Hydrogen atom

Exotic state. Part one

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Introduction

In the scientific community dominates the conviction that the hydrogen atom is the simplest, and existing theories based on equations of Schrödinger and Dirac fully describe all the subtleties of behavior of an electron in a hydrogen atom.

In this paper and in the following articles will be shown that in addition to the known state-based solutions of the Schrödinger and Dirac equations, there are states which were not studied and they were not known, or often simply were discarded with the phrase "have no physical meaning." Further it will be shown that the existing equations of quantum mechanics, namely the Dirac equation, Klein-Gordon equation and especially the Schrödinger equation, can not accurately describe all the subtleties of behavior of an electron in a hydrogen atom.

As a result there will be given a reasonable basis for the feasibility of an experimental search or targeted synthesis of new unknown states of the hydrogen atom.

The solution of equation M2 for the hydrogen atom

In paper [1] it shows the output of the new relativistic equation M2 (1.1). Here is a solution of hydrogen for the isoelectronic series basically states with quantum numbers \( l = 0 \).

\[
\Delta \Psi - \frac{1}{\hbar^2} \left[ \frac{m^4 c^6}{(E - U(r))^2} - m^2 c^2 \right] \Psi = 0 \quad (1.1)
\]

Now let us present the solution of equation M2 considering all possible values of the quantum number \( l \).

To solve the equation (1.1) let us apply the standard technique of separation of variables in spherical coordinates.

In the central field of the nucleus of the hydrogen atom potential energy depends only on one coordinate, the distance from the center. \( U = -\frac{Ze^2}{4\pi\varepsilon_0 r} \) (1.2)

Let us represent the wave function as a product of the radial and angular parts \( \Psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi) \) (1.3)

The Laplace operator in spherical coordinates as follows: \( \Delta_{r, \theta, \varphi} = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{\Delta_{\theta, \varphi}}{r^2} \) (1.4)
By substituting product (1.3) and the potential energy (1.2) in the original equation (1.1).

\[
Y \frac{\partial^2 R}{\partial r^2} + Y \frac{2 \partial R}{r \partial r} + R \frac{\Delta_{\theta \phi} Y}{r^2} - \frac{1}{\hbar^2} \left[ \frac{m^4 c^6}{(E + Ze^2/4\pi\varepsilon_0 r)} - m^2 c^2 \right] R Y = 0
\]

Multiplying the resulting equation in the fraction \( \frac{r^2}{RY} \).

\[
r^2 \frac{\partial^2 R}{\partial r^2} + \frac{2 \partial R}{r \partial r} - \frac{1}{\hbar^2} \left[ \frac{m^4 c^6}{(E + Ze^2/4\pi\varepsilon_0 r)} - m^2 c^2 \right] r^2 = -\Delta_{\theta \phi} \frac{Y}{Y} \quad (1.5)
\]

As you can see the left side of equation (1.5) depends only on the variable \( r \), and the right side of the variables \( \theta \) and \( \phi \). Therefore, both sides are equal to some constant number \( \lambda \). Which allows to separate the radial side of the equation from the corner portion.

\[
\Delta_{\theta \phi} Y = -\lambda Y \quad (1.7)
\]

Next, we represent the function \( Y(\theta, \phi) \) as a product \( Y(\theta, \phi) = \Theta(\theta)\Phi(\phi) \) (1.8). The angular part of the Laplace operator has the following form:

\[
\Delta_{\theta \phi} = \frac{\partial^2}{\partial \theta^2} + \text{ctg} \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (1.9)
\]

By substituting the product (1.8) in an angular equation (1.7) we will get:

\[
\Theta \frac{\partial^2 \Theta}{\partial \theta^2} + \Phi \text{ctg} \theta \frac{\partial \Theta}{\partial \theta} + \Theta \frac{1}{\sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} = -\lambda \Theta \Phi \quad (1.10)
\]

Multiplying equation (1.10) by a fraction \( \frac{\sin^2 \theta}{\Theta \Phi} \) we will get:

\[
\frac{\sin^2 \theta}{\Theta} \frac{\partial^2 \Theta}{\partial \theta^2} + \frac{\sin^2 \theta}{\Theta} \text{ctg} \theta \frac{\partial \Theta}{\partial \theta} + \lambda \sin^2 \theta = -\frac{\partial^2 \Phi}{\Phi \partial \phi^2} \quad (1.11)
\]

The left side of equation (1.11) depends only on the variable \( \theta \) while the right side only on the variable \( \phi \). Therefore, both sides are equal to some constant number, which we denote \( m^2 \) (do not confuse with the mass of the electron). As a result, we obtain two equations:

\[
\frac{\partial^2 \Theta}{\partial \theta^2} + \text{ctg} \theta \frac{\partial \Theta}{\partial \theta} + \lambda \Theta - \frac{m^2 \Theta}{\sin^2 \theta} = 0 \quad (1.12)
\]

\[
\frac{\partial^2 \Phi}{\partial \phi^2} + m^2 = 0 \quad (1.13)
\]

The solution of \( \Phi \) equation (1.13) is well known \( \Phi(\phi) = A \exp(\pm im\phi) \) (1.14). Since identical values of the angle \( \phi \) (0 and \( 2\pi \)) the function must have the same value \( A \exp(\pm im 0) = A \exp(\pm im 2\pi) = A \) and \( \exp(\pm im 2\pi) = 1 \). By using Euler's formula for complex numbers: \( \cos(2\pi m) = \pm i \sin(2\pi m) = 1 \), we will get \( m = 0, \pm 1, \pm 2, \pm 3, \ldots \). In this way, \( m \) can only take integer values. The constant \( A \) is determined from the normalization condition for the function \( \Phi \):

\[
\int_{0}^{2\pi} \Phi^* \Phi d\phi = 1 \quad (1.15)
\]

whence \( A^2 \int_{0}^{2\pi} e^{im\phi} e^{-im\phi} d\phi = A^2 2\pi = 1 \) and \( A^2 = \frac{1}{2\pi} \) finally we obtain the normalized function \( \Phi \) as \( \Phi = \frac{1}{\sqrt{2\pi}} \exp(im\phi) \) (1.16).
For solution \( \Theta \) equation (1.12), let us use the mathematical online resource WolframAlpha [http://www.wolframalpha.com/]

The solution provides:

\[
\Theta(\theta) = c_1 P_l^m(\cos(\theta)) + c_2 Q_l^m(\cos(\theta)) \quad (1.17)
\]

So, the solution is the amount of associated Legendre functions of the first and second kind. Let us make designation 

\[ l = \frac{1}{2} \left( \sqrt{4\lambda + 1} - 1 \right) \quad (1.18) \]

The variable \( l \) will be associated with the azimuthal quantum number. Let us define the range of possible values of the quantum number \( l \). From formula (1.18) follows, that \( 4\lambda + 1 \geq 0 \) therefore \( l \geq -\frac{1}{2} \) (1.19). Rewriting dependency (1.18) relatively \( l \) we will get \( \lambda = l(l+1) \) (1.20) as expected. Thus the angular part of the wave function is of the form:

\[
Y(\theta, \phi) = \left[ c_1 P_l^m(\cos(\theta)) + c_2 Q_l^m(\cos(\theta)) \right] \frac{1}{\sqrt{2\pi}} \exp(im\phi) \quad (1.21)
\]

In the traditional description of the orbital angular momentum quantum numbers \( l \) and \( m \) are integers. In this case, the function \( Q_l^m(\cos(\theta)) \) has particular qualities. Therefore applies \( c_2 = 0 \). In addition it is believed that the quantum number \( l \) cannot take a negative value. This approach automatically excludes consideration of possible solutions of the equation with the value of the quantum number \( l = -\frac{1}{2} \). Which according to the relation (1.19) is not prohibited.

Now we will raise this issue and show that you can get the inseparable wave function at the proper approach (1.21) for the values of the quantum numbers \( l = -\frac{1}{2} \) and \( m = 0 \).

Function \( P_l^m(\cos(\theta)) \) with values \( l = -\frac{1}{2} \) and \( m = 0 \) has a singularity at the pole at \( \theta = \pi \). The function \( Q_l^m(\cos(\theta)) \) with values \( l = -\frac{1}{2} \) and \( m = 0 \) has a singularity at the pole at \( \theta = 0 \). Therefore, we proceed as follows. Let us divide the range of possible values of the variable \( \theta \in [0,\pi] \) to two intervals

\[ \theta \in \left[ 0, \frac{\pi}{2} \right] \quad \text{and} \quad \theta \in \left[ \frac{\pi}{2}, \pi \right] \]

In the first interval the electron behavior will be subject to the Legendre functions of the first kind \( P_l^m(\cos(\theta)) \) and in the second interval the electron behavior will be subject to the Legendre function of the second kind \( Q_l^m(\cos(\theta)) \).

Corresponding switching between functions is accomplished by selecting the integration constants \( c_1 \) and \( c_2 \). That is, in the first interval \( \theta \in \left[ 0, \frac{\pi}{2} \right] \) \( c_1 = 1, c_2 = 0 \) and in the second interval \( \theta \in \left[ \frac{\pi}{2}, \pi \right] \) \( c_1 = 0, c_2 = 1 \).

As a result, we get the following picture:
Pic. 1 The chart of function $P_l^m \cos(\theta)$ at $l = -\frac{1}{2}$ and $m = 0$ in the interval $\theta \in \left[0, \frac{\pi}{2}\right]$.

Pic. 2 The chart of function $Q_l^m \cos(\theta)$ at $l = -\frac{1}{2}$ and $m = 0$ in the interval $\theta \in \left[\frac{\pi}{2}, \pi\right]$.

Now let us combine the two together in one graph below. Pic. 3
Pic. 3 The graph of angular part of the wave function (1.21) with an appropriate choice of the constants of integration and variable intervals $\theta$.

Thus, as mentioned, with proper approach it can be obtained a smooth, unbroken function as a corner portion of the wave function (1.21).

Figuratively speaking, the electron does not go down in the zone of the singular behavior of the wave function and makes a "detour".

Another argument in favor of considering the state with quantum numbers $l = \frac{1}{2}$ and $m = 0$ is the fact that despite the existence of singularities at the poles, the angular wave function (1.21) is square integrable. That is, the integral of the square module $\int|Y(\theta, \phi)|^2 d\Omega$ is convergent.

As the spherical coordinate system, the element of solid angle $d\Omega = \sin(\theta) d\theta d\phi$, then on the poles with $\theta = 0$ and $\theta = \pi$ we will get $\sin(\theta) = 0$. Hence the multiplication by $\sin(\theta) = 0$ eliminates the singularity.

For descriptive graph of the function $|P^m_l \cos(\theta)|^2 \sin(\theta)$ at $l = -\frac{1}{2}$ and $m = 0$, $\theta \in [0, \pi]$, $\phi \in [0, 2\pi]$.

Pic.4.
The chart of function $P_l^m \cos(\theta) \sin(\theta)$ at $l = -\frac{1}{2}$ and $m = 0, \theta \in [0, \pi], \varphi \in [0, 2\pi]$.

The graph is shown in a partially cut open to make it noticeable behavior of the function in the inner region. As you can see, it is a hollow to toroidal surface without any singularity. The same graph is obtained for the Legendre functions of the second kind $Q_l^m \cos(\theta) \sin(\theta)$ and for their sum.

We now turn to the solution of the radial equation $M_2$ (1.6). For that let us use the online mathematical resource WolframAlpha http://www.wolframalpha.com/

Let us rewrite the equation (1.6) with the notation (1.20).

$$\frac{\partial^2 R}{\partial r^2} + \frac{2 \partial R}{r \partial r} - \frac{l(l+1)}{r^2} R - \frac{1}{\hbar^2} \left[ \frac{m^4 c^6}{(E + Ze^2 / 4 \pi \varepsilon_0 r)^2} - m^2 c^2 \right] R = 0 \quad (1.22)$$

Next we will apply the Hartree’s atomic system of units $a_0 = 1, m = 1, \epsilon = 1, \hbar = 1, c = 137.03599971, 4 \pi \varepsilon_0 = 1$. Let us rewrite the equation (1.22) in the Hartree atomic units.

$$\frac{\partial^2 R}{\partial r^2} + \frac{2 \partial R}{r \partial r} - \frac{l(l+1)}{r^2} R - \frac{c^6}{(E + Z/c)^2} c^2 R = 0 \quad (1.23)$$

The solution of equation (1.23) is the sum of two linearly independent parts. Generalized Laguerre polynomials and confluent hypergeometric function of the second kind.

We use the first linearly-independent solutions. That is:

$$R(r) = k \exp \left( \frac{L + c}{E - c} \right) \Gamma(\frac{c + 2L}{2}) L^{\frac{E^2 + c^2 I + 1 + 1}{2(E - c)^2}} \text{LaguerreL} \left( \frac{E + Z}{E - c} \right) \text{LaguerreL} \left( \frac{E + Z}{E - c} \right) \text{LaguerreL} \left( \frac{E + Z}{E - c} \right)$$

where LaguerreL generalized Laguerre polynomial, $k_i$ constant of integration. $L = l(l+1)$ where $l$ is the quantum number.
As it is known, the first parameter of the generalized Laguerre polynomial is the radial quantum number $n_{rad}$. From these considerations, we obtain the equation for determining the energy of the ground state and the excited states of hydrogen ions in the following form:

$$
\left( \frac{\sqrt{4L + \frac{4Z^2c^6}{E^4}} + 1}{e^4} \right) E^4 - c^4 \left( \frac{\sqrt{4L + \frac{4Z^2c^6}{E^4}} + 1}{e^4} \right) E^2 + 2Zc^4 \sqrt{c^6 - E^2c^2} \right) = n_{rad}
$$

The solution of the equation (1.24) with parameters $l = -\frac{1}{2}, n_{rad} = 0, Z = 1, c = 137.03599971$ we define the test energy states of the hydrogen atom. The solution provides an energy value $E_0 = 18776.921448$ in Hartree's atomic units. The energy includes energy electron rest $mc^2$. Considering this we define the energy state of the test and transform it into an electron-volts. $E_0 = 18776.921448 - (137.03599971)^2 = -1.943768$ a.u. In electron-volts we get $E_0 = 27.2 \times (-1.943768) = -52.8705eV$.

Let us determine the constant of integration using the normalization condition $\int_0^\infty k_1^2R(r)^24\pi r^2dr = 1$

$$k_1^2 = \frac{1}{17279.055481388717}$$

By using the formula for the radial wave function, we construct a graph of the normalized radial probability density Pic.5.

Pic.5 Normalized radial probability density at $l = -\frac{1}{2}, E_0 = -52.8705eV$

Let us define the orbital radius, that is the distance from the origin to the point of maximum probability density. $r_0 = 0.25721897$ in atomic units. Multiplying this value by the Bohr radius $a_0 = 52.9 pm$ we will get $r_0 = 0.25721897 \times 52.9 = 13.606883513 pm$. And we get the most appropriate $R(r_0) = 0.114744691$. 
Thus, by solving the equation $M_2$ was proved the possibility of the existence of hitherto unknown state of the hydrogen atom with the following parameters: value of quantum numbers $l = -\frac{1}{2}$, $m = 0$, $n_{rad} = 0$. State energy value $E_0 = -52.8705\, eV$. The value of the orbital radius $r_0 = 13.606883513\, pm$.

We denote the resulting state of the hydrogen atom symbol $H^0$ and will call it "Hydrogen is a zero-valent" [2], as derived characteristics do not allow to enter $H^0$ in chemical compounds.

Drawing the graph of radial wave function $R(r)$ Pic.6.

![Graph of the radial wave function](image)

**Pic.6** The graph of the radial wave function in $l = -\frac{1}{2} \quad E_0 = -52.8705\, eV$

As you can see the wave function tends to infinity $r \to 0$. But such behavior cannot be considered natural because this is a consequence of an infinite increase in the negative direction when the Coulomb potential $r \to 0 \quad Z \quad r \to \infty$. In reality, the potential is different from the purely Coulomb at $r \to 0$ and it is limited from below, since the core is not a point but has dimensions.

It should be noted that other equations of quantum mechanics also have similar solutions. Here is a table to compare the data, without detailed exposition of the relevant decisions.
The Results

The solutions of the equations of quantum mechanics to atomic hydrogen $\text{H}^0$

<table>
<thead>
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<th>Energy in atomic units</th>
<th>Energy eV</th>
<th>Orbital radius in atomic units</th>
<th>Orbital radius pm</th>
</tr>
</thead>
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<td>M2</td>
<td>-1.94376843</td>
<td>-52.8705013</td>
<td>0.25721897</td>
<td>13.60688351</td>
</tr>
<tr>
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<td>Dirac’s</td>
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<td>-54.40289707</td>
<td>0.24997349</td>
<td>13.22359762</td>
</tr>
<tr>
<td>3</td>
<td>Klein-Gordon's</td>
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<td>0.25012141</td>
<td>13.23142259</td>
</tr>
<tr>
<td>4</td>
<td>Schrödinger’s</td>
<td>-2</td>
<td>-54.4</td>
<td>0.25</td>
<td>13.225</td>
</tr>
</tbody>
</table>

As you can see, the results generally coincide with sufficient accuracy for the Dirac equation, Klein-Gordon and Schrödinger. For the equation M2 is a rather noticeable difference. Perhaps in the future, in the experimental finding, that this distinction will allow to correctly identify the state of hydrogen $\text{H}^0$.

M2 equation in cylindrical coordinates

The arguments listed in the first section in favor of the continuity of the angular part of the wave function, can not be sufficiently convincing. Therefore, this section will try to provide additional evidence of the existence of the exotic states of the hydrogen atom $\text{H}^0$ with the parameters obtained above.

Rewriting the equation M2 (1.1) in cylindrical coordinates. The Laplace operator in cylindrical coordinates as follows:

$$\Delta_{r,z,\phi} = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2}$$

(2.1)

The potential energy in cylindrical coordinates has the form of $U(r, z) = -\frac{Ze^2}{4\pi\varepsilon_0 \sqrt{r^2 + z^2}}$ (2.2)

Substituting the expressions obtained in (1.1), we obtain:

$$\frac{\partial^2 \Psi}{\partial r^2} + \frac{1}{r} \frac{\partial \Psi}{\partial r} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{1}{r^2} \frac{\partial^2 \Psi}{\partial \phi^2} - \frac{1}{\hbar^2} \left[ \frac{m^4 c^6}{(E + \frac{Ze^2}{4\pi\varepsilon_0 \sqrt{r^2 + z^2}})^2} - m^2 c^2 \right] \Psi = 0$$

(2.3)

Let us represent the wave function as a product $\Psi(r, z, \phi) = R(r, z) \Phi(\phi)$ (2.4). By substituting product (2.4) in the original equation (2.3).
By multiplying the resulting equation in the fraction $\frac{r^2}{R\Phi}$.

$$\frac{r^2}{R} \frac{\partial^2 R}{\partial r^2} + \frac{r^2}{R} \frac{1}{r} \frac{\partial R}{\partial r} + \frac{r^2}{R} \frac{\partial^2 R}{\partial z^2} - \frac{1}{\hbar^2} \left[ \frac{m^4 c^6}{(E - \frac{Ze^2}{4\pi\varepsilon_0 \sqrt{r^2 + z^2}})^2} - m^2 c^2 \right] r^2 = - \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \varphi^2}$$

(2.6)

Next we apply the Hartree atomic system of units $a_0 = 1, m = 1, e = 1, \hbar = 1, c = 137.03599971, 4\pi\varepsilon_0 = 1$.

Let us rewrite the equation (2.6) in the Hartree atomic units.

As you can see the left-hand side of equation (2.7) depends only on the variables $r$ and $z$ and right on the variable $\varphi$. Therefore, both sides are equal to some constant number which we denote $m^2$ (do not confuse with the mass of the electron) what allows us to select a real part of the equation from the corner portion. As a result, we obtain two equations:

$$\frac{\partial^2 R}{\partial r^2} + \frac{1}{r} \frac{\partial R}{\partial r} + \frac{\partial^2 R}{\partial z^2} - \frac{1}{r^2} R - \left[ \frac{c^6}{(E + \frac{Z}{\sqrt{r^2 + z^2}})^2} - c^2 \right] R = 0 \quad (2.8)$$

$$\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \varphi^2} + m^2 = 0 \quad (2.9)$$

The resulting equation (2.9) coincides with the equation (1.13), so we have the solution $\Phi = \frac{1}{\sqrt{2\pi}} \exp(imp)$ (2.10) and the values for $m = 0, \pm 1, \pm 2, \pm 3, \ldots$.

As we analyze the state with quantum number $m = 0$, we get the value of the wave function $\Phi = \frac{1}{\sqrt{2\pi}}$. And the equation (2.8) takes the form:

$$\frac{\partial^2 R}{\partial r^2} + \frac{1}{r} \frac{\partial R}{\partial r} + \frac{\partial^2 R}{\partial z^2} - \left[ \frac{c^6}{(E + \frac{Z}{\sqrt{r^2 + z^2}})^2} - c^2 \right] R = 0 \quad (2.11)$$

This equation does not contain a corner piece in an explicit form. Therefore, the problem of continuity of the corner portion is removed automatically. But it is necessary to ensure the convergence of the solution of equation (2.11) with the value of the state of energy $E_0 = -52.8705 eV$.

To solve the equation (2.11) by analytical methods will be difficult. So we will use numerical methods. We use a software package for the numerical solution of systems of differential equations FlexPDE http://www.pdesolutions.com/
As a result, the numerical solution of the following values of the parameters of the hydrogen in the state $H^0$. $E_0 = -51.22739\, eV$, $r_0 = 13.82385\, pm$

Which has a good agreement with the analytical solutions.

Numerical solution showed:

1. The equation of state of hydrogen $H^0$ has a sufficiently high convergence.
2. Concerns about the singular behavior of the angular part of the wave function are groundless.
3. Therefore, there are sufficient grounds for the expediency of an experimental hydrogen research in the state $H^0$.

Below we present the results of the decision in the form of two-dimensional and three-dimensional graphs of the wave function and the radial probability density.
Pic. 8 The three-dimensional graph of the wave function

Pic. 9 The two-dimensional graph of the radial probability density
Pic.10 The three-dimensional graph of the radial probability density

Pic.11 The projection of the three-dimensional radial probability density
Results and discussion

The controversy surrounding hydrogen atoms do not cease to this day. It would seem that after the creation of quantum mechanics and the solution of the Schrödinger and Dirac equations all the issues would disappear for a long time. However, from time to time there are hypotheses about the existence of hydrogen energy states with energy lower than the so-called ground state. In particular, such a hypothesis develops his theories and experiments Dr. Randell Mills company founder Brilliant Light Power, Inc. (BLP).

There are numerous works for and against. There are also experimental results with the release of huge amounts of energy, inexplicable from the standpoint of modern science. An example of such an experiment is the device invented by G.G. Arakelyan[2].

The present work demonstrates that all this talk is not unfounded. The existence of states of the hydrogen atom with an energy below the ground state mathematically quite possible. May it be against this, there are other purely physical causes? But the fact that there are sufficient grounds to thoroughly look into the matter, there is no doubt.

Theoretical work in this direction will be continued.

References

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