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On the singular solution of Schroedinger equation

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Abstract

We obtained an exact analytic expression for the second independent solution of Schoedinger equation for the hydrogen atom. The solution consists of a sum of two parts, one of which increases indefinitely over long distances, while the other is limited and contains a logarithmic term. This feature is peculiar to all values of the orbital angular momentums. In known for us textbooks on quantum mechanics, the first regular solution is considered only. To exclude the second linearly independent solution from the general solution, different textbooks give various arguments.

1 Introduction

The problem for the hydrogen atom, as one of the few that allows an exact analytical solution, is considered for methodological reasons in most textbooks on quantum mechanics. One of the two independent solutions of the Schoedinger equation is square integrable and satisfies the boundary conditions at the coordinate origin ($r = 0$) and at infinity ($r \to \infty$). For states with orbital angular momentum $l \geq 1$, the second singular solution gives the divergence of the normalization integral at the point $r = 0$.

However, for the angular momentum $l = 0$, the singularity of the second solution is expressed weakly and does not lead to the divergence of the integral at the origin, but it is rejected by guiding various arguments in various textbooks. These arguments can be classified into three groups. The first group of textbooks [1, 2, 3, 4] indicates the unsatisfactory boundary conditions of the second solution at the origin. In another group of textbooks [5, 6, 7], it is indicated that this solution does not satisfy the Schoedinger equation at the origin of coordinates $r = 0$ due to the appearance of the Dirac function $\delta(r)$. In the practical textbook [8], there is argued that in the singular state of $l = 0$ the mean value of the kinetic energy takes the infinite, therefore this solution is unacceptable.

We tried to deal with this variety of arguments also because if the singular solution for the orbital moment $l = 0$ is possible to normalize, then it represents a state with limited energy of the system but an infinite average kinetic energy ($+\infty$) and infinite potential energy ($-\infty$), that is, the sum of two infinite quantities is finite

$$E = \langle\Psi|\hat{H}|\Psi\rangle = \langle E_K\rangle + \langle E_P\rangle = (+\infty) + (-\infty). \tag{1}$$

To demonstrate our investigation about the singular solution we briefly repeat one of the methods for obtaining the analytical solution of the Schroedinger equation with the Coulomb potential.

2 The radial Schroedinger equation

In the Schroedinger equation

$$H\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{2}$$

with the Coulomb potential for the hydrogen atom

$$H = \frac{\vec{p}^2}{2\mu} + \frac{\alpha}{r}, \tag{3}$$

where μ is a reduced mass of the atom, one separates the variables in the spherical coordinate system

$$\Psi(\vec{r}) = \Psi(r,\theta,\phi) = R_l(r)Y_{lm}(\theta,\phi) = \frac{u_l(r)}{r}Y_{lm}(\theta,\phi), \tag{4}$$

where $Y_{lm}(\theta,\varphi)$ is spherical harmonics. For radial function $u_l(r)$, we obtain the equation

$$u_l^{''} + (-k^2 - \frac{l(l+1)}{r^2} + \frac{2A}{r}) \cdot u_l(r) = 0, \tag{5}$$

where l is the orbital angular momentum, and parameters k and A have the same dimension and are given by expressions

$$k^2 = \frac{2\mu|E|}{\hbar^2}, A = \frac{e^2\mu}{\hbar^2} \tag{6}$$

The normalization of the radial function *u(r)* looks as

$$\int_0^\infty u_l^2(r) \cdot dr = 1. \tag{7}$$

At large distance ($r \to \infty$) equation (5) takes the form

$$u^{''} - k^2 \cdot u(r) = 0, \tag{8}$$

and has two independent solutions e^{-kr} and e^{+kr}. Since the normalization condition is fulfilled for the asymptotic ($r \to \infty$) solution e^{-kr}, the radial function of equation (5) is sought in the form

$$u(r) = f(r) \cdot e^{-kr}, \tag{9}$$

which leads to an equation for the unknown function $f(r)$

$$f^{''} - 2kf^{'} - \frac{l(l+1)}{r^2}f + \frac{2A}{r}f = 0. \tag{10}$$

We shall now look for solution of equation (10) by the power series method

$$f(r) = r^s \cdot \sum_{j=0}^{\infty} a_j r^j, a_0 \neq 0, \tag{11}$$

where s and a_j are unknown parameters that are determined from the substitution of function (11) into equation (10) with subsequent zeroing of coefficients for each power of variable r. The coefficient at the lowest power gives the equation for determining the parameter s

$$a_0(s^2 - s - l^2 - l) = 0. \tag{12}$$

This equation has two solutions $s_1 = l + 1$ and $s_2 = -l$. Since the roots of the indicial equation (12) differ by an integer, according to [9] two independent solutions of the differential equation are defined in the way

$$f_1(r) = r^{l+1} \cdot \sum_{j=0}^{\infty} a_j r^j, \tag{13}$$

$$f_2(r) = r^{-l} \cdot \sum_{q=0}^{\infty} b_q r^q + g \cdot f_1(r) \cdot ln(r), \tag{14}$$

where unknown coefficients a_j, b_q and g are successively determined by substituting the formulas (13) and (14) into equation (10) and equating to zero the coefficients for powers of the variable r.

3 The regular solution

Substituting formula (13) into equation (10) we obtain the following chain of equations for coefficients a_j

$$a_0(k \cdot l + k - A) - a_1(l+1) = 0, a_1(k \cdot l + 2k - A) - a_2(2l+3) = 0, \ldots \tag{15}$$

In the general case, starting with coefficient a_1, the following are sequentially

$$a_j = \frac{2 \cdot (k \cdot (l+j) - A)}{(2l+j+1) \cdot j} \cdot a_{j-1}, j = 1, 2, 3, \ldots \tag{16}$$

The only coefficient a_0 remains indefinite, but it serves as a common factor and defines only the normalization of the function (13). The ratio of the coefficients of the series (13) with the growth of the index j gives the value

$$\lim_{j \to \infty} \frac{a_j}{a_{j-1}} = \frac{2k}{j}, \tag{17}$$

which corresponds to the ratio of coefficients of the Taylor series for the function e^{2kr}. That is, taking into account formula (9), the radial function $u(r)$ will behave like e^{kr}. However, when the coefficients of the series (13) vanish, starting with a_1 we break an infinite series and obtain a polynomial as the first independent solution. The zero value of the coefficient a_J can be achieved by a special choice of the parameter k (eigenvalue of the energy (6))

$$k = \frac{A}{l+J}, J = 1, 2, 3, \ldots \tag{18}$$

The given algorithm allows finding the eigenvalues of energy and the regular radial eigenfunction

$$u_1(r) = f_1(r) \cdot e^{-kr}, \tag{19}$$

where the coefficient a_0 is determined by the condition of normalization (7). In this case, the function $f_1(r)$ is a polynomial with powers of the variable from r^{l+1} up to r^{J+1}.

4 The singular solution

The second independent solution of equation (10) is given by formula (14), which includes the first solution (13). We note that for orbital momentum $l \geq 1$ the solution (14) is singular at zero, which does not allow normalizing the radial function. Therefore, we consider the case $l = 0$, when the solution is regular at zero. To simplify the calculations, we take into account the ground state ($l = 0, J = 1, k = A$) for which the first solution has the form $f_1(r) = a_0 \cdot r$. Then the formula for the second independent solution (14) will take the form

$$f_2(r) = \sum_{q=0}^{\infty} b_q r^q + g \cdot r \cdot ln(r) \tag{20}$$

We substitute formula (20) into equation (10) and consistently vanish coefficients for every degree of variable r (logarithmic members are reduced autonomously). To determine unknown coefficients we obtain a chain of equations

$$2Ab_0 + g = 0, 2b_2 - 2Ag = 0, -2Ab_2 + 6b_3 = 0, \tag{21}$$
$$-4Ab_3 + 12b_4 = 0, -6Ab_4 + 20b_5 = 0, \ldots \tag{22}$$

From these equations, one can sequentially find g, b_2, b_3, b_4, etc. Coefficient b_1 remains uncertain. This reflects the fact that the sum of two independent solutions

$$f(r) = \alpha f_1(r) + \beta f_2(r) \tag{23}$$

is also a solution to the equation (10). For simplicity, the coefficient b_1 can be set to zero. The coefficient b_0 also remains as an indefinite common factor of the function $f_2(r)$. The chain of equations (21) is not interrupted, and the relation of neighboring coefficients with the growth of the index q has the same form as formula (17). Accordingly, an infinite series in (20) behaves asymptotically as e^{2kr}. So the second independent solution of the radial equation (5) will have a term that behaves like e^{kr} as $r \to \infty$.

That is, we have found two independent solutions of the ground state of hydrogen (hydrogen-like atoms) of the forms

$$u_1(r) = a_0 \cdot r \cdot e^{-kr}, \tag{24}$$

$$u_2(r) = (\sum_{q=0}^{\infty} b_q r^q) \cdot e^{-kr} + g \cdot r \cdot \ln(r) \cdot e^{-kr}. \tag{25}$$

The first solution (23) is normalized (regular), and the second solution (24) is not normalized (singular) since the power series behaves like e^{2kr} at large distances.

5 Discussion and conclusion

We found the exact formula (14) of the second independent solution of the Schroedinger equation for the hydrogen atom, which contains a logarithmic term and satisfies the equation at the origin of the coordinate $r = 0$. For the orbital angular momentum $l = 0$, the second independent solution is finite at the origin but exponentially increases at long distances. The exponential behavior of the second independent radial solution at large distances is inherent for every value of the angular momentum l. That is, one independent solution of the radial Schroedinger equation for hydrogen-like atoms has a regular behavior and is normalized on the interval $[0, \infty)$, and the second independent solution is not normalized and exponentially increases at large values of variable r.

The exponential rise of the second independent solution of (5) can be proved by based on general considerations. Namely, at large distances, the Schroedinger equation has two independent solutions $\tilde{u}_1(r) \sim e^{-kr}$ and $\tilde{u}_2(r) \sim e^{kr}$, which don't depend on orbital angular momentum l. At the origin of the coordinates, independent solutions are $u_1(r) \sim r^{l+1}$ and $u_2(r) \sim r^{-l}$. The solution $u_1(r)$ converges to the solution $\tilde{u}_1(r)$ as $r \to \infty$, but the independent solution $u_2(r)$ must converge either to the solution $\tilde{u}_2(r)$ or to linear sum $[\alpha \cdot \tilde{u}_1(r) + \beta \cdot \tilde{u}_2(r)]$ (here $\beta \neq 0$) as $r \to \infty$. That is the second solution exponentially rise at the infinite.

One can note that the Schroedinger equation for the scattering problem of an electron on a proton differs from equation (5) only by a sign of the parameter k^2 ($+k^2$ instead of $-k^2$). For such equation, two independent solutions are well known - the regular $F_l(k,r)$ and irregular (logarithmic) $G_l(k,r)$ Coulomb wave functions [10].

We want to emphasize that for the hydrogen atom with Coulomb potential and for deuteron wave function [11], the logarithmic term in (14) ensures the correct behavior of the solution at the origin. However, for other potentials, it can appear that the coefficient g in equation (14) is zero.

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