A Variational Approach for Numerically Solving the Two-Component Radial Dirac Equation for One-Particle Systems

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ABSTRACT

In this paper we propose a numerical approach to solve the relativistic Dirac equation suitable for computational calculations of one-electron systems. A variational procedure is carried out similar to the well-known Hylleraas computational method. An application of the method to hydrogen isoelectronic atoms is presented, showing its consistency and high accuracy, relative to the exact analytical eigenvalues.

Keywords: One-Electron Systems; 2D Dirac Equation; No-Inertial Frames; Variational Approach

1. Introduction

The study of hydrogen-like models plays an important role to test new approaches, and also in the description of the electronic structure of atomic and molecular systems. In this context, relativistic effects are of the most importance in a complete description of the physical system, mainly as the atomic mass of elements increases. Indeed, these effects play a crucial role in the description of the electronic structure of heavy elements.

Nevertheless, numerical methods used to take into account relativistic effects face several setbacks when the Dirac equation is used due to the existence of a negative continuum energy spectrum associated to the Dirac Hamiltonian operator, e.g., the appearance of instabilities in numerical calculations. Such methodologies are based on straight minimization of the expected values of the Dirac Hamiltonian with respect to a subset of the possible Dirac spinors [1-8]. As it is well known, it is very difficult to describe systems of many-electron atoms and molecules using the relativistic quantum mechanics approach. Even, in the Dirac’s relativistic framework, where a one-electron spinorial solution is a two-vector whose components are scalar wave functions, the description is incomplete. Hence, a full relativistic description of the atomic and molecular electronic structure demands the application of Quantum Electrodynamics methods and consequently, the difficulty of implementing computational treatment for many-electron system increases. A survey of the currently available analytical solutions for relativistic one electron atoms may be found in Maple or Mathematica codes in [9,10] which may be valuable in comparing results of different theories.

In this paper, we propose an alternative approach that allows a simple numerical calculation to attain higher accuracy and allows comparison to other results. We improve the numerical methods to solve the Dirac equation, with special attention to the work of Drake and Goldman [11]. In this way we re-express the problem as one of finding the solution of the variation of a one-dimensional Lagrangian function. This Lagrangian is constructed as a positive definite function for particle energy eigenvalues, the antiparticle ones being get simply by sign reversal. This approach simplifies the procedure of finding the eigenvalues associated with a two-spinor subspace because it avoids automatically the variational collapse problem that always appears when considering the whole eigenvalue spectrum. The numerical procedure is done by calculating the algebraic variations of trial functions. This trial function we calculated in Section 3 for one-electron bound systems, i.e., is similar to the Hylleraas computation method. Furthermore, the reduction to a two-dimensional Dirac-like equation is done by using transformation properties between noninertial frames because it avoids automatically the variational collapse problem that always appears when considering the whole eigenvalue spectrum. The numerical procedure is done by calculating the algebraic variations of trial functions. This trial function we calculated in Section 3 for one-electron bound systems, i.e., is similar to the Hylleraas computation method. Furthermore, the reduction to a two-dimensional Dirac-like equation is done by using transformation properties between noninertial frames, which will be useful in condensed matter such nanostructure, graphene and so on investigation. But for the applications in many-electrons as atomic and molecular systems the analytical equation given in [12] is not applicable. This paper goal is to obtain a numerical solution of the approach given in [12] to be useful in many-electrons applications. We should point out, as far we know...
from the literature, our method to obtain the energy values of the Dirac-Coulomb problem derives directly from the Dirac equation and not from the usual minimization procedures of the Dirac Hamiltonian. In this context the results presented in the paper are new. Although the theoretical aspects have been discussed [12] in order to make the paper more self-contained, we devote Section 2 to a short review of the mathematical tools of that reference. In Section 3 we develop the numerical methods and apply them to hydrogen isoelectronic atoms showing its consistency and high accuracy, relative to the exact analytical eigenvalues. The conclusions are summarized in Section 4.

2. An Irreducible 2D Form for the Dirac Equation

The Dirac wave equation [13] is naturally associated with complex manifolds of the form $C^n \otimes C^n$, with $n \geq 2$. The usual 4D representation demands that $n = 2$ because the electron spin is introduced as an implicit or algebraic degree of freedom, which implies the need of four $4 \times 4$ linearly independent matrices to construct the standard 4-spinor Dirac equation. However, we will show here that an irreducible 2D representation is also possible in $C \otimes C$ for a hydrogen-like problem. In future we expect to generalize the procedure for many electron problems, by considering other $C^n \otimes C^n$ sets.

Since objects of $C \otimes C$, that is the SU2 group are complex $2 \times 2$ quadratic matrices, [14] the corresponding wave function must be a two-spinor of the form $\psi = (\chi_1, \chi_2)$, so that we consider the stationary Hamiltonian problem

$$H(\chi_1, \chi_2) = E(\chi_1, \chi_2),$$

with

$$H = \varphi + i \sigma_i \partial_i - i \sigma_i \partial_i + \sigma_i m,$$

with $\sigma_i$ being the usual Pauli matrices. In order to investigate what angular momentum corresponds to a constant of motion in this model we consider the $z$ component of the angular moment vector

$$J_z = i \left( y \partial_x - x \partial_y \right).$$

Equation (2.3) can easily be verified that do not commute with the Hamiltonian $H$

$$[H, J_z] = \sigma_i \partial_i + \sigma_i \partial_i, \quad (2.4)$$

However, we should observe that

$$[H, J_z] = -2 \left( \sigma_i \partial_i + \sigma_i \partial_i \right),$$

so that the effective operator,

$$M = J_z + \frac{1}{2} \sigma_z,$$

commutes with $H$ and therefore is a constant of motion. In this context, $M$ and $H$ may be simultaneously diagonalized, that is

$$M(\chi_1, \chi_2) = j(\chi_1, \chi_2),$$

where $J$ is an eigenvalue of $M$.

In order to check if our irreducible Dirac equation generates the correct one particle solution, we consider a Coulomb potential $\varphi(r) = -Z \alpha / r$, where $Z$ is the nuclear charge and $\alpha \equiv 1 / 137$ is the fine structure constant and determines the energy levels for hydrogenic atoms.

Equation (2.1) is explicitly written as a two component Dirac-like linear systems of equations

$$\partial_\tau \chi_1 + i \alpha \chi_1 = 0 \quad (2.8a)$$

and

$$\partial_\tau \chi_2 - i \alpha \chi_2 = q \chi_1,$$

where we have introduced $q = m \pm (E + Z \alpha / r)$.

In ordinary polar coordinates $(r, \varphi)$, the differential operators in Equations (2.7) and (2.8) become

$$\partial_\tau \pm i \alpha = e^{i\varphi} \left( \partial_\tau \pm ire^{-i\varphi} \right), \quad J_z = \pm i \alpha$$

By substituting Equation (2.9) into Equation (2.7) and Equations (2.8), it is straightforward to verify that the general solutions are

$$\chi_1(r, \varphi) = e^{i(j \pm \frac{1}{2})} R_1(r), \quad R_1(r) = r^{\frac{3}{2}} e^{-\frac{Z \alpha}{r}} \sum_k a_k r^{k+1} \quad \text{(2.10a)}$$

$$\chi_2(r, \varphi) = e^{i(j \pm \frac{1}{2})} R_2(r), \quad R_2(r) = r^{\frac{3}{2}} e^{-\frac{Z \alpha}{r}} \sum_k a_{2k+1} r^{k+1} \quad \text{(2.10b)}$$

The exact solution has recursion relations given by

$$a_{2k+2} = \frac{2(n - k + j)}{(n + k + 1)(n + k + 2)} \frac{c_{s+2} ^{y_1} c^{y_2} z_2 a_{2k}}{\gamma_1 s + \gamma_2 (s + v + j)}, \quad (2.11a)$$

$$a_{2k+1} = \frac{(s + v + j)}{\gamma_1 + \gamma_2 z_2 a_{2k}}, \quad (2.11b)$$

where $s = \sqrt{j^2 - Z^2 \alpha^2}$, $a_0 = 1$, $0 \leq v \leq n_0 = n - j$ with $1 \leq j \leq n = 1, 2, \ldots$. The remaining parameters are given by $\gamma_1 = \left( m^2 - E^2 \right)^{1/2}$ and $\gamma_2 = m - E$. Finally, Equations (2.11) form a polynomial solution of finite degree for Equations (2.7) and (2.8), if and only if, the corresponding energy eigenvalues are given exactly by

$$E_{n, l} = m \left[ 1 + \frac{Z^2 \alpha^2}{(n-j+\sqrt{j^2 - Z^2 \alpha^2})^2} \right]^{1/2} \quad \text{(2.13)}$$

$$\cong m \left[ 1 - \frac{Z^2 \alpha^2}{2n^2} + \frac{Z^2 \alpha^2}{n^2} - \frac{3}{4} \right]$$

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The first two radial functions $R_{n_{11}}(r)$ and $R_{2(n_{11})}(r)$ for the hydrogen ground state are

$$R_{n_{11}} = \frac{1}{2} r^2 e^{-\sqrt{2} r}, \quad (2.14a)$$

$$R_{2(n_{11})} = \frac{Z\alpha}{2} R_{n_{11}}. \quad (2.14b)$$

We would like to point out that the proportionality between $R_{2(n_{11})}$ (the so called small component) and $R_{n_{11}}$ (the so called large component) observed in Equation (2.14) occurs only when $n = j$; otherwise these functions are linearly independent.

3. Numerical Hylleraas-Like Variational Problem

We have seen in [12] that the method is analytically successful for one-electron atoms. We now formulate a numerical version, which is based in a Hylleraas-like variational approach given in [15], and aims to be extended to two or more electron systems in a future work. This time, instead of solving analytically the system composed of Equations (2.8), we isolate

$$\chi_2 = \frac{-\partial_x X_1 + i\partial_y X_1}{q}, \quad (3.1)$$

and substitute into Equation (2.8b), obtaining

$$-\left(\partial_x - i\partial_y\right)\left(\partial_x X_1 + i\partial_y X_1\right) + q, X_1 = 0 \quad (3.2)$$

We now express Equations (2.8) by means of an extremum problem in which the space integral of a general Lagrangean density $L(x, y, \chi(x, y), \partial_x \chi(x, y))$ is stationary against small algebraic variations in the form of $\chi(x, y)$ about the form of the exact eigenfunctions $\chi_j(x, y)$ and

$$\chi_j(r, \varphi) = e^{(j-\frac{1}{2})\varphi} R_j(r), R_j(r) = r^{-\frac{1}{2}} e^{-r^2} \sum_{n} a_{n} r^{n-1}, \quad (3.3)$$

given by

$$\delta \int L dx dy = 0, \quad (3.4)$$

which leads to the corresponding differential equation obeyed by the Lagrangean:

$$\partial_x \frac{\partial L}{\partial (\partial_x \chi)} + \partial_y \frac{\partial L}{\partial (\partial_y \chi)} - \frac{\partial L}{\partial \chi} = 0, \quad (3.5)$$

where $\chi^*$ is the complex conjugate of $\chi$ that satisfies the asymptotic condition $\lim_{r \to \infty} \chi = 0$.

By comparing Equation (3.3) with Equation (3.5), it is clear that the only possible Lagrangean should be

$$L = \left(\partial_x \chi^* - i\partial_y \chi^*\right)\left(\partial_x \chi + i\partial_y \chi\right)/q + q, \chi^* \chi, \quad (3.6)$$

For $\chi = \chi_1$, we recover Equation (2.10a) or, making use of Equation (2.9) one obtains Equations (2.8). Now we construct a variation function by a product of a power series and undetermined coefficients times the exact solution in Equation (2.10b)

$$\chi(r, \varphi) = e^{(j-\frac{1}{2})\varphi} R_j(r), R_j(r) = R_j(r) \sum_{n} c_n r^n \quad (3.7)$$

where $N$ is an integer and to be specified later.

The variation process implied in Equation (3.4) is then performed directly, by requiring the vanishing of the partial derivatives of the integral of $L$ with respect to the undetermined power series coefficients $c_n$, whose values produce the algebraic variation of the form of $\chi(x, y)$ about the form of the exact eigenfunction $\chi_j(x, y)$, i.e.,

$$\delta \int L dx dy = 0 \Rightarrow \frac{\partial}{\partial c_n} \int_0^L dx dy \bigg|_{n=0,1,2,...} = 0. \quad (3.8)$$

More explicitly, after substituting Equation (3.7) into Equation (3.6), the modified Lagrangean becomes

$$L = \frac{1}{q} \left(\frac{dR_j}{dr} - \frac{j-\frac{1}{2}}{r} R_j\right)^2 + q, |R_j|^2. \quad (3.9)$$

Because the function $\chi_j(x, y)$ is not in general an eigenfunction of the Hamiltonian operator, Equation (3.7) does not lead naturally to a finite system of equations, as can be seen in Equation (2.8). Then it is necessary to truncate the power series of the modified function at some order of precision given by the integer $N$. In fact, Equation (3.7) leads us to an infinite system of linear equations such that the determinant must vanish in order to have a non trivial solution, so it has to be truncated, as usual in Hylleraas-like calculations, at a given order of precision [15]. The whole computational process is so simple that we could express and run the corresponding numerical algorithm using only what is available in Maple algebraic software.

The numerical results of energies $E_{n_{1j}} = E_{n_{1j}} - m$ in atomic units are calculated for the ground state and several excited states of hydrogen atom and are given in Table 1, in which $\delta$dED stands for the numerical deviation with respect to the exact analytical values given in Equation (2.13). To obtain these results we have used $N = 5$ in Equation (3.7) and 4 iterations. Table 2 shows the set of

<table>
<thead>
<tr>
<th>$(n_{1j})$</th>
<th>Energy (a.u.)</th>
<th>$\delta$dED</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1</td>
<td>-0.5000066564993</td>
<td>10^{-28}</td>
</tr>
<tr>
<td>2,1</td>
<td>-0.1250020801588</td>
<td>10^{-30}</td>
</tr>
<tr>
<td>2,2</td>
<td>-0.1250004160228</td>
<td>10^{-28}</td>
</tr>
<tr>
<td>3,1</td>
<td>-0.0555562951656</td>
<td>10^{-29}</td>
</tr>
<tr>
<td>3,2</td>
<td>-0.0555558020877</td>
<td>10^{-28}</td>
</tr>
<tr>
<td>3,3</td>
<td>-0.0555556737326</td>
<td>10^{-31}</td>
</tr>
</tbody>
</table>
Table 2. Set of fine structures with quantum number \( n = 10 \) for atomic hydrogen.

<table>
<thead>
<tr>
<th>( j )</th>
<th>Energy (a.u.)</th>
<th>dED</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.0050000246288</td>
<td>10^{-33}</td>
</tr>
<tr>
<td>2</td>
<td>-0.0050000113158</td>
<td>10^{-33}</td>
</tr>
<tr>
<td>3</td>
<td>-0.0050000068872</td>
<td>10^{-34}</td>
</tr>
<tr>
<td>4</td>
<td>-0.0050000046594</td>
<td>10^{-34}</td>
</tr>
<tr>
<td>5</td>
<td>-0.0050000033281</td>
<td>10^{-34}</td>
</tr>
<tr>
<td>6</td>
<td>-0.0050000024406</td>
<td>10^{-34}</td>
</tr>
<tr>
<td>7</td>
<td>-0.0050000018067</td>
<td>10^{-35}</td>
</tr>
<tr>
<td>8</td>
<td>-0.0050000013132</td>
<td>10^{-36}</td>
</tr>
<tr>
<td>9</td>
<td>-0.0050000009614</td>
<td>10^{-36}</td>
</tr>
<tr>
<td>10</td>
<td>-0.0050000006656</td>
<td>10^{-37}</td>
</tr>
</tbody>
</table>

fine structure levels for the quantum numbers \( 1 \leq j \leq n = 10 \) of the hydrogen atom, where we have used \( N = 7 \) and the order of precision \( \text{dED} \) was obtained after 4 iterations.

The energy levels for several hydrogen isoelectronic atoms calculated by the present theory are shown in Table 3. In this table \( \eta \) is the number of iterations for a given order of precision, \( N \) is the truncation integer of the power series in Equation (3.7) and \( \text{dED} \) gives the comparative accuracy between the exact analytical Dirac solution and our numerical results. Using \( N = 9 \) to calculate the energy of Ba \( ^{10} \) we have obtained a precision of \( 10^{-18} \) at \( 10^{-31} \) for \( N = 11 \). In the case of \( Z = 55 \) we have obtained the precision of \( 10^{-9}, 10^{-23} \) and \( 10^{-31} \) for \( N = 9, N = 11 \) and \( N = 15 \), respectively. In order to improve precision, we have to increase the value of \( N \) in the series in Equation (3.7). We can also observe in Table 3 that when \( Z \) increases, the interaction is slower and it is necessary to increase \( N \) as well. In Table 4 we compare the results obtained by our approach with the results found in the literature. The order of precision of our results (\( \text{dED} \)), in Table 4, is \( 10^{-30} \). The numerical applications shown in Tables 1-4 indicates that our method has a high accuracy with respect to the analytical results obtained by Dirac.

### 4. Conclusions

In this paper, we have shown that there is an irreducible two dimension representation for the Dirac equation with a special solution generates the same set of energy eigenvalues as the usual four dimension representation and further that it makes possible to construct a numerical method which is a mirror of the Dirac differential equations, from what comes highly accurate approximations for the energy eigenvalues. Finally we would like to stress that the novelty our method to obtain the energy values of the Dirac-Coulomb problem derives directly from the Dirac equation, and not from the usual minimization procedures of the Dirac Hamiltonian.
Table 4. Relativistic energy of the ground state of Hydrogen-like atoms (Z = 2, 10, 24, 26, 50, 90 and 110) results by this work and by others authors.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy (a.u.)</th>
<th>This work</th>
<th>Others authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>He+</td>
<td>-2.000106512497</td>
<td>-2.000106514</td>
<td>Ref. [7]</td>
</tr>
<tr>
<td>Ne+9</td>
<td>-50.06674103932</td>
<td>-50.066742026</td>
<td>Ref. [8]</td>
</tr>
<tr>
<td>Cr23+</td>
<td>-290.2429399596</td>
<td>-290.2428</td>
<td>Ref. [7]</td>
</tr>
<tr>
<td>Fe25+</td>
<td>-341.0977911403</td>
<td>-341.097839</td>
<td>Ref. [4]</td>
</tr>
<tr>
<td>Sn+49</td>
<td>-1294.625449024</td>
<td>-1294.62590</td>
<td>Ref. [8]</td>
</tr>
<tr>
<td>Th89+</td>
<td>-4617.746550797</td>
<td>-4617.75</td>
<td>Ref. [7]</td>
</tr>
<tr>
<td>Ds109+</td>
<td>-7579.653261351</td>
<td>-7579.65</td>
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<tr>
<td></td>
<td></td>
<td>-7549.57702</td>
<td>Ref. [8]</td>
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REFERENCES


