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On the Spectrum and Eigenfunctions of the Equivariant General Boundary Value Problem Outside the Ball for the Schrödinger Operator with Coulomb Potential

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Abstract: We consider the Schrödinger equation for hydrogen-like atom with Coulomb potential and non-point ball nucleus. The eigenvalues and eigenfunctions of the operator given by an arbitrary rotation-invariant boundary value problem on the spherical boundary of the nucleus are found and as it is proved to be the eigenvalues are independent on selection of any such boundary value problem and they are the same as for point nucleus.

Keywords: Boundary value problem, the Schrödinger equation, ball nucleus

In this paper the emission (absorption) spectrum of a hydrogen-like atom with nontrivial nucleus radius was found, it is understood as the discrete spectrum of the operator in the title. Assume that the nuclear charge is distributed spherically symmetric. As is well known, spherically symmetric body beyond its limits creates the same gravitational field, as a material point of the same mass, which is located in the center of the body. Therefore we use the Coulomb potential, using the analogy with gravity. Usually two restrictions are imposed on the wave function, that is a solution of the Schrödinger equation with the Coulomb potential, they are a limitation at zero and the decrease at infinity [8]. In present paper, the wave function is not defined in a neighborhood of zero, instead it we consider a boundary value problem for solution in the exterior of a sphere of radius ρ_0. We do not know what the boundary conditions should be placed on the surface of the nucleus, but we assume that they must be spherically symmetric. This leads to the formulation of the general equivariant boundary value problem. In this paper we consider the general external rotation-invariant boundary value problem for the Schrödinger equation with the Coulomb potential. The eigenvalues and the corresponding eigenfunctions of the problem were obtained. It is proved to be that obtained energy values are the same as radiation energy of the point size atom, that sounds awesome, although, of course, the eigenfunctions are other. The Schrödinger equation is usually studied in the whole space, boundary value problems for the Schrödinger type equation have been studied in some papers, for instant in the works [1,2,10], but the setting as above has not been considered. Remark that arbitrary rotation-invariant boundary value problems for the PDEs have been considered in the book [4].

Let us consider the stationary Schrödinger equation for the wave function of an electron of mass M and the Coulomb attractive potential in the exterior of the ball $K = \{x \in \mathbf{R}^3, |x| < \rho_0\}$ with a general boundary value problem :

$$\left(\triangle_{x,y,z} + \frac{2M}{\hbar^2}\left(\frac{Ze^2}{r} + E\right)\right)\psi(r,\varphi,\theta) = 0, \qquad (1)$$

$$A\psi|_{\partial K} + B\psi'_{\nu}|_{\partial K} = 0. \qquad (2)$$

Here $-\frac{Ze^2}{r}$ – potential, e – electron charge, Ze – nucleus charge, E – eigenvalue, $\hbar$ – Dirac constant, $\psi(r,\varphi,\theta)$ – unknown wave function. We assume that the boundary value problem (2) with normal ν is invariant with respect to ball rotations that is the operators A and B are invariant.

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Let's consider the quasi-regular unitary representation $T : G \to U(L_2(S^2))$, $[T(g)f](\xi) = f(g^{-1}\xi)$, $f(\xi) \in L_2(S^2), g \in G$ of the Lie group $G = SO(3)$. It is well-known [7] that every linear operator in $L_2(S^2)$ which commutes with all operators $T(g)$ of quasi-regular representation is convolutional. Therefore we will consider boundary problems of the form

$$\psi|_{\partial K} * \alpha + \psi'_v|_{\partial K} * \beta = 0, \quad \alpha^2 + \beta^2 \neq 0. \qquad (3)$$

Here α and β are arbitrary given functions on the sphere ∂K. At infinity we have set the condition of disappearance. We want to find the eigenvalues of operator from (1) with condition (2) and show that these eigenvalues don't depend on functions α and β.

For investigation of this problem we will use the well-known way specified in the standard books [9,5]. It appears that the method of separation of variables is also suitable in this case of Schödinger equation with the general boundary value problem. First, let's write the general solution of equation (1). Suppose that the solution in polar coordinates is represented in the form

$$\psi(r,\varphi,\theta) = \hat{C}\sum_{l=0}^{\infty}\sum_{m=-l}^{l} R_{l,m}(r)Y_{l,m}(\varphi,\theta), \qquad (4)$$

where $Y_{l,m} = \frac{1}{\sqrt{2\pi}}e^{im\varphi}(-1)^m\sqrt{\frac{2l+1}{2}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)$ are spherical functions that are eigenfunctions of the square of the angular momentum with eigenvalues $l(l+1), l = 0,1,2..\infty$, $P_l^m(\cos\theta)$ are associated Legendre functions, $\hat{C}$ is a constant, which is convenient for us to enter at once but choose it later and $R_{l,m}(r)$ are unknown radial functions.

Substituting (4) into (1) we obtain the following equation for the radial parts of the wave function

$$R''_{l,m} + \frac{2}{r}R'_{l,m} + $$
$$+R_{l,m}\left(-l(l+1)\frac{1}{r^2} + \frac{2MZe^2}{\hbar^2}\frac{1}{r} + \frac{2ME}{\hbar^2}\right) = 0. \qquad (5)$$

Let's find a solution of equation (5) explicitly by making the change $R_{l,m}(r) = \widehat{R}_{l,m}(\rho)\rho^l e^{-\rho/2}$, $\rho = 2nr$.

For convenience we introduce the notation

$$\sqrt{-2ME}\,/\,\hbar = n$$

considering the case $E < 0$.

Then we obtain the following equation

$$\rho\widehat{R}''_{l,m} + (2l+2-\rho)\widehat{R}'_{l,m} + \widehat{R}_{l,m}\left(\frac{Me^2}{n\hbar^2} - l + 1\right) = 0. \qquad (6)$$

The last equation is degenerate hypergeometric equation and solutions are the Kummer functions with the first parameter $-\frac{Me^2}{n\hbar^2} + l - 1$ and with the second parameter $2l + 2$. Therefore, in terms of the degenerate hypergeometric functions of the first and second kinds, we get [3]

$$\widehat{R}_{l,m}(\rho) = C_1(l,m)\rho^l e^{-\rho/2}\Phi\left(l - \frac{Me^2}{n\hbar^2} - 1, 2l+2, \rho\right) +$$
$$+C_2(l,m)\rho^l e^{-\rho/2}\rho^{-2l-1}\Psi\left(-l - \frac{Me^2}{n\hbar^2} - 2, -2l, \rho\right). \qquad (7)$$

Note that the function $\widehat{R}_{l,m}$ also depend on n (further on k). Let's investigate the behavior of the radial part of the wave function at infinity using equation (5). Let r take large values, then some terms can be neglected in equation (5), namely those which are multiplied by $\frac{1}{r}$ or $\frac{1}{r^2}$. We obtain the equation $R'' + \frac{2ME}{\hbar^2}R = 0$. It has a finite solution at infinity $R = e^{-nr}$. Hence, the solution of equation (5) at infinity should decrease as e^{-nr}. It means that the function $\Phi(-\frac{Me^2}{n\hbar^2} + l - 1, 2l+2, \rho)$ should not grow at infinity too fast. However, it is well-known[3] that generic degenerate hypergeometric functions increases as the exponent of its argument.

In order to the degenerate hypergeometric function of the first kind in (7) does not spoil the behavior of the radial function at infinity, it is necessary that the first parameter would be a negative integer.

$$\Phi(\alpha,\beta,z) = 1 + \frac{\alpha}{\beta}\frac{z}{1!} + \frac{\alpha(\alpha+1)}{\beta(\beta+1)}\frac{z^2}{2!} +$$
$$+ \frac{\alpha(\alpha+1)(\alpha+2)}{\beta(\beta+1)(\beta+2)}\frac{z^3}{3!} + \ldots \qquad (8)$$

As it can be seen from the definition of the degenerate hypergeometric function (8), if the first parameter α is an integer negative then all the terms in the series will be nulled, except for the first some terms. Thus, the function Φ from (8) becomes a polynomial function and hence the corresponding term in (8) disappearances at infinity. Denote a negative integer value of the parameter α in (8) by $-\frac{Me^2}{n\hbar^2} + l - 1 = -k + l - 1$. It is clearly that the parameter k (known as the principal quantum number) can be any positive integer, $k \geq l-1, l \geq 0$. So, $n = \frac{Me^2}{\hbar^2 k}$.

Let's see how the function $\Psi(-k-l-2,-2l,x)$ behaves at infinity[3].

$$\Psi(-k-l-2,-2l,\rho) \approx$$
$$\approx \sum_{p=0}^{N}(-1)^p\frac{(-l-k-2)_p(l-k-1)_p}{p!}\rho^{l+k+2-p} + \qquad (9)$$
$$+O(|x|^{l+k+2-N-1}).$$

From the last equation it is clear that the function at infinity behaves as a polynomial.

Returning to (6) we can see that the energy values are

$$E_k = \frac{-Me^4}{2\hbar^2 k^2},\ k = \overline{1..\infty}. \qquad (10)$$

Note that in this case the energy levels is the same as in the classical case of a point nucleus.

Return to the general boundary value problem (3): $\psi|_{\partial K} * \alpha + \psi'_\nu|_{\partial K} * \beta = 0$. Let $\alpha = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} \alpha_l^m Y_{l,m}$, $\beta = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} \beta_l^m Y_{l,m}$ – decompositions of functions in Fourier series on sphere S^2. The function ψ from (4) depend on E or on k by virtue of (10). For different k we have different eigenfunctions ψ_k. For the eigenfunction ψ_k also $\psi_k|_{\partial K} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} a_{k,l}^m Y_{l,m}$, $\psi'_{k\nu}|_{\partial K} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} b_{k,l}^m Y_{l,m}$. $*$ – convolution on ∂K, that is $\psi_k|_{\partial K} * \alpha = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} a_{k,l}^m \alpha_l^0 Y_{l,m}$

Here we are in the following situation and we will use the following results. As usual, an operator A is called invariant with respect to a group G of transformations if the operator A commutes with transformations of G, more accurate, if the operator A commutes with each operator of quasiregular representation of the group G in the action space of A. For the space $E = L_2(S^2)$ and the group $G = SO(3,\mathbf{R})$ acting on S^2 by rotations a quasiregular representation $T : G \to GL(E)$ is given by definition by the formula[7] $T(g)f(x) = f(g^{-1}x,\ f(x) \in E,\ g \in G$. This representation is unitary and has the decomposition in the direct sum of irreducible representations $T = \sum_{l=0}^{\infty} T^l$, where irreducible component T^l acts on the space $\gamma(H^l)$, γ is the operator of contraction of functions from $\mathbf{R^3}$ onto sphere S^2, H^l is the space of homogeneous harmonic polynomials of degree l on $\mathbf{R^3}$ and the spherical functions $\{Y_{m,l}\}_{m=-l}^{l}$ constitute a basis in H^l. We will consider any function on sphere S^2 as a function on the group G that is a constant on each left coset in $G/SO(2,\mathbf{R})$. The following statements[6] hold:

1). For any linear operator $\mathscr{A}$ in the space E which commutes with each operator $T(g)$ of quasiregular representation there exists a function $\psi_{\mathscr{A}} \in L_2(S^{n-1})$ such that $[\mathscr{A}\varphi](g) = \int\limits_{g_1 \in G} \varphi(g_1)\psi_{\mathscr{A}}(g_1^{-1}g)dg_1 = [\varphi * \psi_{\mathscr{A}}](g)$ for each $\varphi \in L_2(S^{n-1})$. Vise verse any convolution operator commutes with each $T(g)$.

2). Let us have $f_1 * f_2(g) = \sum_{l=0}^{\infty}\sum_{m=1}^{h(l)} \gamma_l^m t_{m1}^l(g)$ is decomposition of convolution of functions $f_1(g)$ $f_2(g)$ that are constants on left cosets in Fourier expansion. Here $t_{m1}^l(g) = \left(T^l(g)e_1, e_m\right)$ are matrix entries of irreducible representation T^l, e_1 is an invariant with respect to H vector in the space T^l, $h(l) = \dim T^l$. Then $\gamma_l^m = \lambda_l^m \cdot \mu_l^1$, where λ_l^m and μ_l^m are Fourier coefficients of functions $f_1(g)$ and $f_2(g)$ respectively. For our case we have the basis t_{m1}^l corresponds to $Y_{l,m}$, the index 1 in μ_l^1 means zonal harmonic $Y_{l,0}$.

Boundary value problem (3) in terms of the Fourier coefficients for each k can be written as

$$a_{k,l}^m \alpha_l^0 + b_{k,l}^m \beta_l^0 = 0. \tag{11}$$

$a_{k,l}^m = \widehat{R}_{k,l,m}|_{\rho=\rho_0}$ is given by (4),(7) and $b_{k,l}^m = \frac{1}{\rho_0}\frac{\partial \widehat{R}_{k,l,m}(\rho)}{\partial \rho}\Big|_{\rho=\rho_0}$. Note that tesseral harmonics in α and β can be omit.

Thus, the boundary value problem can be written as

$$\begin{aligned}
&\{C_1(k,l,m)\rho_0^{2l+3}\Phi(l-k-1,2l+2,\rho_0)+\\
&+C_2(k,l,m)\rho_0^2\Psi(-k-l-2,-2l,\rho_0)\}\alpha_l^0+\\
&+\{C_1(k,l,m)\rho_0^{2l+1}(l\Phi(l-k-1,2l+2,\rho_0)-\\
&-1/2\rho_0\Phi(l-k-1,2l+2,\rho_0)+\\
&+\rho_0\frac{l-k-1}{2l+2}\Phi(l-k,2l+3,\rho_0))+\\
&+C_2(k,l,m)((-l-1)\Psi(-k-l-2,-2l,\rho_0)-\\
&-1/2\rho_0\Psi(-k-l-2,-2l,\rho_0)+\\
&+\rho_0(l+k+2)\Psi(-k-l-1,-2l+1,\rho_0))\}\beta_l^0=0.
\end{aligned} \tag{12}$$

We can assume that $C_2(k,l,m) \equiv 1$, since both sides of (12) can be divided into an arbitrary constant. The equality (12) allows us to find unknown constant $C_1(k,l,m)$.

Normalization condition allows us to find the last unknown constant $\hat{C}$ from (4): $\int_{r_0}^{\infty} |\psi_k(r,\varphi,\theta)|^2 dr = 1$. *Eigenvalues and the corresponding eigenfunctions of the problem (1), (2), in the above notation, are*

$$E_k = \frac{-Me^4}{2\hbar^2 k^2},\ k = \overline{1..\infty},$$

$$\begin{aligned}
\psi_k(r,\varphi,\theta) = \hat{C}\sum_{l=0}^{k}\sum_{m=-l}^{l} &(C_1(k,l,m)(2nr)^l e^{-nr}\\
&\times\Phi(l-k-1,2l+2,2nr)+\\
+(2nr)^{-l-1}e^{-nr}\Psi(-l-k-2,&-2l,2nr))Y_{l,m}(\varphi,\theta).
\end{aligned}$$

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