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Two-fermion relativistic bound states: hyperfine shifts

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Abstract

We discuss the hyperfine shifts of the positronium levels in a relativistic framework, starting from a two-fermion wave equation where, in addition to the Coulomb potential, the magnetic interaction between spins is described by a Breit term. We write the system of four first-order differential equations describing this model. We discuss its mathematical features, mainly in relation to possible singularities that may appear at finite values of the radial coordinate. We solve the boundary value problems both in the singular and non-singular cases and we develop a perturbation scheme, well suited for numerical computations, that allows us to calculate the hyperfine shifts for any level, according to well-established physical arguments that the Breit term must be treated at the first perturbative order. We discuss our results, comparing them with the corresponding values obtained from semi-classical expansions.

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1. Introduction

The relativistic description of the fine structure of the hydrogen atom levels was first proposed by Darwin [1] in a semi-classical treatment of the Dirac equation. This was immediately followed by the Breit proposal of a two-body relativistic equation [2] that, in addition to the Coulomb potential, included a quasi-static magnetic term where the velocities were substituted by the Dirac $\vec{\alpha}$ -matrices according to a proposal of Heisenberg. Shortly later Fermi calculated the spectrum of a Dirac electron interacting with a Pauli nucleus and deduced the values of nuclear magnetic momenta from the measured hyperfine splitting [3], using the Schrödinger non-relativistic wavefunctions to calculate the averages near the origin. In fact, following a Pauli suggestion, also the Breit paper contained a semi-classical expansion along the lines of the Darwin work, but eventually Breit himself was doubtful about the actual predictivity of his equation and two years later he reached the conclusion that the Coulomb interaction should be treated exactly, while the magnetic term had to be considered as a first-order self-consistent perturbation, so that only its diagonal matrix elements on the exact Coulomb eigenstates were brought to bear. Since then, major achievements were obtained by Pirenne [4], Berestetski and Landau [5]. Still using the Breit semi-classical approximation and the non-relativistic

Coulomb wavefunctions, they were able to produce analytical approximations for the shifts of the parapositronium levels and for the ground state of the orthopositronium. In their approach they also included the annihilation term. In the early 1950s, the appearance of the Schwinger [6] and of the Bethe–Salpeter equations [7, 8] made it possible to calculate up to the order α^5 ($\alpha =$ fine structure constant) the shifts of the first excited levels of the positronium, by accounting for the effects of one and two virtual photons, self-energy and vacuum polarization, but still keeping the semi-classical perturbative scheme [9, 10]. Later, in the 1970s, due to the great improvement in the experimental analysis of the atomic spectra, [11], to the qualitative changes in the mathematical and physical framework of symmetries and mainly to the new ideas of hadrons as composed by quarks, interest in the bound states and for the relativistic wave equations arose again and has never weakened since [12–24]. The challenge of the completely relativistic calculation of the hyperfine splitting was again pushed on foreground and various models for two spin- $\frac{1}{2}$ interacting particles were proposed, with special attention to the positronium that constituted an ideal system both from a theoretical and an experimental point of view: it appears, however, that the use of the semi-classical expansion and non-relativistic Coulomb wavefunctions as a starting point has maintained his role. Even in a later paper [13], where a non-perturbative treatment is claimed, the solutions of the Breit equation are calculated analytically but expanding the equation up to the second order in α . This latter procedure, in particular, may be assumed somewhat safely in atomic physics, where the velocities are of the same order of the fine structure constant, so that the expansion in α in fact corresponds to a semi-classical approximation. It becomes less and less justified in view of an extension of the method to quark bound states (see, e.g., [25, 26]), where an expansion in the coupling constant is not allowed and where it would be worth dealing from the very beginning with relativistic states.

In the present paper, we fill this old gap and present a completely relativistic treatment of the hyperfine splitting based on the Breit approach, providing an effective method for its computation for any spectral level. We thus analyse an approximate interaction within the framework of an exact kinematics. It is rather evident that analytic results will be possible only for the initial steps of our treatment, i.e. for establishing the system of equations to be discussed and their reduction due to conserved quantities. Analytic expressions will also be available when looking for series or asymptotic solutions, but finding the spectrum will necessarily be achieved by numerical methods. Moreover we shall omit from our treatment the annihilation term.

The starting point is thus the two-fermion relativistic wave equation we presented in [27]. In that paper, using a canonical reduction of the relativistic kinematics of the two-body problem, we introduced Lorentz-invariant interactions dependent upon the reduced coordinates and gave a solution of the relative time problem. We then quantized the model assuming a fermion nature for both of the two particles and deduced a completely Lorentz covariant internal dynamics, which was reduced by separating the radial part in a multipole scheme exploiting the conservations of angular momentum and parity. A further reduction of the radial equations produced a final linear system of order four containing the spectral parameter to be determined. We proved that the Dirac and the non-relativistic limits were recovered and compared our model with other existing models, [14, 17–19], finding a general agreement. The complete spectral curves from Dirac to positronium for pure Coulomb interaction were plotted for ground and higher states and the crossing of terms inferred in [17] was precised and made concrete. In that paper we also looked at the possibility of using the eigenfunctions of the degenerate singlet–triplet ground states of the positronium to set up a direct perturbative calculation of the hyperfine splitting, using the usual perturbative terms for the magnetic interaction: the answer was negative even for the ground state, since the behaviour of the

relativistic wavefunctions in the origin was not compatible with the magnetic interaction terms obtained by the semiclassical approximation.

In order to investigate the hyperfine structure, we shall therefore add to our pure Coulomb wave equation a Breit term in a Lorentz covariant way. The radial reduction of the problem is again done by using the still holding conservations of angular momentum and parity and here also the final wave equation reduces to a fourth-order linear system. Unfortunately the situation is now not as nice as in the pure Coulomb case, since a singularity of the wave equation appears at finite positive values of the radial coordinate. This occurrence had already been notified (see [28]) and, to our knowledge, has prevented up to date any correct integration attempt. However, a careful investigation shows that the behaviour of the system is not so bad. Indeed the singularity can be ‘bridged’ and the spectrum can be determined although, as previously said, only the first perturbative order in the Breit interaction makes sense and higher order corrections should be dealt with using the QED [24]. Therefore we are going to present a perturbative approach that allows the complete numerical calculation of the contribution to the shift of any level of the para- and the orthopositronium due to the Breit term. We shall show that in almost any case the presence of the additional singularity can be avoided: only for the levels with odd parity and angular momentum $j = 0$ this is impossible and the analysis has to be refined. However, in order to provide numerical evidence of the correctness of the Breit argument concerning the perturbative nature of the magnetic interaction, we further investigate the singular cases connected to the ground states. A numerical approach based on a different starting point and on Padé approximation techniques has been successful in calculating the shifts of the parapositronium singlets to the order α^4 [29]. The principal merit of our scheme from a numerical point of view is that we are able to obtain the results uniquely by means of the numerical values of spectral levels, without any need to use the eigenfunctions in order to calculate the matrix elements for the Breit term: in the full relativistic case this leads to a faster and more precise approach for finding the spectrum, especially for the orthopositronium triplets. When comparing our results to the values of the hyperfine levels computed in the semi-classical scheme and expressed in terms of simple fractions of powers of α^2 , [10, 30], we find an excellent agreement up to the order α^4 . This is rather remarkable, since the pure Coulomb contribution—where the correct kinematics and the recoil effects are exactly accounted for—and the magnetic perturbative terms are here separately different with respect to the corresponding semi-classical contributions (more details are given in section 4). We want to stress that, apart from some technical obstacles, our general method has a great conceptual simplicity: besides its applications to any excited level of electromagnetic bound states with components of arbitrary mass ratio, we believe that it should also be relevant for models of different nature, for which non-relativistic calculations are less reliable.

The paper is organized as follows. In section 2, we briefly recall the derivation of the wave equation for the two-fermion system with a general radial interaction and present the new equation with the additional Breit term together with its reduction that defines the spectral problem to be solved. The procedure is completely parallel to that of the pure Coulomb interaction explained in the previous paper [27], which we refer to for detailed expressions, as, for instance, the explicit form of the even and odd state vectors. The nature of the mathematical problem and the numerical methods we have used for its solution are explained in section 3. Here we also investigate the possible presence of singularities at a non-vanishing finite value of the radial coordinate and we comment on their properties. Finally, in section 4, we present the results and discuss them. A revisit of the perturbative expansion as we have used it in our computations (up to second order in the proof, but evidently valid at any order) is given in the appendix.

In the following we use units such that $\hbar = c = 1$.

2. The system for the Coulomb and Breit interaction

In the paper [27] we have described the method for obtaining a Lorentz covariant wave equation for two fermions interacting by means of a scalar potential. Obviously, we cannot reproduce the derivation here and have to refer to [27] for details. It is, however, necessary to recall the main definitions in order to have a minimum of self-consistency of the treatment.

2.1. The canonical variables

Denote by $x_{(i)}^\mu$ and $p_{(i)}^\mu$ the Minkowski coordinates and the momenta of two pointlike fermions with masses m_i , $i = 1, 2$. Define the tensor

$$\varepsilon_a^\mu(P) = \eta_a^\mu - \frac{P_a [P^\mu + \eta_0^\mu \sqrt{P^2}]}{\sqrt{P^2} [P_0 + \sqrt{P^2}]}, \quad \varepsilon_0^\mu(P) = P^\mu / \sqrt{P^2} \quad (2.1)$$

where η is the Lorentz metric and $P^\mu = p_{(1)}^\mu + p_{(2)}^\mu$ is the total momentum. It satisfies the identities

$$\eta_{\mu\nu} \varepsilon_\alpha^\mu(P) \varepsilon_\beta^\nu(P) = \eta_{\alpha\beta}, \quad \eta_{\alpha\beta} \varepsilon_\alpha^\mu(P) \varepsilon_\beta^\nu(P) = \eta^{\mu\nu} \quad (2.2)$$

and therefore it represents a Lorentz transformation to the $\vec{P} = 0$ reference frame. We can use (2.1) for the construction of a canonical transformation to the variables

$$\begin{aligned} Z^\mu &= X^\mu + \frac{\varepsilon_{abc} P_a \eta_b^\mu L_c}{\sqrt{P^2} [P_0 + \sqrt{P^2}]} + \frac{\varepsilon_a^\mu}{\sqrt{P^2}} (q_a \check{r} - r_a \check{q}) + \frac{P^\mu}{P^2} \check{q} \check{r} \\ \check{q} &= \varepsilon_0^\mu q_\mu, \quad \check{r} = \varepsilon_0^\mu r_\mu, \quad q_a = \varepsilon_a^\mu q_\mu, \quad r_a = \varepsilon_a^\mu r_\mu \end{aligned} \quad (2.3)$$

where

$$X^\mu = \frac{1}{2} (x_{(1)}^\mu + x_{(2)}^\mu), \quad r^\mu = x_{(1)}^\mu - x_{(2)}^\mu, \quad q^\mu = \frac{1}{2} (p_{(1)}^\mu - p_{(2)}^\mu). \quad (2.4)$$

Both r_a and q_a are Wigner vectors of spin one, as well as Z_a is a Newton–Wigner position vector for a particle with angular momentum $L_a = \varepsilon_{abc} r_b q_c$. In terms of (2.3), the two-particle mass shell conditions $p_{(i)}^2 = m_i^2$ can be put into the form

$$(q_a q_a + m_1^2)^{1/2} + (q_a q_a + m_2^2)^{1/2} = \lambda, \quad \lambda \check{q} = \frac{1}{2} (m_1^2 - m_2^2), \quad (2.5)$$

where $\lambda = \sqrt{P^2}$ while the variable \check{q} can be fixed and generates a canonical reduction of the phase space. Its conjugate coordinate, namely the relative time coordinate \check{r} , is cyclic and becomes a kind of a gauge function that is chosen *a posteriori* in order to recover the complete Minkowski description for each of the two particles. For instance, a useful choice could be $\check{r} = 0$, although there is no necessity of requiring such a condition. It is now straightforward introducing a Lorentz covariant interaction by changing the mass shell condition (2.5) with the addition of a scalar potential depending upon the Lorentz invariant relative separation $r = (r_a r_a)^{1/2}$. Thus a relativistic two-body system interacting by means of a potential $V(r)$ is described by (2.5) where λ will be substituted by $h(r) = \lambda - V(r)$.

2.2. The two-fermion quantum system

Let us now quantize equation (2.5) assuming that both particles are fermions. In order to determine the structure of the wave equation, it is sufficient to consider the case of two free fermions, since the interaction will then be introduced in the way previously described. The two-particle wavefunction is simply the tensor product of the two single-particle wavefunctions, and must therefore satisfy the two separate Dirac equations determined by the operators $D_1 = (\frac{1}{2} P_\mu + q_\mu) \gamma_{(1)}^\mu - m_1$ and $D_2 = (\frac{1}{2} P_\mu - q_\mu) \gamma_{(2)}^\mu - m_2$, where we adopt

the notation $\gamma_{(1)}^\mu = \gamma^\mu \otimes \mathbf{I}_4$, $\gamma_{(2)}^\mu = \mathbf{I}_4 \otimes \gamma^\mu$ and where \mathbf{I}_4 is the unity matrix in four dimensions. Introducing the new set of γ -matrices $\check{\gamma} \equiv \check{\gamma}(P) = \varepsilon_0^\mu(P)\gamma_\mu$, $\gamma_a \equiv \gamma_a(P) = \varepsilon_a^\mu\gamma_\mu$ and using the canonical operators corresponding to the variables (2.3), we easily find

$$\lambda = q_a(\check{\gamma}_{(1)}\gamma_{(1)a} - \check{\gamma}_{(2)}\gamma_{(2)a}) + \check{\gamma}_{(1)}m_1 + \check{\gamma}_{(2)}m_2, \quad \lambda\check{q} = \frac{1}{2}(m_1^2 - m_2^2). \quad (2.6)$$

System (2.6) has exactly the same content as the initial system of the two independent Dirac equations. However, put in this form, we see that the variable \check{q} remains fixed, in a complete agreement with the classical canonical reduction. The cyclic character of \check{r} is also evident from the Lorentz scalar identity for the phase of plane waves $p_{(1)}^\mu x_{(1)\mu} + p_{(2)}^\mu x_{(2)\mu} = P^\mu Z_\mu - q_a r_a$. Moreover the definition of $\check{\gamma}$, γ_a is actually a unitary transformation on the γ^μ 4-vector. Hence, as long as P is conserved, the matrices can be represented by the usual γ matrices. The first of equations (2.6) is thus the Lorentz-invariant equation for the two-fermion free system. Its 16 eigenvalues are immediately calculated, yielding the expected four singular values

$$\lambda = \pm(q_a q_a + m_1^2)^{1/2} \pm (q_a q_a + m_2^2)^{1/2}, \quad \pm(q_a q_a + m_1^2)^{1/2} \mp (q_a q_a + m_2^2)^{1/2}, \quad (2.7)$$

each singular value having multiplicity four.

The equation for the interacting system is simply obtained by substituting λ with $h(r) = \lambda - V(r)$ in the first of the (2.6) equations. For future discussions, we find it useful to introduce the mass parameters $M = m_1 + m_2$, $\mu = m_1 - m_2$, $\rho = \mu/M$ and to reorder the basis of the states making a linear transformation on the tensor product of the two spinor spaces such that the system at rest is diagonalized and the four singular values (2.7) are put in the order M , $-M$, $-\mu$ and μ . We then make a further linear transformation such that, in each four-dimensional eigenspace corresponding to the above energy eigenvalues, the square and the third component of the total spin $\mathbf{S} = \mathbf{I}_4 \otimes \sigma + \sigma \otimes \mathbf{I}_4$ (where σ is the Dirac spin) are also diagonalized and ordered with the triplet always following the singlet.

We finally recall that the global parity transformation is given by the product of orbital and internal parity transformations. In our picture the internal parity is $\check{\gamma} \otimes \check{\gamma} = \text{diag}(\mathbf{I}_8, -\mathbf{I}_8)$. It can be verified that the global angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ and the parity are conserved, so that, together with λ , they provide a classification of the states of the global symmetry.

2.3. The radial equations

In the basis we have chosen, the free Hamiltonian operator H_0 is a 16×16 matrix of the form

$$H_0 = \begin{pmatrix} \mathcal{J}_M & \mathcal{H}_0 \\ \mathcal{H}_0 & \mathcal{J}_\mu \end{pmatrix}, \quad (2.8)$$

where $\mathcal{J}_\Lambda = \Lambda \text{diag}(\mathbf{I}_4, -\mathbf{I}_4)$, $\Lambda = M, \mu$ and \mathcal{H}_0 is a 8×8 matrix whose elements are spherical differential operators (see [27] for the explicit form). We next construct the ‘even’ and ‘odd’ states Ψ_\pm with assigned angular momentum (j, m) and given parity $(-)^j$ or $(-)^{j+1}$, whose 16 components are collected in 4 groups indexed by the eigenvalues $\pm\Lambda$ of the free system at rest:

$$\Psi_\pm = {}^t(\Psi_\pm^{(M)}, \Psi_\pm^{(-M)}, \Psi_\pm^{(-\mu)}, \Psi_\pm^{(\mu)}). \quad (2.9)$$

In each group the components are singlet–triplet ordered, namely

$$\Psi_\pm^{(\Lambda)} = {}^t(\psi_{\pm,0}^{(\Lambda)}, \psi_{\pm,1_+}^{(\Lambda)}, \psi_{\pm,1_0}^{(\Lambda)}, \psi_{\pm,1_-}^{(\Lambda)}), \quad (2.10)$$

where the subscript ‘0’ refers to the singlet component, while ‘1₊, 1₀, 1₋’ denote the triplet components. The explicit expressions have been determined using the standard algorithms of the composition of angular momenta by means of Clebsch–Gordan coefficients and are therefore linear combinations of spherical harmonics. They are fully reported in [27].

By applying the Hamiltonian operator (2.8) to the states (2.9) we obtain a system of radial differential equations by requiring the vanishing of the coefficients of the different spherical harmonics in each component of the resulting vector. Indeed we get a large number of differential equations (e.g. 34 when starting with $\Psi = \Psi_+$), but of course, as one should expect, only eight of them are independent for each state with definite parity. Moreover a closer look at them shows that four of these eight equations are algebraic relations that can be used, by an appropriate choice of the unknown functions, to obtain a system of only four differential equation for each of the two state vectors Ψ_+ and Ψ_- . Finally, adding a Lorentz invariant interaction as specified in item (a), the fourth-order system reads

$$\frac{dY(r)}{dr} + \mathcal{M}Y(r) = 0, \quad (2.11)$$

where $Y(r) = (y_1(r), y_2(r), y_3(r), y_4(r))$ and \mathcal{M} is a matrix with general structure

$$\mathcal{M} = \begin{bmatrix} 0 & E(r) & F(r) & 0 \\ E(r) & \frac{1}{r} & 0 & -F(r) \\ G(r) & 0 & \frac{2}{r} & E(r) \\ 0 & -G(r) & E(r) & \frac{1}{r} \end{bmatrix}. \quad (2.12)$$

The explicit expressions of $E(r)$, $F(r)$ and $G(r)$ for the even case are the following ones,

$$\begin{aligned} E(r) &= \frac{\sqrt{j(j+1)}\mu}{rh(r)}, & F(r) &= \frac{\mu^2 - h^2(r)}{2h(r)}, \\ G(r) &= \frac{h(r)}{2} \left(1 - \frac{r^2 M^2 + 4j(j+1)}{r^2 h^2(r)} \right) \end{aligned} \quad (2.13)$$

and they specialize to the Coulomb interaction when $h(r) = \lambda + \alpha/r$, α being the fine structure constant.

As explained in [27], the odd coefficients are obtained from the previous ones by a parity transformation, whose action simply results in the change $M \rightarrow -\mu$ and $\mu \rightarrow -M$. In [27], it has also been shown how the Dirac and the non-relativistic limits are recovered from (2.12). We finally observe that for $E(r) = 0$ (e.g. for $j = 0$ or for $\mu = 0$ in the even case) the fourth-order system splits into separate second-order subsystems, making it easier the numerical solution of the spectral problem. In the general case, however, the complete fourth-order system has to be considered.

2.4. The addition of the Breit term

The spin–spin interaction can be described by introducing a Breit term, in addition to the Coulomb interaction, in the relation (2.6) that becomes

$$\begin{aligned} \lambda + \frac{\alpha}{r} \left[1 - \frac{1}{2} \left(\check{\gamma}_{(1)} \gamma_{(1)a} \check{\gamma}_{(2)} \gamma_{(2)a} + \left(\check{\gamma}_{(1)} \gamma_{(1)a} \frac{r_a}{r} \right) \left(\check{\gamma}_{(2)} \gamma_{(2)b} \frac{r_b}{r} \right) \right) \right] \\ = q_a (\check{\gamma}_{(1)} \gamma_{(1)a} - \check{\gamma}_{(2)} \gamma_{(2)a}) + \check{\gamma}_{(1)} m_1 + \check{\gamma}_{(2)} m_2. \end{aligned} \quad (2.14)$$

The Hamiltonian matrix must be modified with respect to (2.8) in order to account for the presence of the additional γ -matrices. This modification as well as the change of the basis are straightforward. The angular momentum and parity are conserved and the radial equations are again deduced by applying the new Hamiltonian to the states Ψ_{\pm} , as in the pure Coulomb

case. The general features of the systems of radial equations are also preserved and the final result is again a fourth-order linear system. In the even case and with $h(r) = \lambda + \alpha/r$, the matrix \mathcal{B} of this system reads

$$\mathcal{B} = \begin{bmatrix} 0 & E(r) & F(r) & 0 \\ E_\varepsilon(r) & \frac{1}{r} & 0 & F_\varepsilon(r) \\ G_{1,\varepsilon}(r) & 0 & \frac{2}{r} & E_\varepsilon(r) \\ 0 & G_{2,\varepsilon}(r) & E(r) & \frac{1}{r} \end{bmatrix} \quad (2.15)$$

where $E(r)$ and $F(r)$ are given in (2.13). The remaining matrix elements read

$$\begin{aligned} E_\varepsilon(r) &= \frac{\sqrt{j(j+1)}\mu}{rh(r) - 2\alpha\varepsilon}, & F_\varepsilon(r) &= \frac{(h^2(r) - \mu^2)r^2 - (2\alpha\varepsilon)^2}{2r(rh(r) - 2\alpha\varepsilon)} \\ G_{1,\varepsilon}(r) &= \frac{h(r)}{2} + \frac{4\alpha\varepsilon + \frac{4j(j+1)}{2\alpha\varepsilon - rh(r)} + \frac{r^2M^2}{4\alpha\varepsilon - rh(r)}}{2r} \\ G_{2,\varepsilon}(r) &= \frac{2j(j+1)}{r^2h(r)} + \frac{4\alpha^2\varepsilon^2 + (-h(r)^2 + M^2)r^2}{2r(rh(r) - 2\alpha\varepsilon)}. \end{aligned} \quad (2.16)$$

Again the matrix of the odd system is obtained by changing $M \rightarrow -\mu$ and $\mu \rightarrow -M$. It is also immediate to verify that for $\varepsilon = 0$ (2.15) reduces to (2.12).

Some remarks are in order. In the first place, we observe that in the matrix (2.15) we have introduced a parameter ε , not present in (2.14) and reproducing the latter for the $\varepsilon = 1/2$. We shall see in the following that an appropriate use of this parameter permits the calculation of the first perturbative terms in the Breit interaction in a way that is numerically much more efficient than the usual computations by means of the eigenfunctions. Secondly in (2.14) and therefore in the system produced by (2.15) no anomalous magnetic moment is present. This absence would constitute a drawback for the calculation of the hyperfine structure of the hydrogen atom, but remains an acceptable approximation for the positronium, which is the only case we are going to consider later on. Finally, in the even and odd systems describing the positronium, we will let $\mu = 0$ and $M = 2m_e$, where m_e is the electron mass.

3. The numerical treatment of the Breit interaction

We now discuss some general properties of the equations for the positronium with a particular attention to the possible presence of singularities other than the origin and the infinity. We find it useful to introduce the new dimensionless independent variable x and the new eigenvalue w as follows:

$$x = m_e r, \quad w = \left(\frac{m_e}{2} \alpha^2 \right)^{-1} (\lambda - 2m_e). \quad (3.1)$$

The value of the fine structure constant has been assumed as $\alpha = 0.007\,297\,372\,568$, [31]. In the following we distinguish the discussion of the even case, which develops essentially according to the classical ODE theory [32], from the odd case, that poses some new problems.

3.1. The even case

We begin from the case with even parity. From (2.15) we see that $\mathcal{B}_{12} = \mathcal{B}_{21} = \mathcal{B}_{34} = \mathcal{B}_{43} = 0$ when $\mu = 0$. This means that the fourth-order system generated by (2.15) decouples into

two second-order systems for the unknown functions $(y_1(x), y_3(x))$ and $(y_2(x), y_4(x))$ that, in turn, can be reduced to two second-order differential equations for $y_1(x)$ and $y_2(x)$. It has also been shown in [27] that for $j = 0$ only the system for $(y_1(x), y_3(x))$ makes sense, while for $j > 0$ both systems contribute to determining the levels. The first of these two equations, introducing the unknown function $u(x)$ defined by $y_1(x) = [(4 + \alpha^2 w)x + 2\alpha]^{1/2} x^{-3/2} u(x)$, reads

$$\frac{d^2}{dx^2} u(x) + \left[-\frac{8\alpha\varepsilon}{(4 + \alpha^2 w)x - 2\alpha(4\varepsilon - 1)} - \frac{3\alpha^2}{((4 + \alpha^2 w)x + 2\alpha)^2 x^2} - \frac{1}{16x^2} \right. \\ \left. \times (-\alpha^2 w(8 + \alpha^2 w)x^2 - 4\alpha(4 + \alpha^2 w)(2\varepsilon + 1)x - 4\alpha^2(4\varepsilon + 1) + 16j(j + 1)) \right. \\ \left. - \frac{4\alpha\varepsilon j(j + 1)}{((4 + \alpha^2 w)x - 2\alpha(2\varepsilon - 1))x^2} \right] u(x) = 0 \quad (3.2)$$

It can be seen that, in addition to the usual singularities in the origin and at infinity, the equation presents a new singularity at the point $x = 2\alpha(4\varepsilon - 1)/(\alpha^2 w + 4)$, which assumes finite positive values for $\varepsilon > 1/4$. Although we shall show that solutions exist also for $\varepsilon > 1/4$ —in fact we shall give an explicit solution for $\varepsilon = 1/2$, in carrying out our perturbative program we can avoid this singularity, as well as almost all those we shall encounter in later developments. Indeed, according to the perturbative approach we are going to explain below—and whose proof is given in appendix A, it is sufficient to solve the equation for values $\varepsilon < 1/4$. There is, however, one instance in the case with odd parity where the singularity must be explicitly taken into account.

If $y_2(x) = [(4 + \alpha^2 w)x + 2\alpha(2\varepsilon + 1)]^{1/2} x^{-3/2} z(x)$, the second equation of the even case in $z(x)$ is

$$\frac{d^2}{dx^2} z(x) + \left[-\frac{8\alpha\varepsilon}{(4 + \alpha^2 w)x + 2\alpha(1 - 2\varepsilon)} - \frac{3\alpha^2(2\varepsilon + 1)^2}{((4 + \alpha^2 w)x + 2\alpha(2\varepsilon + 1))^2 x^2} - \frac{1}{16x^2} \right. \\ \left. \times (-\alpha^2 w(8 + \alpha^2 w)x^2 - 4\alpha(4 + \alpha^2 w)(2\varepsilon + 1)x - 4(2\varepsilon + 1)^2 \alpha^2 + 16j(j + 1)) \right. \\ \left. - \frac{4\alpha\varepsilon j(j + 1)}{((4 + \alpha^2 w)x + 2\alpha)x^2} + \frac{2\alpha(2\varepsilon + 1)}{((4 + \alpha^2 w)x + 2\alpha(2\varepsilon + 1))x^2} \right] z(x) = 0. \quad (3.3)$$

This equation develops a new singularity at $x = 2\alpha(2\varepsilon - 1)/(4 + \alpha^2 w)$, which assumes positive values for $\varepsilon > 1/2$. This new singularity is therefore not effective for the same reasons explained above. It would be such also when considering the Breit term as non-perturbative, and it would only act through a modification of the singularity in the origin.

The boundary value problem posed by (3.2) and (3.3) for sufficiently small values of ε , namely without the additional singularity, is very classical. Both the boundary points, the origin and the infinity, are singular and what we have to do for starting the numerical procedure is to determine the initial conditions in the neighbourhood of those points by looking for analytic approximations of the solutions in the form of series or asymptotic expansions respectively. We then apply the double shooting method in order to determine the value of the spectral parameter with the desired accuracy. As a matter of fact, both the series and the asymptotic expansions produce two linearly independent solutions, but in each case only one solution can be accepted: we are thus in the so-called limit point case of the Weyl classification of the boundary value problems [32] and therefore there is no ambiguity in choosing the appropriate solution for giving the initial conditions and starting the numerical integration, once the spectral parameter has been assigned a numerical value that will be adjusted in the successive integrations until when the two solutions coming from zero and infinity, as well as their derivatives, match within the required accuracy. This is actually the spectral condition that simply reduces to checking the equality of logarithmic derivatives at a chosen crossing

point, whose location is immaterial for the result. The regular series solutions for the first and second equations of the even case are of the form $y_i(x) = A_i x^{\rho_i} S_i(x)$, $i = 1, 2$, where A_i are integration constants, $S_i(x)$ are power series in x with the zeroth-order term equal to unity and ρ_i are the positive indices

$$\begin{aligned}\rho_1 &= \frac{1}{2} + \frac{1}{2(1-2\varepsilon)} [(1-2\varepsilon)^2(4-\alpha^2(4\varepsilon+1)) + 4(1-2\varepsilon)j(j+1)]^{1/2} \\ \rho_2 &= \frac{1}{2} + \frac{1}{2} [4(1+2\varepsilon)j(j+1) - (1+2\varepsilon)^2\alpha^2]^{1/2}.\end{aligned}\quad (3.4)$$

The asymptotic solutions for the two equations are of the form $y_i(x) = B_i \exp[-\kappa_i x] x^{\nu_i} T_i(x)$, $i = 1, 2$, where B_i are again integration constants, $T_i(x)$ are power series in $1/x$ with zeroth-order term equal to unity, while the two positive numbers κ_i and the two indices ν_i coincide for both equations and are equal to κ and ν , where

$$\kappa = \frac{1}{4} \sqrt{-w(\alpha^2 w + 8)}, \quad \nu = \frac{\alpha^2 w(8 + \alpha^2 w)(2\varepsilon + 1) + 16}{2(4 + \alpha^2 w) \sqrt{-w(8 + \alpha^2 w)}}. \quad (3.5)$$

We finally remark that only the first terms of the series and asymptotic expansions have been determined analytically. The following ones have been calculated by numerical codes, and the number of terms to be taken has been chosen according to the following criterion: in the point where the initial conditions for the numerical integrations were assigned the result of the substitution of the solution into the differential equation divided by the solution itself had to be less than 10^{-15} . We also remark that tests have been made also for the arithmetic precision of the calculations and the number of meaningful figures has always been kept sufficiently high.

Let us now discuss the solution of equation (3.2) for the even ground state, $j = 0$, with $\varepsilon = 1/2$, that presents a singularity at the positive point $x_s = 2\alpha/(4 + \alpha^2 w)$. We can study the series solutions in x_s and realize that this singular point is in the case of the *limit cycle* of the Weyl classification [32], independently of the value of w in the physical domain. This means that in the neighbourhood of x_s the equation admits two finite solutions that can be used for matching the solution and its derivative coming from the origin to the solution and the corresponding derivative coming from infinity, forming therefore what in mathematics is referred to as a ‘classical solution’ of the differential equation. Procedures of this type and also with more elaborate matching conditions have been occasionally considered, see e.g. [33], but usually more as an investigation of mathematical possibilities, than under the real necessity of solving a specific problem. The first terms of the solution in the neighbourhood of x_s are

$$y_s(x) = A(x - x_s) \left(1 + \frac{2\alpha(x - x_s)}{\alpha^2 w + 4} \right) + B \left(1 + \frac{4\alpha(x - x_s) \ln(|x - x_s|)}{\alpha^2 w + 4} \right) \quad (3.6)$$

The index in the origin is $\rho = \frac{1}{2}(1 + \sqrt{4 - 3\alpha^2})$, while the parameters for the asymptotic solution are those given in (3.5) with $\varepsilon = 1/2$. The results will be discussed in the next section.

3.2. The odd case

From the remarks following (2.15), we see that the matrix for the odd system is obtained by substituting $M = 0$ and $\mu = -2m_e$ in (2.15). In the dimensionless variables (3.1), the explicit

expression of the system we get is

$$\begin{aligned}
\frac{d}{dx}y_1(x) - \frac{2\sqrt{j(j+1)}}{rh(x)}y_2(x) + \frac{1}{2}\frac{(4-h^2(x))}{h(x)}y_3(x) &= 0 \\
\frac{d}{dx}y_2(x) - \frac{2\sqrt{j(j+1)}y_1(x)}{xh(x)-2\alpha\varepsilon} + \frac{1}{x}y_2(x) + \frac{1}{2}\frac{(-4\alpha^2\varepsilon^2+(h^2(x)-4)x^2)y_4(x)}{x(xh(x)-2\alpha\varepsilon)} &= 0 \\
\frac{d}{dx}y_3(x) + \frac{1}{2}\left(h(x) + \frac{1}{x}\left(4\alpha\varepsilon + \frac{4j(j+1)}{2\alpha\varepsilon - xh(x)}\right)\right)y_1(x) + \frac{2}{x}y_3(x) - \frac{2\sqrt{j(j+1)}}{xh(x)-2\alpha\varepsilon}y_4(x) &= 0 \\
\frac{d}{dx}y_4(x) + \frac{1}{2}\left(\frac{4j(j+1)}{x^2h(x)} + \frac{4\alpha^2\varepsilon^2 - x^2h^2(x)}{x(xh(x)-2\alpha\varepsilon)}\right)y_2(x) - \frac{2\sqrt{j(j+1)}y_3(x)}{xh(x)} + \frac{1}{x}y_4(x) &= 0
\end{aligned}
\tag{3.7}$$

where $h(x) = 2 + \alpha^2 w/2 + \alpha/x$. The system decouples only for $j = 0$ so that, for the moment, we will assume $j > 0$ (remark that the triplet ground state has $j = 1$).

A superficial check of the coefficients shows the presence of an irrelevant singularity at positive values of x for $\varepsilon > 1/2$. The situation, however, is not so simple and there actually exists a further hidden singularity that reveals itself when trying to integrate numerically the system in a direct way. This unexpected singularity becomes manifest when deducing the fourth-order differential equation equivalent to the system (3.7). Both the partial and the final results when obtaining this equation are very cumbersome: the final analytic expression has been calculated and managed only by means of a systematic use of computer algebra and cannot be reported here. We simply give the steps of the method we have followed to get the equation and that in mathematics is known as the prolongation method. First we isolate $y_2(x)$ from the first equation and $y_4(x)$ from the third; we then substitute $y_2(x)$, its derivative and $y_4(x)$ into the second equation, obtaining a second order equation in $y_1(x)$ where $y_3(x)$ and its first derivative only appear. We then substitute $y_4(x)$, its derivative and $y_2(x)$ into the fourth equation, obtaining a second-order equation in $y_3(x)$ where $y_1(x)$ and its first derivative only appear. We next consider the prolongations of this system: this means that we differentiate these two second-order equations and substitute the second-order derivatives obtained by the second-order equation themselves. The third-order equation for $y_1(x)$, thus, contains $y_3(x)$ and its first derivative only. We differentiate once more this equation and finally from this, the two third-order and the two second-order equations we can eliminate $y_3(x)$ and its first, second and third derivatives, finally obtaining a fourth-order differential equation for $y_1(x)$.

In the denominator of the coefficients of the fourth-order equation we find a factor responsible for the appearance of the new singularity given by a root of the corresponding equation:

$$\begin{aligned}
& -(\alpha^2 w + 4)(16 + \alpha^2 w(\varepsilon^4 \alpha^2 + 1)(\alpha^2 w + 8))x^3 - 2\alpha(\varepsilon^4 \alpha^4 w(\alpha^2 w + 8)(3 + 2\varepsilon) \\
& - (\alpha^2 w + 4)^2(2\varepsilon - 3) + 32\varepsilon^4 \alpha^2)x^2 + 4\alpha^2(-\varepsilon^4(4\varepsilon + 3)\alpha^2 - 3 - 4\varepsilon(\varepsilon^2 - \varepsilon - 1) \\
& + 4\varepsilon^4 j(j + 1))(\alpha^2 w + 4)x + 8\alpha^3(4\varepsilon^4 j(j + 1) - (2\varepsilon + 1)(2\varepsilon - 1)^2 - \varepsilon^4(2\varepsilon + 1)\alpha^2) = 0.
\end{aligned}
\tag{3.8}$$

For the typical values $j = 1$ and $w = -0.5$ it has a solution $x > 0$ for $\varepsilon \simeq 0.36014$. Here also we stress that the presence of this singularity does not affect the perturbative approach to the hyperfine interaction, but must be considered if one is willing to integrate the odd equation as it stands.

We have solved the fourth-order equation for small enough values of ε —so as to prevent the presence of the additional singularity—as well as for $\varepsilon = 1/2$. In both cases, taking

into account the due differences, the method is conceptually a variant of the double shooting procedure described in the previous paragraph. For small values of ε we have to take care of the origin and infinity, that are the only two singular points. It turns out that in each one of them there exist two regular solutions that can provide the necessary initial conditions for starting the numerical integration. The spectral condition is now given by the matching of function, first, second and third derivatives in a fixed crossing point x_c , so to recover the ‘classical solution’ of the equation. This amounts to the vanishing of the following determinant:

$$\det \begin{pmatrix} y_{0,1}(x_c) & y_{0,2}(x_c) & y_{\infty,1}(x_c) & y_{\infty,2}(x_c) \\ y_{0,1}^{(I)}(x_c) & y_{0,2}^{(I)}(x_c) & y_{\infty,1}^{(I)}(x_c) & y_{\infty,2}^{(I)}(x_c) \\ y_{0,1}^{(II)}(x_c) & y_{0,2}^{(II)}(x_c) & y_{\infty,1}^{(II)}(x_c) & y_{\infty,2}^{(II)}(x_c) \\ y_{0,1}^{(III)}(x_c) & y_{0,2}^{(III)}(x_c) & y_{\infty,1}^{(III)}(x_c) & y_{\infty,2}^{(III)}(x_c) \end{pmatrix} = 0 \quad (3.9)$$

where $y_{0,i}, y_{\infty,i}$, ($i = 1, 2$), are the two regular solutions coming from the origin and from the infinity respectively and the superscripts denote the order of the derivatives. As in the even case, the two acceptable series solutions in the neighbourhood of the origin are of the form $y_i(x) = A_i x^{\rho_i} S_i(x)$, where, for $j > 0$ and $\varepsilon < 1/2$,

$$\rho_1 = -1 + \frac{1}{2(1-2\varepsilon)} [(1-2\varepsilon)^2(4-\alpha^2(4\varepsilon+1)) - 4(-1+2\varepsilon)j(j+1)]^{1/2} \quad (3.10)$$

$$\rho_2 = \frac{1}{2} [-\alpha^2(2\varepsilon+1)^2 + 4(2\varepsilon+1)j(j+1)]^{1/2}.$$

The search for the asymptotic solutions is a bit more delicate. Indeed they are still of the form $y_i(x) = B_i \exp[-\kappa_i x] x^{\nu_i} T_i(x)$, $i = 1, 2$, and again $\kappa_1 = \kappa_2 = \kappa$, with

$$\kappa = \frac{\alpha}{4} [-w(8+\alpha^2 w)]^{1/2} \quad (3.11)$$

while the indices are

$$\nu_1 = -1 + \frac{16 + \alpha^2 w(8 + \alpha^2 w)(2\varepsilon + 1)}{2(4 + \alpha^2 w)[-w(8 + \alpha^2 w)]^{1/2}} \quad \nu_2 = \nu_1 - 2. \quad (3.12)$$

Although an integer difference of the indices could imply solutions of different types, the present case is the simplest one and a second non-logarithmic solution is found.

We now consider the odd ground state for $\varepsilon = 1/2$. We have then to discuss the fourth-order differential equation with $j = 1$ in the presence of a singularity located, almost independently of the value of w , around $x \simeq 0.001\,6478$. The two regular asymptotic solutions are of the type already described and the corresponding parameters are obtained from (3.11) and (3.12) with $\varepsilon = 1/2$. The second solution is again non-logarithmic. The behaviour in the origin, however is here different. In fact we have one of the two regular solutions of the form $y_1(x) = x^{\sqrt{4-\alpha^2}} S_1(x)$, but the second one, due to the fact that the singularity in the origin is irregular, must be searched in a more general form [34], and results in

$$y_2(x) = \exp \left[-\frac{4\sqrt{\alpha(4+\alpha^2 w)}}{(4+\alpha^2 w)\sqrt{x}} \right] x^{-3/4} S_2(\sqrt{x}) \quad (3.13)$$

where $S_2(\sqrt{x})$ is a power series in \sqrt{x} with zeroth-order term equal to unity. Finally four regular solutions are found in a neighbourhood of the singular point: their indices are 0, 1, 2, 49/16, but despite the integer differences all of them are non-logarithmic. These solutions together with their first three derivatives are used to bridge the two solutions from

the origin to the two solutions from infinity. From a numerical viewpoint, however, this is not very simple due to the critical sensitivity of the coefficients of the differential equation to tiny variations of the coordinate x . Indeed the ordinary integration codes present errors too large to be accepted, so that, in order not to lose in accuracy when integrating out of the singularity, we have chosen a mesh of sufficiently close points (all of them obviously regular with respect to the differential equations): for each point we have constructed four regular series solutions with a number of terms sufficiently large to respect the accuracy requirements, and we have connected all these solutions by matching functions and derivatives up to order 3.

We finally discuss the spectral solution of the odd case with $j = 0$. We have already stated that now the system decouples and gives rise to a pair of second-order differential equations. As in the even case, only one of these equations, namely the equation coming from the (y_1, y_3) subsystems, has a physical meaning. From (3.7) we easily find

$$\begin{aligned} \frac{d^2}{dx^2}y(x) + \frac{2}{x} \left[1 + \frac{\alpha}{\alpha^2 w x + 2\alpha + 8x} - \frac{\alpha}{4x + \alpha^2 w x + 2\alpha} + \frac{1}{x\alpha w + 2} \right] \frac{d}{dx}y(x) \\ + \left[\frac{\alpha^2 w (\alpha^2 w + 8)}{16} + \frac{\alpha^2 (4\varepsilon + 1)}{4x^2} + \frac{\alpha (\alpha^2 w + 4)(2\varepsilon + 1)}{4x} \right. \\ \left. - \frac{8\alpha\varepsilon}{(4 + \alpha^2 w)x + 2\alpha} \right] y(x) = 0 \end{aligned} \quad (3.14)$$

and we see that the coefficient of the first derivative has a singularity at the point $x = -2/(w\alpha)$, independent of ε . Since for the bound states we are studying w assumes negative values, the singularity is therefore located at a finite positive value of x and must be accounted for in the integration for any value of ε . The situation is similar to what we have already seen and may be briefly summarized as follows: the index for the acceptable series solution in the origin is $\rho = -1 + \frac{1}{2}\sqrt{4 - \alpha^2(4\varepsilon + 1)}$. The two constants of the asymptotic solution are the same κ as in (3.11) and $\nu = \nu_1$ as given in (3.12). In the neighbourhood of the singular point the indices are 0, 2 and there exist two non-logarithmic solutions.

4. Discussion of the results

To begin the discussion of the results we report the values we have obtained in [27] for the levels of the pure Coulomb interacting system. The classification scheme we used in that paper was fit to describe the spectral terms for systems with variable mass ratio. For convenience in comparing our levels with the corresponding values existing in the literature [11, 10] and obtained by semi-classical expansions, we will adopt the commonly accepted classification of the positronium levels³.

Our results for the relativistic two-body equation with pure Coulomb interaction are as follows. For the ground states we have

State	w_{Coulomb}	State	w_{Coulomb}
1^1s_0	-0.499 995 0109	1^3s_1	-0.499 995 0109

³ Although not necessary for the discussion, it is straightforward to recognize the following correspondence between [27] and [11]: $(+, 0, I) \rightarrow 1^1s_0, (-, 1, I) \rightarrow 1^3s_1, (+, 0, II) \rightarrow 2^1s_0, (+, 1, I) \rightarrow 2^3p_1, (+, 1, II) \rightarrow 2^1p_1, (-, 0, I) \rightarrow 2^3p_0, (-, 1, II) \rightarrow 2^3s_1, (-, 2, I) \rightarrow 2^3p_2$.

For the first excited states, the data are:

State	w_{Coulomb}	State	w_{Coulomb}
2^1s_0	-0.124 999 6884	2^3s_1	-0.124 999 6884
2^1p_1	-0.125 000 2427	2^3p_1	-0.125 000 5200
2^3p_0	-0.125 000 7974	2^3p_2	-0.124 999 9654

As explained in appendix A, the levels accounting for the first-order perturbative effects of the Breit terms are given by

$$w_{\text{Breit}} = w_{\text{Coulomb}} + \frac{1}{2} \left. \frac{dw(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=0}. \quad (4.1)$$

The derivative of w in $\varepsilon = 0$ was calculated by computing the eigenvalues corresponding to $\varepsilon = 0.1$ and $\varepsilon = 0.2$ and then looking for the three-point Lagrangian interpolation through them and through ($\varepsilon = 0, w = w_{\text{Coulomb}}$). The results have been checked by repeating the same procedure for other values of ε sufficiently close to the origin and the differences are at most of some unities in the last figure for the states s and even less for the states p. Even if we take the values we have calculated for $\varepsilon = 1/2$ —and reported below—to construct the interpolation, we see that the results for the hyperfine ground levels differ only for some unities in the ninth figure. In the following table we summarize the data we have obtained. Remark that the calculations have been done with a number of figures sufficiently large to prevent the rounding errors.

State	$w_{\varepsilon=0.1}$	$w_{\varepsilon=0.2}$	$dw/d\varepsilon _{\varepsilon=0}$
1^1s_0	-0.500 000 8658	-0.500 002 4624	$-0.798 407 7369 \times 10^{-4}$
1^3s_1	-0.499 995 5437	-0.499 995 3671	$-0.887 489 6904 \times 10^{-5}$
2^1s_0	-0.125 000 5867	-0.125 000 9527	$-0.116 441 3908 \times 10^{-4}$
2^3s_1	-0.124 999 9215	-0.125 000 0659	$-0.277 440 1032 \times 10^{-5}$
2^1p_1	-0.125 000 3204	-0.125 000 2205	$-0.166 409 1904 \times 10^{-5}$
2^3p_1	-0.125 000 7197	-0.125 000 8750	$-0.221 861 1453 \times 10^{-5}$
2^3p_0	-0.125 001 2966	-0.125 001 7959	$-0.499 227 1268 \times 10^{-5}$
2^3p_2	-0.125 000 0186	-0.125 000 0452	$-0.664 616 5115 \times 10^{-6}$

The spectral values with $\varepsilon = 1/2$ for 1^1s_0 and 1^3s_1 are the following:

State	$w_{\varepsilon=1/2}$	State	$w_{\varepsilon=1/2}$
1^1s_0	-0.499 981 6915	1^3s_1	-0.499 990 5793

The differential equations producing these last values present a singularity at finite values of the radial coordinate. This singularity is in fact non-disturbing for the integration and one can ‘pass through’ by imposing the matching conditions as explained in section 3. The results however confirm the Breit idea: indeed they present a qualitatively wrong configuration, with the singlet higher than the triplet.

Let us now compare our results with the known data. We recall the formula giving the first terms of the semi-classical expansion for the singlets [5]:

$$w = -\frac{1}{2n^2} + \frac{\alpha^2}{2n^4} \left(\frac{11}{16} - \frac{n}{j + \frac{1}{2}} \right) + O(\alpha^4). \quad (4.2)$$

It is well known that the 1^3s_1 level has a value

$$w = -\frac{1}{2} + \frac{1}{96}\alpha^2 \quad (4.3)$$

omitting the annihilation term, which contributes for an additional $\alpha^2/2$ to the singlet–triplet splitting. From [11] we take the approximations for the $n = 2$ triplets obtained from [10]. The results are

$$w(2^3p_0) = -\frac{1}{8} + \frac{95}{1536}\alpha^2 \quad (4.4)$$

and

$$w(2^3p_j) = w(2^3p_0) + \delta(j), \quad w(2^1p_1) = w(2^3p_0) + \delta' \quad (4.5)$$

with

$$\delta(1) = \frac{5}{160}\alpha^2, \quad \delta(2) = \frac{9}{160}\alpha^2, \quad \delta' = \frac{1}{24}\alpha^2. \quad (4.6)$$

Finally $w(2^3s_1)$ is deduced from the relation [9]

$$w(2^3s_1) - w(2^1s_0) = \frac{1}{8}(w(1^3s_1) - w(1^1s_0)). \quad (4.7)$$

The comparison with our results is summarized in the following table:

State	w_{num}	$w_{\text{semi-classical}}$
1^1s_0	-0.500 034 9313	$-\frac{1}{2} - \frac{21}{32}\alpha^2 = -0.500 034 9462$
1^3s_1	-0.499 999 4484	$-\frac{1}{2} + \frac{1}{96}\alpha^2 = -0.499 999 4453$
2^1s_0	-0.125 005 5105	$-\frac{1}{8} - \frac{53}{512}\alpha^2 = -0.125 005 5123$
2^3s_1	-0.125 001 0756	$-\frac{1}{8} - \frac{31}{1536}\alpha^2 = -0.125 001 0747$
2^1p_1	-0.125 001 0747	$-\frac{1}{8} - \frac{31}{1536}\alpha^2 = -0.125 001 0747$
2^3p_1	-0.125 001 6293	$-\frac{1}{8} - \frac{47}{1536}\alpha^2 = -0.125 001 6294$
2^3p_0	-0.125 003 2935	$-\frac{1}{8} - \frac{95}{1536}\alpha^2 = -0.125 003 2935$
2^3p_2	-0.125 000 2977	$-\frac{1}{8} - \frac{43}{7680}\alpha^2 = -0.125 000 2982$

A couple of final comments on the results are in order. In the first place we observe that the pure Coulomb levels calculated in the semi-classical approximation or, equivalently, using the expansion in α differ from the levels calculated by the two-body relativistic equation by a quantity of the same order of the approximation itself. In order to produce a concrete example we let $\varepsilon = 0$ in (3.2) and use the ‘atomic variable’ $z = \frac{1}{2}\alpha x$. Expanding in α up to the second order, we find

$$\frac{d^2}{dz^2}y(z) + \left(\frac{w^2\alpha^2}{4} + 2w + \frac{4 + \alpha^2 w}{2z} + \frac{\alpha^2}{4z^2} \right) y(z) \quad (4.8)$$

with the regular solution

$$y(z) = z^{1/2} + (1/2)\sqrt{1 - \alpha^2} e^{-(1/2)\sqrt{-w(\alpha^2 w + 8)}z} \cdot {}_1F_1\left(\frac{1}{2} + \frac{\sqrt{1 - \alpha^2}}{2} - \frac{\alpha^2 w + 4}{2\sqrt{-w(\alpha^2 w + 8)}}, 1 + \sqrt{1 - \alpha^2}, \sqrt{-w(\alpha^2 w + 8)}z\right). \quad (4.9)$$

From the vanishing of the first argument of the hypergeometric we get the ground level

$$w = \frac{1}{\alpha^3} (2 + 2\sqrt{1 - \alpha^2})\sqrt{2 - 2\sqrt{1 - \alpha^2}} - \frac{4}{\alpha^2} \simeq -\frac{1}{2} - \frac{5}{32}\alpha^2 + O(\alpha^4) \quad (4.10)$$

Comparing (4.10) with our relativistic pure Coulomb result $w = -0.499\,995\,0109$, that can be approximated as $w = -1/2 + 3\alpha^2/32 + O(\alpha^4)$, we find a difference of about $\alpha^2/4$. In contrast, when looking at the data presented in the final table, we see that the difference reduces to less than $\alpha^3/26$ and becomes even more negligible for the levels with higher orbital angular momentum.

A second observation concerns the degeneracy of the states 2^3s_1 and 2^1p_1 that is predicted from the perturbative expansion and that is completely confirmed from the numerical calculations. The existing difference of about $0.01\alpha^2$ for the pure Coulomb interaction disappears when introducing the Breit term. A similar phenomenon in the perturbative framework had been noted in [14] with respect to the Lamb shift in the hydrogen atom, produced by a pure relativistic Coulomb interaction and reabsorbed by the presence of the magnetic term.

To conclude, in this paper we have presented a relativistic calculation of the hyperfine structure of the positronium, providing the theoretical and mathematical instruments to obtain the results. We have pursued our approach without any semi-classical approximation or expansion in the fine structure constant: the only due perturbative treatment has been reserved to the magnetic interaction term. Along this way, almost unexplored, we have proved some other aside facts. In particular, we have discussed the nature and the properties of the singularities arising in the development and have found that they bear no serious consequences either in the integration of the wave equations, or in their spectral behaviour, but for lengthy technical complications: this, in a sense, can be considered an indirect test of the reliability of the approach to bound states through relativistic wave equations up to the quantum field theoretic corrections. We have also indicated possible applications of the method, which are now under investigation.

Appendix. A perturbative expansion

In this appendix we prove the relationships between the derivative of the spectral values with respect to a parameter ε and the perturbative expansion in that parameter.

Consider the Hermitian operators H , Q and the sum

$$K(\varepsilon) = H + \varepsilon Q. \quad (\text{A.1})$$

Let $U(\varepsilon)$ be the unitary operator such that

$$K_d(\varepsilon) = U^{-1}(\varepsilon)K(\varepsilon)U(\varepsilon) \quad (\text{A.2})$$

is diagonal. Denoting by a dot the derivatives with respect to ε and letting $U = U(0)$, $U^{-1} = U^{-1}(0)$, $\dot{U} = \dot{U}(\varepsilon)|_{\varepsilon=0}$, we expand equation (A.2) to the first order in ε obtaining

$$K_d + \varepsilon \dot{K}_d = H_d + \varepsilon([H_d, U^{-1}\dot{U}] + U^{-1}QU) \quad (\text{A.3})$$

where $K_d = K_d(0)$, $\dot{K}_d = \dot{K}_d(\varepsilon)|_{\varepsilon=0}$. Obviously $K_d \equiv H_d \equiv U^{-1}HU$ and \dot{K}_d are diagonal matrices. Moreover the diagonal elements of $[H_d, U^{-1}\dot{U}]$ are vanishing, so that

$$(\dot{K}_d)_{ii} = (U^{-1}QU)_{ii} \equiv \langle V_i, QV_i \rangle, \quad [H_d, U^{-1}\dot{U}]_{ij} + (U^{-1}QU)_{ij} = 0, \quad i \neq j, \quad (\text{A.4})$$

where V_i is the i th normalized eigenvector of H . Hence

$$K_d(\varepsilon)_{ii} = (H_d)_{ii} + \varepsilon \langle V_i, QV_i \rangle + O(\varepsilon^2) \quad (\text{A.5})$$

and we recover the usual first-order correction of the perturbative expansion.

The procedure goes over to any order. Although in our framework we do not use anything but the first order, we want just to outline how the second order is also obtained. A straightforward computation gives

$$\ddot{K}_d = [H_d, U^{-1}\dot{U}] + 2U^{-1}\dot{U}[U^{-1}\dot{U}, H_d] + 2[U^{-1}QU, U^{-1}\dot{U}] \quad (\text{A.6})$$

where, in the usual notations, $\ddot{K}_d = d^2K_d(\varepsilon)/d\varepsilon^2|_{\varepsilon=0}$ and the same for \ddot{U} . Again the diagonal part of $[H_d, U^{-1}\dot{U}]$ vanishes. Using the second equation of (A.4) and expanding the commutators, we find

$$\frac{1}{2}(\ddot{K}_d)_{ii} = \sum_{j \neq i} (U^{-1}\dot{U})_{ij}(U^{-1}QU)_{ji} + \sum_j (U^{-1}QU)_{ij}(U^{-1}\dot{U})_{ji} - \sum_j (U^{-1}\dot{U})_{ij}(U^{-1}QU)_{ji} \quad (\text{A.7})$$

or equivalently, taking carefully into account the summation ranges,

$$\frac{1}{2}(\ddot{K}_d)_{ii} = \sum_{j \neq i} (U^{-1}QU)_{ij}(U^{-1}\dot{U})_{ji}. \quad (\text{A.8})$$

Observing that from the second equation of (A.4) we have

$$(U^{-1}\dot{U})_{ji} = \frac{(U^{-1}QU)_{ij}}{(H_d)_{ii} - (H_d)_{jj}}, \quad j \neq i \quad (\text{A.9})$$

we find the usual second-order contribution

$$\frac{\varepsilon^2}{2}(\ddot{K}_d)_{ii} = \varepsilon^2 \sum_{j \neq i} \frac{|\langle V_i, QU_j \rangle|^2}{(H_d)_{ii} - (H_d)_{jj}}. \quad (\text{A.10})$$

It appears therefore the advantage achieved for a numerical evaluation of the perturbative corrections in our problem as previously explained.

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