Bound-state properties of the positronium negative ion Ps^-

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Various geometrical and energetical (bound-state) properties of the positronium negative ion (Ps^- or $e^-e^+e^-$) are determined by using highly accurate variational wave functions. These wave functions have been constructed by applying the advanced two-stage strategy proposed by Frolov [Phys. Rev. A **57**, 2436 (1998)]. The determined total energy of the ground state $E=-0.262\ 005\ 070\ 232\ 975\ 7$ a.u. is the lowest and most accurate value obtained for this system to date (the corresponding binding energy equals $-0.326\ 674\ 721\ 317\ 821$ eV). The computation of the second-order relativistic corrections ($\simeq\alpha^2$) to the total energy is discussed also. The general form of the Breit-Pauli Hamiltonian in the relative coordinates for the Ps^- ion is presented. [S1050-2947(99)04910-0]

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In our previous work [2] published a few years ago, the results of highly accurate calculations for some properties in the Ps^- ion have been reported. Recently, however, significant progress has been made in performing such calculations. In particular, the advanced two-stage procedure proposed in [1] produces extremely accurate wave functions for various three-body systems. As a result, the final accuracy of highly accurate, three-body, bound-state calculations has been increased drastically. In general, such wave functions give us additionally two to three correct significant decimal figures in the total energy. Also, our present knowledge about the bound-state properties in three-body (and four-body) systems is far beyond the level that we had even four years ago. Finally, now we can compute significantly more bound-state properties and compare them with the expected or predicted values. Furthermore, the whole system of independent tests can be used today in order to check these properties and find more appropriate definitions for them.

On the other hand, the Ps^- ion is of increasing interest for theoretical studies and various applications. For instance, a complete theoretical analysis of the one-photon annihilation in this system has been made recently [3–7] (see also [1]). It was shown that the probability of this process is determined by the expectation value of the three-particle δ function (i.e., $\langle\delta_{321}\rangle$). In many similar studies, the knowledge of other bound-state properties for the Ps^- ion is critically important (see, e.g., [8]). Another example is the present work, where we discuss the second-order relativistic corrections to the ground-state energy of the Ps^- ion. This requires numerical calculations of expectation values of some specific operators (see below). Actually, one of the goals of this work is to compute a large number of nonrelativistic properties for the Ps^- ion. In principle, our present study can be considered as a ''nonrelativistic basis'' for future relativistic considerations.

It should be mentioned that the stability of the Ps^- ion was demonstrated for the first time by Wheeler [9] and Hylleraas [10]. Today, there are a few hundred publications which deal with various properties of this system. But in a paper of this size it is clearly impossible to discuss every aspect or property of the Ps^- ion. Presently, we restrict ourselves only to the discussion of works which contain the results of highly accurate bound-state calculations. Note that the first highly accurate calculations have been stimulated by earlier theoretical studies for the Ps^- ion performed by Ho and Bhatia and Drachman [11–13]. In particular, these papers as well as the two experimental works by Mills [14] have stimulated my own interest in the study of the Ps^- ion. The first highly accurate calculations of the bound-state properties for this system have been made by Ho [15]. Our earlier works [16] related with the Ps^- ion include only the bound-state energy computations. In [2] we considered the same properties as in [15]. The next paper [6] contains a large number of new properties for the Ps^- ion. However, Ho in [17] used an improved technique to construct a very accurate wave function for the Ps^- ion. Our method used in [6] could not provide even comparable accuracy. Moreover, all earlier attempts to improve our method [6] have failed. Finally, after a few years of extensive calculations a successful approach [1] was found in some alternative direction. In [1] the new, advanced, two-stage procedure has been developed in order to construct extremely accurate wave functions for the three-body systems.

Let us remember, that in this approach the trial wave function Ψ is represented by the sum of the very well optimized, short-term function Ψ_1 with the N_0 basis functions and roughly optimized (or even nonoptimized) long-term function Ψ_2. If the total number of basis functions equals N and each of the basis functions contains m nonlinear parameters, then we may write $\Psi(N)=\Psi_1(N_0)+\Psi_2(N-N_0)$, where $N_0\ll N$. The mN_0 nonlinear parameters in the short-term or booster function $\Psi_1(N_0)$ are optimized very carefully. This problem is not very complicated, since the booster function $\Psi_1(N_0)$ contains only a relatively small number (mN_0) of the nonlinear parameters. The long-term function $\Psi_2(N-N_0)$ with $m(N-N_0)$ nonlinear parameters is constructed with an approximate optimization or even without any optimization of the nonlinear parameters. A detailed description of the choice of nonlinear parameters in the booster and long-term functions can be found in [1].

In the present work, the exponential variational expansion is used. For the considered case of the (ground) $1\ ^1S$ state in the Ps^- ion this expansion takes the form

TABLE I. The total energies (E) in atomic units ($m_e=1$, $\hbar=1$, $e=1$) for the ground states of the Ps^- ion. N designates the number of basis functions used.

N	E
200[a]	−0.2620050702293112
400	−0.2620050702322065
500	−0.2620050702326614
600	−0.2620050702328437
700	−0.2620050702329184
800	−0.2620050702329484
900	−0.2620050702329598
950	−0.2620050702329634
1000	−0.2620050702329674
1200	−0.2620050702329726
1400	−0.2620050702329749
1600[b]	−0.2620050702329757

[a]This case corresponds to the short-term, booster function $\Psi_1(N_0)$, where $N_0=200$.

[b]The three most accurate variational energies obtained previously are −0.262 005 070 232 855 a.u. [17], −0.262 005 070 232 950 [28] a.u., and −0.262 005 070 232 965 a.u. [1].

$$\Psi=\frac{1}{2}(1+\hat{P}_{21})\sum_{i=1}^{N} C_i \exp(-\alpha_i r_{32}-\beta_i r_{31}-\gamma_i r_{21}). \quad (1)$$

Here C_i are linear (or variational) parameters and α_i, β_i, and γ_i are nonlinear parameters. The operator $\hat{P}_{21}$ is the permutation of the two identical (1 and 2) particles (electrons) in the Ps^- ion. For the two-stage procedure in the present study we have chosen $N_0=200$ and $N_{\max}=1600$. As is mentioned above, the first stage produces a very compact and highly accurate wave function Ψ_1. This function includes only $3N_0=600$ nonlinear parameters. The appropriate energy contains approximately 12–13 correct decimal figures (in atomic units). The second stage of the procedure gives as a rule 3–4 additional correct decimal figures to the total energy, and generates extremely accurate wave functions, which is used to compute various properties of the Ps^- ion.

The total variational energies from Table I are represented quite well by the following approximate formula:

$$E(N)=E(\infty)+\frac{A}{N^p}. \quad (2)$$

Here, A and p are the two positive constants, N is the number of basis functions used to compute $E(N)$, and $E(\infty)$ is the asymptotic value of energy which corresponds, in principle, to the infinite number of basis functions. If any three energies $E(N_i)$ have been computed, then all three constants p, A, and $E(\infty)$ in the last equation can be determined easily. For instance, by using the $E(N)$ values for $N=800$, 1000, and 1200 from Table I, one finds $E(\infty)=-0.262\ 005\ 070\ 232\ 975\ 79$ a.u., while for $N=900$, 1000, and 1200 the analogous result is $E(\infty)=-0.262\ 005\ 070\ 232\ 974\ 75$ a.u. Note that as a rule $E(\infty)$ contains one to two extra correct significant figures in comparison with $E(N_{\max})$. Finally, in terms of the results given in Table I we have estimated the $E(\infty)$ value as follows:

$$E(\infty)=-0.262005070232978\pm 4\times 10^{-15}\ \text{a.u.} \quad (3)$$

Note that our asymptotic and variational energies are very close to each other.

The numerical values for some of the properties (i.e., expectation values) can be found in Table II. In this table only stable figures from calculations with the higher N are presented for most of the Ps^- properties. For the two- and three-particle cusps, only the best results are given in Table II. All properties are given in atomic units ($m_e=1$, $e=1$, and $\hbar=1$). The physical meaning for all of the expectation values in Table II is quite clear from the notations used (for more detail, see also [1]). So, here we wish to make only a few following remarks. In all the formulas given below and also in Table II, the notations 1 and 2 mean electrons, while the notation 3 designates the positron. The notations δ_{31}, δ_{21}, and δ_{321} stand for the two- and three-particle Dirac δ functions, respectively. The two-body cusp ratios are determined in a traditional manner [18,19]:

$$\nu_{ij}=\frac{\left\langle \delta(\mathbf{r}_{ij})\dfrac{\partial}{\partial r_{ij}}\right\rangle}{\langle \delta(\mathbf{r}_{ij})\rangle}, \quad (4)$$

where $\delta_{ij}=\delta(\mathbf{r}_{ij})$ is the appropriate Dirac δ function and $(ij)=(21)$ and (31). The exact value of ν_{ij} equals

$$\nu_{ij}=q_i q_j\frac{m_i m_j}{m_i+m_j}, \quad (5)$$

where q_i and q_j are the charges and m_i and m_j are the masses of the particles.

The expectation values of the two interparticle cosine functions are determined traditionally:

$$\tau_{ij}=\langle\cos(\mathbf{r}_{ik}\mathbf{r}_{jk})\rangle=\left\langle\frac{\mathbf{r}_{ik}\cdot\mathbf{r}_{jk}}{r_{ik}r_{jk}}\right\rangle, \quad (6)$$

where $(i,j,k)=(1,2,3)$. The quantity $\langle f\rangle$ is expressed in terms of the relative coordinates (r_{31},r_{32},r_{21}) or perimetric coordinates (u_1,u_2,u_3) [where $u_i=\frac{1}{2}(r_{ij}+r_{ik}-r_{jk})$ and $(i,j,k)=(1,2,3)$] as follows:

$$\langle f\rangle=\left\langle\psi\left|\frac{u_1}{r_{32}}\frac{u_2}{r_{31}}\frac{u_3}{r_{21}}\right|\psi\right\rangle$$
$$=\int\int\int|\psi(u_1,u_2,u_3)|^2 u_1u_2u_3du_1du_2du_3. \quad (7)$$

The value $\langle f\rangle$ can be calculated directly or by applying τ_{ij}. Their coincidence indicates that these $\tau_{21},\tau_{32},\tau_{31}$ and $\langle f\rangle$ have been computed correctly. The equalities

$$\tau_{21}+\tau_{32}+\tau_{31}=1+4\langle f\rangle \quad (8)$$

hold for an arbitrary three-body system. For the symmetric Ps^- ion, we have $\tau_{32}=\tau_{31}$.

The virial factor η is determined as follows:

TABLE II. The expectation values $\langle X_{ij}\rangle$ in atomic units ($m_e=1,\ \hbar=1,\ e=1$) of some properties for the ground states of the Ps^- ion. The notations 1 and 2 designate the two electrons, while 3 stands for the positron (e^+).

$\langle X_{ij}\rangle$		$\langle X_{ij}\rangle$	
$\langle r_{21}^{-2}\rangle$	0.03602205848	$\langle r_{21}^{-1}\rangle$	0.15563190565266
$\langle r_{31}^{-2}\rangle$	0.27932654211	$\langle r_{31}^{-1}\rangle$	0.33982102305927
$\langle r_{21}\rangle$	8.54858065516	$\langle r_{21}^{2}\rangle$	93.178633855
$\langle r_{31}\rangle$	5.48963325238	$\langle r_{31}^{2}\rangle$	48.418937230
$\langle r_{21}^{3}\rangle$	1265.5804487	$\langle r_{21}^{4}\rangle$	21054.45349
$\langle r_{31}^{3}\rangle$	607.29563001	$\langle r_{31}^{4}\rangle$	9930.638730
$\langle (r_{31}r_{32})^{-1}\rangle$	0.0909353465282	$\langle \mathbf{r}_{31}\cdot\mathbf{r}_{32}\rangle$	1.82962030209
$\langle (r_{31}r_{21})^{-1}\rangle$	0.0606976902876	$\langle \mathbf{r}_{31}\cdot\mathbf{r}_{21}\rangle$	46.5893169266
$\langle (r_{32}r_{31}r_{21})^{-1}\rangle$	0.0220342378947		
$\langle -\frac{1}{2}\nabla_1^2\rangle$	0.066619294535873	$\langle \boldsymbol{\nabla}_1\cdot\boldsymbol{\nabla}_2\rangle$	-0.004472107910576
$\langle -\frac{1}{2}\nabla_3^2\rangle$	0.12876648116117	$\langle \boldsymbol{\nabla}_1\cdot\boldsymbol{\nabla}_3\rangle$	-0.12876648116117
τ_{31}	0.5919817011492	$\langle \delta_{31}\rangle$	0.0207331976
τ_{21}	0.0197696328167	$\langle \delta_{21}\rangle$	0.17099692×10^{-3}
$\langle f\rangle$	0.05093325877879	$\langle \delta_{321}\rangle$	0.35875×10^{-4}
ν_{31}	-0.499999795011881	ν_{21}	0.499983153136046
ν_{31}[a]	-0.5	ν_{21}[a]	0.5
ξ_{123}	-0.221846010657566	η	$\leqslant 0.559715\times10^{-14}$
ξ_{123}[b]	-0.25	ε(eV)	-0.326674721317821[c]

[a]The exact value from Eq. (4).

[b]The exact value, from Eq. (11).

[c]To compute this value, we assume that the corresponding conversion factor equals 27.211 396 1 (eV/a.u.) exactly.

$$\eta=\left|1+\frac{\langle V\rangle}{2\langle T\rangle}\right|, \tag{9}$$

where $\langle T\rangle$ and $\langle V\rangle$ are the expectation values of the kinetic and potential energy, respectively. The deviation of the factor η from zero indicates, in principle, the quality of the wave function used. The appropriate binding energies ε are given in eV (the conversion factor is 1 a.u. $=27.211\ 396\ 1$ eV). Note however, that even exact coincidence of the factor η with 0 does not indicate the high quality of the wave function. Indeed, by using the so-called scaling transformation ($\vec{r}_i=\alpha\vec{r}_i$) one can make the factor η very close to zero for an arbitrary wave function. Analogously, an excellent coincidence between computed and expected cusp values can be found in some cases (or easily made) for wave functions which *a priori* have a very poor quality. In particular, one can easily construct the three-term trial function Eq. (1) which provides a stable bound state for the Ps^- ion and ''exact'' values for both the ν_{21} and ν_{31} cusps. But for other properties the quality of such a function will be very poor. In general, the wave function has a high quality if (and only if) it reproduces very accurately a large number of bound-state properties.

The numerical values for the properties in Table II agree quite well with the values known from previous highly accurate calculations (see [1,2,6], and [17]). The convergence for the properties upon the number of basis functions used was considered in detail in [2,6] and [17]. Note, however, that some of the properties have never been computed before. For instance, the so-called symmertrized three-particle cusp,

$$\xi_{123}=\xi_{12;3}+\xi_{13;2}+\xi_{23;1}, \tag{10}$$

where

$$\xi_{ik;j}=\frac{\left\langle \delta_{ijk}\dfrac{\partial^2}{\partial r_{ij}\partial r_{jk}}\right\rangle}{\langle \delta_{ijk}\rangle}=\frac{\left\langle \delta(\mathbf{r}_{ij})\,\delta(\mathbf{r}_{jk})\dfrac{\partial^2}{\partial r_{ij}\partial r_{jk}}\right\rangle}{\langle \delta(\mathbf{r}_{ij})\,\delta(\mathbf{r}_{jk})\rangle} \tag{11}$$

is of specific interest. Its numerical value for the exact Coulomb three-body wave function equals $\pm\infty$ (for more detail see, e.g., [20]). But for an arbitrary finite-term analytical trial function [e.g., Eq. (1)], all $\xi_{ik;j}$ cusps are finite [21], and moreover, they can be expressed through Kato's two-body cusps. Indeed, following Kato [18], we can determine the so-called cusp operators $\hat{\nu}_{ij}$:

$$\hat{\nu}_{ij}=\delta(\mathbf{r}_{ij})\frac{\partial}{\partial r_{ij}}, \tag{12}$$

where $(ij)=(32)$, (31), (21) and $(ij)=(ji)$. For an arbitrary three-body Coulomb wave function $\Psi(r_{32},r_{31},r_{21})$ the three following conditions are obeyed [18]:

$$\hat{\nu}_{ij}\Psi(r_{32},r_{31},r_{21})=\nu_{ij}\delta(\mathbf{r}_{ij})\Psi(r_{32},r_{31},r_{21}), \tag{13}$$

where the eigenvalues ν_{ij} are given by Eq. (4). Now, from Eq. (11) one finds for the ξ_{123} cusp

$$\xi_{123}=\nu_{12}\nu_{13}+\nu_{12}\nu_{23}+\nu_{13}\nu_{23}. \tag{14}$$

For the Ps^- ion the expected value for the ξ_{123} cusp is -0.25 (in atomic units). The comparison of the ξ_{123} value

with -0.25 can be found in Table II. Note, however, that the definition of the three-particle cusps can be given in a few different ways and for some of the definitions the observed agreement with excepted values is better (for more detail, see [20]).

Note that some expectation values in Table II can be expressed as the linear combinations of other properties. For instance, for the three relative vectors $\vec{r}_{32}$, $\vec{r}_{31}$, and $\vec{r}_{21}$ we have

$$\vec{r}_{32}-\vec{r}_{31}+\vec{r}_{21}=\vec{0}. \tag{15}$$

Therefore, the three equalities $[(i,j,k)=(1,2,3)]$

$$\vec{r}_{ik}\cdot\vec{r}_{jk}=\frac{1}{2}(r_{ik}^2+r_{jk}^2-r_{ij}^2) \tag{16}$$

hold in any case. For the appropriate expectation values, one finds (see Table II)

$$\langle\vec{r}_{ik}\cdot\vec{r}_{jk}\rangle=\frac{1}{2}(\langle r_{ik}^2\rangle+\langle r_{jk}^2\rangle-\langle r_{ij}^2\rangle). \tag{17}$$

Analogously, since $\vec{p}_1+\vec{p}_2+\vec{p}_3=\vec{0}$, then we write

$$\vec{p}_i\cdot\vec{p}_j=\frac{1}{2}(p_k^2-p_i^2-p_j^2) \tag{18}$$

and

$$\langle\vec{p}_i\cdot\vec{p}_j\rangle=\frac{1}{2}(\langle p_k^2\rangle-\langle p_j^2\rangle-\langle p_i^2\rangle), \tag{19}$$

respectively $[(i,j,k)=(1,2,3)]$. Moreover, if the three $\vec{p}_i$ are determined by the relations $\vec{p}_i=(-\imath)\vec{\nabla}_i$ in Cartesian coordinates, then one finds

$$\langle\vec{\nabla}_i\cdot\vec{\nabla}_j\rangle=\langle-\tfrac{1}{2}\nabla_k^2\rangle-\langle-\tfrac{1}{2}\nabla_i^2\rangle-\langle-\tfrac{1}{2}\nabla_j^2\rangle, \tag{20}$$

where $(i,j,k)=(1,2,3)$. The expectation values from both sides of this equality can be found in Table II. Note, however, that the last three equalities are obeyed only in Cartesian coordinates, where we have $\vec{\nabla}_i=\imath\vec{p}_i$. In the present study, all $\vec{\nabla}_i$ operators are written in Cartesian coordinates, and therefore $\langle\vec{\nabla}_i\cdot\vec{\nabla}_j\rangle$ can be expressed through $\langle-\frac{1}{2}\nabla_i^2\rangle$ and vice versa. Moreover, in the symmetric systems we have $\langle p_1^2\rangle=\langle p_2^2\rangle$ and $\langle\vec{r}_{31}\cdot\vec{r}_{21}\rangle=\langle\vec{r}_{32}\cdot\vec{r}_{12}\rangle$, respectively. This simplifies some of the equations presented above. Moreover, for the symmetric systems one easily finds that $\langle\vec{\nabla}_1\cdot\vec{\nabla}_2\rangle$ is always negative, since $\langle\vec{\nabla}_1\cdot\vec{\nabla}_2\rangle=-\langle-\frac{1}{2}\nabla_3^2\rangle<0$.

Now, by using the expectation values for the δ functions from Table II, we can calculate the total and one-photon annihilation rates (analytical expressions can be found, e.g., in [13] and [1]):

$$\Gamma=2\pi\alpha^4 c a_0^{-1}\left[1-\alpha\left(\frac{17}{\pi}-\frac{19\pi}{12}\right)\right]\langle\delta_{31}\rangle$$
$$=100.617\ 480\ 9\times10^9\langle\delta_{31}\rangle\ \mathrm{sec}^{-1}, \tag{21}$$

$$\Gamma_{1\gamma}=\frac{4}{9}\frac{16\pi^2}{3}\alpha^8 c a_0^{-1}\langle\delta_{321}\rangle=1065.757\ 44\langle\delta_{321}\rangle\ \mathrm{sec}^{-1},$$

where $\alpha=0.729\ 735\ 308\times10^{-2}$ is the fine-structure constant, $c=0.299\ 792\ 458\times10^9$ m sec^{-1} is the velocity of light, and the Bohr radius a_0 equals $0.529\ 177\ 249\times10^{-10}$ m [22]. Now, by applying the expectation values for the appropriate Dirac δ functions from Table II, one finds from the last equalities that $\Gamma=2.086\ 122\ 114\times10^9$ sec^{-1} and $\Gamma_{1\gamma}=3.823\ 40\times10^{-2}$ sec^{-1}. The deviations from the appropriate results computed earlier (see, e.g., [1] and [17]) do not exceed 50 sec^{-1} and $7\cdot10^{-4}$ sec^{-1} for Γ and $\Gamma_{1\gamma}$, respectively. The other annihilation rates $\Gamma_{2\gamma},\Gamma_{3\gamma},\ldots$ can be easily estimated by using the $\langle\delta_{31}\rangle$ value and formulas from [23].

Now, let us discuss the calculations of relativistic corrections of the lowest orders. The energies and other properties discussed above are essentially nonrelativistic. The first nonzero correction corresponds to the second-order terms upon α [24]. The Hamiltonian which includes terms $\simeq\alpha^2$ is called the Breit-Pauli Hamiltonian. In the next approximation $\simeq\alpha^3$ one needs to consider terms which represent emission, absorption, and scattering of radiation [24]. In the fourth-order approximation upon α, electron-positron annihilation in the Ps^- ion will affect the energy levels in this system. In fact, the closed solution can be found only in the second-order approximation upon α. It should be mentioned that this problem has been considered earlier [25].

Here, we want to discuss the calculation of the second-order corrections upon α in detail. For an arbitrary three-body system $(m_1,m_2,m_3;q_1,q_2,q_3)$, the Breit-Pauli Hamiltonian H_{BP} takes the following general form (in atomic units; see, e.g., [26]):

$$H_{\mathrm{BP}}=\left\{\frac{1}{2m_1}p_1^2+\frac{1}{2m_2}p_2^2+\frac{1}{2m_3}p_3^2+\frac{q_1q_2}{r_{21}}+\frac{q_1q_3}{r_{31}}+\frac{q_2q_3}{r_{32}}\right\}$$
$$-\frac{\alpha^2}{8}\left[\frac{1}{m_1}p_1^4+\frac{1}{m_2}p_2^4+\frac{1}{m_3}p_3^4\right]+\alpha^2\hat{U}_1(\vec{p}_3,\vec{p}_2,\vec{r}_{32})$$
$$+\alpha^2\hat{U}_2(\vec{p}_1,\vec{p}_3,\vec{r}_{31})+\alpha^2\hat{U}_3(\vec{p}_2,\vec{p}_1,\vec{r}_{21}), \tag{22}$$

where m_1, m_2, and m_3 are the particle masses and q_1, q_2, and q_3 are their charges. $\alpha\approx7.297\ 353\ 08\times10^{-3}$ is the fine-structure constant. $\vec{r}_i$ and $\vec{p}_i$ are the coordinate and momentum vectors, respectively $(i=1,2,3)$. In order to make the formulas below more compact, the following notations are used: $\vec{r}_{ij}=\vec{r}_j-\vec{r}_i$ and $\vec{p}_i=(-\imath)\vec{\nabla}_i$. The terms without α^2 represent the nonrelativistic Hamiltonian H_0. The terms $\simeq p^4$ correspond to the corrections related with the relativistic $m(v)$ dependence. The operator $\hat{U}_3(\vec{p}_2,\vec{p}_1,\vec{r}_{21})$ takes the form

$$\hat{U}_3(\vec{p}_2,\vec{p}_1,\vec{r}_{21})$$
$$=-\frac{\pi q_1q_2}{2}\left(\frac{1}{m_1^2}+\frac{1}{m_2^2}\right)\delta(\vec{r}_{21})-\frac{q_1q_2}{2m_1m_2r_{21}}$$
$$\times\left[\vec{p}_1\cdot\vec{p}_2+\frac{\vec{r}_{21}(\vec{r}_{21}\cdot\vec{p}_1)\cdot\vec{p}_2}{r_{21}^2}\right]$$

$$-\frac{q_1q_2}{4m_1^2r_{21}^3}(\vec{r}_{21}\times\vec{p}_1)\cdot\hat{\vec{\sigma}}_1+\frac{q_1q_2}{4m_2^2r_{21}^3}(\vec{r}_{21}\times\vec{p}_2)\cdot\hat{\vec{\sigma}}_2$$

$$-\frac{q_1q_2}{4m_1m_2r_{21}^3}[(\vec{r}_{21}\times\vec{p}_1)\cdot\hat{\vec{\sigma}}_2-(\vec{r}_{21}\times\vec{p}_2)\cdot\hat{\vec{\sigma}}_1]$$

$$+\frac{q_1q_2}{4m_1m_2}\left[\frac{\hat{\vec{\sigma}}_1\cdot\hat{\vec{\sigma}}_2}{r_{21}^3}-3\frac{(\hat{\vec{\sigma}}_1\cdot\vec{r}_{21})(\hat{\vec{\sigma}}_2\cdot\vec{r}_{21})}{r_{21}^5}\right.$$

$$\left.-\frac{8\pi}{3}\hat{\vec{\sigma}}_1\cdot\hat{\vec{\sigma}}_2\delta(\vec{r}_{21})\right], \tag{23}$$

where $\hat{\vec{\sigma}}=(\hat{\sigma}_x,\hat{\sigma}_y,\hat{\sigma}_z)$, and $\hat{\sigma}_x,\hat{\sigma}_y$ and $\hat{\sigma}_z$ are the usual Pauli (2×2) matrices (see, e.g., [26]). The other two operators $\hat{U}_1(\vec{p}_3,\vec{p}_2,\vec{r}_{32})$ and $\hat{U}_2(\vec{p}_1,\vec{p}_3,\vec{r}_{31})$ can be found from $\hat{U}_3(\vec{p}_2,\vec{p}_1,\vec{r}_{21})$ by cyclic permutations. For the Ps^- ion, all masses m_1,m_2, and m_3 are equal to each other, and furthermore, all of them equal 1 (in atomic units). This simplifies the operator $\hat{U}_3(\vec{p}_2,\vec{p}_1,\vec{r}_{21})$ significantly:

$$\hat{U}_3(\vec{p}_2,\vec{p}_1,\vec{r}_{21})$$

$$=-\pi q_1q_2\delta(\vec{r}_{21})-\frac{q_1q_2}{2r_{21}}\left[\vec{p}_1\cdot\vec{p}_2+\frac{\vec{r}_{21}(\vec{r}_{21}\cdot\vec{p}_1)\cdot\vec{p}_2}{r_{21}^2}\right]$$

$$+\frac{q_1q_2}{4r_{21}^3}[-(\hat{\vec{\sigma}}_1+2\hat{\vec{\sigma}}_2)(\vec{r}_{21}\times\vec{p}_1)$$

$$+(\hat{\vec{\sigma}}_2+2\hat{\vec{\sigma}}_1)\cdot(\vec{r}_{21}\times\vec{p}_2)]$$

$$+\frac{q_1q_2}{4}\left[\frac{\hat{\vec{\sigma}}_1\hat{\vec{\sigma}}_2}{r_{21}^3}-3\frac{(\hat{\vec{\sigma}}_1\cdot\vec{r}_{21})(\hat{\vec{\sigma}}_2\cdot\vec{r}_{21})}{r_{21}^5}\right.$$

$$\left.-\frac{8\pi}{3}\hat{\vec{\sigma}}_1\cdot\hat{\vec{\sigma}}_2\delta(\vec{r}_{21})\right]. \tag{24}$$

The first line in this equation represents the so-called orbital (or L^2) corrections. The second line corresponds to the spin-orbital (or LS) interaction, while the last line includes the corrections related with the spin-spin (or S^2, or tensor) interaction. In principle, all terms in the last equation have the same or quite comparable order of magnitude, and *a priori* we cannot neglect any of them.

Now, in the first approximation we can calculate the expectation value of this Hamiltonian $H_{\rm BP}$ using the eigenfunction $\Psi(N)$ determined above for the H_0 nonrelativistic H_0 Hamiltonian. In this approximation, all LS terms equal zero identically (see, e.g., [27]). Furthermore, the ground-state Ps^- ion wave function is represented in the form $\Phi_S(r_{32},r_{31},r_{21})(\bar{\alpha}_1\bar{\beta}_2-\bar{\alpha}_2\bar{\beta}_1)\bar{\alpha}_3$, where $\Phi_S(r_{32},r_{31},r_{21})$ is the coordinate (or positional, or spatial) function, which is symmetric with respect to the pair interchange of particles 1 and 2 (i.e., electrons). The function $(\bar{\alpha}_1\bar{\beta}_2-\bar{\alpha}_2\bar{\beta}_1)\bar{\alpha}_3$ is the appropriate spin function, which is antisymmetric with respect to the same interchange (i.e., it changes the sign). The definition of the basis spin functions $\bar{\alpha}_i$ and $\bar{\beta}_i$ $(i=1,2,3)$ is traditional:

$$(\hat{\sigma}_z)_i\bar{\alpha}_i=(+1)\bar{\alpha}_i,\quad (\hat{\sigma}_z)_i\bar{\beta}_i=(-1)\bar{\beta}_i. \tag{25}$$

Now, by using the identity $\hat{\vec{\sigma}}_i\cdot\hat{\vec{\sigma}}_j=2\vec{S}_{ij}^2-3$ (see, e.g., [26]) we can write the following expression for the expectation value of the Breit-Pauli Hamiltonian, or in other words for the Breit-Pauli energy $E_{\rm BP}$:

$$E_{\rm BP}=\langle H_{\rm BP}\rangle=E_0-\frac{\alpha^2}{8}[2\langle p_1^4\rangle+\langle p_3^4\rangle]$$

$$-\frac{\alpha^2}{2}\left[\left\langle\frac{\vec{p}_1\cdot\vec{p}_2}{r_{21}}\right\rangle+\left\langle\frac{\vec{r}_{21}(\vec{r}_{21}\cdot\vec{p}_1)\cdot\vec{p}_2}{r_{21}^2}\right\rangle\right]$$

$$+\alpha^2\left[\left\langle\frac{\vec{p}_1\cdot\vec{p}_3}{r_{31}}\right\rangle+\left\langle\frac{\vec{r}_{31}(\vec{r}_{31}\cdot\vec{p}_1)\cdot\vec{p}_3}{r_{31}^2}\right\rangle\right]$$

$$+\alpha^2\left(\pi-\frac{4\pi}{3}\cdot\vec{S}_{21}^2\right)\langle\delta(\vec{r}_{21})\rangle$$

$$-\alpha^2\left(2\pi-\frac{4\pi}{3}(\vec{S}_{31}^2+\vec{S}_{32}^2)\right)\langle\delta(\vec{r}_{31})\rangle, \tag{26}$$

where the symmetry between particles 1 and 2 (electrons) is taken into account. For the $(\bar{\alpha}_1\bar{\beta}_2-\bar{\alpha}_2\bar{\beta}_1)\bar{\alpha}_3$ spin function mentioned above, we have $\vec{S}_{21}^2=0$ and $\vec{S}_{31}^2+\vec{S}_{32}^2=1$. This produces the final expression for the $E_{\rm BP}$ energy. The last expression contains a few expectation values, which have never been calculated before. Their computation is our goal for the nearest future.

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