Variational spectrum of the relativistic Coulomb problem in a non-orthogonal basis

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We use the concept of "sign spin" in order to perform calculations of the relativistic spectra of hydrogen-like atoms in a Sturm-Coulomb basis. With one single variational parameter, we obtain very good results for the energy eigenvalues of the bound states, accounting correctly for the fine structure. We show explicit results for the hydrogen atom and the single-electron uranium ion to illustrate the power of our variational method, and discuss also a subtlety associated with the angular momentum quantum labels.

Keywords: Relativistic variational method; Dirac equation; Sturm-Coulomb basis; sign spin; hydrogen

Usando el concepto de "espín de signo", calculamos el espectro relativista de átomos hidrogenoides en la base de Sturm-Coulomb. Con un sólo parámetro variacional obtenemos muy buenos resultados para las energías de los estados ligados, incluyendo la estructura fina. Para ilustrar el poder de nuestro método variacional relativista, mostramos resultados explícitos para el átomo de hidrógeno y para el ion de uranio monoelectrónico. También discutimos una sutileza relacionada con los números cuánticos del impulso angular.

Descriptores: Métodos variacionales relativistas; ecuación de Dirac; base de Sturm-Coulomb; espín de signo; hidrógeno

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1. Introduction

The variational method has been used extensively in order to approximate eigenvalues in quantum mechanics. Since Dirac's famous paper in 1928 [1], where he established relativistic quantum mechanics, many approximate methods have been developed in atomic and molecular physics to deal with relativistic Hamiltonians. In this work, we illustrate how to solve variationally the relativistic Coulomb problem in a non-orthogonal basis, using the Sturm-Coulomb non-relativistic wave functions. We discuss the Hamiltonian for the Dirac equation with a Coulomb interaction in the language of sign spin [2] that allows us to write the Dirac matrices as the direct product of two 2×2 matrices, one associated with the ordinary spin, and the other with the sign spin. The latter is associated with the sign of the energy and, mathematically, it is identical to isospin. The advantage of the sign spin is that it decouples from the spin, which in turn couples with the angular momentum to yield the (conserved) total angular momentum.

We focus on the relativistic Coulomb Hamiltonian because the exact spectrum is known, and we can thus compare with the energy eigenvalues obtained from our variational analysis. As we shall show, the method is remarkably powerful. This is due to the fortunate choice of a variational basis, which is not quite naive. In a previous paper [3], a similar computation with the orthogonal wave-functions of the harmonic oscillator was performed; the results were off by more than 10%. Now, we find agreement with the Dirac formula to one part in a million for $Z = 1$, or better than one percent for $Z = 92$.

2. The variational hamiltonian

In atomic units ($e = \hbar = m = 1$, $c \approx 1/137$), the single-particle Dirac equation with a Coulomb interaction for an energy eigenstate is

$$\left(c\vec{\alpha} \cdot \vec{p}\,' + c^2\beta - \frac{Z}{r'}\right)\psi(\vec{r}\,') = E\psi(\vec{r}\,'), \qquad (1)$$

where the wave-function $\psi(\vec{r}')$ is a Dirac spinor depending only on the relative radial co-ordinate $\vec{r}'$.

Letting

$$r' = \frac{r}{2\lambda}, \qquad \vec{p}\,' = 2\lambda\vec{p}, \qquad (2)$$

with $\lambda \geq 0$ the variational parameter, we obtain the variational Hamiltonian

$$\tilde{H}_\lambda = 2\lambda c\vec{\alpha} \cdot \vec{p} + c^2\beta - \frac{2\lambda Z}{r}. \qquad (3)$$

We can write the Dirac matrices as direct products of 2×2 matrices [2]:

$$\vec{\alpha} = 4\vec{s} \otimes t_1,$$
$$\beta = 2\, I \otimes t_3, \qquad (4)$$

where $s_i = t_i = \sigma_i/2$, with σ_i the Pauli matrices. The s_i matrices act on the ordinary spin, whereas t_i act on the sign spin. This formalism is identical to Wigner's supermultiplet theory [4], where the t_i are associated with isospin.

Subtracting the rest energy c^2 from the Hamiltonian, we find

$$H_\lambda = 8\lambda c(\vec{s}\cdot\vec{p})\otimes t_1 + c^2(2I\otimes t_3 - I\otimes I) - \frac{2\lambda Z}{r}(I\otimes I). \quad (5)$$

Before we plunge into solving the relativistic eigenvalue equation variationally, let us point out that we have also carried out these variational calculations for the non-relativistic Coulomb problem. Because the variational test functions yield the exact solutions to the problem, we obtain with a 1×1 matrix the exact ground state energy at the minimum, with $\lambda = 1$. For $\lambda = 2/n$ the n-th Sturm-Coulomb wave-function has a minimum and is in fact the exact solution. If we truncate the infinite basis to the first n Sturm-Coulomb functions, for any $\lambda > 0$, we have n orthogonal states with different energy eigenvalues. Applying the variational method to these functions, we obtain the energy values of the first n excited states [5].

The interest of our work is to extend the above procedure to the relativistic (but not field-theoretical) case. An important ingredient is the astute choice of basis for the Dirac matrices which splits clearly the spin in a two-dimensional subspace: the group theory simplifies considerably and can be managed with standard, though laborious, mathematical methods. The non-orthogonal basis of wavefunctions chosen for this particular problem is also a crucial ingredient in the extraordinarily rapid convergence of the numerical computations.

3. The Sturm-Coulomb basis

The states on which the Hamiltonian acts are expected to be of the form

$$|\, n(\ell,\tfrac{1}{2})jm;\tau\rangle = \sum_{\mu,\sigma}\langle \ell\mu,\tfrac{1}{2}\sigma \mid jm\rangle R_{n\ell}(r)Y_{\ell\mu}(\theta,\phi)\chi_\sigma \mid \tfrac{1}{2}\tau\rangle. \quad (6)$$

The part related with the sign spin is denoted by the ket $|\,\frac{1}{2}\tau\rangle$, with the eigenvalue of t_3 being $\tau = \pm\frac{1}{2}$. The numbers $\langle \ell\mu,\frac{1}{2}\sigma \mid jm\rangle$ are Clebsch-Gordan coefficients. The labels j, m (resp. ℓ, μ) indicate the total (resp. orbital) angular momentum and its projection; j, m are conserved. The $Y_{\ell\mu}(\theta,\phi)$ are the usual spherical harmonics and $R_{n\ell}(r)$ are the Sturm-Coulomb functions

$$|\, n\ell\rangle = R_{n\ell}(r) = \sqrt{\frac{n!}{(2\ell+n+1)!}}\, r^\ell e^{-r/2} L_n^{(2\ell+1)}(r), \quad (7)$$

where $L_n^{(2\ell+1)}(r)$ are the associated Laguerre polynomials [6].

The Sturm-Coulomb functions are orthogonal with respect to the measure $r\,dr$:

$$\int_0^\infty R_{n'\ell}(r)R_{n\ell}(r)r\,dr = \delta_n^{n'}, \quad (8)$$

but with respect to the volume element $r^2\,dr$ they are only tri-diagonal [7]:

$$\langle n'\ell \mid n\ell\rangle = \sqrt{(n+2\ell+2)(n+1)}\,\delta_{n+1}^{n'} - 2(n+\ell+1)\delta_n^{n'} - \sqrt{n(n+2\ell+1)}\,\delta_{n-1}^{n'}. \quad (9)$$

Because of this non-orthogonality, the variational calculations call for the secular equation

$$\det\langle|\, H_\lambda - E\,|\rangle = 0. \quad (10)$$

In order to solve this equation, we need the explicit Clebsch-Gordan and Racah coefficients [8] in terms of δ-functions, such as

$$W(\ell\ell' jj';0\tfrac{1}{2}) = \frac{(-1)^{-\ell-j'+1/2}\delta_\ell^{\ell'}\delta_j^{j'}}{\sqrt{(2\ell'+1)(2j'+1)}} \quad (11)$$

and

$$\langle \ell\ell, 1-1 \mid \ell'\ell'\rangle = \delta_{\ell-1}^{\ell'}\sqrt{\frac{2\ell-1}{2\ell+1}}. \quad (12)$$

The explicit matrix elements with the above naive wavefunctions are

$$\begin{aligned}\langle n'(\ell',\tfrac{1}{2})jm;\tau' \mid H_\lambda - E \mid n(\ell,\tfrac{1}{2})jm;\tau\rangle &= -2\lambda Z\delta_n^{n'}\delta_\ell^{\ell'}\delta_\tau^{\tau'} \\ &- \left(2c^2\delta_{-\frac{1}{2}}^{\tau'}\delta_\tau^{-\frac{1}{2}} + E\delta_\tau^{\tau'}\right)\delta_\ell^{\ell'}\left[\sqrt{(n+2\ell+2)(n+1)}\,\delta_{n+1}^{n'} - 2(n+\ell+1)\delta_n^{n'} + \sqrt{n(n+2\ell+1)}\,\delta_{n-1}^{n'}\right] \\ &+ 2i\lambda c\left(\delta_{\ell+1}^{\ell'}\delta_{-\frac{1}{2}}^{\tau'}\delta_\tau^{\frac{1}{2}} - \delta_{\ell-1}^{\ell'}\delta_{\frac{1}{2}}^{\tau'}\delta_\tau^{-\frac{1}{2}}\right)\left[\frac{\left(j+\ell+\frac{5}{2}\right)\left(j+\ell+\frac{1}{2}\right)\left(\ell+\frac{3}{2}-j\right)\left(j-\ell+\frac{1}{2}\right)}{(2\ell+1)(2\ell+3)}\right]^{\frac{1}{2}} \\ &\times\left[\frac{1}{2}\sqrt{(n+2\ell+2)(n+1)}\,\delta_{n+1}^{n'} - (\ell+1)\delta_n^{n'} - \frac{1}{2}\sqrt{n(n+2\ell+1)}\,\delta_{n-1}^{n'}\right]. \quad (13)\end{aligned}$$

The naive states above are formed by combining the non-relativistic Sturm-Coulomb wave-functions

$$\mid n\ell\rangle \mid \ell\mu\rangle = R_{n\ell}(r)Y_{\ell\mu}(\theta,\phi), \tag{14}$$

with the spin-1/2 states $\mid \chi_\sigma\rangle$ ($\sigma = \pm 1/2$) to form eigenstates of the total angular momentum. Whereas in the non-relativistic case only ∇^2 appears, the Dirac equation is linear in ∇. This implies, curiously, that the identification between the second label of the radial wave-function $R_{n\ell}$ and the orbital angular momentum is lost. In other words, the variational trial wave-functions (6) are not the most appropriate to the problem. Keeping ℓ for the angular momentum variable appearing in the spherical harmonics, and introducing L for the second label of the radial wave-functions, we are forced to use, instead of the above, trial states of the form

$$\mid nL(\ell,\tfrac{1}{2})jm;\tau\rangle = R_{nL}(r)\sum_{\mu,\sigma}\langle \ell\mu,\tfrac{1}{2}\sigma \mid jm\rangle Y_{\ell\mu}(\theta,\phi)\chi_\sigma \mid \tfrac{1}{2}\tau\rangle. \tag{15}$$

The label L is still an integer but now, instead of being always equal to ℓ, it is equal to the minimum value of ℓ in the collection of states. Given j, we know that $\ell = j \pm \frac{1}{2}$, and thus $L = j - \frac{1}{2}$ always, independently of ℓ.

Accordingly, the secular equation to be solved is not (13) but rather

$$\begin{aligned}
\langle n'L(\ell',\tfrac{1}{2})jm;\tau' \mid H_\lambda - E \mid nL(\ell,\tfrac{1}{2})jm;\tau\rangle \;&= -2\lambda Z\delta_n^{n'}\delta_\ell^{\ell'}\delta_\tau^{\tau'} \\
&- \left(2c^2\delta_{-\frac{1}{2}}^{\tau'}\delta_\tau^{-\frac{1}{2}} + E\delta_\tau^{\tau'}\right)\delta_\ell^{\ell'}\left[\sqrt{(n+2L+2)(n+1)}\,\delta_{n+1}^{n'} - 2(n+L+1)\delta_n^{n'} + \sqrt{n(n+2L+1)}\,\delta_{n-1}^{n'}\right] \\
&+ 2i\lambda c\left(\delta_{\ell+1}^{\ell'}\delta_{-\frac{1}{2}}^{\tau'}\delta_{\frac{1}{2}}^{\frac{1}{2}} - \delta_{\ell-1}^{\ell'}\delta_{\frac{1}{2}}^{\tau'}\delta_\tau^{-\frac{1}{2}}\right)\left[\frac{\left(j+\ell+\frac{5}{2}\right)\left(j+\ell+\frac{1}{2}\right)\left(\ell+\frac{3}{2}-j\right)\left(j-\ell+\frac{1}{2}\right)}{(2\ell+1)(2\ell+3)}\right]^{\frac{1}{2}} \\
&\times\left[\frac{1}{2}\sqrt{(n+2L+2)(n+1)}\,\delta_{n+1}^{n'} - (L+1)\delta_n^{n'} - \frac{1}{2}\sqrt{n(n+2L+1)}\,\delta_{n-1}^{n'}\right].
\end{aligned} \tag{16}$$

4. Relativistic spectra of hydrogen-like atoms

To illustrate concretely the general discussion above, let us concentrate on the states with lowest total angular momentum, namely $j = \frac{1}{2}$. In this case, $L = 0$ always, and of course the spin σ and the orbital angular momentum ℓ are completely correlated. Furthermore, the states split in two disjoint sets, meaning that the matrix elements of $H_\lambda - E$ between them all vanish. One set contains the states with positive sign spin $\tau = \frac{1}{2}$ and angular momentum $\ell = 0$ and also the states with negative sign spin $\tau = -\frac{1}{2}$ and $\ell = 1$. The other set contains the states with $\tau = \frac{1}{2}$, $\ell = 1$ and those with $\tau = -\frac{1}{2}$ and $\ell = 0$. In this simple case with $j = \frac{1}{2}$, the parity-preserving form of the Hamiltonian enforces thus an accidental but useful one-to-one correspondence between the sign spin and the angular momentum. Each set of states contains one of lowest energy, and they have opposite parity. We will consider only the set of states containing the true ground state, of even parity: $\ell = 0$ and $\tau = \frac{1}{2}$.

Exploiting the correlation between τ and ℓ, we may simplify the notation for the set of trial states to be considered:

$$\mid n0(\ell,\tfrac{1}{2})\tfrac{1}{2};\tau\rangle \rightleftharpoons \mid n, 2\tau\rangle \quad 2\tau = \pm 1, \quad n = 0,1,2,\ldots, \tag{17}$$

where $\ell = 0$ if $\tau = \frac{1}{2}$, and $\ell = 1$ if $\tau = -\frac{1}{2}$, and the ground state ($n = \ell = 0$) of even parity is included. Explicitly, to perform numerical computations, we order these states as $\mid 0+\rangle, \mid 0-\rangle, \mid 1+\rangle, \mid 1-\rangle, \mid 2+\rangle, \mid 2-\rangle, \ldots$, and truncate the semi-infinite matrix

$$\langle n', 2\tau' \mid H_\lambda - E \mid n, 2\tau\rangle$$

to a finite one, with $n, n' \leq N$. For each N, we must evaluate the determinant of a $2N \times 2N$ matrix, find its eigenvalues, and then vary λ to minimize those of the bound states. When $\lambda = 0$, there are N states with zero energy and N states with energy $-2c^2$. As λ becomes positive, the degeneracy disappears completely. The N negative energy states sink forever into the Dirac sea with increasing λ, but the N states which start at zero first decrease, then reach a minimum, and then increase forever.

We begin with 2×2 matrix, (*i.e.* we take only the $n = 0$, $\ell = 0, 1$ states). For each λ there are two energy eigenvalues: one associated to the ground state, the other to a state in the Dirac sea. The minimal value is $E_0 \simeq -0.500067$, close to Dirac's $E_0^D \simeq -0.500070$. When we increase the dimension of the basis the excited states appear and the minimal energy eigenvalues improve tremendously.

In Table I, we compare Dirac's values with the energy minima of the bound states of hydrogen calculated using our variational method in an 18×18 matrix. For this case, we can compare with the series expansion in c, the fine structure constant in our units. According to Dirac's formula [9], the bound state energies for $j = \frac{1}{2}$ are

$$E_\nu = c^2\left\{-1 + \left[1 + \frac{Z^2/c^2}{(\nu - 1 + \sqrt{1 - Z^2c^2})^2}\right]^{-\frac{1}{2}}\right\} \tag{18}$$

where the principal quantum number is $\nu = n + \ell + 1$. Ex-

TABLE I. The difference between the variational minima and Dirac's formula for the first nine bound states of hydrogen is shown with two significant digits. The last two entries for hydrogen, marked with an (*), are the coefficients of c^5 in the difference, not c^7; the first seven states come out stupendously well, the last two not so great. Also shown are the approximate values of the variational parameter λ at the minima.

Relativistic bound state energies for hydrogen		
ν	$c^{-7}(E^{\rm var} - E^{\rm Dirac})$	λ
1	0.11	1.44
2	0.029	0.6
3	0.16	0.28
4	0.18	0.27
5	0.33	0.20
6	0.052	0.17
7	5.3	0.15
8	2.3*	0.13
9	7.6*	0.11

TABLE II. Variational energies for the first nine bound states of the uranium single-electron ion. We quote the difference in percent between the variational energy and Dirac's relativistic value, as well as the values of the variational parameter λ for which a minimum is attained. We used $c = 1/137.0359895$.

Relativistic bound state energies for uranium				
ν	$E^{\rm Dirac}$	$E^{\rm var}$	λ	% diff
1	−4861.64	−4861.64	326	3.5×10^{-5}
2	−1257.54	−1254.43	326	0,25
3	−539.141	−538.225	66	0.17
4	−295.279	−293.724	36	0.53
5	−185.496	−184.712	28.5	0.42
6	−127.1	−125.939	19.5	0.92
7	−92.4448	−91.7230	16.5	0.79
8	−70.2282	−69.1485	12.5	1.6
9	−55.1453	−54.1900	10.5	1.8

panding in $c \simeq 1/137$, this is

$$E_\nu = -\frac{1}{2\nu^2}Z^2 - \left(\frac{1}{2\nu^3} - \frac{3}{8\nu^4}\right) Z^4 c^2 - \left(\frac{1}{8\nu^3} + \frac{3}{8\nu^4} - \frac{3}{4\nu^5} + \frac{5}{16\nu^6}\right) Z^6 c^4 + O\left(Z^8 c^6\right). \quad (19)$$

With our variational method, we pick up the non-relativistic term, of course, and also, to an excellent approximation, the relativistic corrections.

Table II shows the energy minima for the bound states of single-electron uranium ion, for which $Z = 92$ and thus the perturbative expansion of (18) converges very slowly. Clearly, the variational method used with the Sturm-Coulomb basis is very good.

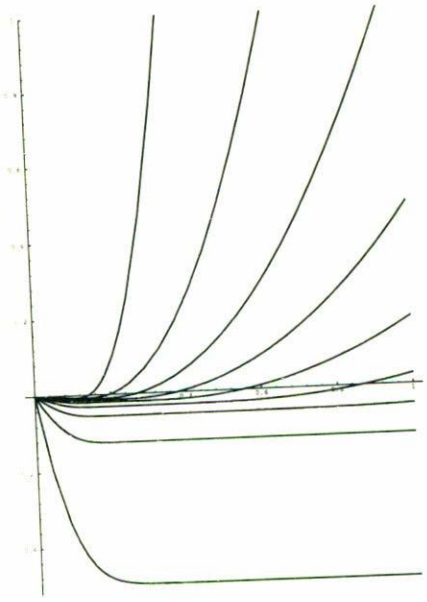

FIGURE 1. Variational energy levels E_ν for the first nine bound states of the hydrogen atom, in units of c^4. The flat curves increase for higher λ and have a unique minimum. There are also nine other curves, not shown, with energies starting at $-2c^2$, which sink forever.

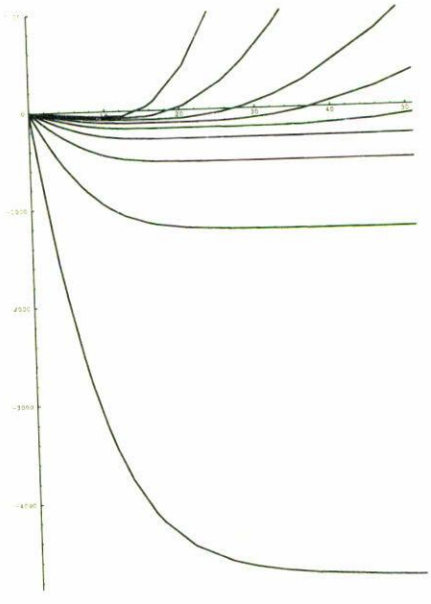

FIGURE 2. Variational energy levels E_ν for the first nine bound states of the uranium single-electron ion, in units of c^4, as a function of the dimensionless variational parameter λ.

In Figs. 1 and 2 we show how the first nine bound states of hydrogen change with the variational parameter, for $Z = 1$ (hydrogen) and $Z = 92$ (single-electron uranium ion).

5. Conclusions

In the relativistic case we observe clearly a gap between the curves of positive and negative energies. The energy minima are very stable with respect to small variations of parameter λ.

The idea of sign spin [2], which simplifies considerably the computations via standard group-theoretical tricks, is just that the Dirac matrices $\vec{\alpha}$ and β can be written, in some basis, as $a \otimes b$, where a acts only on the usual spin and b on the "sign" spin. This is helpful because in the construction of a variational basis the spin and the angular momentum combine to yield the total angular momentum, which is a constant of motion, whereas the sign spin decouples from the angular momentum.

Our results are much better than the ones calculated with harmonic oscillator basis [3], and show the fine structure in the spectra of hydrogen-like atoms. Actually, the energy eigenvalues that we obtain have an unexpectedly good agreement with Dirac's exact formula.

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