A 2D Formulation for the Helium Atom Using a Four-Spinor Dirac-like Equation and the Discussion of an Approximate Ground State Solution

D. L. Nascimento[1*] and A. L. A. Fonseca[1]

[1]*Institute of Physics and International Center of Condensed Matter, University of Brasília, 70919-970, Brasília, DF, Brazil.*

Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

Article Information

Original Research Article

ABSTRACT

We present a two-dimensional analysis of the two-electron problem which comes from the classical conservation theorems and from which we obtain a version of the Dirac equation for the helium atom. Approximate solutions for this equation are discussed in two different methods, although in principle it can be solved analytically. One method is variational, of the Hylleraas type, the execution of which is left for a later communication. In contrast, the other method will have a more complete treatment, in which the set of equations will be separated into its angular and radial components. Furthermore, an exact solution for the angular component will be displayed as well as an approximate solution for the radial component, valid only for the fundamental state of the atom.

Keywords: Helium atom; Dirac equation; relativistic quantum mechanics; variational methods; Hylleraas method; semi analytic solutions.

_____

*Corresponding author: E-mail: daniel@fis.unb.br;

1. INTRODUCTION

Since the beginning of quantum chemistry in the 1920s the implementation of purely computational calculations of the Hartree-Fock type [1] has prevailed, due to their high performance and easy implementation, over more analytical structures such as those of the Hylleraas type [2]. Nevertheless some authors have tried to give an analytical basis to their iterative calculations, some of which have become the source of inspiration to start this line of work [3-6].

Following this analytical aim [7,8], we try to explore the Classical Theorems of Conservation *before* any quantization procedure is performed. We believe that they can reduce the dimensions of the coordinate systems that are necessary to formulate the problem in the quantum domain. More recently [9], we demonstrated that it is possible to use, in the analytical solution of the Dirac equation [10] for the hydrogen atom, Dirac 2x2 matrices rather than the usual 4x4 matrices, which leads to a considerable reduction in complexity of the problem. Moreover, our method led us to a new approach to the relativistic Hylleraas procedure in which the Dirac equation is derived from an extremum problem. This procedure was used to carry out numeric calculations for hydrogen-like atoms that resulted in extremely accurate energy eigenvalues with respect to the exact values, which are well known [11].

In this paper we treat the problem of the helium atom in a similar way to what we did in the case of the hydrogen atom. This treatment has allowed us to use Dirac 4x4 matrices instead of the 16x16 matrices of the Breit theory for the same atom [12], although it should be mentioned that we do not consider here the time retardation effects. Therefore we have developed a dual procedure: on the one hand we obtain a Dirac-like system of partial differential equations and on the other a Lagrangian density to carry out a variational calculation of the Hylleraas type, whose execution is however left to an upcoming article.

For the Dirac-like procedure we take into account the trivial fact of the Theory of Relativity that we cannot add together the geodesics of individual particles. Then we consider a system formed by a single electron plus the nucleus, i.e., the He$^+$ ion, as a substrate on which an outer electron is introduced gradually through a penetration parameter. The gradual superposition of the corresponding Hamiltonians yields a system of differential equations that is dependent on the parameter of penetration, which should be used at the end of the calculation to obtain the minimum energy of the two-electron system. Considering now the Hylleraas-like procedure, the Hamiltonian is used in the traditional way in which the system is treated as a whole, without distinction of individual equations for each electron. For both procedures we try to express the system of equations in a truly covariant form, in which we can introduce later the retardation effects without breaking this fundamental requirement of the Theory of Relativity.

In the last section of the paper we separate the angular and radial components of the Dirac-like system of partial differential equations for the helium atom [13]. We find the angular eigenfunctions that allow us to separate the system of radial equations and an asymptotic form of the wave function that is a solution of this system for the ground state of the atom. From this we get a determination of the atom energy eigenvalue that agrees with the experimental data within 0.1% of accuracy and we also check that it tends to the exact value of the ion energy when the outer electron is displaced to infinity.

2. THEORY

In the infinity mass nucleus rest frame, the relativistic classical Hamiltonians for the individual electrons of the Helium atom in natural units $\hbar = c = 1$ and $\alpha = e^2 \cong 1/137$ are

$$H_1 = \sqrt{\mathbf{p}_1^2 + m^2} - \frac{2\alpha}{r_1} + \frac{\alpha}{r_{12}},$$

$$H_2 = \sqrt{\mathbf{p}_2^2 + m^2} - \frac{2\alpha}{r_2} + \frac{\alpha}{r_{12}}, \qquad (1a,b)$$

where $r_{12} = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}$. We see that the repulsion energy entries fully for each electron in this case, on the other hand, if we consider the energy of the whole system, not taking into account the electrons individually, we arrive at the usual classical Hamiltonian

$$H = \sqrt{\mathbf{p}_1^2 + m^2} + \sqrt{\mathbf{p}_2^2 + m^2} - \frac{2\alpha}{r_1} - \frac{2\alpha}{r_2} + \frac{\alpha}{r_{12}}, \quad (1c)$$

in which the repulsion energy entries only once.

Still in the infinity mass nucleus rest frame, we choose to use a coordinate system in which the motion occurs in the plane defined by the nucleus and the two electrons, i.e., $p_z = 0$, whose z axis may be moving at constant velocity with respect to the z axis of another inertial system, so that the system is invariant against space translations in this direction. In this frame, the only non vanishing components of the classical angular momentum $\mathbf{J}_1 = \mathbf{r}_1 \times \mathbf{p}_1$ and $\mathbf{J}_2 = \mathbf{r}_2 \times \mathbf{p}_2$ and of the total angular momentum $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$ are their z components, namely, $J_{1z} = x_1 p_{1y} - y_1 p_{1x}$, $J_{2z} = x_2 p_{2y} - y_2 p_{2x}$ and $J_z = J_{1z} + J_{2z}$ respectively. Now, we know from Classical Mechanics [14] that the Poisson Bracket for each electron angular momentum with respect to the Classical Hamiltonian (1c) is not null and that they are symmetric with respect to each other, i.e., $\{H, J_{1z}\} = r_1 r_2 r_{12}^{-3} \sin\theta = -\{H, J_{2z}\}$, in which $\theta = \theta_2 - \theta_1$, so that the summation of them is null and hence the total angular momentum J_z becomes a constant of the motion. This happens because the repulsion force between the electrons is a non central force and hence it produces a torque in each electron that makes it oscillating about the axis that join the nucleus to the other electron. In the Poisson Bracket it appears due to the implicit derivatives of $1/r_{12}$ with respect to x_1, y_1 or x_2, y_2 , which produces the symmetric terms because $r_{12} = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}$ in Cartesian coordinates. Therefore, a 2D formulation of the problem is, at least in principle, perfectly possible and we shall present two possibilities of it below.

In this way, besides the usual Hamiltonian for the whole system (1c), an alternative approach for the problem would be to define an effective Hamiltonian function for the two electron system which would be composed of a inner Hamiltonian H_1 of the ion H_e^+ and another Hamiltonian H_2 which would take into account an outer electron, which is superposed to the former through a penetration factor σ, that is

$$ H_\sigma = (1 - \sigma) H_1 + 2\sigma H_2 . \tag{1d} $$

We see that $\sigma = 0$ corresponds to the ion limit when $r_{12} \to \infty$ and the electron 2 is not present;

on the other hand, $\sigma = 1$ correspond to the limit when the two electrons form a single system with perfectly symmetric positions so that the system Hamiltonian becomes two times the Hamiltonian of one of the electrons, which was chosen by convenience to be the electron 2. In fact, it will be seen that $\langle r_{12} \rangle$ becomes a function of σ, so that the equations of the system are solved for $r_{12} =$ constant and then, at the final of the calculation, this constant is varied through σ in order the equilibrium configuration may be obtained.

We now search for a Dirac equation corresponding to the quantization of the classical Eqs. (1c) and (1d), in the infinity mass nucleus rest frame. The quantization is done in a way similar to that performed by Breit [12], in which each square root is "linearized" individually:

$$ \mathbf{p}_1^2 + m^2 = \left(\gamma^5 p_{1y} - \gamma^3 p_{1x} + m\gamma^0 \right)^2 , \tag{2a} $$

$$ \mathbf{p}_2^2 + m^2 = \left(\gamma^1 p_{2y} - \gamma^2 p_{2x} + m\gamma^0 \right)^2 . \tag{2b} $$

We need five 4×4 anticommuting matrices, which are the four usual γ^μ Dirac matrices together with the γ^5 matrix which always appears connected with Dirac´s theory:

$$ \gamma^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad \boldsymbol{\gamma} = \begin{pmatrix} 0 & i\boldsymbol{\sigma} \\ -i\boldsymbol{\sigma} & 0 \end{pmatrix}, $$
$$ \gamma^5 = -i\gamma^0\gamma^1\gamma^2\gamma^3 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{3} $$

where σ_x , σ_y , σ_z are the Pauli spin matrices. As is well known [1], the γ matrices obey $\gamma^\mu\gamma^\nu + \gamma^\nu\gamma^\mu = 2\delta^{\mu\nu}$, for $\mu, \nu = 0, 1, 2, 3, 5$, that is, are unitary and anticommute in pairs, as required to make equal the two sides of Eqs. (2).

---

[1] *There are several possibilities of defining these matrices according to the rules of the Clifford Algebra; we have chosen the only one that makes all products $\gamma^\mu\gamma^\nu$ to be real and positive along with γ^μ be diagonal for $\mu = 0$ and anti-diagonal for $\mu > 0$. These conditions are necessary for the Eq.(6b) and Eq.(8) below reduce to the one-electron 2D Dirac equation [9] when $\sigma \to 0$, which is a fundamental contour condition of our approach.*

By using the momentum operators $\mathbf{p}_1 = -i\nabla_1$ and $\mathbf{p}_2 = -i\nabla_2$, the linear Hamiltonian-like matrix operator associated with Eq.(1c) and Eq.(1d) becomes

$$\hat{H} = i\left(\gamma^3\partial_{x_1} - \gamma^5\partial_{y_1}\right) - \frac{2\alpha}{r_1} + i\left(\gamma^2\partial_{x_2} - \gamma^1\partial_{y_2}\right) - \frac{2\alpha}{r_2} + 2m\gamma^0 + \frac{\alpha}{r_{12}}.$$ (4a)

$$\hat{H}_\sigma = (1-\sigma)\left[i\left(\gamma^3\partial_{x_1} - \gamma^5\partial_{y_1}\right) - \frac{2\alpha}{r_1}\right] + 2\sigma\left[i\left(\gamma^2\partial_{x_2} - \gamma^1\partial_{y_2}\right) - \frac{2\alpha}{r_2}\right] + (1+\sigma)\left(m\gamma^0 + \frac{\alpha}{r_{12}}\right).$$ (4b)

In our coordinate system the total angular momentum operator becomes the z component alone, i.e.

$$\hat{J}_z = iy_1\partial_{x_1} - ix_1\partial_{y_1} + iy_2\partial_{x_2} - ix_2\partial_{y_2}.$$ (5)

Now, as it is well known, the operator $\hat{J}_z$ does not commute with $\hat{H}$ or $\hat{H}_\sigma$. However, it can be verified immediately that total angular operator $\hat{M} = \hat{J}_z + \frac{1}{2}\alpha_{1z} + \frac{1}{2}\alpha_{2z}$, which includes the electron spins, commutes with both $\hat{H}$ and $\hat{H}_\sigma$, that is $\left[\hat{H},\hat{M}\right] = 0$ as well as $\left[\hat{H}_\sigma,\hat{M}\right] = 0$. Here, in the definition of the operator $\hat{M}$ were introduced the two-electron spin matrices $\alpha_{1,z} = -i\gamma^5\gamma^3 = \begin{pmatrix} -\sigma_z & 0 \\ 0 & \sigma_z \end{pmatrix}$ and $\alpha_{2,z} = -i\gamma^2\gamma^1 = \begin{pmatrix} -\sigma_z & 0 \\ 0 & -\sigma_z \end{pmatrix}$ and the diagonalization problems to be solved become therefore $\hat{H}\psi = E\psi$ or $\hat{H}_\sigma\psi = E\psi$ and $\hat{M}\psi = j\psi$, where $\psi = (\chi_1,\chi_2,\chi_3,\chi_4)$ is a four-spinor.

Now, in order to get a truly covariant equation, we left-multiply the energy eigenvalue problem by γ^0, for both operators in (4), so that we get

$$\left[(\phi_{12} - E)\gamma^0 + i\left(\gamma^0\gamma^5\partial_{x_1} - \gamma^0\gamma^3\partial_{y_1}\right) + i\left(\gamma^0\gamma^1\partial_{x_2} - \gamma^0\gamma^2\partial_{y_2}\right) + 2m\right]\psi = 0,$$ (6a)

$$\left[(\phi_{12\sigma} - E)\gamma^0 + i(1-\sigma)\left(\gamma^0\gamma^5\partial_{x_1} - \gamma^0\gamma^3\partial_{y_1}\right) + 2i\sigma\left(\gamma^0\gamma^1\partial_{x_2} - \gamma^0\gamma^2\partial_{y_2}\right) + (1+\sigma)m\right]\psi = 0,$$ (6b)

where $\phi_{12} = -\frac{2\alpha}{r_1} - \frac{2\alpha}{r_2} + \frac{\alpha}{r_{12}}$ and $\phi_{12\sigma} = -\frac{2(1-\sigma)\alpha}{r_1} - \frac{4\sigma\alpha}{r_2} + \frac{(1+\sigma)\alpha}{r_{12}}$ are the total potential energy functions. It may immediately be seen that Eqs.(6) can be put in the explicit covariant form $\left[\sigma_1\zeta_{1\mu}\pi_1^\mu + \sigma_2\zeta_{2\mu}\pi_2^\mu\right]\psi = 0$, by rewriting them in terms of the matrix operators $\zeta_{1\mu} = \left(1, -\gamma^0\gamma^5, \gamma^0\gamma^3, \gamma^0\right)$, $\zeta_{2\mu} = \left(1, -\gamma^0\gamma^1, \gamma^0\gamma^2, \gamma^0\right)$ and the effective momentum operators $\hat{\pi}_k^\mu = \left(m, -i\partial_{x_k}, -i\partial_{y_k}, -\frac{2\alpha}{r_k} + \frac{\alpha}{\sigma_3 r_{12}} - \frac{E}{2\sigma_k}\right)$, where $k = 1,2$; $\sigma_1 = \sigma_2 = 1$, $\sigma_3 = 2$ for (6a) and $\sigma_1 = 1 - \sigma$, $\sigma_2 = 2\sigma$, $\sigma_3 = 1$ for (6b).

Explicitly, Eq.(6a) becomes the following system of linear partial differential equations

$$q_+\chi_1 - \left(\partial_{x_1} + i\partial_{y_1}\right)\chi_3 + \left(-\partial_{x_2} + i\partial_{y_2}\right)\chi_4 = 0,$$ (7a)

$$q_+\chi_2 + \left(\partial_{x_1} - i\partial_{y_1}\right)\chi_4 - \left(\partial_{x_2} + i\partial_{y_2}\right)\chi_3 = 0 \quad , \quad (7b)$$

$$q_-\chi_3 + \left(-\partial_{x_1} + i\partial_{y_1}\right)\chi_1 + \left(-\partial_{x_2} + i\partial_{y_2}\right)\chi_2 = 0 \quad , (7c)$$

$$q_-\chi_4 + \left(\partial_{x_1} + i\partial_{y_1}\right)\chi_2 - \left(\partial_{x_2} + i\partial_{y_2}\right)\chi_1 = 0 \quad , \quad (7d)$$

and Eq.(6b) as well becomes

$$q_{\sigma+}\chi_1 - (1-\sigma)\left(\partial_{x_1} + i\partial_{y_1}\right)\chi_3 + 2\sigma\left(-\partial_{x_2} + i\partial_{y_2}\right)\chi_4 = 0 , \quad (8a)$$

$$q_{\sigma+}\chi_2 + (1-\sigma)\left(\partial_{x_1} - i\partial_{y_1}\right)\chi_4 - 2\sigma\left(\partial_{x_2} + i\partial_{y_2}\right)\chi_3 = 0 , \quad (8b)$$

$$q_{\sigma-}\chi_3 + (1-\sigma)\left(-\partial_{x_1} + i\partial_{y_1}\right)\chi_1 + 2\sigma\left(-\partial_{x_2} + i\partial_{y_2}\right)\chi_2 = 0 , \quad (8c)$$

$$q_{\sigma-}\chi_4 + (1-\sigma)\left(\partial_{x_1} + i\partial_{y_1}\right)\chi_2 - 2\sigma\left(\partial_{x_2} + i\partial_{y_2}\right)\chi_1 = 0 , \quad (8d)$$

in which the new potential functions $q_\pm = 2m \pm (\phi_{12} - E)$ and $q_{\sigma\pm} = (1+\sigma)m \pm (\phi_{12\sigma} - E)$ were introduced for shortness.

At this point we shall need to split the paper in two parts. In the first one, we shall present a variational version of Eqs.(7) that allows us to make numerical calculations of the energy eigenvalues in the Hylleraas scheme, as we did with high accuracy in the case of one-electron atoms [11]. But we shall only introduce the problem, which will be treated fully in a next paper. To do this, firstly we solve the last two equations of (7) for χ_3 and χ_4, what yields

$$\chi_3 = \frac{\left(\partial_{x_1} - i\partial_{y_1}\right)\chi_1 + \left(\partial_{x_2} - i\partial_{y_2}\right)\chi_2}{q_-} ,$$

$$\chi_4 = \frac{-\left(\partial_{x_1} + i\partial_{y_1}\right)\chi_2 + \left(\partial_{x_2} + i\partial_{y_2}\right)\chi_1}{q_-} , \quad (9)$$

then we substitute them into the first two of (7), left-multiply each one by the complex conjugated vectors χ_1^* and χ_2^* respectively and sum up the resulting equations to form a real quadratic function in (χ_1, χ_2) which defines the following Lagrangean density

$$L = \frac{\left|\partial_{x_1}\chi_1 - i\partial_{y_1}\chi_1\right|^2 + \left|\partial_{x_1}\chi_2 + i\partial_{y_1}\chi_2\right|^2 + \left|\partial_{x_2}\chi_1 + i\partial_{y_2}\chi_1\right|^2 + \left|\partial_{x_2}\chi_2 - i\partial_{y_2}\chi_2\right|^2}{q_-} + q_+\left|\chi_1\right|^2 +$$

$$+\Re\left[\frac{(\partial_{x_1}\chi_1^* + i\partial_{y_1}\chi_1^*)(\partial_{x_2}\chi_2 + i\partial_{y_2}\chi_2) - (\partial_{x_2}\chi_1^* + i\partial_{y_2}\chi_1^*)(\partial_{x_1}\chi_2 + i\partial_{y_1}\chi_2)}{q_-}\right] + q_+\left|\chi_2\right|^2 \quad . \quad (10)$$

The extremum problem

$$\delta\int L\,dx_1 dx_2 dy_1 dy_2 = 0 \quad (11)$$

is then solved, in the same way as done with the hydrogen-like atoms [11], by the requirement that the integral in (11) be stable against small variations of the algebraic forms of (χ_1, χ_2) about the corresponding exact solutions of (7) or some suitable approximation of them:

$$\chi_\ell = \chi_{\ell ap} \sum_{\mu+\nu+\lambda=0}^{N} c_{\ell\mu\nu\lambda} r_1^\mu r_2^\nu r_{12}^\lambda \quad (12)$$

for $\ell = 1, 2$ in which $\chi_{\ell ap}$ are the approximations for the exact solutions of (7), $c_{\ell\mu\nu\lambda}$ are the variational coefficients corresponding to each function $\chi_{\ell ap}$ and N is the least integer necessary to a given order of precision to be reached. The variation becomes thus

$$\frac{\partial}{\partial c_{\ell\mu\nu\lambda}} \int L\, dx_1 dx_2 dy_1 dy_2 \bigg|_{N=0,1,2,\ldots} = 0,$$
(13)

which produces two systems of linear equations in $c_{\ell\mu\nu\lambda}$, the determinants of which generate a polynomial function on the atom energy, the roots of which yield the energy eigenvalues for the atom. It should be remarked that the need to know $\chi_{\ell ap}$ in advance is in fact the great limitation of the Hylleraas methodology because, in practice, only asymptotic solutions are known, so that the use of arbitrary intermediary functions becomes the only way to perform the calculation. It is by this reason that we are proposing below the sigma variation procedure, in which we retain the almost exact form of the one-electron solution and perform the variation through a macro parameter that is related to the average values of the radial variables. The Hylleraas-like problem will be reconsidered formally in a next paper.

3. APPROXIMATE GROUND STATE SOLUTION FOR THE SIGMA HAMILTONIAN

Now, considering the second part of the paper, we shall perform the variation through the parameter sigma which allows using one-electron solutions to provide an analytical approximation for the solution of the Eqs. (8). Thus, in order to separate the angular part of Eqs. (8), we must first address the angular momentum problem, $\hat{M}\psi = j\psi$, which written in the polar coordinates of the electrons 1 and 2 becomes $\left(\partial_{\theta_1} + \partial_{\theta_2}\right)\chi_k = i\left(j + \lambda_k\right)\chi_k$, where $\lambda_1 = 1$, $\lambda_2 = -1$, $\lambda_3 = \lambda_4 = 0$, are the diagonal values of $-\frac{1}{2}\left(\alpha_{1z} + \alpha_{2z}\right)$ and $j = j_1 + j_2$. In accordance, the most general forms for the solutions of the angular equation are the set of eigenfunctions

$$\chi_k = f_k e^{i\Phi_k}, \quad f_k = f_k\left(r_1, r_2, r_{12}\right), \quad k = 1,..,4,$$
(14)

where the phase functions are

$$\Phi_1 = \left(j_1 + \tfrac{1}{2}\right)\theta_1 + \left(j_2 + \tfrac{1}{2}\right)\theta_2 + g_1,$$
$$\Phi_2 = \left(j_1 - \tfrac{1}{2}\right)\theta_1 + \left(j_2 - \tfrac{1}{2}\right)\theta_2 + g_2,$$
(15a,b)

$$\Phi_3 = \left(j_1 - \tfrac{1}{2}\right)\theta_1 + \left(j_2 + \tfrac{1}{2}\right)\theta_2 + g_3,$$
$$\Phi_4 = \left(j_1 + \tfrac{1}{2}\right)\theta_1 + \left(j_2 - \tfrac{1}{2}\right)\theta_2 + g_4,$$
(15c,d)

with $g_k = g_k\left(r_1, r_2, r_{12}\right)$. Since $r_{12} = r_{12}(r_1, r_2, \theta)$, the dependence of f_k and g_k on r_{12} has evidently no effect on the values of the angular momentum, but this dependence is necessary when considering a complete solution of the problem in the radial variables r_1, r_2, r_{12}.

Formally, the substitution of χ_k in Eq. (8) makes all complex phases and angular variables vanish and yields a new set of linear equations depending only on the radial variables r_1, r_2, r_{12}. To see this we consider the first order derivatives appearing in (8) expressed in the polar system $\left(r_1, r_2, \theta_1, \theta_2\right)$ and considering also the implicit dependence of the Cartesian coordinates in $r_{12} = r_{12}(r_1, r_2, \theta)$, from this we get the following differential operators

$$\partial_{x_1} \pm i\partial_{y_1} = e^{\pm i\theta_1}\left(\partial_{r_1} \pm \frac{i}{r_1}\partial_{\theta_1}\right) + \frac{r_1 e^{\pm i\theta_1} - r_2 e^{\pm i\theta_2}}{r_{12}}\partial_{r_{12}},$$
(16a)

$$\partial_{x_2} \pm i\partial_{y_2} = e^{\pm i\theta_2}\left(\partial_{r_2} \pm \frac{i}{r_2}\partial_{\theta_2}\right) - \frac{r_1 e^{\pm i\theta_1} - r_2 e^{\pm i\theta_2}}{r_{12}}\partial_{r_{12}}$$
(16b)

Substituting the solution (14) together with the operators (16) into (8) and next separating it in their real and imaginary parts would bring two sets of linear partial differential equations in the radial variables r_1, r_2, r_{12} connecting f_k and g_k with their derivatives, whose analytical solution is completely out of hand at the moment.

However, in this work, we shall limit ourselves to search for solutions satisfying the constraint $\rho = \langle r_{12}\rangle = $ constant, so that in effect we arrive at $f_k = f_k\left(r_1, r_2\right)$ and further assume that $g_k = 0$, which will simplify considerably the resulting equations and also yields the variational relation $\rho = \rho(\sigma)$ that will be used to get the equilibrium configuration of the system. In these circumstances, we arrive at a unique system of equations given by the real part of (8), the imaginary one vanishing identically, that is

$$q_{\sigma+}f_1 - (1-\sigma)\left(\frac{\partial f_3}{\partial r_1} + \frac{j_1 - \frac{1}{2}}{r_1}f_3\right) - 2\sigma\left(\frac{\partial f_4}{\partial r_2} - \frac{j_2 - \frac{1}{2}}{r_2}f_4\right) = 0$$

(17a)

$$q_{\sigma+}f_2 + (1-\sigma)\left(\frac{\partial f_4}{\partial r_1} + \frac{j_1 + \frac{1}{2}}{r_1}f_4\right) - 2\sigma\left(\frac{\partial f_3}{\partial r_2} + \frac{j_2 + \frac{1}{2}}{r_2}f_3\right) = 0$$

(17b)

$$q_{\sigma-}f_3 - (1-\sigma)\left(\frac{\partial f_1}{\partial r_1} + \frac{j_1 + \frac{1}{2}}{r_1}f_1\right) - 2\sigma\left(\frac{\partial f_2}{\partial r_2} + \frac{j_2 - \frac{1}{2}}{r_2}f_2\right) = 0$$

(17c)

$$q_{\sigma-}f_4 + (1-\sigma)\left(\frac{\partial f_2}{\partial r_1} - \frac{j_1 - \frac{1}{2}}{r_1}f_2\right) - 2\sigma\left(\frac{\partial f_1}{\partial r_2} + \frac{j_2 + \frac{1}{2}}{r_2}f_1\right) = 0$$

(17d)

Since the limitations described above do not allow us to get general solutions, we shall limit ourselves to get the simplest solution of Eq. (17), valid only for the ground state of the atom:

$$f_k = e^{-\beta_1 r_1 - \beta_2 r_2} \sum_{\mu+\nu=0}^{1} a_{k\mu\nu} r_1^{s_1+\mu} r_2^{s_2+\nu} , \quad k = 1,2,3,4 \quad (18)$$

because the approximation made above restricts severely the possibility of obtaining energy sub-states, which depend strongly on power series of higher degrees. The substitution of Eq. (18), together with its first derivatives

$$\partial_{r_1} f_k = e^{-\beta_1 r_1 - \beta_2 r_2} \sum_{\mu+\nu=0}^{1} a_{k\mu\nu} \left(\frac{s_1+\mu}{r_1} - \beta_1\right) r_1^{s_1+\mu-1} r_2^{s_2+\nu} ,$$

$$k = 1,2,3,4 ,$$

(19a)

$$\partial_{r_2} f_k = e^{-\beta_1 r_1 - \beta_2 r_2} \sum_{\mu+\nu=0}^{1} a_{k\mu\nu} \left(\frac{s_2+\nu}{r_2} - \beta_2\right) r_1^{s_1+\mu} r_2^{s_2+\nu-1} ,$$

(19b)

into the system (17) yields the new set of equations (summation on μ,ν is omitted for shortness):

$$\left[\gamma_{2\rho} - \frac{2\alpha(1-\sigma)}{r_1} - \frac{4\alpha\sigma}{r_2}\right]a_{1\mu\nu} + (1-\sigma)\left(\beta_1 + \frac{j_1 - s_1 - \frac{1}{2}}{r_1}\right)a_{3\mu\nu} + 2\sigma\left(\beta_2 + \frac{j_2 - s_2 - \frac{1}{2}}{r_2}\right)a_{4\mu\nu} = 0$$

(20a)

$$\left[\gamma_{2\rho} - \frac{2\alpha(1-\sigma)}{r_1} - \frac{4\alpha\sigma}{r_2}\right]a_{2\mu\nu} + 2\sigma\left(\beta_2 - \frac{j_2 + s_2 + \frac{1}{2}}{r_2}\right)a_{3\mu\nu} + (1-\sigma)\left(\frac{j_1 + s_1 + \frac{1}{2}}{r_1} - \beta_1\right)a_{4\mu\nu} = 0$$

(20b)

$$\left[\gamma_{1\rho} + \frac{2\alpha(1-\sigma)}{r_1} + \frac{4\alpha\sigma}{r_2}\right]a_{3\mu\nu} + 2\sigma\left(\beta_2 + \frac{j_2 - s_2 - \frac{1}{2}}{r_2}\right)a_{2\mu\nu} + (1-\sigma)\left(\beta_1 - \frac{j_1 + s_1 + \frac{1}{2}}{r_1}\right)a_{1\mu\nu} = 0$$

(20c)

$$\left[\gamma_{1\rho} + \frac{2\alpha(1-\sigma)}{r_1} + \frac{4\alpha\sigma}{r_2}\right]a_{4\mu\nu} - (1-\sigma)\left(\beta_1 + \frac{j_1 - s_1 - \frac{1}{2}}{r_1}\right)a_{2\mu\nu} + 2\sigma\left(\beta_2 - \frac{j_2 + s_2 + \frac{1}{2}}{r_2}\right)a_{1\mu\nu} = 0$$

(20d)

where $\gamma_{1\rho} = (1+\sigma)m + E - \frac{(1+\sigma)\alpha}{\rho}$ and $\gamma_{2\rho} = (1+\sigma)m - E + \frac{(1+\sigma)\alpha}{\rho}$.

Now we start with the determination of the coefficients and parameters by observing that the system of equations formed by each negative power $1/r_1$ and $1/r_2$ must vanish separately in order the coefficients a_{k00} do not vanish:

$$-2\alpha a_{100} + \left(j_1 - s_1 - \tfrac{1}{2} \right) a_{300} = 0 \;,$$
(21a)

$$-2\alpha a_{200} + \left(j_1 + s_1 + \tfrac{1}{2} \right) a_{400} = 0 \;,$$
(21b)

$$-\left(j_1 + s_1 + \tfrac{1}{2} \right) a_{100} + 2\alpha a_{300} = 0 \;,$$
(21c)

$$-\left(j_1 - s_1 - \tfrac{1}{2} \right) a_{200} + 2\alpha a_{400} = 0 \;,$$
(21d)

and equally

$$-4\alpha a_{100} + \left(j_2 - s_2 - \tfrac{1}{2} \right) a_{400} = 0 \;,$$
(22a)

$$-4\alpha a_{200} - \left(j_2 + s_2 + \tfrac{1}{2} \right) a_{300} = 0 \;,$$
(22b)

$$-\left(j_2 + s_2 + \tfrac{1}{2} \right) a_{100} + 4\alpha a_{400} = 0 \;,$$
(22c)

$$\left(j_2 - s_2 - \tfrac{1}{2} \right) a_{200} + 4\alpha a_{300} = 0 \;.$$
(22d)

For this condition to be fulfilled it is necessary that the determinants of the systems (21) and (22) vanish, from which we get $s_1 = -\tfrac{1}{2} + \sqrt{j_1^2 - 4\alpha^2}$ and $s_2 = -\tfrac{1}{2} + \sqrt{j_2^2 - 4\alpha^2}$.

Now get back to the original system (20), assume that $a_{k\mu\nu} = a_{k\nu\mu}$, for $\mu \neq \nu = 0,1$, and equate the coefficients of the system of equations for the same powers, from which we get the system of recurrence equations

$$\gamma_{2\rho} a_{100} + (1-\sigma)\beta_1 a_{300} + 2\sigma\beta_2 a_{400} - 2\alpha(1+\sigma) a_{110} - (1-\sigma) s_1 a_{310} - 2\sigma s_2 a_{410} = 0 \;,$$
(23a)

$$\gamma_{2\rho} a_{200} + 2\sigma\beta_2 a_{300} + (1-\sigma)\beta_1 a_{400} - 2\alpha(1+\sigma) a_{210} - 2\sigma s_2 a_{310} + (1-\sigma) s_1 a_{410} = 0 \;,$$
(23b)

$$(1-\sigma)\beta_1 a_{100} + 2\sigma\beta_2 a_{200} + \gamma_{1\rho} a_{300} + 2\alpha(1+\sigma) a_{310} - (1-\sigma) s_1 a_{110} - 2\sigma s_2 a_{210} = 0 \;,$$
(23c)

$$2\sigma\beta_2 a_{100} - (1-\sigma)\beta_1 a_{200} + \gamma_{1\rho} a_{400} + 2\alpha(1+\sigma) a_{410} - 2\sigma s_2 a_{110} + (1-\sigma) s_1 a_{210} = 0 \;.$$
(23d)

In order the series (18) can stop, the part of the coefficients a_{k00} in the recurrence must vanish separately of that of the coefficients $a_{k\mu\nu}$ for $\mu \neq \nu = 0,1$, that is

$$\gamma_{2\rho} a_{100} + (1-\sigma)\beta_1 a_{300} + 2\sigma\beta_2 a_{400} = 0 \;,$$
(25a)

$$\gamma_{2\rho} a_{200} + 2\sigma\beta_2 a_{300} + (1-\sigma)\beta_1 a_{400} = 0 \;,$$
(25b)

$$(1-\sigma)\beta_1 a_{100} + 2\sigma\beta_2 a_{200} + \gamma_{1\rho} a_{300} = 0 \;,$$
(25c)

$$2\sigma\beta_2 a_{100} - (1-\sigma)\beta_1 a_{200} + \gamma_{1\rho} a_{400} = 0 \;,$$
(25d)

and also

$$-2\alpha(1+\sigma) a_{110} - (1-\sigma) s_1 a_{310} - 2\sigma s_2 a_{410} = 0 \;,$$
(26a)

$$-2\alpha(1+\sigma) a_{210} - 2\sigma s_2 a_{310} + (1-\sigma) s_1 a_{410} = 0 \;,$$
(26b)

$$2\alpha(1+\sigma) a_{310} - (1-\sigma) s_1 a_{110} - 2\sigma s_2 a_{210} = 0 \;,$$
(26c)

$$2\alpha(1+\sigma) a_{410} - 2\sigma s_2 a_{110} + (1-\sigma) s_1 a_{210} = 0 \;.$$
(26d)

Therefore in order the system (25) have a non trivial solution its determinant must vanish, from what we get $\beta_1 = \dfrac{\sqrt{\gamma_{1\rho}\gamma_{2\rho} - 4\sigma^2\beta_2^2}}{1-\sigma}$ as a function of β_2 and the other parameters.

Now, the non trivial solution for the homogeneous system of equations (25) in the coefficients a_{k00} can be obtained from the kernel associated to β_1, whose basis is given by the two linearly independent column vectors

$$\psi_1 = \begin{pmatrix} -(1-\sigma)\beta_1/\gamma_{2\rho} \\ -2\sigma\beta_2/\gamma_{2\rho} \\ 1 \\ 0 \end{pmatrix},$$

$$\psi_2 = \begin{pmatrix} -2\sigma\beta_2/\gamma_{2\rho} \\ -(1-\sigma)\beta_1/\gamma_{2\rho} \\ 0 \\ 1 \end{pmatrix}, \qquad (27a,b)$$

out of which $\psi = a_{300}\psi_1 + a_{400}\psi_2$ is a general kernel vector. These basis vectors generate by its turn relations among the power series coefficients given by $a_{100} = -(1-\sigma)\beta_1 a_{300}/\gamma_{2\rho}$, $a_{200} = -2\sigma\beta_2 a_{300}/\gamma_{2\rho}$, $a_{400} = 0$ for the former vector and $a_{100} = -2\sigma\beta_2 a_{400}/\gamma_{2\rho}$, $a_{200} = -(1-\sigma)\beta_1 a_{400}/\gamma_{2\rho}$, $a_{300} = 0$ for the later one.

The last step in order to be able to make the evaluation of the energy eigenvalue of the system is as follows. First form a null line vector corresponding to the system (23), i.e., $R = [23a, 23b, 23c, 23d]$ and second make a contraction of it with one of the kernel vectors. Since it may be seen that both kernel vectors produce the same energy eigenvalue, so that the solutions in a_{300} and a_{400} are degenerated, we have chosen to make the contraction with the first kernel vector, that is, $R\psi_1 = 0$. This operation, as expected, eliminates the coefficients a_{k00} and produces a new relation connecting the coefficients a_{k10}:

$$\left[\frac{2\alpha(1-\sigma^2)\beta_1}{\gamma_{2\rho}} - (1-\sigma)\left(\frac{3}{2} + s_1 + j_1\right) \right] a_{110} + 2\sigma \left[\frac{2\alpha(1+\sigma)\beta_2}{\gamma_{2\rho}} - \frac{3}{2} - s_2 + j_2 \right] a_{210} +$$

$$+ \left[\left(\frac{3}{2} + s_1 - j_1\right)\frac{(1-\sigma)^2\beta_1}{\gamma_{2\rho}} + 4\sigma^2\beta_2\left(\frac{3}{2} + s_2 + j_2\right) + 2\alpha(1+\sigma) \right] a_{310} = 0$$

. (28)

Third, decrease the indices µ by one step, in order we can obtain another relation for the coefficients a_{k00}, and use the relation given by the kernel vector ψ_1 to eliminate them:

$$-\left[\frac{2\alpha(1-\sigma^2)\beta_1}{\gamma_{2\rho}} - (1-\sigma)\left(\frac{1}{2} + s_1 + j_1\right) \right](1-\sigma)\frac{\beta_1}{\gamma_{2\rho}} - 4\sigma^2\left[\frac{2\alpha(1+\sigma)\beta_2}{\gamma_{2\rho}} - \frac{1}{2} - s_2 + j_2 \right]\frac{\beta_2}{\gamma_{2\rho}} +$$

$$+ \left(\frac{1}{2} + s_1 - j_1\right)\frac{(1-\sigma)^2\beta_1}{\gamma_{2\rho}} + 4\sigma^2\beta_2\left(\frac{1}{2} + s_2 + j_2\right) + 2\alpha(1+\sigma) = 0.$$

(29)

Before we can follow, we should note that the determinant of the system (26) is not null, so that the only possible solution for (26) is the trivial solution, i.e., $a_{k10} = 0$, so that the solution (18) for the system of differential equations reduces to the elementary form

$$f_k = a_{k00} r_1^{s_1} r_2^{s_2} e^{-\beta_1 r_1 - \beta_2 r_2}, \quad k = 1, 2, 3, 4,$$ (30)

where we have redefined the coefficients a_{k00} as $a_{100} = -(1-\sigma)\beta_1/\gamma_{2\rho}$, $a_{200} = -2\sigma\beta_2/\gamma_{2\rho}$, $a_{300} = 1$ and $a_{400} = 0$.

Now, we write by convenience $\beta_2 = h\beta_1$, where h is to be determined below. As a consequence, substituting β_1 found above and after a little of algebra, we get from (29)

$$\gamma_{1\rho}\gamma_{2\rho} = \frac{4\alpha^2\left(1+\sigma\right)^2\left[\left(1-\sigma\right)^2 + 4\sigma^2h^2\right]\left(\gamma_{1\rho} - \gamma_{2\rho}\right)^2}{\left(1-\sigma^2\right)\left(s_1 + \frac{1}{2}\right) + 4\sigma^2h\left(s_2 + \frac{3}{2}\right)}$$ (31)

which is the fundamental relation that connects the electron parameters. Next, we substitute into (31) the expressions for $\gamma_{1\rho}$ and $\gamma_{2\rho}$ defined above to get finally an algebraic expression for the energy eigenvalues we are searching for

$$E = \frac{\alpha\left(1+\sigma\right)}{\rho} + \frac{\left(1+\sigma\right)m}{\sqrt{1 + \dfrac{4\alpha^2\left(1+\sigma\right)^2\left[\left(1-\sigma\right)^2 + 4\sigma^2h^2\right]}{\left(1-\sigma^2\right)\left(s_1 + \frac{1}{2}\right) + 4\sigma^2h\left(s_2 + \frac{3}{2}\right)}}}$$ (32)

However, this is not yet the final step, since we still need to find out a value for h and the connection between σ and ρ, so that we can obtain a numerical evaluation of the atom energy. This is done by considering the values of the radii for which the probability given by the radial function (30) is a maximum, that is, for which the first derivatives (19) vanish. From this come the relations $r_{10} = s_1 / \beta_1$ and $r_{20} = s_2 / \beta_2$ among the most likely orbital radii and the points of maxima of the radial part of the wave function.

Further we assume that $\rho = \langle r_{12}\rangle$ at the equilibrium configuration may be approximated by $\rho = r_{10} + r_{20}$ and also a linear connection $r_{10} = \sigma r_{20}$ between the electron equilibrium radii which assures the contour condition $r_{20} \to \infty$ when $\sigma \to 0$. From these relations we finally get $h = \sigma s_2 / s_1$. At this point we have finally fulfilled all the steps toward getting an expression for the energy eigenvalues in terms of the basic electron properties along with the variation factor σ:

$$E = \frac{2\sigma m\alpha^2\left(1+\sigma\right)^2}{C_1} + \frac{\left(1+\sigma\right)m}{C_2}$$ (33)

where use has been made of the parameters

$$C_1 = \sqrt{\left[\left(1-\sigma\right)^2\left(s_1 + \frac{1}{2}\right)s_1 + 4\sigma^3\left(s_2 + \frac{3}{2}\right)s_2\right]^2 + 4\alpha^2\left(1+\sigma\right)^2\left[\left(1-\sigma\right)^2 s_1^2 + 4\sigma^4 s_2^2\right]}$$ (34a)

$$C_2 = \sqrt{1 + \frac{4\alpha^2\left(1+\sigma\right)^2\left[\left(1-\sigma\right)^2 s_1^2 + 4\sigma^4 s_2^2\right]}{\left[\left(1-\sigma\right)^2\left(s_1 + \frac{1}{2}\right)s_1 + 4\sigma^3\left(s_2 + \frac{3}{2}\right)s_2\right]^2}}$$ (34b)

We also get, together with Eq. (33), a determination of the equilibrium distance between the electrons as a function of σ, i.e., $\rho = \dfrac{C_1}{2\sigma m\alpha(1+\sigma)}$, as was aimed at the beginning of the paper. And finally the equilibrium radii becomes $r_{10} = \dfrac{\sigma}{1+\sigma}\rho$ and $r_{20} = \dfrac{\rho}{1+\sigma}$.

At this point we can make a plot of the energy excess $\Delta E = E - (1+\sigma)m$ of the system against the effective mass $(1+\sigma)m$. After considering the unit conversion factors, the Hartree $m\alpha^2 \cong 27\,eV$ and the Bohr radius $a_0 = 1/(m\alpha) \cong 0.53 A^\circ$, we get dimensionless forms for the energy excess ΔE and for the distance ρ as follows:

$$\Delta E = \frac{2\sigma(1+\sigma)^2}{C_1} + \left[\frac{(1+\sigma)}{C_2} - 1 - \sigma\right]\frac{1}{\alpha^2}, \quad (35)$$
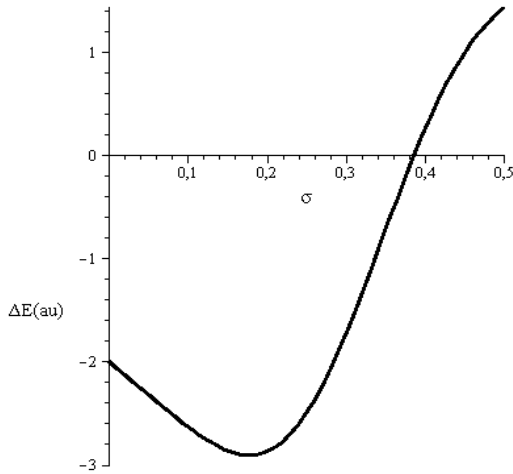
$$\rho = \frac{C_1}{2\sigma(1+\sigma)}. \quad (36)$$

Fig. 1. Excess energy variation ΔE in au against the dimensionless parameter σ

The plot of the energy excess (in au) as a function of σ is shown in Fig. 1 (above), from which we immediately see that the ion ground state limit $\Delta E = -2$ occurs for σ = 0 or $\rho = \infty$. The minimum of the energy excess for $j_1 = j_2 = 1$ corresponds to the inner orbital state of the parahelium atom (or the state 1s-1s of the Spectroscopy). By solving the equation $\frac{d}{d\sigma}\Delta E = 0$, we see that the equilibrium value occurs approximately for $\sigma = 0.17753$, for whose value we get an energy ground state of $\Delta E = -2.9059$, which agrees with the experimental value $\Delta E_{Exp} = -2.9033$ within 0.1% of accuracy. This means that the approximations done to get the determination of the ground state energy of the atom, although rather rough, were

consistent with the dynamics of the physical system. Besides, the equilibrium radii found $r_{10} = 0.130$, $r_{20} = 0.732$ and $\rho = 0.862$ seem also to be in a reasonable agreement with the known values [15].

4. CONCLUSION

In this work we have considered a 2D formulation of the Helium Atom, derived a four-spinor Dirac-like equation and found the suitable matrices. The work has been developed within two methods of approach: on the one hand through a total Hamiltonian in a Hylleraas context that ends in an extremum problem to be solved in a next paper. And on the other hand through a pair of Hamiltonians for an ion-atom and for an outer electron respectively. This second approach stands for a process controlled by a macro-parameter of variation which is connected with the average values of the radial variables and that contains the ion helium atom ground state as a limit case. For this case we have discussed the general structure of the equations, separated the system of equations, found the angular eigenfunctions that decouple the system and a solution for the radial equation, in the approximation of constant inter-electron distance. This made possible to calculate the ground state energy eigenvalue of the atom, whose value agrees with the experimental data within 0.1% of accuracy.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Hartree DR. The calculation of atomic structures. New York (NY): John Wiley; 1957.

2. Hylleraas EA. Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium. Z. fur Physik. 1929;54:347-366.

3. Eisenhart LP. Separation of the variables of the two-particle wave equation. Proc. N. A. Soc. 1949;35:490-94.

4. Kato T. On the existence of solutions of the Helium wave equation. Trans. Am. Math. Soc. 1951;70:212–218.

5. Nakatsuji H, Nakashima H. Analytically solving the relativistic Dirac-Coulomb

equation for atoms and molecules. Phys. Rev. Letters. 1995;95:050407/1-4.

6. Pont M, Shakeshaft R. Decomposition of the two-electron-atom eigenvalue problem. Phys. Rev. A. 2005;51(1):257-265.

7. Nascimento DL, Fonseca ALA, Portilho O. Determination of the Helium atom ground state through the Hamilton–Jacobi equation. Int. J. Q. Chem. 2005;103:505–508.

8. Nascimento DL, Fonseca ALA. New approach to researches in relativistic quantum chemistry using Hamilton-Jacobi Equation, in Quantum Chemistry Research Trends, chap. 5; 173-204. Edited by Kaisas MP, Nova Science Publishers, Inc; 2007.

9. Nascimento DL, Fonseca ALA. A 2D spinless version of Dirac's equation written in a noninertial frame of reference. Int. J. Q. Chem. 2011;111;1361-69.

10. Dirac PAM. The quantum theory of the electron. Proc. Royal Society. 1928; A117(778):610-24.

11. Nascimento DL, Fonseca ALA, Monteiro FF, Amato MA. A variational approach for numerically solving the two-component radial Dirac equation for one- particle systems. J. Mod. Phys. 2012;3:350-354.

12. Breit G. The effect of retardation on the interaction of two electrons. Phys. Rev. 1929;34:553-573.

13. Nascimento DL, Fonseca ALA. Derivation of a four-spinor Dirac-like equation for the Helium atom and an approximate ground state solution. arXiv:1304.5581; 2013.

14. Goldstein H. Classical mechanics, 2nd Ed. Addison-Wesley, Reading, Mass; 1980.

15. Available:http://periodictable.com/Properties/A/AtomicRadius.an.html

_____

Peer-review history:
The peer review history for this paper can be accessed here:
http://sciencedomain.org/review-history/13496