WHAT IS THE BOUNDARY CONDITION FOR RADIAL WAVE FUNCTION OF THE SCHRODINGER EQUATION ?

Anzor A. Khelashvili[a)]
Inst. of High Energy Physics, Iv. Javakhishvili Tbilisi State University, University Str. 9, 0109, Tbilisi, Georgia and St.Andrea the First-called Georgian University of Patriarchy of Georgia, Chavchavadze Ave.53a, 0162, Tbilisi, Georgia
Teimuraz P. Nadareishvili[b)]
Inst. of High Energy Physics, Iv. Javakhishvili Tbilisi State University, University Str. 9, 0109, Tbilisi, Georgia

Abstract. The mathematical physics literatures as well as quantum mechanics textbooks on spherically symmetric potentials are enormous. Despite of these there is no unique point of view about the boundary behavior of the radial function at the origin, in particular, for singular potentials. Since at least the work of K.Case , it has been known that Weyl limit-point, limit-circle analysis provides the right way to understand the boundary conditions at the origin. This is now textbook material, as discussed in books of Reed and Simon, for example. But these books are very difficult to understand for students. Despite of this in our opinion there is no necessity of deepening into such profound mathematics. Strict derivation of radial Schrodinger equation shows an appearance of new delta function term during reduction of Laplace operator in spherical coordinates. As a result, regardless of behavior of potential, an additional constraint is imposed on the radial wave function in form of a vanishing boundary condition at the origin.

Keywords: Schrodinger equation, radial equation, boundary condition, singular potentials.

PACS numbers: 03.65.-w, 03.65.Ca, 03.65.Ta

I. INTRODUCTION

According to general principles of quantum mechanics wave functions of physical states must obey certain requirements, such as continuity (more precisely, two-fold differentiability), uniqueness and square integrability. In many quantum mechanical problems the knowledge of the behavior of wave function is needed at points where the potential under consideration has some singularities (e.g. wells and so on). Below we consider problems in central symmetric fields, for which the separation of variables performed in spherical coordinates. It is well known that the transition to spherical coordinates is singular transformation with respect to the origin. Indeed the transition from Cartesian to spherical coordinates is not unambiguous, because the Jacobean of this transformation equals to $J = r^2 \sin\theta$ and it is singular at $r = 0$ and $\theta = n\pi (n = 0,1,2,...)$. Angular part is unambiguously fixed by the requirements of continuity and uniqueness.[1] It gives the unique spherical harmonics $Y_l^m(\theta,\varphi)$.

We also note that though $\vec{r} = 0$ is an ordinary point in full Schrodinger equation, it is a point of singularity in the radial equation and thus, knowledge of specific boundary behavior is required.

For this, at the first sight simple problem, there is no definite answer in the framework of general principles. We have in mind the radial wave function $u(r)$, for which the equation consists of only the second derivative

$$\frac{d^2u(r)}{dr^2} - \frac{l(l+1)}{r^2}u(r) + 2m[E - V(r)]u(r) = 0 \tag{1}$$

From this equation the behavior of the radial wave function at the origin will depend upon behavior of potential, in particular, whether it is regular or singular. Whereas for regular potentials there exist a relatively definite answer, for singular potentials situation is totally unclear.[2]

Our aim is to elucidate things in this problem. Therefore we reconsider derivation of radial equation in more detail. We show that the status of radial equation in itself is depended on the behavior of $u(r)$ at the origin.

This article is organized in the following manner: In section II we consider consequences of general principles. We will show that there is no unambiguous answer. In section III we consider the transition to the radial equation carefully and obtain the new delta-like term, elimination of which provides definite constraint on the radial wave function at the origin. Only after fulfillment of this constraint the equation takes its usual form (1). At the same time this constraint has the form of boundary condition for radial wave function at the origin. In section IV we give concluding remarks, while in the Appendix we remember how the delta function appears.

II. BOUNDARY CONDITION AT THE ORIGIN ACCORDING TO GENERAL REQUIREMENTS OF QUANTUM MECHANICS

The question is what is the maximal singularity that the radial function $R(r)$ or $u(r) = rR(r)$ can have at the origin $r = 0$. We remember here some of definitions:

Full 3-dimensional wave function is presented as

$$\psi(\vec{r}) = R(r)Y_l^m(\theta,\varphi); r > 0;\ \ 0 \le \theta \le \pi;\ \ 0 \le \varphi \le 2\pi \tag{2}$$

and the equation for full radial function $R(r)$ takes form

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + 2m[E - V(r)]R - \frac{l(l+1)}{r^2}R = 0 \tag{3}$$

The traditional change of variables in quantum mechanics eliminates the first derivative term from this equation by the following substitution

$$R(r) = \frac{u(r)}{r}, \tag{4}$$

which in turn, gives the equation (1) for the new radial wave function $u(r)$. This well known equation plays an important role in quantum mechanics since its birth.

From the continuity of wave function $R(r)$ at $r = 0$ it follows that $u(0) = 0$ insuring the finiteness of probability at this point.[3] However one can weaken this condition by requiring the finiteness of differential probability in the spherical slice $(r, r + dr)$

$$dW = |R|^2 r^2 dr d\Omega < \infty \tag{5}$$

Then, if at origin $R \sim r^s$, it follows that $s > -1$, or $u(0) = 0$.

Another generalization is to require a finiteness of total probability inside of sphere with a small radius a

$$\int_0^a |R|^2 r^2 dr < \infty \tag{6}$$

In this case more singular behavior is permissible, namely

$$\lim_{r\to 0} u(r) \approx \lim_{r\to 0} r^{-1/2} \to \infty \tag{7}$$

The same follows from the finiteness of the norm.

$$\int_0^\infty |R(r)|^2 r^2 dr < \infty \tag{8}$$

One can use also more strong argument by Pauli[4] namely, *time independence of the norm.* To explore it we proceed below in analogy to the book by Blokhincev.[5]

In quantum mechanics the norm of wave function is independent of time

$$\frac{dN}{dt} \equiv \frac{d}{dt}\int \psi^* \psi dV = 0 \tag{9}$$

Using the time dependent Schrodinger equation we transform previous relation into

$$\frac{dN}{dt} = -\frac{i}{\hbar}\int \left[\psi^*(H\psi) - (H\psi)^*\psi\right] dV = 0 \tag{10}$$

Therefore, time independence of probability means that the Hamiltonian must be Hermitian (symmetric) operator. By introducing the density of probability current

$$\vec{J} = \mathrm{Re}\left[\psi^* \frac{h}{im}\vec{\nabla}\psi\right], \tag{11}$$

it is easy to show that

$$div\vec{J} = \frac{i}{\hbar}\left[\psi^*(H\psi) - (H\psi)^*\psi\right] \tag{12}$$

Therefore the equation of conservation of probability takes form (after using the Gauss theorem)

$$\frac{d}{dt}\int \psi^*\psi dV = -\int div\vec{J} dV = -\int J_N dS \tag{13}$$

Let us propose that at $r = 0$ the Hamiltonian has a singular point. At this point the Gauss theorem in the previous form is not applicable. We must exclude this point from the integration volume, surrounding it by small sphere of radius a. In this case the surface integral is divided into two parts: infinitely separated surface, which envelops the total volume, and the surface of sphere of radius a:

$$\lim_{a\to 0} a^2 \int J_a d\Omega + \int_\infty J_N ds = 0 \tag{14}$$

In the first integral we have expressed the surface element of sphere as $ds = a^2 d\Omega$, where $d\Omega$ is an element of body angle. Because of vanishing of wave functions at infinity, the second term turns to zero. Substituting $J_a = \frac{i\hbar}{2m}\left(\psi \frac{\partial \psi^*}{\partial r} - \psi^* \frac{\partial \psi}{\partial r}\right)_{r=a}$ and supposing $\psi = \frac{\tilde{u}}{r^s}$, where $\tilde{u}$ is regular at $r \to 0$, we obtain

$$\lim_{a\to 0} \frac{a^2}{a^{2s}} \int \left(\tilde{u} \frac{\partial \tilde{u}^*}{\partial r} - \tilde{u}^* \frac{\partial \tilde{u}}{\partial r}\right)_{r=a} d\Omega = 0 \qquad (15)$$

This condition is fulfilled if $s < 1$. It follows that the wave function $R(r)$ does not rise at infinity more quickly than $1/r^s$, with $s < 1$, which means that $\lim_{r\to 0} u(r) \approx \lim_{r\to 0} r^{-s+1} \to 0$.

We see that the different arguments lead to different conclusions for wave function behavior at the origin. Finiteness of the norm allows divergent growth of $u(r)$ at the origin, but time independence of the norm gives vanishing behavior.

The following question arises naturally: Does the boundary behavior at the origin have some physical meaning? For this reason let us start from the radial equation (1) and consider the well known example of regular potential

$$\lim_{r\to 0} r^2 V(r) = 0 \qquad (16)$$

For this case after substitution at the origin $u \sim r^a$ from indicial equation it follows, that $a(a-1) = l(l+1)$, which gives two solutions $u_{r\to 0} \sim c_1 r^{l+1} + c_2 r^{-l}$. For nonzero l the second term is not locally square integrable and is ignored usually. But for $l = 0$, many authors discuss how to deal with this solution,[6,7] which is square integrable at origin. Messiah[7] in his book writes: "*The foregoing argument does not apply when* $l = 0$. *But in that case, the corresponding wave function* ψ_0 *(*R_0 *in our notation) does not satisfy the Schrodinger equation [condition (a)]. In fact,* ψ_0 *behaves as* $(1/r)$ *at the origin, and since* $\Delta(1/r) = -4\pi\delta(\vec{r})$,

$$(H - E)\psi_0 = \frac{2\pi\hbar^2}{m}\delta(\vec{r}) \qquad (17)$$

One must therefore keep only so-called "regular" solutions, that is, the solutions satisfying the condition $[u(0) = 0]$. *With such a solution we can be sure that the function* ψ_l^m *is a solution of the Schrodinger equation everywhere, including the origin; moreover, since the normalization integral converges at the origin, the condition that* ψ_l^m *or its eigen differential belong to Hilbert space depends solely upon the behavior of this solution at infinity".*

However this solution corresponds only to the case of regular potential. Things change drastically when potential is singular. Indeed, let consider the case of so-called transitive singular potential

$$\lim_{r\to 0} r^2 V(r) = -V_0 = const \qquad (18)$$

$V_0 > 0$ corresponds to the attraction, while $V_0 < 0$ - to repulsion.

For this potential the indicial equation takes form $a(a-1)=l(l+1)-2mV_0$, which has two solutions: $a=\frac{1}{2}\pm\sqrt{\left(l+\frac{1}{2}\right)^2-2mV_0}$. Therefore

$$\underset{r\to 0}{u}\sim c_1 r^{\frac{1}{2}+P}+c_2 r^{\frac{1}{2}-P} \quad ; \quad P=\sqrt{\left(l+\frac{1}{2}\right)^2-2mV_0} \tag{19}$$

It seems that both solutions are square integrable near the origin as long as $0\le P<1$. Exactly this range is studied in most papers in connection with self-adjoint extension of the radial Hamiltonian.[8,9] It corresponds to the case (6) above. On the other hand, in case (5) this parameter is restricted as follows $0\le P<1/2$. The difference is essential. Indeed, in this notation the radial equation takes the form

$$u''(r)-\frac{P^2-1/4}{r^2}u(r)+2mEu(r)=0 \tag{20}$$

Depending on whether P exceeds 1/2 or not, the sign in front of the fraction changes and one can derive attraction in case of repulsive potential and vice versa, whereas the condition (5) forbids this undesirable solution with $1/2\le P<1$.

It seems that the choice $u(0)=0$ is more preferable. But this condition does not follow directly from the equation (1). Therefore we think that there is a reason to reconsider the derivation of eq. (1) in more detail.

II. MORE PROFOUND DERIVATION OF THE RADIAL EQUATION OR WHEN IS THE RADIAL EQUATION VALID?

Now we return to the rigorous derivation of radial equation for $u(r)$. Note that after substitution of representation (3) into the equation (2) the following equation follows

$$\frac{1}{r}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)u(r)+u(r)\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)\left(\frac{1}{r}\right)+2\frac{du}{dr}\frac{d}{dr}\left(\frac{1}{r}\right)-\left[\frac{l(l+1)}{r^2}-2m(E-V(r))\right]\frac{u}{r}=0 \tag{21}$$

We write equation in this form deliberately, showing action of radial part of Laplacian on relevant factors explicitly. It seems that the first derivatives of $u(r)$ cancelled and we are faced with the following equation

$$\frac{1}{r}\left(\frac{d^2u}{dr^2}\right)+u\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)\left(\frac{1}{r}\right)-\frac{l(l+1)}{r^2}\frac{u}{r}+2m(E-V(r))\frac{u}{r}=0 \tag{22}$$

Now if we differentiate the second term "naively", we'll derive zero. But it is true only in case, when $r\neq 0$. Below we show that in general this term is proportional to the 3-dimensional delta function. Indeed, taking into account that

$$\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}=\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)\equiv\Delta_r \tag{23}$$

is the radial part of the Laplace operator and therefore[10](See also Appendix)

$$\Delta_r\left(\frac{1}{r}\right)=\Delta\left(\frac{1}{r}\right)=-4\pi\delta^{(3)}(\vec{r}) \tag{24}$$

we obtain the equation for $u(r)$

$$\frac{1}{r}\left[-\frac{d^2u(r)}{dr^2}+\frac{l(l+1)}{r^2}u(r)\right]+4\pi\delta^{(3)}(\vec{r})u(r)-2m[E-V(r)]\frac{u(r)}{r}=0 \qquad (25)$$

We see the extra delta-function term appears in the equation (25). It's presence in the radial equation has no physical meaning and thus it must be eliminated. Note that when $r \neq 0$, this extra term vanishes owing to the property of the delta function and if, in this case, we multiply this equation by r, we'll obtain the ordinary radial equation (1).

However if $r = 0$, multiplication by r is not permissible and this extra term remains in Eq. (25). Therefore one has to investigate this term separately and find another ways to discard it.

The term with 3-dimensional delta-function must be comprehended as being integrated over $d^3r = r^2 dr \sin\theta d\theta d\varphi$. On the other hand[10]

$$\delta^{(3)}(\vec{r}) = \frac{1}{|J|}\delta(r)\delta(\theta)\delta(\varphi) \qquad (26)$$

Taking into account all the above mentioned relations, one is convinced that extra term still survives, but now in the one-dimensional form

$$u(r)\delta^{(3)}(\vec{r}) \to u(r)\delta(r) \qquad (27)$$

Its appearance as a point-like source breaks many fundamental principles of physics, which is not desirable. The only reasonable way to remove this term without modifying Laplace operator or including compensating delta function term in the potential $V(r)$, is to impose the requirement

$$u(0) = 0 \qquad (28)$$

(note, that multiplication of Eq. (25) by r and then elimination of this extra term owing the property $r\delta(r) = 0$ is not legitimated procedure, because effectively it is equivalent to multiplication of this term on zero).

Therefore we conclude that the radial equation (1) for $u(r)$ is compatible with the full Schrodinger equation (2) if and only if the condition $u(0) = 0$ is satisfied. *The radial equation* (1) *supplemented by the condition* (28) *is equivalent to the full Schrodinger equation* (2). It is in accordance with the Dirac requirement[11], that the solutions of the radial equation must be compatible with the full Schrodinger equation. It is remarkable to see that the supplementary condition (28) has a form of boundary condition at the origin.

We already seen above that there is some ambiguity in formulation of boundary condition for radial wave function from general principles of quantum mechanics. Therefore various boundary behaviors were considered in physical literature, especially for singular potentials. Now we have proven that the radial equation is valid only together with condition (28) independently of the potential, whether it is regular or singular.

It seems very curious that this fact (appearance of Delta function while reduction of Schrodinger equation) was unnoted until now.

Therefore it is interesting to know what will be the influence of this observation on physical results obtained previously.

It is evident, that papers, in which this boundary condition was explored, are correct. On the other hand, papers without this boundary condition are not correct from physical point of view.

It is well known that in most textbooks only regular potentials are considered with this boundary condition. Therefore all those results are correct. The only exclusion concerns to the above mentioned $l = 0$ state, refined attention by A.Messiah[7] , and may be, by others. But we practically proven his assumption, because of that the second solution must be ignored for any l, including $l = 0$.

More far-reaching consequences follow in case of singular potentials, which recently are the subjects of active interest, in connection with the self-adjoint extension. Many authors neglected boundary condition entirely and were satisfied only by square integrability. But this treatment, after leakage into the forbidden regions and through a self-adjoint extension procedure, sometimes yields curious unphysical results.

IV. CONCLUSIONS

We have shown that a rigorous reduction of the Laplace operator in spherical coordinates leads to the previously unnoticed delta function term. Careful investigation of this term gives a definite constraint on the radial function behavior at the origin. This constraint has a boundary condition form, $u(0) = 0$. Therefore a *unique* boundary condition follows for both regular and singular potentials in the radial Schrodinger equation. Only the character of turning to zero depends on the behavior of potential at the origin.

As we noted in the ABSTRACT, since at least the work of K.Case,[12] it has been known that Weyl limit-point, limit-circle analysis provides the right way to understand the boundary conditions for Eq. (1) at the origin[13]. We have nothing against these strong mathematical treatments; however it follows from above considerations that the radial wave equation is valid only together with condition $u(0) = 0$ .Therefore, a self-adjoint extension, performed in many papers without this condition, has only mathematical importance and has nothing in common with physics without above mentioned boundary condition.

Lastly, we note that the same holds for radial reduction of the Klein-Gordon equation, because in three dimensions it has the following form

$$\left(-\Delta + m^2\right)\psi(\vec{r}) = \left[E - V(r)\right]^2 \psi(\vec{r}) \tag{29}$$

and the reduction of variables in spherical coordinates will proceed to absolutely same direction as in Schrodinger equation.

ACKNOWLEDGEMENTS

We want to thank Profs. John Chkareuli, Sasha Kvinikhidze and Parmen Margvelashvili for valuable discussions. One of us (A.Kh.) is indebted to thank Prof. Boris Arbuzov for reading the manuscript.

APPENDIX: HOW THE DELTA FUNCTION APPEARS

Let us remember appearance of delta function. In this aim below we'll follow to the book[10].

Let us consider following differentiation

$$\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)\left(\frac{1}{r}\right)$$

By naive calculation we get zero. But separate terms in this expression are highly singular, therefore we must regularize them. Let us choose the following regularization near the origin

$$\frac{1}{r}\to\lim_{a\to 0}\frac{1}{\sqrt{r^2+a^2}}$$

If we differentiate now, we get

$$\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}\right)\left(\frac{1}{r^2+a^2}\right)^{1/2}=-\frac{3a^2}{\left(r^2+a^2\right)^{5/2}}$$

It is well behaved everywhere for nonvanishing a, but as $a\to 0$ it becomes infinite at $r=0$ and vanishes for $r\neq 0$. So it seems that we are close to the Delta function. Indeed, integration over sphere gives

$$-4\pi\int\frac{3a^2}{\left(r^2+a^2\right)^{5/2}}r^2dr$$

Let us divide full volume of integration into two parts: sphere with center at the origin of radius R and outside region. Imagine that that $a<<R$ and tending to zero. Then integral from the exterior of the sphere will vanish like a^2 as $a\to 0$.
We thus need consider only the contribution from inside the sphere. Here we can neglect r^2 in the numerator, because the integrand varies very slowly with r.
After this the integral becomes equal to

$$\frac{3a^2}{\left(a^2\right)^{5/2}}\frac{a^3}{3}=\frac{a^5}{a^5}=1$$

Thus we have all properties of the Delta function.

[a)] Electronic mail: anzor.khelashvili@tsu.ge
[b)] Electronic mail: teimuraz.nadareishvili@tsu.ge

[1] L.Schiff, *Quantum Mechanics*, 3rd ed. (MC Graw-Hill Book Company, New York-Toronto-London, 1968).
[2] R. Newton, *Scattering Theory of Waves and Particles*, 2nd ed. (Dover Publications, 2002), pp.389-392.
[3] See any textbook on quantum mechanics
[4] W.Pauli , *Die allgemeinen Prinzipen der Wellenmechanik* In *Handbuch der Physik*,Bd.5,vol .1(Berlin: Aufl 1958)
[5] D. Blokhincev , *Foundations of Quantum Mechanics* ,6th ed. (Nauka, Moscow,1983) (In Russian), pp.648-650.
[6] Thomas F. Jordan, "Conditions on wave functions derived from operator domains," Am.J.Phys. **44** (6), 567-569 (1976).

[7] A Messiah, *Quantum mechanics* , Two Volumes Bound as One. (Dover Publications, 1999), p.352.

[8] P.Giri, K.Gupta, S. Meljanac and A.Samsarov, "A Electron Capture and Scaling Anomaly in Polar Molecules**,"** Phys. Lett. **A372** (17), 2967-2970 (2008).

[9] H.Falomir, M.A.Muschietti, and P.A.Pisani, "On the resolvent and spectral functions of a second order differential operator with a regular singularity," J.Math. Phys. **45** (12), 4560-4577 (2004).

[10] J.D.Jackson, *Classical Electrodynamics*, 3rd ed.(John Wiley &Sons. Inc, New York-London, 1999), p.120.

[11] P.A.M.Dirac, *The Principles of Quantum Mechanics*, 4th ed.(Univ. Press, Oxford, 1958), pp.155-156.

[12] K.Case, "Singular potentials", Phys.Rev. **80** (5),797-806 (1950).

[13] M.Reed and B.Simon.*Methods of Modern Mathematical Physics*.Vol 4 (Academic Press. New York,1978].