 10.053968 |
| $v_{ep}$ | 0.49999997 | 0.49999997 | 0.49999998 | 0.50000000 | 0.49999994 |
| $\Gamma$ ($10^9 \text{s}^{-1}$) | 1.8975596 | 1.8975599 | 1.8975600 | 1.8975601 | 1.8975601 |

We compare our results with highly accurate ones given by Frolov[10] below. Table 3 summarizes the total energy, the ionization potential (IP), the averaged inter-particle distances $\langle r_1 \rangle$ and $\langle r_{12} \rangle$, and the electron-positron pair annihilation rate given by RHF, SEHF, and Frolov[10]. Although Frolov's results published in 2007[11] are the most accurate, we compare our results with Frolov's results published in 1999[10] because they are in agreement to an 8-digit accuracy each other. To calculate ionization potentials, the conversion factor 27.2113961 eV/hartree is employed.

For the total energy, the SEHF calculation gives 98.1% of Frolov's total energy. Although it is a simple method, the results of the total energy value are very reasonable. The difference between SEHF and Frolov's total energies is 0.00508520 hartree; this is caused by a lack of the electron-electron angular correlation effect. Although the RHF calculation yields 93.1% of Frolov's total energy, the RHF ionization potential is a negative value because the ionization potential is small.

For the electron-positron pair annihilation rate, the RHF and SEHF calculations yield 69.9% and 91.0% of Frolov's value, respectively. The SEHF method gives considerably good values for the electron-positron pair annihilation rate. Compared with the RHF value, the electron-electron

radial correlation effect improves the electron-positron pair annihilation rate by 20.1% of Frolov's value. Hence, the electron-electron correlation effects are also important in calculating an accurate electron-positron pair annihilation rate.

For the averaged inter-particle distances, the RHF method underestimates both of $\langle r_1 \rangle$ and $\langle r_{12} \rangle$. On the contrary, the SEHF method overestimates both the values. The errors of RHF calculations are smaller than those of SEHF calculations. Although the RHF and SEHF wave functions include the electron-positron distances, calculations of $\langle r_1 \rangle$ need to include electron-electron correlation effects.

Based on the above discussion, we conclude that introducing the electron-electron radial correlation effect is important for calculations in obtaining the accurate total energy and expectation values. The total energy and the expectation values are further improved by introducing the electron-electron angular correlation effect. Therefore, it is of particular interest to estimate the contributions to the total energy and the expectation values from higher angular momentum orbitals in the CI calculation.

Table 3. Total energy ($E$), ionization potential (IP), averaged inter-particle distances ($\langle r_1 \rangle$ and $\langle r_{12} \rangle$), and electron-positron pair annihilation rate ($\Gamma$) given by RHF, SEHF, and Frolov.

|  | $-E$ (hartree) | IP (eV) | $\langle r_1 \rangle$ (au) | $\langle r_{12} \rangle$ (au) | $\Gamma$ ($10^9 \mathrm{s}^{-1}$) |
|---|---|---|---|---|---|
| RHF[1] | 0.24396487 | −0.16422431 | 5.0079193 | 7.4785480 | 1.4582933 |
| SEHF[1] | 0.25691975 | 0.18829606 | 6.2354473 | 10.053964 | 1.8975601 |
| Frolov[2] | 0.2620050702329757 | 0.326674721 | 5.48963325238 | 8.54858065516 | 2.086122114 |

[1] This work.

[2] Reference 10.

Although we tried to calculate the $^3$S state of Ps$^-$, we could not obtain an energetically stable root. Because electron spin multiplicity is a triplet, the electron-electron correlation energy may be small. Hence, calculations that considered the electron-electron correlation effects may also result in energetically unstable roots. However, it is expected that electronic triplet spin states of Ps$^-$ may stabilize on white dwarfs and neutron stars (i.e. Ps$^-$ in strong magnetic fields) because magnetic fields lower energies of high spin states. It is our continued interest to calculate total energies and electron-positron pair annihilation rates for high spin states of Ps$^-$ in strong magnetic fields. The study of Ps$^-$ in strong magnetic fields and CI calculations for the ground state of Ps$^-$ are in progress.

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