Relativistic and QED energy shifts in positronium ion

M. Grigorescu and G. W. F. Drake

Department of Physics
University of Windsor
Windsor, Ontario, Canada

Abstract: The leading relativistic and QED corrections to the ground state energy of the three-body system $e^- e^+ e^-$ are calculated numerically using a Hylleraas correlated basis set. The accuracy of the nonrelativistic variational ground state wave function is discussed with respect to the convergence properties at the increase of the basis dimension and to the variance of the energy expectation value. Recent progress in the numerical procedure used to calculate expectation values for products of various physical operators is presented. It is shown that the nonrelativistic ground state energy can be calculated with an accuracy below the level width. The corrections to this energy include the lowest order Breit interaction, the vacuum polarization potential, one and two photon exchange contributions, the annihilation interaction, and spin-spin contact terms. The relativistic effects and the residual interactions considered here decrease the one electron binding energy from the nonrelativistic value of $0.012\,005\,070\,232\,980\,10(3)$ a.u. to $0.011\,981\,051\,246(2)$ a.u..

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I. Introduction

The positronium negative ion (Ps$^-$) is the simplest system composed of three equal mass fermions, \( e^-e^+e^- \), bounded only by electromagnetic interactions. Similar examples of three-body systems, bounded by increasingly complex interactions, are provided by three-quark systems such as the proton and neutron, and three-nucleon systems, as the $^3$H, $^3$He nuclei.

In a nonrelativistic approach, accurate numerical approximations to the bound eigenstates of three quantum particles interacting by Coulomb forces can be obtained by using the Rayleigh-Ritz variational method. A suitable set of coordinates and basis states for the three-body problem was proposed by Hylleraas [1] during the early days of quantum mechanics, and it was used to calculate the ground state energy of the helium atom. With respect to this set, the matrix elements of various two-body operators can be expressed in analytical form [2], and extensive high-precision calculations become feasible [3] [4].

The relativistic quantum many-body problem can be approached either from the field theory, or by using a Schrödinger equation with an "action at a distance" type Hamiltonian, defined by quantizing the classical relativistic system [5]. Though, a puzzling result in classical mechanics is the no interaction theorem [6], which apparently rules out any instantaneous action-at-a-distance Hamiltonian. This theorem states that in a classical many-body system, the relativistic invariance of the equations of motion (the physical laws) is compatible with the "manifest relativistic invariance", of the world lines determined by these equations, only if there is no interaction between the particles. However, this strong result can be avoided if the interacting particles have a structure, as the condition of manifest invariance becomes ambiguous [7] [8].

The approach to the bound state problem based on field theory leads to a relativistically invariant Bethe-Salpeter equation [9], p. 196. In the case of two relativistic electrons, approximate Lorentz invariance to the first order is introduced by the Breit interaction, which can be seen as the quantum correspondent to the Darwin term in classical electromagnetism [10].

In the helium atom, the two electrons move in the Coulomb field created by a composite, heavy nucleus, which to a first approximation can be considered as center of mass (CM). The case of Ps$^-$ is different, because all three particles are elementary, have the same mass, and move to the same degree
The existence of a bound ground state in the $e^-e^+e^-$ system was predicted by Wheeler [11] and was observed by Mills [12] passing a positron beam through a thin carbon film in vacuum. The measured $\text{Ps}^- \rightarrow (2\gamma)e^-$ decay rate $\lambda = 2.09(9) \text{nsec}^{-1}$ [12] corresponds to a $\text{Ps}^-$ lifetime of 0.478 nsec, intermediate between that of para (singlet) $\text{Ps}$ (0.125 nsec) and ortho (triplet) $\text{Ps}$ (140 nsec) [13].

Accurate nonrelativistic numerical calculations for the ground-state properties of $\text{Ps}^-$ are presented in refs. [14] to [17]. The autoionization states have been studied in [18], while several low-lying resonances have been predicted recently [19], by using a combination between the stochastic variational method (SVM) with correlated Gaussians and the complex scaling method.

The accuracy of the $\text{Ps}^-$ ground-state wave functions given by SVM in a Gaussian basis, was studied by comparison to the direct solution of the Schrödinger equation in [16]. It was shown that despite the fact that in SVM the convergence properties of the expectation values for most operators are better, the wave function is less accurate.

In this work, the accuracy of the $\text{Ps}^-$ nonrelativistic variational ground state is studied by using beside the convergence properties of the energy with basis size, also the variance of the Hamiltonian. The numerical procedure used to calculate matrix elements is presented in Sect. II. It is shown that in agreement with [16], the variance is larger than the accuracy resulting from convergence. Estimates of the relativistic correction terms and the leading QED corrections are presented in Sect. III. Tables containing the expectation values of singular operators appearing in the correction terms, such as $p^4$ and delta functions are given in the Appendix. The main results and the concluding remarks are summarized in Sect. IV.

II. The Nonrelativistic Quantum Three-Body Problem

The nonrelativistic Hamiltonian of the three-body system $e^-e^+e^-$ (or $e^+e^-e^+$) is

$$H_0 = \left( -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - f \nabla_1 \cdot \nabla_2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}} \right) f \text{ a.u.} \quad (1)$$

where $f = \mu/m$, $\mu = m/2$ is the reduced mass, $\nabla_i \equiv \partial_{\vec{r}_i}$, $\vec{r}_i = \vec{R}_i/a_\mu$, 

with respect to the CM.
\( i = 1, 2, 3 \) denote the position vectors in the CM frame of the two electrons \((i = 1, 2)\), and of the positron \((i = 3)\) in \(a_\mu\) units, while \(r = |\vec{r}_1 - \vec{r}_2|\), \(r_1 = |\vec{r}_1 - \vec{r}_3|\) and \(r_2 = |\vec{r}_2 - \vec{r}_3|\) are the relative distances. The space coordinates unit is \(a_\mu = a_0/f\), where \(a_0 = \hbar^2/(me^2) = 0.529\ 177\ 249(24)\ \text{Å}\) is the Bohr radius. By this choice, the Hamiltonian is naturally expressed in reduced atomic units of energy \(f\) a.u. (= 13.605 698 1(40) eV = 1Ry if \(f = 0.5\), where 1 a.u. = \(e^2/a_0 = \alpha^2mc^2\) is the atomic unit of energy and \(\alpha = e^2/(\hbar c) = 0.007\ 297\ 353\ 08(32)\) is the fine structure constant.

Approximate eigenfunctions of this Hamiltonian are obtained by using the variational method. The trial function is a finite linear combination

\[
\Psi(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2) = \sum_{a,b,c,l_1,l_2} [q_{abc}^{l_1l_2}(1, 2) \Phi_{abc \ l_1l_2LM}(\vec{r}_1, \vec{r}_2) + q_{abc}^{l_2l_1}(2, 1) \Phi_{abc \ l_2l_1LM}(\vec{r}_2, \vec{r}_1)] \psi_{S_{m_s}}(\vec{s}_1, \vec{s}_2)
\]

of \(N_b\) basis elements \(\Phi_{abc \ l_1l_2LM}\). The orbital component \(\Phi_{abc \ l_1l_2LM}\) is represented by the Hylleraas correlated wave function [1]

\[
\Phi_{abc \ l_1l_2LM}(\vec{r}_1, \vec{r}_2) = r_1^a r_2^b r_1^{c} e^{-\alpha r_1 - \beta r_2} Y_{LM}^{l_1l_2}(1, 2)
\]

which is a product between a polynomial in all relative radial variables and the orbital angular momentum eigenstates

\[
Y_{LM}^{l_1l_2}(1, 2) = \sum_{m_1 + m_2 = M} C_{m_1m_2M}^{l_1l_2} Y_{l_1m_1}(\hat{r}_1) Y_{l_2m_2}(\hat{r}_2),
\]

where \(\hat{r}_i = \vec{r}_i/r_i, \ i = 1, 2, \ \hat{r} = \vec{r}/r\) are unit vectors.

The spin function

\[
\psi_{S_{m_s}} = \sum_{\mu_1 + \mu_2 = m_s} C_{\mu_1\mu_2m_s}^{l_1l_2S} |1/2\mu_1\rangle |1/2\mu_2\rangle
\]

corresponds to singlet \((S = 0)\) or triplet \((S = 1)\) configurations, when the orbital part is symmetric \(q_{abc}^{l_1l_2}(1, 2) = q_{abc}^{l_2l_1}(2, 1)\) or antisymmetric \(q_{abc}^{l_1l_2}(1, 2) = -q_{abc}^{l_2l_1}(2, 1)\), respectively. The expansion coefficients \(q_{abc}^{l_1l_2}(1, 2)\), and the nonlinear parameters \(\alpha, \beta\), have been determined previously [17] by using the variational equations

\[
\delta_{q,\alpha,\beta} \frac{\langle \Psi | H_0 | \Psi \rangle}{\langle \Psi | \Psi \rangle} = 0.
\]
The kinetic energy operator for the electron 1 is \(-\nabla_1^2/2\), and its effective action in the Hylleraas model space is given by

\[
\nabla_1^2 \Phi = \left[ \frac{1}{r_1^2} \frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\vec{l}_1^2}{r_1^2} \right] \Phi
\]  

\[+ \frac{2(r_1 - r_2 \hat{r}_1 \cdot \hat{r}_2)}{r} \frac{\partial^2}{\partial r_1 \partial r} - \frac{2}{r_1 r_2} \vec{r}_1 \cdot \nabla_1 Y \frac{\partial}{\partial r} \Phi \]  

where \(\vec{l}_1 = \vec{r}_1 \times \vec{p}_1\) and \(\nabla_1^2 = -i \hat{r}_1 \times \vec{l}_1\). A similar expression, obtained by permuting the indices 1 and 2, yields \(\nabla_2^2 \Phi\).

The action of such operators on the Hylleraas basis states is complicated, and in the case of their product becomes tedious, involving hundreds of polynomial terms, spherical harmonics, and singular delta functions. Therefore, in this work the matrix elements have been calculated by using a new procedure, based on the representation of the physical operators as linear combinations within a set \(\mathcal{E} = \{E_k, k = 1, 2, ..., n\}\) of \(n\) elementary operators. Although \(\mathcal{E}\) is not a Lie algebra, this approach makes the numerical calculation more flexible, because the components \(E_k\) can be programmed individually, and they can be assembled as needed to form various complicated operators. By a suitable choice, the set \(\mathcal{E}\) may account for several physical operators of interest. Some of the elementary operators used in the present calculation are presented in Appendix, Table I.

The accuracy of the wave function improves with the dimension \(N_b\) of the basis set. When \(N_b\) increases, the expectation value of the Hamiltonian \(\langle H_0 \rangle (N_b) = \langle \Psi | H_0 | \Psi \rangle\) decreases, and in principle, at the limit \(N_b \to \infty\) the series \(\langle H_0 \rangle (N_b)\) approaches the exact ground state energy. Thus, a measure of the accuracy is provided by the deviation from 0, the known limit value, of the "convergence speed" \(\left[ \langle H_0 \rangle (N''_b) - \langle H_0 \rangle (N'_b) \right]/(N''_b - N'_b)\), where \(N'_b\) and \(N''_b\) are two consecutive values of \(N_b\). A different measure of the accuracy is the variance \(\sigma = \sqrt{\langle H_0^2 \rangle (N_b) - \langle H_0 \rangle (N_b)^2}\). The variational ground state energy \(E_g = \langle H_0 \rangle (N_b)\) [17] and the present results obtained for \(\sigma^2\) are given in Appendix, Table II. The effective value defined in the Appendix-(b) is \(E^{eff}_g = -0.524 010 140 465 960 215 38(56)\) f a.u.. Previous estimates of \(E_g\) in Ps\(^-\) by using the correlation-function hyperspherical-harmonic method and the stochastic variational method are \(-0.524 010 139 0\) f a.u., respectively \(-0.524 010 140 452\) f a.u. [16]. The effective value obtained in [15] by
using the extrapolation formula \( E_g(N_b) = E_g^{\text{eff}} + A/N_b^p \) is \(-0.524 \, 010 \, 140 \, 465 \, 956(8)\) f.a.u..

### III. Relativistic and QED Corrections

The quantum description of a relativistic charged fermion based on Dirac equation requires two spin-1/2 wave functions, \( |\psi_+\rangle \) and \( |\psi_-\rangle \), corresponding to the retarded and advanced waves, respectively. For the particle eigenstates with energy \( E \sim mc^2 \), \( |\psi_-\rangle \sim K|\psi_+\rangle \), \( K = \vec{\sigma} \cdot \vec{p}/(2mc) \), and the normalization condition \( \langle \psi_+ | \psi_+ \rangle + \langle \psi_- | \psi_- \rangle = 1 \), can be written in terms of the large components as \( \langle \phi | \phi \rangle = 1 \), where \( |\phi\rangle = (1 + K^2/2)|\psi_+\rangle \). The antiparticle eigenstates are related in principle to the solutions with \( E \sim -mc^2 \), when \( |\psi_-\rangle \) become the large components. Therefore, in general, the normalized eigen state of a nonrelativistic Schrödinger equation for a particle or antiparticle should be seen as an approximation for \( |\phi\rangle \approx (1 + K^2/2)|\psi_+\rangle \), where \( |\psi_+\rangle \) denotes the corresponding large component. By definition, if \( H_L|\psi_L\rangle = E_L|\psi_L\rangle \), then \( H_{L,K}|\phi\rangle = E_L|\phi\rangle \), where \( H_{L,K} = H_L + [K^2, H_L]/2 \) includes both the nonrelativistic Hamiltonian and the lowest order correction terms.

In the interacting \( e^-e^+e^- \) system \( H_{L,K} \) will be restricted to \( H_0 + H_1 + H_2 \), where \( H_0 \) is given by Eq. (1). The term

\[
H_1 = -\frac{1}{8m^2c^2} (p_1^4 + p_2^4 + p_3^4)
\]

(\( p_i = |\vec{p}_i| \)) takes into account the relativistic variation of the mass with velocity, and

\[
H_2 = -\frac{1}{8m^2c^2} \sum_{i=1}^{3} [\vec{p}_i \cdot [\vec{p}_i, V]]
\]

derives from the sum between the term \( 2(\vec{p}V) \cdot \vec{p})/(2mc)^2 \) of \( H_L \) and the commutator \([K^2, V]/2 = 2[p^2, V]/(4mc)^2 \). Here \( V(R, R_1, R_2) = e^2(1/R - 1/R_1 - 1/R_2) \equiv V f \) a.u. and \( R = a_\mu r, R_{1,2} = a_\mu r_{1,2} \).

The magnetic current-current interaction plus the retardation correction corresponding to the lowest-order Breit interaction are described by the additional term

\[
M_2 = -\frac{e^2}{2m^2c^2} \left\{ R_1^{-1} [\vec{p}_1 \cdot \vec{p}_2 + \vec{r} \cdot (\vec{r} \cdot \vec{p}_1)\vec{p}_2] 
- R_1^{-1} [\vec{p}_1 \cdot \vec{p}_3 + \vec{r}_1 \cdot (\vec{r}_1 \cdot \vec{p}_1)\vec{p}_3] 
- R_2^{-1} [\vec{p}_2 \cdot \vec{p}_3 + \vec{r}_2 \cdot (\vec{r}_2 \cdot \vec{p}_2)\vec{p}_3] \right\}
\]
such that the total Hamiltonian for $Ps^-$ that will be considered here is $H = H_0 + H_1 + H_2 + M_2$. In a classical relativistic many-body system, the dynamical CM defined by the condition $\sum_i \vec{p}_i = 0$, is not necessarily the same as the geometrical centre of mass, located at $\vec{R}_{CM} = \sum_i m_i \vec{R}_i / \sum_i m_i$. In the present case, if $H = H_0 + H_1 + H_2 + M_2$, only the dynamical CM is inertial, because $[\vec{p}_1 + \vec{p}_2 + \vec{p}_3, H] = 0$, while $[\vec{r}_1 + \vec{r}_2 + \vec{r}_3, H]$ is not a constant. The use of the Hylleraas basis ensures that the present calculation takes place in the dynamical CM frame, because by the choice of the coordinates $-i\nabla_i = \vec{p}_i/(f\alpha mc)$ and $\nabla^3 \Phi = (-\nabla_1 - \nabla_2) \Phi$ for any variational wavefunction $\Phi$.

The expectation value $\langle H_1 \rangle = -(1/64)\langle \nabla_1^4 + \nabla_2^4 + \nabla_3^4 \rangle \alpha^2 f$ a.u. can be calculated either directly, or by assuming that in the ground state $\langle H_0 \langle \psi \rangle \rangle = \langle \mathcal{O}_p H_0 \rangle = \mathcal{E}_g (\mathcal{O}_p) \langle \omega \rangle$ for any operator $\mathcal{O}_p$, and using the equalities $\nabla_1^2 + \nabla_2^2 = 2(\vec{H}_0 - \vec{V} + f \vec{\nabla}_1 \cdot \vec{\nabla}_2)$, with $\vec{H}_0 = \vec{H}_0/(f\text{a.u.})$, and

$$
\nabla_1^4 + \nabla_2^4 = 4(\vec{H}_0 - \vec{V} + f \vec{\nabla}_1 \cdot \vec{\nabla}_2)^2 - 2\nabla_1^2 \nabla_2^2 ,
$$

$$
\nabla_3^4 = (-\vec{\nabla}_1 - \vec{\nabla}_2)^2 = \nabla_1^4 + \nabla_2^4 + 4(\nabla_1 \cdot \nabla_2)^2 + 2\nabla_1^2 \nabla_2^2 + 4(\nabla_1^2 + \nabla_2^2) \nabla_1 \cdot \nabla_2 .
$$

Although formally the same, within a finite basis the two expressions give slightly different results ($\langle \nabla_1^4 \rangle$, $\langle \nabla_1^4 \rangle_E$), presented in the Appendix, Table III. In the numerical estimates we have used only $\langle \nabla_1^4 \rangle_E$, because of its rapid convergence and higher accuracy in the effective value.

The term $H_2$ contains the singular operators $\Delta_1 \vec{V} = -4\pi [\delta(\vec{r}) - \delta(\vec{r}_1)]$, $\Delta_2 \vec{V} = -4\pi [\delta(\vec{r}) - \delta(\vec{r}_2)]$, and $\Delta_3 \vec{V} = 4\pi [\delta(\vec{r}_1) + \delta(\vec{r}_2)]$, which yield

$$
\langle H_2 \rangle = \alpha^2 \pi \langle \delta(\vec{r}_1) + \delta(\vec{r}_2) - \delta(\vec{r}) \rangle f^3 \text{ a.u.}
$$

Previous estimates of $\langle \delta(\vec{R}_1) \rangle$ ($= a_{\mu}^{-3} \langle \delta(\vec{r}_1) \rangle$) in $Ps^-$ by using the correlation - function hyperspherical - harmonic method and the stochastic variational method are 0.020 733 14(6)$a_0^{-3}$, respectively 0.020 731 048 976 $a_0^{-3}$ [16]. The same methods give for $\langle \delta(\vec{R}) \rangle$ the values 0.000 170 997(2)$a_0^{-3}$ and 0.000 171 112 600 741 $a_0^{-3}$, respectively [16]. The results of the present calculation, in the same units ($a_0^{-3}$), are listed in Appendix, Table IV as a function of the dimension $N_0$ of the basis set.

The expectation values which appear in the calculus of $\langle M_2 \rangle$, obtained when $N_0 = 324$ are

$$
u_{ee} = \langle r^{-1} \nabla_1 \cdot \nabla_2 \rangle = -0.008 267 646 67 ,$$
\[ v_{ee} = \langle r^{-1} \hat{r} \cdot (\hat{r} \cdot \nabla_1) \nabla_2 \rangle = 0.019 \, 610 \, 925 \, 35 \]

and for \( i = 1, 2 \)

\[ u_{ep} = \langle r^{-1}_i (\nabla_i \cdot \nabla_3) \rangle = 1.535 \, 434 \, 049 \, 31 \]
\[ v_{ep} = \langle r^{-1}_i \hat{r}_i \cdot (\hat{r}_i \cdot \nabla_3) \nabla_i \rangle = -0.555 \, 009 \, 821 \, 912 \, . \]

In terms of these variables, \( \langle M^2 \rangle = 0.5 \alpha^2 \) a.u. with \( w = u_{ee} + v_{ee} - 2u_{ep} - 2v_{ep} = -1.949 \, 505 \, 176 \, 125 \). For the 2528-dimensional basis set \( w = -1.949 \, 505 \, 250 \, 368 \). The average of the last three consecutive values, obtained for \( N_b = 1990, 2276 \) and 2528 gives the effective matrix element \( w^{\text{eff}} = -1.949 \, 505 \, 250 \, 368 \).

The effective sum of the spin independent relativistic correction terms \( \langle H_1 \rangle \), \( \langle H_2 \rangle \) and \( \langle M^2 \rangle \) is \( -0.145 \, 476 \, 184 \, 397(8) \alpha^2 f \) a.u. which decrease the Ps\textsuperscript− ground state energy to

\[ E^\text{eff}_g = \langle H \rangle^\text{eff} = E^\text{eff}_g - 0.145 \, 476 \, 184 \, 397(8) \alpha^2 f \text{ a.u.} \, . \]  

(14)

The same calculations yield for the corrected ground state energy \( E^0_g \), in neutral positronium \( E^0_g = -(0.5 + 5\alpha^2/32) f \) a.u.. However, for this relativistic two-body system the finite mass corrections to the energy provided by the one-body Dirac equation can be obtained exactly up to the order \( \alpha^2 \text{Ry} \) by using the formula [20]

\[ E_{(n,j,Z)} = \frac{1}{\alpha^2} \left[ \frac{1}{\sqrt{1 + (Z \alpha)^2/(n - \nu)^2}}, \nu = j + 1/2 - \sqrt{(j + 1/2)^2 - (Z \alpha)^2} \right] f \text{ a.u.} \]  

(15)

where \( \eta = 1/\sqrt{1 + (Z \alpha)^2/(n - \nu)^2}, \nu = j + 1/2 - \sqrt{(j + 1/2)^2 - (Z \alpha)^2} \). The expansion \( E_{(1,1/2,1)} \approx -(0.5 + 5\alpha^2/32) f \) a.u. reproduces \( E^0_g \), showing that the relativistic corrections given by the expectation value of \( H \) are reliable.

Within QED the constituents of the three body-system \( e^- e^+ e^- \) cease to be "elementary", because they are subject not only to the mutual two-body Coulomb-Breit interaction, but are also coupled to the vacuum fluctuations of the electromagnetic field \( \vec{A} \) [21]. The interaction terms accounting for this coupling are represented by an infinite series of increasingly complicated Feynman diagrams with closed photon lines. However, the complexity is increased recursively, by taking into account at each order three basic processes, represented by the anomalous magnetic moment (vertex) corrections,
electron self-mass and vacuum polarization diagrams.

Although formally complicated, the main effect of the coupling to the field degrees of freedom is simply a change in the charge and mass parameters $e$ and $m$ of the theory. This contribution has already been taken into account, because it is included in the measured values of $e$ and $m$ used to define the atomic unit of energy. Though, the QED corrections in the interacting three body-system $e^- e^+ e^-$ are not the same as for the free particles, and the differences still need to be considered.

The vacuum polarization properties have been studied first by Heisenberg [22] and Uehling [23], showing that a given charge density $\rho(\vec{R})$ induces a polarization charge $\delta\rho(\vec{R}) = -(\alpha/15\pi)\lambda_0^2 \nabla^2 \rho(\vec{R})$, where $\lambda_0 = \hbar/mc$ is the Compton wavelength of the electron. The induced charge leads to deviations from the standard Coulomb interaction. Thus, the vacuum behaves as an inhomogeneous dielectric, in which the mutual potential energy between two point-like charges $Z_1$ and $Z_2$ is [23]

$$V(R) = \frac{Z_1 Z_2 e^2}{R} \left[ 1 - \frac{\alpha}{\pi} U(R) \right],$$

by $U(R)$ denoting the Uehling potential. This potential is singular at $R = 0$, falls of exponentially for $R > 0$, and satisfies the integral condition $\int d^3 R U(R) = -4\pi \lambda_0^2 / 15$. Therefore, it can be well approximated by a delta function, $U(R) = -4\pi (\lambda_0^2 / 15) \delta(R)$. In the case of Ps$^-$, the correction term introduced by this potential is

$$\langle H_{vp} \rangle = \frac{4}{15} \alpha^3 \langle \delta(\vec{r}) - \delta(\vec{r}_1) - \delta(\vec{r}_2) \rangle f^3 \text{ a.u.}$$

By using the effective values given in Appendix, Table IV, the contribution of the vacuum polarization to the Ps$^-$ ground state energy is $\langle H_{vp} \rangle^{eff} = -0.022 024 212 934 6(7) \alpha^3$ f a.u.. It is important to remark that this value takes into account the positron recoil (the “mass polarization” term) because the wave functions are obtained by minimizing the full nonrelativistic Hamiltonian. In neutral positronium, $\langle \delta(\vec{R}_1) \rangle_{Ps} = 1/(\pi a_0^3) = 1/(8\pi a_0^3)$, and the vacuum polarization correction is $-1/(15\pi) \alpha^3$ f a.u.. As it was shown early by the Lamb shift measurements [24], the main QED correction appears however from the coupling to the vacuum fluctuations of the field rather than from the vacuum polarization ( [21] p. 59). For
a free electron the ground state energy is given by its rest mass \( m = m_b + \delta m \), consisting of the uncoupled value \( m_b \) and the positive renormalization term \( \delta m = (3\alpha m_b/2\pi) \ln(\Lambda/m_b) \) due to the electromagnetic self-energy, where \( \Lambda \) is a large (formally infinite) cutoff mass.

Similarly, the coupling to the field modes also affects the intrinsic excitations of a many-body system. In a bounded \( N \)-particle system, the shift \( \Delta E_n \) in the energy \( E_n = \langle n|H_0|n \rangle \) of the level \( |n \rangle \) due to the exchange of a transverse photon can be obtained by using the time-independent second-order perturbation expression

\[
\Delta E_n = -\langle n, 0_f|H_c(\vec{A})\frac{1}{H_0 + H_A - E_n}H_c(\vec{A})|n, 0_f \rangle .
\]  

(18)

Here \( H_c(\vec{A}) = \sum_{i=1}^{N} h_i(\vec{A}) \) is the sum over all particles of the one-body coupling terms \( h_i(\vec{A}) = -e_i \vec{\alpha}_i \cdot \vec{A}(\vec{r}_i) \), \( \vec{\alpha}_i \approx \vec{p}_i/(m_i c) \),

\[
\vec{A}(\vec{r}) = \frac{\hbar c}{2\pi} \int \frac{d^3k}{\sqrt{k}} \sum_{\lambda=1,2} \vec{e}_\lambda (\hat{a}^\dagger_{k\lambda} e^{-i\vec{k} \cdot \vec{r}} + \hat{a}_{k\lambda} e^{i\vec{k} \cdot \vec{r}})
\]

(19)

is the quantized transverse vector potential of the photon \((\vec{e}_\lambda \cdot \vec{k} = 0, \vec{e}_\lambda^2 = 1)\), \( H_A = \int d^3k \sum_{\lambda=1,2} \hbar c k a^\dagger_{k\lambda} a_{k\lambda} \) is the free field Hamiltonian, and \(|0_f \rangle \) denotes the photon vacuum. This shift has the form \( \Delta E_n = \sum_{i=1}^{N} X_i^n + \sum_{i<j} Y_{ij}^n \), where

\[
X_i^n = -\langle n, 0_f|h_i(\vec{A})\frac{1}{H_0 + H_A - E_n}h_i(\vec{A})|n, 0_f \rangle
\]

(20)

and

\[
Y_{ij}^n = -2\text{Re}[\langle n, 0_f|h_i(\vec{A})\frac{1}{H_0 + H_A - E_n}h_j(\vec{A})|n, 0_f \rangle]
\]

(21)

It is important to remark that the interaction with the vacuum field fluctuations may affect not only the intrinsic dynamics, but also the center of mass. In a classical two-body system coupled to the field, \( H_c \) can be written in terms of the canonical pairs \((\vec{r}, \vec{p}_\mu) \equiv (\vec{R}_1 - \vec{R}_2, \mu \vec{p}_1/m_1 - \mu \vec{p}_2/m_2) \) and \((\vec{R}_{CM}, \vec{P}_{CM}) \equiv (\mu \vec{R}_1/m_2 - \mu \vec{R}_2/m_1, \vec{P}_1 + \vec{P}_2) \) of intrinsic and respectively, center of mass variables, as

\[
\vec{p}_\mu \cdot \left[ \frac{e_2}{m_2} \vec{A}(\vec{R}_2) - \frac{e_1}{m_1} \vec{A}(\vec{R}_1) \right] - \frac{\mu}{m_1 m_2} \vec{P}_{CM} \cdot \left[ e_1 \vec{A}(\vec{R}_1) + e_2 \vec{A}(\vec{R}_2) \right]
\]
This expression shows that in a neutral two-body system (such as Ps) the center of mass energy is not affected by the field only if \( \vec{A}(R_1) = \vec{A}(R_2) \), or when the size of the system is negligible compared to the photon wavelength (dipole approximation).

In a quantum \( N \)-body system it is convenient to take advantage of the finite size effects by writing \( \vec{A} \) as the incoherent sum of long and short wavelength components, \( \vec{A}_L \) and \( \vec{A}_S \), obtained by decomposing \( \int d^3k \) as \( \int_{|\vec{k}|<k_L} d^3k + \int_{k_L<|\vec{k}|<k_M} d^3k \), where \( k_L \) and \( k_M \) are cutoff parameters. Each domain brings its own contribution to the matrix elements, which can be similarly decomposed as

\[
X^n_i = X^{Ln}_i + X^{Sn}_i, \quad Y^n_{ij} = Y^{Ln}_{ij} + Y^{Sn}_{ij}.
\] (22)

At the end of the calculation \( k_L \) should disappear, while \( k_M \to \infty \).

If \( H_0 \) consists of the kinetic energy term plus a local potential \( V \), then a non-relativistic calculation within the dipole approximation yields

\[
X^{Ln}_i = -\frac{\alpha}{3\pi m^2 c^2} [2\hbar c k_L \langle n|\vec{p}_i^2|n\rangle + \langle n|[\vec{p}_i, [\vec{p}_i, V]]|n\rangle] \ln \frac{k_L}{k_R} - 2B^n_{ii},
\] (23)

where \( k_R = R_M/\hbar c \), \( R_M \) is a dimensional constant with units of energy, and \( B^n_{ii} \) are the diagonal elements of the matrix \( [B^n_{ij}] \) defined by

\[
B^n_{ij} = \sum_m (E_n - E_m) \text{Re}(\langle n|\vec{p}_i|m\rangle \cdot \langle m|\vec{p}_j|n\rangle) \ln \frac{|E_n - E_m|}{R_M}.
\] (24)

The first term depends only on the kinetic energy, and it can be written as \(-\delta m_L \langle n|\vec{p}_i^2|n\rangle/(2m^2)\), \( \delta m_L = 4\pi r_e k_L/(3\pi) \), where \( r_e = \alpha \hbar / (mc) \) denotes the classical radius of the electron. It contributes also to the energy of a free particle (\( V = 0 \)) and has the structure of a first-order perturbation shift induced by a variation \( \delta m_L \) of the nonrelativistic mass. Thus, such terms can be taken into account simply by a redefinition of the cutoff mass \( \Lambda \).

A relativistic calculation of the one-body QED correction arising from the exchange of a transverse hard photon at a Coulomb vertex [25], [21] p.177, yields

\[
X^{Sn}_i = \frac{\alpha \hbar^2}{3\pi m^2 c^2} (\ln \frac{mc}{2\hbar k_L} + \frac{5}{6}) \langle n|\Delta_i V|n\rangle,
\] (25)

\( (5/6 = 11/24 + 3/8) \) such that

\[
X^n_i = -\frac{\delta m_L}{2m^2} \langle n|\vec{p}_i^2|n\rangle + \frac{\alpha}{3\pi m^2 c^2} \hbar^2 (\ln \frac{mc}{2\hbar k_R} + \frac{5}{6}) \langle \Delta_i V \rangle_n + 2B^n_{ii}.
\] (26)
The quantity $Y_{ij}^{L_n}$ can be expressed as

$$Y_{ij}^{L_n} = -\frac{\delta m_L}{m^2} \frac{e_i e_j}{e^2} \langle \vec{p}_i \cdot \vec{p}_j \rangle_n - \frac{2\alpha}{3\pi m^2 c^2} \frac{e_i e_j}{e^2} \{\langle [\vec{p}_i', [\vec{p}_j, V]] \rangle_n \ln \frac{k_L}{k_R} - 2B_{ij}^n \} .$$ (27)

In the case of $\text{Ps}^-$ there are three terms $X_i^n$, one for each electron ($i = 1, 2$) and one for the positron ($i = 3$), and three terms $Y_{ij}^{L_n}$, $i < j$. The contribution to $\Delta E_n$ arising from the terms linear in $\delta m_L$ of $X$ and $Y^L$ is $\delta E_n = -\delta m_L \langle n| (\vec{p}_1 + \vec{p}_2 - \vec{p}_3)^2 | n \rangle / (2m^2)$. In the dynamical CM frame, this energy shift can be accounted, for example, by an effective variation $3\delta m_L$ in the total mass of the electron-electron pair and $\delta m_L$ in the mass of the positron, or by a variation of $4\delta m_L$ in only one of them.

The definition of the Bethe logarithm $\beta_n \equiv 2B_{33}^n / \langle [\vec{p}_3, [\vec{p}_3, H_0]] \rangle_n$, and the identity $m^2 \sum_{i,j} e_i e_j B^n(i,j)/(m_i m_j) = e^2 B^n(3,3)(1 + m/m_3)^2$ (valid if $m_1 = m_2 = m$ and $\langle n| \sum_i \vec{p}_i | n' \rangle = 0$ for any $n, n'$), show that $\sum_i X_i^n + \sum_{i<j} Y_{ij}^{L_n} = \delta_0 E_n + \delta_1 E_n + \delta_2 E_n$, where

$$\delta_1 E_n = \frac{\alpha \hbar^2}{3\pi m^2 c^2} [-4\beta_n \langle \Delta_3 V \rangle_n + (\ln \frac{mc}{2\hbar k_R} + \frac{5}{6}) \sum_{i=1}^3 \langle \Delta_i V \rangle_n] \quad (28)$$

$$= \frac{4\alpha^3}{3} \left[-4\beta_n \langle \delta^3(r_1) + \delta^3(r_2) \rangle_n + 2(\ln \frac{mc}{2\hbar k_R} + \frac{5}{6}) \langle \delta^3(\mathbf{r}_1) + \delta^3(\mathbf{r}_2) - \delta^3(\mathbf{r}) \rangle_n \right] f^3 \text{ a.u.}$$

and $\delta_2 E_n \equiv \sum_{i<j} \langle W_{ij}^{L} \rangle_n$ is given by the expectation value of the potential

$$W_{ij}^{L}(k_L) = \frac{8\alpha^3}{3} \ln \frac{k_L}{k_R} \delta^3(\mathbf{r}_{ij}) f^3 \text{ a.u.} \quad (29)$$

The term $Y_{ij}^{S_n}$ due to the exchange of a short wavelength (hard) transverse photon between different particles will be decomposed as $Y_{ij}^{S_n} = Y_{ij}^{S_{2n}} + Y_{ij}^{S_{3n}}$, according to the expansion $1/(H_0 + H_A - E_n) \approx 1/H_A - (H_0 - E_n)/(H_A)^2$. The contribution from $1/H_A$ is

$$Y_{ij}^{S_{2n}} = -2\langle n, 0_f | h_i(\hat{A}_S) H_A^{-1} h_j(\hat{A}_S) | n, 0_f \rangle . \quad (30)$$

In the limit $k_L \to 0, k_M \to \infty$, the integral over $k$ in this matrix element can be evaluated by using the identity

$$\int \frac{d^3k}{k^2} e^{i\vec{k} \cdot \vec{r}} (\vec{A} \cdot \vec{B} - \hat{k} \cdot \hat{A} \cdot \hat{B}) = \frac{\pi}{r} (\vec{A} \cdot \vec{B} + \hat{r} \cdot \hat{A} \hat{r} \cdot \vec{B}) .$$
showing that the sum $\sum_{i<j} Y_{ij}^{S2n}$ becomes the two-body term $\langle M_2 \rangle_n$ of order $\alpha^2 \text{Ry}$, already taken into account. Thus, the only new contribution is the next-order term

$$Y_{ij}^{S3n} = 2 \text{Re} \langle n, 0_f | h_i(\vec{A}_S) \frac{H_0 - E_n}{H^2} h_j(\vec{A}_S) | n, 0_f \rangle$$

which is the expectation value of the two-body potential

$$W_{ij}^S(k_L, k_M) = \frac{2\alpha^3}{3\pi} \left[ \frac{3}{2} f(k_L, k_M, r_{ij}) + 4\pi \delta^3(r_{ij}) \ln \frac{k_M}{k_L} \right] f^3 \text{ a.u.}$$

Here $f(k_L, k_M, r) = \frac{2}{3} \left[ j_0(k_M r) + j_2(k_M r) - j_0(k_L r) - j_2(k_L r) \right] / (3r^3)$ is the function introduced by Araki [26], written in terms of the spherical Bessel functions $j_0, j_2$. When $k_L \rightarrow 0, k_M \rightarrow \infty$, $f(0, \infty, r) = -2/(3r^3)$, but the logarithmic factor in the second term of $W_{ij}$ is divergent at both limits. However, the divergence in $k_L$ is cancelled by the low-energy term, and the sum $W_{ij}(k_M) = W_{ij}^L(k_L) + W_{ij}^S(k_L, k_M)$,

$$W_{ij}(k_M) = \frac{2\alpha^3}{3\pi} \left[ \frac{3}{2} f(0, k_M, r_{ij}) + \frac{\delta(r_{ij})}{r_{ij}^2} \ln \frac{k_M}{k_R} \right] f^3 \text{ a.u.} ,$$

is independent of $k_L$. The divergent factor containing $k_M$ contributes only when $|n\rangle$ is an $S$ state, but in this case the expectation value $\langle 1/r^3 \rangle_n$ is also logarithmically divergent. It is however possible to define a limit for the sum of these infinite terms in the sense of the principal value. Let

$$D(a, r) = \frac{\theta(r - a)}{r^3} - \frac{\delta(r)}{r^2} \ln \frac{a}{a} \mu$$

be a distribution depending on the positive radius parameter $a = \eta/k_M$, where $\eta$ is a positive scale factor. Because $r^2 \partial_a D(a, r) = [\delta(r) - \delta(r - a)]/a$, when $k_M \rightarrow \infty$ the expectation value $\langle D(a, r) \rangle_n$ is finite. In terms of this distribution we can define the principal value

$$\mathcal{P} \left[ \frac{3}{2} f(0, k_M, r) + \frac{\delta(r)}{r^2} \ln \frac{k_M}{k_R} \right] \big|_{k_M \rightarrow \infty} = 4\pi \delta^3(r) \ln \frac{\eta}{a_\mu k_R} - \lim_{a \rightarrow 0} D(a, r) .$$

The choice of a scale factor $\eta = e^{4/3 - \gamma}$, where $\gamma$ is the Euler’s constant, yields the formula used by Araki [26]

$$\langle W_{ij} \rangle_n = -\frac{2\alpha^3}{3\pi} \left[ Q_{ij}^n + 4\pi \langle \delta^3(r_{ij}) \rangle_n \ln a_\mu k_R - \frac{4}{3} \right] f^3 \text{ a.u.} ,$$

(36)
\[ Q_{ij}^n = \lim_{a \to 0} \langle D(a, r) + 4\pi \gamma \delta^3(r_{ij}) \rangle_n. \]

In $\text{Ps}^-$ this yields for the effective two-body contribution $\delta_2 E_n = \delta_{2L} E_n + \sum_{i<j} \langle W_{ij}^S \rangle_n = \sum_{i<j} \langle W_{ij} \rangle_n$ the expression

\[ \delta_2 E_n = -2\alpha^3 \frac{3}{3\pi} \left[ Q_{12}^n + Q_{13}^n + Q_{23}^n \right] + 4\pi \left( \ln a_k R - \frac{4}{3} \right) \langle n| \delta^3(r_1) + \delta^3(r_2) + \delta^3(r)|n \rangle \right] f^3 \text{ a.u.}. \]

Summarizing these results, the effective QED contribution of order $\alpha^3$ to the energy level $E_n$ of $\text{Ps}^-$ due to the exchange of a transverse photon is

\[ \delta_{1P} E_n = \delta_1 E_n + \delta_2 E_n. \]

This sum is independent of the arbitrary energy unit $R_M$, as it should, but for the purpose of numerical calculations we choose $R_M = f \text{Ry}$. With this choice, $a_\mu k_R = \alpha/2$, and $mc/(2\hbar k_R) = 1/(f \alpha^2)$.

The corresponding terms for positronium can be obtained from the expressions given above simply by neglecting all the expectation values containing the variables $r_2$ and $r$, involving the second electron. For the Ps ground state $Q_{13}^{P_1} = -4 \ln 2$, while $\beta_g^{P_1} = \gamma_g$ is the same as the Bethe logarithm for hydrogen $\beta_g^H = 2.984 128 555 765 497 611(4)$, each Bethe logarithm being calculated using the corresponding reduced Rydberg constant [27]. For the $\text{Ps}^-$ ground state the numerical values of $Q_{12}^P$ and $Q_{13}^P$ used in the present estimates are listed in Table V, while $\beta_g = 3.005 030(2)$ [27] (including the finite mass correction).

To the same order we should consider also the double photon exchange term (including the Coulomb part) $\delta_{2\mu} E_n$ [26] [28]

\[ \delta_{2\mu} E_n = -2\alpha^3 \frac{3}{3\pi} \left[ Q_{12}^n + Q_{13}^n + Q_{23}^n \right] \]

\[ -4\pi \left( \ln f \alpha - \frac{4}{3} \ln 2 + \frac{13}{6} \right) \langle n| \delta^3(r_1) + \delta^3(r_2) + \delta^3(r)|n \rangle \right] f^3 \text{ a.u.}, \]

and the energy shift associated with the two-photon decay.

In general, any coupling which makes the levels unstable produces a complex energy shift $\Delta_c E_n = \delta_c E_n - i\Gamma_c^n/2$, where $\delta_c E_n$ is a correction to the level centroid, $\lambda_c^n = \Gamma_c^n/h$ is the decay rate, and $c$ denotes the decay channel.

Neutral positronium normally decays by spontaneous $e^+e^-$ annihilation into two photons if the total spin $S_{ep} = 0$, ($S_{ep} = \vec{s}_e \cdot \vec{s}_p$), and in three photons if $S_{ep} = 1$ [29]. The corresponding decay rates are such that $\Gamma_{3\gamma} \sim \alpha \Gamma_{2\gamma}$. 

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and the first correction arises from two photon annihilation. In this channel
\[ \delta_2\gamma E_n/\Gamma_{2\gamma}^n = -(1 - \ln 2)/\pi \] [30], where
\[ \Gamma_{2\gamma}^n = 2\pi\alpha^3 \langle (2 - \vec{S}_{cp})\delta^3(r_1) \rangle_{nf} f^3 \text{ a.u.} \] (39)

For the Ps ground state (\( \vec{S}_{cp} = 0 \)) this yields a decay rate
\[ \lambda_{(Ps,2\gamma)} = \alpha^3\text{Ry}/\hbar = 8.04\text{nsec}^{-1} \], in good agreement with the experimental result 7.99(11)nsec\(^{-1} \) [31].

In the Ps\(^- \) ground state the electron spins are coupled to 0, and the two-photon annihilation can take place between the positron and any of the two electrons. The total rate depends on
\[ \langle \vec{S}_{13}^2 + \vec{S}_{23}^2 \rangle_g = 3 \], and can be expressed in the form
\[ \Gamma_{(Ps^-,2\gamma)} = 2\pi\alpha^3 \langle \delta^3(r_1) \rangle f^3 \text{ a.u.} \] (40)

The effective ground state expectation value \( \langle \delta(\vec{R}_1/a_0) \rangle \) given in the Appendix, Table IV, yields \( \lambda_{(Ps^-,2\gamma)} = 2.092 797(1)\text{nsec}^{-1} \), in good agreement with the previous estimates [32] and the experimental result 2.09(9) nsec\(^{-1} \) [12]. The corresponding level shift is
\[ \delta_2\gamma E_g = -(1 - \ln 2)\Gamma_{(Ps^-,2\gamma)}/\pi. \]

Summarizing the results of these calculations, the effective ground state expectation values of the nonrelativistic Hamiltonian and the first relativistic and QED corrections for Ps and Ps\(^- \) are collected in the following table

| \( E_{g} \text{[Ry]} \) | Ps | Ps\(^- \) | \( E_{Ps} - E_{Ps^-} \) |
|------------------|------------------|-----------------|------------------|
| \( H_1/\alpha^2 \) | -5/32 | -0.161 254 673 938 50(6) | 0.005 004 673 938 50(6) |
| \( H_2/\alpha^2 \) | 1/4 | 0.259 466 645 837(8) | -0.009 466 645 837(8) |
| \( M_2/\alpha^2 \) | -1/4 | -0.243 688 156 296 0(1) | 0.006 311 843 704 0(1) |
| \( H_{vp}/\alpha^3 \) | -1/(15\pi) | -0.022 024 212 934 6(7) | 0.000 803 553 855 7(7) |
| \( \delta_{1p} E_g/\alpha^3 \) | 2.766 873 00(3) | 3.006 491 9(9) | -0.239 618 9(9) |
| \( \delta_{2p} E_g/\alpha^3 \) | -0.585 335 778(7) | -0.510 831 605(7) | -0.074 504 17(1) |
| \( \delta_{2\gamma} E_g/\alpha^3 \) | -(1 - \ln 2)/\pi | -0.025 448 161 055(1) | -0.072 226 124 976(1) |

In Ps\(^- \) the nonrelativistic one electron binding energy 0.024 010 140 465 960 215 38(56) Ry is practically the same as the one determined in [15], and close to the older estimate of 0.024 010 113 Ry [32]. The effect of the correction terms is to decrease slightly this energy to
\[ B' = [0.024 010 140 465 960 215 38(56) - 0.010 773 815 602(8)\alpha^2] \] (41)
In positronium the observed hyperfine splitting of $1.160 \ 963(9)\alpha^2$ Ry between the otherwise degenerate ground state components corresponds to an additional spin-spin contact term [30]

$$\delta_{ep}^e E_n^0 = 2\pi \alpha^2 \langle \delta^3(r_1) \{ \frac{4}{3} \vec{s}_e \cdot \vec{s}_p (1 - \frac{\alpha}{2\pi}) + \frac{1}{2} \vec{s}_{ep} \cdot \vec{s}_{ep} \{ 1 - (\frac{26}{9} + \ln 4) \frac{\alpha}{\pi} \} \} \rangle_n \ f^3 \text{ a.u.} , (42)$$

shifting the energy of the singlet by $\delta_{ep}^s E_g^0 = -2\alpha^2 (1 - \alpha/2\pi)f^3\text{a.u.} = -0.265 \ 947 \ 576(23) \times 10^{-4}\text{Ry}$. In $\text{Ps}^-$ the electron-electron spin-spin dependent energy shift is [26]

$$\delta_{ee}^e E_g = -\frac{8\pi}{3} \alpha^2 (1 + \frac{5}{2\pi} \alpha) \langle \vec{s}_1 \cdot \vec{s}_2 \delta^3(r) \rangle \ f^3 \text{ a.u.} , (43)$$

while the two electron-positron spin-spin contact terms contribute by

$$\delta_{2ep}^e E_g = \pi \alpha^2 \langle \delta^3(r_1) (\vec{s}_{13}^2 + \vec{s}_{23}^2) [1 - (\frac{26}{9} + \ln 4) \frac{\alpha}{\pi}] \rangle \ f^3 \text{ a.u.} . (44)$$

These formulas yield an additional shift of the $\text{Ps}^-$ ground state energy $\delta_s E_g = \delta_{ee}^e E_g + \delta_{2ep}^e E_g = 0.207 \ 196 \ 744(18) \times 10^{-4} \text{Ry}$, and a contribution to its binding energy of $\delta_{ep}^e E_g^0 - \delta_s E_g = -0.473 \ 144 \ 32(3) \times 10^{-4}\text{Ry}$. Including the spin-spin contact terms, the binding energy becomes

$$B'' = B' + \delta_{ep}^e E_g^0 - \delta_s E_g = 0.023 \ 962 \ 102 \ 492(3)\text{Ry} . (45)$$

### IV. Summary and Conclusions

The calculation of the relativistic and QED corrections to the energy levels of a quantum three-body system represents a challenging problem for the modern theory. Difficulties appear both at conceptual and computational levels, as there is no satisfactory relativistic many-body quantum theory, and the nonrelativistic problem is not integrable.

A quantum three-body system thoroughly investigated since the early days of quantum mechanics is the helium atom. In this system a major simplification occurs, because the reduced electron mass $\mu$ is smaller than the
mass of the positive charge by a factor $1.3707 \times 10^{-4}$, and to a first approximation the relative motion of the nucleus in the center of mass frame can be neglected. The relativistic invariance is partly restored by the Breit interaction, and highly accurate nonrelativistic wave functions can be obtained numerically, from variational calculations. Within this framework, a perturbative treatment of the relativistic and QED corrections gives energy levels in remarkable agreement with experiment [3] [4].

The same procedure was applied in this work to the negative positronium ion. However, by contrast to helium, all three particles have equal mass, and a perturbative treatment of the positron motion becomes inappropriate.

The accuracy of the nonrelativistic energy and variational ground state wave function was discussed in Sect. II. The effective value of $E_g$ estimated here is $-0.262\,005\,070\,232\,980\,107\,69 (28)$ a.u., the same as in [15], [17] and close within $10^{-8}$ to estimates obtained by other methods [16]. The variance of the Hamiltonian for the largest (2528-dimensional) basis set is $2.78 \times 10^{-8}$ a.u., smaller than the level width $\Gamma = \hbar \lambda = 5.06 \times 10^{-8}$ a.u. due to the $(2\gamma)e^-\text{ decay.}$

The calculation of the first relativistic and QED corrections has been presented in Sect. III. Formal expressions of these correction terms have been known for a long time, but the mass polarization term, which cannot be neglected for Ps$^-$, increases dramatically the complexity of the numerical calculations. In this work the calculations have been performed by representing the action of the physical operators on the Hylleraas basis states in terms of a suitable set of elementary operators (Appendix, Table I). The numerical values obtained for some of the most important matrix elements are summarized in the Tables II-V of the Appendix. It was found that the spin independent relativistic terms contribute to the Ps$^-$ ground state energy by $-0.072\,738\,092\,198(4)\alpha^2$ a.u. and the lowest order QED corrections by $1.224\,094\,00(44)\alpha^3$ a.u.. These terms decrease the ground state energy to $E_{g}^{\text{eff}} = -0.262\,008\,467\,959\,9(4)$ a.u.. Both contributions decrease slightly also the one electron binding energy, from the nonrelativistic value $0.012\,005\,070\,232\,980\,10(3)$ a.u. to $0.012\,004\,708\,462\,43(3)$ a.u.. A much larger contribution appears however from the spin-dependent contact terms, which raise the ground state energy to $E_{g}^{\text{eff}} = -0.261\,998\,108\,122(1)$ a.u., and further decrease the binding energy to $0.011\,981\,051\,246(2)$ a.u.. The calculated decay rate by two photon emission is $2.092\,797(1)$ nsec$^{-1}$, close to the previous theoretical results and to the measured value [12].
The binding and ground state energies are shifted also by relativistic corrections of order $\alpha^3$Ry containing spin-orbit magnetic interactions. These contributions are also important, and should be included in the further attempts to improve the accuracy of the present estimates.

**Appendix**

(a) **Elementary operators**

In terms of the elementary operators defined in Table I, the nonrelativistic Hamiltonian contains linear combinations such as

$$
\left( -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 \right) \Phi = (E_2 + E_3 - E_4 + E_5 + E_6 - 0.5E_9

-0.5E_{10} - 0.5E_{11} - 0.5E_{12}) \Phi
$$

for the kinetic energy part, $\tilde{V} \Phi = -E_{13} \Phi$ for the potential energy and

$$\nabla_1 \cdot \nabla_2 \Phi = (E_1 + E_2 + E_3 - E_4 + E_5 + E_6 + E_7 + E_8) \Phi
$$

for the recoil term. The action on the basis states of a linear combination

$$\hat{O}_p = \sum_k f_{pk} E_k,$$

has the general form

$$\hat{O}_p \Phi \equiv \sum_{t=1}^{N_p} q_{px}^t A_t \Phi_{xt},$$

where $x$ denotes the whole set of indices of $\Phi$, $q_{px}^t$ is a factor determined by $x$ and the action of $E_k$ on the radial functions, while $A_t$ denotes the remaining angular operator. In this sum the same state $A_t \Phi_{xt}$ (or $A_t A_{tr} \Phi_{xtr}$ in the case of a product) may appear several times with different scalar factors $q$. Therefore, in general it is possible to reduce the number of terms from $N_p$ to $N_r < N_p$ by partial summations, before the effective calculation of the matrix elements. The reduction increases the speed of the numerical calculation, because $N_r$ can be significantly smaller than $N_p$. For example, $N_p : N_r$ is 20 : 18 in the case of $\nabla_1 \cdot \nabla_2$, 400 : 235 for $(\nabla_1 \cdot \nabla_2)^2$, while for $H_0$ and $H_0^2$ is 31 : 24 and 961 : 427, respectively.
In the computer program the action of $E_k$ consists of both arithmetic and symbolic operations. The arithmetic operations are determined by its action on the radial function $r_1^a r_2^b e^{-\alpha r_1 - \beta r_2}$. The number $n_k$ of distinct polynomial terms generated by this action is given in the second column of Table I. The symbolic operation corresponds to the action of $E_k$ on the spherical harmonics in $Y_{LM}$, and is coded by a character denoting angular operators such as $\hat{r}_1 \cdot \hat{r}_2$ or $\nabla_1 Y \cdot \nabla_2 Y$.

(b) Error estimates

The series of numerical values presented in Tables II-V appear to be convergent, but for comparison with experiment, it is useful to provide also a single effective value, representing the expected result of the present calculation when $N_b \to \infty$. The procedure adopted here to define this value depends on the manner of convergence. In the case of a sequence $\{f_n\}$ convergent as an alternating series, the effective value $f_{eff} = f_{n_y} - f_{n_x}$, given in the last row, was defined as the arithmetic average of its last three consecutive terms, by $f_{eff} = (f_{n_x} + f_{n_y} + f_{n_z})/3$, $n_x < n_y < n_z$, and $\sigma_f^2 = [(f_{n_x} - f_{eff})^2 + (f_{n_y} - f_{eff})^2 + (f_{n_z} - f_{eff})^2]/3$. If $\{f_n\}$ approaches the limit by monotonous increase or decrease, then we can assume that the series can be extended to infinity by the function $F(n) = f_{eff} + Ae^{-\gamma n}$. The matching equations $F(n_x) = f_{n_x}$, $F(n_y) = f_{n_y}$, $F(n_z) = f_{n_z}$ between $F(n)$ and the last three calculated numerical values yield the parameter $f_{eff}$ in the form [17]

$$f_{eff} = f_{n_y} + \frac{f_{n_y} - f_{n_x}}{R - 1}.$$  

Here $R \equiv e^{\gamma (n_y - n_x)}$ is the solution of the equation $R - 1 = R_y [1 - R^{(n_y - n_z)/(n_y - n_x)}]$, where

$$R_y = \frac{f_{n_y} - f_{n_z}}{f_{n_z} - f_{n_y}}.$$  

The error is assumed to be

$$\sigma_f = |f_{n_y} - f_{eff}| = \frac{|f_{n_y} - f_{n_x}|}{R - 1}.$$  

If $n_y - n_x = n_z - n_y$, then $R = R_y$. When $n$ is simply $N_b$, then $n_y - n_x = 286$ is larger, but close to $n_z - n_y = 252$, and $R = R_y$ still provides a reasonable
(c) **Expectation values of $p^4$**

The expectation values $\langle \nabla_4^1 \rangle = \langle \nabla_2^1 \rangle$ for electrons in the $\text{Ps}^-$ ground state can be calculated numerically either directly, as

$$\langle \nabla_4^1 \rangle = 4\langle (E_2 - 0.5E_4 + E_6 - 0.5E_9 - 0.5E_{11})^2 \rangle$$

or as $\langle \nabla_4^1 \rangle_E = 0.5\langle \nabla_4^1 + \nabla_2^1 \rangle_E = 0.5\langle (\nabla_1^2 + \nabla_2^2)^2 \rangle_E - \langle \nabla_1^2 \nabla_2^2 \rangle$, where the first term is expressed in the form

$$0.5\langle (\nabla_1^2 + \nabla_2^2)^2 \rangle_E = 2\langle (\tilde{E}_g - \tilde{V} + f\nabla_1 \cdot \nabla_2)^2 \rangle$$

$$= 2[\tilde{E}_g^2 - 2\tilde{E}_g(\tilde{V} - f\nabla_1 \cdot \nabla_2) + (\tilde{V} - f\nabla_1 \cdot \nabla_2)^2)]$$

($\tilde{E}_g \equiv E_g/f \text{ a.u.}$) by assuming that the variational ground state is practically eigenstate of $H_0$. Although formally the same at the limit $N_b \to \infty$, the numerical values obtained for $\langle \nabla_4^1 \rangle$ and $\langle \nabla_4^1 \rangle_E$ at finite $N_b$ are slightly different. These estimates are given as a function of the basis size $N_b$ in the first two columns of Table III. The third column contains the relativistic correction term for the positron, given by

$$\langle \nabla_3^4 \rangle_E = \langle (\nabla_1 + \nabla_2)^4 \rangle_E = 2\langle \nabla_1^4 \rangle_E + 2\langle \nabla_2^2 \nabla_2^2 \rangle - 8\langle (\tilde{E}_g - \tilde{V})\nabla_1 \cdot \nabla_2 \rangle.$$  

(d) **QED corrections of order $\alpha^3$ in the limit $m_3 \to \infty$**

When $m_3 \to \infty$ the vacuum polarization term and the contribution of the electron-electron spin dependent contact interaction $\delta_{se}^E E_n|\alpha^3 = -(20/3)\langle \tilde{s}_1 \cdot \tilde{s}_2 \delta^3(r) \rangle_n \alpha^3 f^3 \text{ a.u.}$ remain the same, but $X_n^2 = 0$, $Y_n^3 = 0$, and $\delta_{1p}E_n$ becomes

$$\delta_{1p}E_n^\infty = \alpha^3\left[\frac{4}{3}\ln\frac{mc}{2\hbar k_R} + \frac{5}{6} - \beta_n\right] \langle \delta^3(r_1) + \delta^3(r_2) \rangle_n$$

$$-\frac{8}{3}\left[\ln\frac{mc}{2\hbar k_R} - \frac{1}{2} + \ln a_p k_R\right] \langle \delta^3(r) \rangle_n - \frac{2}{3\pi} Q_{12}^n f^3 \text{ a.u.}.$$ 

The two-photon contribution reduces to

$$\delta_{2p}E_n^\infty = \alpha^3\left[-\frac{Q_{12}^n}{2\pi} + 2\ln f \alpha - \frac{4}{3} \ln 2 + \frac{13}{6}\right] \langle \delta^3(r) \rangle_n f^3 \text{ a.u.}$$.
and the total correction $\delta E_{n}^{\infty} = \delta_{1p} E_{n}^{\infty} + \delta_{2p} E_{n}^{\infty} + \delta_{s} E_{n}^{\infty} + \langle H_{sp} \rangle_{n}$ is

$$\delta E_{n}^{\infty} = \alpha^{3} \left[ \frac{4}{3} \left( \frac{19}{30} - \ln f \alpha^{2} - \beta_{n} \right) (\delta^{3}(r_{1}) + \delta^{3}(r_{2}))_{n} + \frac{14}{3} \ln f \alpha + \frac{164}{15} \right] \langle \delta^{3}(r) \rangle_{n} - \frac{7}{6\pi} Q_{12}^{n} ] f^{3} \text{ a.u.} .$$

**Table captions**

Table I. Elementary operators $\{E_{k}, k = 1, 15\}$ used in the calculation of the expectation values. $n_{k}$ denotes the number of distinct polynomial terms generated by the action of $E_{k}$ on a basis state.

Table II. The ground state expectation values $E_{g} = \langle H_{0} \rangle$, $\langle H_{0}^{2} \rangle$ and $\sigma^{2} = \langle H_{0}^{2} \rangle - E_{g}^{2}$ as a function of the basis dimension $N_{b}$.

Table III. Ground state expectation values of the singular differential operators $\langle \nabla_{1}^{4} \rangle_{E}$, $\langle \nabla_{1}^{3} \rangle_{E}$ and $\langle \nabla_{3}^{3} \rangle_{E}$ as a function of the basis dimension $N_{b}$.

Table IV. Ground state expectation values of the singular Dirac distributions $\langle \delta(\vec{R}_{1}) \rangle$ and $\langle \delta(\vec{R}) \rangle$ as a function of the basis dimension $N_{b}$.

Table V. The ground state expectation values $Q_{12}^{g}$ and $Q_{13}^{g}$ defined by $Q_{ij}^{g} = \lim_{a \to 0} \langle \theta(r_{ij} - a)/r_{ij}^{3} + 4\pi[\gamma + \ln(a/a_{\mu})]\delta^{3}(r_{ij}) \rangle$, as a function of the basis dimension $N_{b}$.
| \( k \) | \( n_k \) | \( E_k \) |
|---|---|---|
| 1 | 4 | \( \hat{r}_1 \cdot \hat{r}_2 \partial^2_{r_1r_2} \) |
| 2 | 4 | \( r^{-1}(r_2 \hat{r}_1 \cdot \hat{r}_2 - r_1) \partial^2_{r_1r} \) |
| 3 | 4 | \( r^{-1}(r_1 \hat{r}_1 \cdot \hat{r}_2 - r_2) \partial^2_{r_2r} \) |
| 4 | 1 | \( \partial^2_r + 2r^{-1} \partial_r \) |
| 5 | 1 | \( r_1(r_2 r)^{-1} \hat{r}_1 \cdot \nabla^Y \partial_r \) |
| 6 | 1 | \( r_2(r_1 r)^{-1} \hat{r}_2 \cdot \nabla^Y \partial_r \) |
| 7 | 4 | \( r_2^{-1} \hat{r}_1 \cdot \nabla^Y \partial r_1 + r_1^{-1} \hat{r}_2 \cdot \nabla^Y \partial r_2 \) |
| 8 | 1 | \( (r_1 r_2)^{-1} \nabla^Y \partial^2 \) |
| 9 | 3 | \( \partial^2_r + 2r_1^{-1} \partial_{r_1} \) |
| 10 | 3 | \( \partial^2_{r_2} + 2r_2^{-1} \partial_{r_2} \) |
| 11 | 1 | \( r_1^{-2} \nabla^Y \partial^2 \) |
| 12 | 1 | \( r_2^{-2} \nabla^Y \partial^2 \) |
| 13 | 3 | \( r_1^{-1} + r_2^{-1} - r^{-1} \) |
| 14 | 1 | \( -l_1(l_1 + 1)r_1^{-2} \) |
| 15 | 1 | \( -l_2(l_2 + 1)r_2^{-2} \) |
Table II

| $N_b$ | $E_g$[Ry] | $\langle H_3^2 \rangle$[Ry$^2$] | $\sigma^2 \times 10^{14}$[Ry$^2$] |
|-------|-----------|-------------------------------|----------------------------------|
| 324   | $-0.524\ 010\ 140\ 413\ 399\ 000\ 28$ | $0.274\ 586\ 632\ 449\ 596$ | $519\ 352.588\ 780\ 183\ 9$ |
| 411   | $-0.524\ 010\ 140\ 455\ 551\ 566\ 88$ | $0.274\ 586\ 628\ 565\ 868$ | $126\ 562.113\ 711\ 645\ 6$ |
| 512   | $-0.524\ 010\ 140\ 464\ 139\ 040\ 54$ | $0.274\ 586\ 627\ 626\ 769$ | $31\ 752.227\ 055\ 472\ 07$ |
| 630   | $-0.524\ 010\ 140\ 465\ 665\ 621\ 87$ | $0.274\ 586\ 627\ 375\ 932$ | $6\ 508.536\ 436\ 039\ 192$ |
| 764   | $-0.524\ 010\ 140\ 465\ 918\ 375\ 12$ | $0.274\ 586\ 627\ 323\ 102$ | $1\ 199.051\ 083\ 460\ 867$ |
| 918   | $-0.524\ 010\ 140\ 465\ 954\ 391\ 13$ | $0.274\ 586\ 627\ 313\ 704$ | $255.472\ 732\ 778\ 647\ 0$ |
| 1089  | $-0.524\ 010\ 140\ 465\ 959\ 038\ 66$ | $0.274\ 586\ 627\ 311\ 885$ | $73.086\ 762\ 209\ 023\ 06$ |
| 1283  | $-0.524\ 010\ 140\ 465\ 960\ 002\ 45$ | $0.274\ 586\ 627\ 311\ 421$ | $26.589\ 554\ 852\ 763\ 07$ |
| 1495  | $-0.524\ 010\ 140\ 465\ 960\ 160\ 85$ | $0.274\ 586\ 627\ 311\ 222$ | $6.672\ 153\ 792\ 304\ 994$ |
| 1733  | $-0.524\ 010\ 140\ 465\ 960\ 203\ 19$ | $0.274\ 586\ 627\ 311\ 175$ | $1.965\ 916\ 264\ 831\ 472$ |
| 1990  | $-0.524\ 010\ 140\ 465\ 960\ 212\ 96$ | $0.274\ 586\ 627\ 311\ 165$ | $0.965\ 692\ 558\ 621\ 058$ |
| 2276  | $-0.524\ 010\ 140\ 465\ 960\ 214\ 82$ | $0.274\ 586\ 627\ 311\ 160$ | $0.465\ 897\ 417\ 244\ 748$ |
| 2528  | $-0.524\ 010\ 140\ 465\ 960\ 215\ 25$ | $0.274\ 586\ 627\ 311\ 158$ | $0.308\ 152\ 352\ 372\ 668$ |
| eff   | $-0.524\ 010\ 140\ 465\ 960\ 215\ 4(6)$ | $0.274\ 586\ 627\ 311\ 156(4)$ | $0.23(23)$ |

Table III

| $N_b$ | $\langle \nabla_1^4 \rangle_E$ | $\langle \nabla_1^4 \rangle$ | $\langle \nabla_3^4 \rangle_E$ |
|-------|----------------|----------------|----------------|
| 324   | $2.532\ 451\ 004\ 442\ 6$ | $2.532\ 445\ 719\ 29$ | $5.255\ 396\ 862\ 891$ |
| 411   | $2.532\ 451\ 050\ 420\ 6$ | $2.532\ 451\ 697\ 56$ | $5.255\ 397\ 122\ 254$ |
| 512   | $2.532\ 451\ 056\ 877\ 0$ | $2.532\ 450\ 741\ 84$ | $5.255\ 397\ 117\ 353$ |
| 630   | $2.532\ 451\ 009\ 132\ 0$ | $2.532\ 449\ 964\ 61$ | $5.255\ 397\ 051\ 034$ |
| 764   | $2.532\ 451\ 018\ 719\ 1$ | $2.532\ 450\ 992\ 21$ | $5.255\ 397\ 086\ 467$ |
| 918   | $2.532\ 451\ 022\ 453\ 6$ | $2.532\ 451\ 056\ 52$ | $5.255\ 397\ 094\ 127$ |
| 1089  | $2.532\ 451\ 021\ 529\ 7$ | $2.532\ 451\ 023\ 43$ | $5.255\ 397\ 091\ 672$ |
| 1283  | $2.532\ 451\ 020\ 589\ 3$ | $2.532\ 451\ 019\ 49$ | $5.255\ 397\ 091\ 024$ |
| 1495  | $2.532\ 451\ 020\ 595\ 0$ | $2.532\ 451\ 022\ 17$ | $5.255\ 397\ 090\ 993$ |
| 1733  | $2.532\ 451\ 020\ 587\ 2$ | $2.532\ 451\ 020\ 24$ | $5.255\ 397\ 090\ 958$ |
| 1990  | $2.532\ 451\ 020\ 559\ 2$ | $2.532\ 451\ 019\ 92$ | $5.255\ 397\ 090\ 940$ |
| 2276  | $2.532\ 451\ 020\ 559\ 6$ | $2.532\ 451\ 020\ 43$ | $5.255\ 397\ 090\ 949$ |
| 2528  | $2.532\ 451\ 020\ 560\ 0$ | $2.532\ 451\ 020\ 42$ | $5.255\ 397\ 090\ 945$ |
| eff   | $2.532\ 451\ 020\ 559\ 6(3)$ | $2.532\ 451\ 020\ 2(2)$ | $5.255\ 397\ 090\ 945(4)$ |

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Table IV

| $N_b$ | $\langle \delta(\vec{R}_1) \rangle [a^{-3}]$ | $\langle \delta(\vec{R}) \rangle [a^{-3}]$ |
|-------|-------------------------------------|-------------------------------------|
| 324   | 0.020 733 174 230 2                 | 0.000 171 000 000 8 |
| 411   | 0.020 733 203 838 1                 | 0.000 170 999 383 2 |
| 512   | 0.020 733 199 804 5                 | 0.000 170 999 967 2 |
| 630   | 0.020 733 193 292 2                 | 0.000 170 997 306 7 |
| 764   | 0.020 733 197 986 7                 | 0.000 170 996 885 4 |
| 918   | 0.020 733 198 238 9                 | 0.000 170 996 811 0 |
| 1089  | 0.020 733 198 094 3                 | 0.000 170 996 832 4 |
| 1283  | 0.020 733 197 999 5                 | 0.000 170 996 756 0 |
| 1495  | 0.020 733 198 024 3                 | 0.000 170 996 767 3 |
| 1733  | 0.020 733 198 007 4                 | 0.000 170 996 760 1 |
| 1990  | 0.020 733 198 003 4                 | 0.000 170 996 757 7 |
| 2276  | 0.020 733 198 005 3                 | 0.000 170 996 757 1 |
| 2528  | 0.020 733 198 005 0                 | 0.000 170 996 756 8 |
| $eff$ | 0.020 733 198 004 6(8)              | 0.000 170 996 756 7(4) |

Table V

| $N_b$ | $Q_{12}^{g} [a^{-3}]$ | $Q_{13}^{g} [a^{-3}]$ |
|-------|----------------------|----------------------|
| 324   | 0.095 757 780 75     | -2.776 563 295       |
| 411   | 0.095 757 975 79     | -2.776 588 343       |
| 512   | 0.095 757 804 27     | -2.776 583 829       |
| 630   | 0.095 758 749 78     | -2.776 578 687       |
| 764   | 0.095 758 904 03     | -2.776 582 810       |
| 918   | 0.095 758 930 40     | -2.776 582 894       |
| 1089  | 0.095 758 918 40     | -2.776 582 776       |
| 1283  | 0.095 758 949 78     | -2.776 582 694       |
| 1495  | 0.095 758 944 76     | -2.776 582 722       |
| 1733  | 0.095 758 947 86     | -2.776 582 703       |
| 1990  | 0.095 758 949 04     | -2.776 582 700       |
| 2276  | 0.095 758 949 31     | -2.776 582 702       |
| $eff$ | 0.095 758 949 4(3)   | -2.776 582 702(1)    |
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