The presence of non-analyticities and singularities in the wavefunction and the role of "invisible" delta potentials

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Abstract
This article examines the suggestion made in Ref. [1] that a solution to a particle in an infinite spherical well model, if it is square-integrable, is a physically valid solution, even if at the precise location of the singularity there is no underlying physical cause, therefore, the divergence would have to be a nonlocal phenomenon caused by confining walls at a distance. In this work we examine this claim more carefully. By identifying the correct differential equation for a divergent square-integrable solution and rewriting it in the form of the Schrödinger equation, we infer that the divergent wavefunction would be caused by the potential $V(r) \approx -\delta(r)$, which is a kind of attractive delta potential. Because of its peculiar form and the fact that it leads to a divergent potential energy $\langle V \rangle = -\infty$, the potential $V(r)$ and the divergent wavefunction associated with it are not physically meaningful.

1. Introduction
The present article starts out as an examination of a claim made in Ref. [1] that a divergent wavefunction represents a valid physical state for a particle in a spherical well model, a model that apart from confining walls has no other potential that could be regarded as a physical cause of a singularity. This essentially would make a singularity a non-local phenomenon. In addition to directly engaging with the claim in Ref. [1], the article examines other "physically valid" cases where some sort of non-analyticity arises and looks carefully into mathematical structure associated with that non-analyticity, as well as into a general question: is a divergent wavefunction physically meaningful in any system?

Besides mathematical concerns, there are physical consequences of accepting a divergent solution as a physical wavefunction. For example, by changing the shape of the confining well from a cube to a sphere we would give rise to a state with a divergent wavefunction – since we know of no divergent wavefunction for a particle in a box model.

Besides quantum mechanics, there are many other physical systems described by the wave equation. For example, standing acoustic waves in a spherical cavities [2], or the standing electromagnetic waves inside a spherical cavity that give rise to Casimir forces. The conclusions of Ref. [1] if correct would have far reaching repercussion.

To summarize the claim of Ref. [1], the authors indicate that a particle in a spherical well model, in addition to the usual class of regular solutions, represented by the spherical Bessel functions $j_l(kr)$, admits another class of solutions that diverge at $r = 0$, corresponding to the spherical Neumann functions denoted as $n_l(kr)$.

Conventionally, the functions $n_l(kr)$ are deemed unphysical on account of their divergence at the center of the spherical well, $n_l(r) \approx r^{l+1}$, where $l = 0, 1,\ldots$ The authors note, however, that since the relevant physical quantity is the density, $\rho(r) \approx r^{-2l+1}$, the correct criterion should not be whether or not a wavefunction diverges, but rather that it be square-integrable. Such a divergent but square-integrable solution happens to be for $l = 0$, in which case the Neumann function becomes $n_0(kr) = -\cos(kr)/(kr)$. The authors then include this solution among valid states of the system. And as square-integrability is the sole criterion of physicality, no concern is given about a physical cause underlying the occurrence of the singularity and/or a mathematical term that gives rise to it.

This paper is organized as follows. We start with the discussion in Sec. 2 of the Coulomb cusp condition, as a well known example of a system with a wavefunction containing non-analyticity. In Sec. 3, we look into the cusp from a different angle, by reformulating the Schrödinger equation and introducing an "invisible" delta potential that strictly speaking is correct but unnecessary. Yet maintaining it in the formalism leads to rigorous link between the hydrogen atom and the delta-potential model. In Sec. 4 we consider the divergent solution for the particle in an infinite spherical well model and identify the correct differential equation associated with that solution. By rewriting this equation in the form of the Schrödinger equation, we infer the delta potential at the location of the divergence and that gives rise to it.

2. Coulomb cusp condition
As a starting point, we review the case of a Coulomb cusp condition where the cusp in the wavefunction can be considered as a weak singularity (or a non-analyticity) whose presence can be traced to the Coulomb potential and the position of the proton. The well defined link between the non-analyticity and its
physical causes are formally expressed in the relation known as the Kato’s cusp condition or the Kato theorem \[3\].

The Schrödinger equation for the hydrogen atom model is

\[
\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\varepsilon r}\right)\psi(r) = E\psi(r).
\]

Being interested in the ground state, the wavefunction of which is spherically symmetric, we consider only the radial part of the Laplacian operator, for an arbitrary dimension \(D\) given by \[4, 5\]

\[
\nabla^2 \rightarrow \left[ \frac{\partial^2}{\partial r^2} + \frac{D-1}{r} \frac{\partial}{\partial r} \right],
\]

so that the Schrödinger equation simplifies to

\[
\frac{\partial^2 \psi(r)}{\partial r^2} + \frac{D-1}{r} \frac{\partial \psi(r)}{\partial r} + \frac{2Z}{a_0 D} \psi(r) = k^2 \psi(r),
\]

where

\[k = \sqrt{\frac{2mE}{\hbar^2}},\]

is a positive number (since \(E < 0\)) and \(a_0 = \frac{4\pi\varepsilon^2\hbar^2}{Ze^2}\) is the Bohr radius. A \(D\)-dependent Schrödinger equation might be of interest to systems under strong confinement, which effectively reduce dimensionality.

In the neighborhood of the point \(r = 0\), the Schrödinger equation in Eq. (2) is completely dominated by the terms proportional to \(1/r\),

\[
\frac{\partial \psi(r)}{\partial r} + \frac{Z}{a_0 D - 1} \psi(r) = 0, \quad \text{as} \quad r \to 0.
\]

After rearranging the above result, we get the cusp condition as it is known in its more familiar form

\[
\left. \frac{1}{\psi(0)} \frac{d\psi(r)}{dr} \right|_{r=0} = -\frac{Z}{a_0} \frac{2}{D-1}.
\]

It turns out that the ground state wavefunction satisfies Eq. (3) not only in the neighborhood of \(r = 0\) but in the entire range of \(r\). Since the solution to Eq. (3) is

\[
\psi_D(r) \propto e^{-\frac{Z}{a_0} \frac{2}{D-1} r},
\]

inserting this result to Eq. (2) yields

\[
k = \frac{2Z}{a_0(D - 1)},
\]

so that the ground state energy is

\[
E = -\frac{2Z^2\hbar^2}{ma_0^2} \left( \frac{1}{D-1} \right)^2.
\]

The above expression indicates that the more degrees of freedom the system has, the higher the energy of its ground state. In the limit \(D \to \infty\) the electron in the ground state should become unbounded. On the other hand, \(E\) diverges as \(D \to 1\), and judging from the wavefunction in Eq. (5) and the corresponding density \(\rho(r) = \vert\psi(r)\vert^2\), the electron appears to be collapsing into proton \[6, 7\].

In the case of \(D = 1\), instead of the Coulomb potential, there is another bounding potential which produces an exponential wavefunction and the cusp condition. This is the delta potential \(V(x) = -\alpha \delta(x)\) and the Schrödinger equation that results is

\[
\psi''(x) + \alpha' \delta(x) \psi(x) = k^2 \psi(x), \quad \text{where} \quad \alpha' = \frac{2ma}{\hbar^2}.
\]

The cusp condition is obtained by operating on this equation with the operator \(\lim_{a \to 0} \int_a^0 dx\) at the location of the delta potential leading to

\[
\left. \frac{1}{\psi(0)} \frac{d\psi(x)}{dx} \right|_{x=0} = -\alpha' \frac{2}{a^2}.
\]

3. The second look at the Coulomb cusp condition

In this section we take a little different view of the cusp condition. Since both the hydrogen atom and the delta potential model produce the same type of non-analyticity, we look for a deeper connection between the two models. The idea is to look for the presence of a hidden delta function in the Schrödinger equation at the location of a cusp, that from the physical point of view may play no role but is useful for mathematical consistency.

Consider the ground-state wavefunction for the hydrogen atom model for a general \(D\)-dimension, first shown in Eq. (5). For the case \(D = 3\) the dominant terms in the neighborhood \(r = 0\) are

\[
\psi(r) \propto 1 - \left( \frac{Z}{a_0} \right) r + \ldots.
\]

Because the expansion does not include the term \(r^{-1}\), it is assumed that that the Laplacian equation of that solution does not include the delta function.

To demonstrate that strictly speaking this is not the case, we define the identity

\[1 = \frac{r}{r},\]

then take the Laplacian of its both sides,

\[0 = \nabla^2 \left( \frac{r}{r} \right).
\]

After expanding the right hand side we get

\[0 = r \nabla^2 \left( \frac{1}{r} \right) + \frac{1}{r} \nabla^2 r + 2 \left( \nabla \cdot \frac{1}{r} \right) \cdot \nabla r,
\]

then using the identity \(\nabla^2 r^{-1} = -4\pi \delta(r)\) and \(\nabla r = \mathbf{r}\) and \(\nabla r^{-1} = -\mathbf{r} r^{-2}\), we get

\[\nabla^2 r = 2 \frac{r}{r^2} + 4\pi r^2 \delta(r),
\]

As the first term can be obtained by straightforward application of the spherically symmetric part of the Laplacian operator, \(\left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) r\), the emergence of the delta function is less obvious.
What essentially this means is that the Laplacian of the wavefunction $\psi(r) \propto e^{-\frac{k}{r}}$ is

$$\nabla^2 \psi(r) = k^2 \psi(r) - \left(\frac{4\pi Z}{a_0}\right)^2 \delta(r),$$

and by rewriting this as the Schrödinger equation we get we would write

$$\begin{align*}
-\nabla^2 - \frac{2Z}{a_0} \frac{1}{r} - \frac{Z}{a_0} 4\pi r^2 \delta(r) \psi(r) &= k^2 \psi(r),
\end{align*}$$

so that the potential energy term is

$$V(r) = -\frac{Z\hbar^2}{2ma_0} 4\pi r^2 \delta(r),$$

such that

$$\langle V \rangle = -\frac{Z\hbar^2}{2ma_0} \int dr 4\pi r^2 \psi^2(r) \delta(r) = -\frac{Z\hbar^2}{2ma_0} \lim_{r \to 0} 4\pi r^2 \psi^2(r) = 0.$$ \hspace{1cm} (12)

The potential $V(r)$, therefore, is completely invisible. We can generalize the result in Eq. (10) to any dimension.

$$\nabla_r^2 = D - 1 + \Omega_D r^{D-1} \delta(r),$$

where

$$\Omega_D = \frac{2\pi^{D/2}}{\Gamma(D/2)}$$

is the $D$-dependent solid angle factor such that $\Omega_1 = 2$, $\Omega_2 = 2\pi$, and $\Omega_3 = 4\pi$. The generalized $D$-dependent Schrödinger equation then becomes

$$\begin{align*}
-\nabla^2 - \frac{2Z}{a_0} \frac{1}{r} - \frac{Z}{a_0} D - 1 r^{D-1} \delta(r) \psi_D(r) &= k^2 \psi_D(r),
\end{align*}$$

so that the $D$-dependent delta potential is

$$V_D(r) = -\frac{Z\hbar^2}{ma_0} D - 1 \delta(r).$$ \hspace{1cm} (14)

Up to this point, it is not clear what advantage there is to using the Schrödinger equation in Eq. (13), since the potential $V_D(r)$ in Eq. (14) is “invisible” and not a part of a physical system. We will next show that including the “invisible” delta potential in Eq. (13) can lead to some mathematical consistencies.

If we scale the Coulomb potential as as $Z' = Z(D - 1)$, so that the Schrödinger equation for the hydrogen atom for an arbitrary dimension $D$ becomes

$$\begin{align*}
-\nabla^2 - \frac{2Z(D - 1)}{a_0} \frac{1}{r} - \frac{Z}{a_0} D - 1 \delta(r) \psi(r) &= k^2 \psi(r),
\end{align*}$$

and then continuously change $D$ from $D = 3 \to 1$, even if we transform the Schrödinger equation, the wavefunction remains the same $\psi(r) \propto e^{-\frac{k}{r}}$. Because for $D = 1$ the Coulomb potential vanishes, it is not clear what physical feature of the Schrödinger equation produces the exponential wavefunction. It happens that at exactly $D = 1$ the delta potential in Eq. (14) becomes “invisible”,

$$-\frac{d^2}{dx^2} - \frac{4Z}{a_0} \delta(x) \psi(x) = k^2 \psi(x),$$ \hspace{1cm} (16)

and because the physical cause of the exponential wavefunction and the cusp condition. The delta potential system in Eq. (16) is frequently referred to as the hydrogen atom, because the wavefunction of its bound state has the same functional form as the ground-state wavefunction of the hydrogen atom in $D = 3$. The mathematical connection established above, through the combined presence of an “invisible” delta and the Coulomb potential and the application of dimensional transformation reveals a deeper mathematical link.

4. Particle in a spherical box model

We next turn to a particle in an infinite spherical well model governed by the following Schrödinger equation

$$\nabla^2 \psi(r) = -k^2 \psi(r), \quad \text{for } |r| \leq a,$$ \hspace{1cm} (17)

where

$$k = \sqrt{\frac{2mE}{\hbar^2}},$$

and $E > 0$. Anywhere outside the spherical well, $r \geq a$, the wavefunction vanishes.

Considering only spherically symmetric solutions which include the ground state, the Schrödinger equation for $D = 3$ reduces to

$$\frac{\partial^2 \psi(r)}{\partial r^2} + \frac{2}{r} \frac{\partial \psi(r)}{\partial r} = -k^2 \psi(r).$$ \hspace{1cm} (18)

The two families of possible spherically symmetric solutions, as pointed out in Ref. [1], are

$$\psi_g(r) \propto \frac{\sin(k_a r)}{k_a r}, \quad k_a = \frac{n\pi}{a}, \quad \text{for } n = 1, 2, \ldots, \hspace{1cm} (19)$$

and

$$\psi_s(r) \propto \frac{\cos(k_n r)}{k_n r}, \quad k_n = \frac{(2n - 1)\pi}{2a}, \quad \text{for } n = 1, 2, \ldots, \hspace{1cm} (20)$$

where the ground state corresponds to the principal number $n = 1$. Even though both solutions vanish at $r = a$, they have very different properties in the neighborhood $r = 0$. The solution $\psi_R$ is regular in the neighborhood $r = 0$,

$$\psi_R(r) \propto \frac{\sin(kr)}{kr} = 1 - \frac{k^2 r^2}{6} + \ldots,$$
while the solution \( \psi_S \) in the same neighborhood has singularity

\[
\psi_S(r) \propto \frac{\cos(kr)}{kr} = \frac{1}{kr} - \frac{kr}{2} + \ldots
\]

Both solutions \( \psi_R \) and \( \psi_S \) can be constructed from the functions \( \frac{e^{ikr}}{kr} \), whose Laplacian is given by

\[
\nabla^2 \left( \frac{e^{ikr}}{kr} \right) = -k^2 \frac{e^{ikr}}{kr} - \frac{4\pi}{k} \delta(r),
\]

and where the delta function is the result of the identity

\[
\nabla^2 \left( \frac{1}{4\pi r} \right) = -\delta(r).
\]

In the case of the regular solution \( \psi_R \), the delta function is cancelled out,

\[
\nabla^2 \left( \frac{\sin kr}{kr} \right) = -k^2 \left( \frac{\sin kr}{kr} \right),
\]

meaning that \( \psi_R \) is a true solution to Eq. (17). On the other hand, the solution \( \psi_S \) retains the delta function,

\[
\nabla^2 \left( \frac{\cos kr}{kr} \right) = -k^2 \left( \frac{\cos kr}{kr} \right) - \frac{4\pi}{k} \delta(r),
\]

and, in consequence, \( \psi_S \) cannot be considered solution of the original system in Eq. (17). It is rather a solution of an alternative differential equation given by

\[
\nabla^2 \psi_S(r) = -k^2 \psi_S(r) - \frac{4\pi}{k} \delta(r).
\]

A related differential equation is encountered in other physical situations. Within the Debye-Hückel theory of electrostatics, the electrostatic potential \( \phi \) is governed by the following linear differential equation [8, 9]

\[
\nabla^2 \phi(r) = k^2 \phi(r) - 4\pi\lambda_0 \delta(r),
\]

where \( k \) is the screening parameter and \( \lambda_0 \) is the Bjerrum length.

The delta function in the above equation has a definite physical meaning, the electrostatic potential \( \phi \) is governed by the following differential equation [8, 9]

\[
-\nabla^2 - 4\frac{\delta(r)}{k} \psi_S(0) \right) \psi_S(r) = k^2 \psi_S(r).
\]

Since in the neighborhood \( r = 0 \), \( \psi_S(r) \propto (kr)^{-1} \), the above equation can be further modified into

\[
-\nabla^2 - 4\pi r \delta(r) \right) \psi_S(r) = k^2 \psi_S(r).
\]

The potential energy that emerges,

\[
V(r) = -\frac{\hbar^2}{2m} 4\pi r \delta(r),
\]

is a kind of an attractive delta potential, apart for the factor \( r \).

At first sight the potential appears "invisible", since at the origin \( r \) vanishes and should have no effect on observable quantities. However, since any physical quantity depends on the density \( \rho(r) = |\psi_S(r)|^2 \), and since this density diverges as \( r^{-2} \), the average value of the potential is not zero but quite contrary, it diverges

\[
\langle V \rangle = -2\pi \hbar^2 \frac{m}{C_n} \int dr r |\psi_S^2(r)| \delta(r)
\]

\[
= -2\pi \hbar^2 \frac{m}{C_n} \lim_{r \to 0} r |\psi_S^2(r)| = -2\pi \hbar^2 \frac{m}{mk_n^2} \lim_{r \to 0} \frac{C_n^2}{r},
\]

where \( C_n \) is the normalization factor, \( \psi_S = C_n \cos kr/k_0 r \), given by

\[
C_n = (2n - 1) \sqrt{\frac{\pi}{8a^3}}.
\]

Despite the divergent potential energy, the total energy is finite, indicating that the kinetic energy has its own positive divergence that exactly cancels out the negative divergence of the potential energy. The total energy is given by

\[
E_n = \frac{k_n^2 \hbar^2}{2m},
\]

where \( k_n \) is defined in Eq. (20).

If we compare the ground state energies corresponding to the principal number \( n = 1 \) for both wavefunctions \( \psi_R \) and \( \psi_S \) and their corresponding Hamiltonians we get

\[
E_1^R = \frac{\pi^2 \hbar^2}{2ma^2}, \quad E_1^S = \frac{\pi^2 \hbar^2}{8ma^2},
\]

so that

\[
E_1^R = 4E_1^S.
\]

The fact that \( E_1^S < E_1^R \) can be traced to the presence of the attractive potential \( V(r) \), which lowers an overall energy but fails to trap a particle, even if it produces a divergent wavefunction. The average position of a particle in each system is

\[
\langle r \rangle_R = \frac{1}{2}, \quad \langle r \rangle_S = \frac{1}{2} - \frac{2}{\pi^2},
\]

so that the average position for the system with the potential \( V(r) \) occupies a more central position.

It is difficult to imagine that the potential \( V(r) \) in Eq. (29) represents an actual physical system, (1) due to its peculiar functional form, in particular, the fact that it vanishes at the origin, (2) because it leads to a divergent potential energy \( \langle V \rangle \), and it has no independent parameter of strength, namely, its magnitude is completely determined by the particle mass. This lack of flexibility does not make \( V(r) \) a good candidate for a physical potential and implies that it is a mathematical oddity that arises by imposing the physical meaning to the divergent wavefunction \( \psi_S(r) \).
5. Hydrogen atom in an infinite spherical well: unbounded states

As the last example of an example where a divergent solution may arise, we consider a hydrogen atom trapped in an infinite spherical well. A hydrogen molecule in confinement has been of interest since early days of quantum mechanics and in recent years it received renewed interest due to its connection to realistic systems, one prominent example being quantum dots. Like the particle in a spherical well, this system, too, admits of a divergent solution so that one could attempt to force physical interpretation.

The maximum value of Z at which a particle remains unbounded by the Coulomb potential occurs when the negative potential energy is completely cancelled by the kinetic energy, \( \langle V \rangle = -(K) \). This means \( E = 0 \), or \( k = 0 \), in which case the Schrödinger equation in Eq. (2) for the case \( D = 3 \) reduces to

\[
\frac{\partial^2 \psi(r)}{\partial r^2} + \frac{2}{r} \frac{\partial \psi(r)}{\partial r} + \frac{2Z}{a_0} \psi(r) = 0. \tag{31}
\]

The non-divergent ground-state solution is

\[
\psi(r) \propto j_1 \left( \sqrt{2Za} / a_0 \right), \tag{32}
\]

where \( j_1(x) \) is the Bessel function of the first kind. The requirement that the wavefunction vanishes at \( r = a \) provides us with the relation

\[
v_k = \sqrt{2Za} / a_0,
\]

where \( v_k \) are zeros of the Bessel function and the lowest zero \( v_1 \) = 3.83171 corresponds to the ground-state.

The wavefunction in Eq. (32) satisfies the cusp condition in Eq. (4). This can be shown by expanding the wavefunction around \( r = 0 \), where the initial terms are

\[
j_1 \left( \sqrt{2Za} / a_0 \right) \propto 1 + Z / a_0 r + \ldots,
\]

and which satisfy the cusp relation

\[
\frac{1}{\psi(0)} \left. \frac{\partial \psi(r)}{\partial r} \right|_{r=0} = \frac{Z}{a_0}.
\]

A divergent solution to Eq. (31) is given by

\[
\psi(r) \propto -y_1 \left( \sqrt{2Za} / a_0 \right),
\]

where \( y_1(x) \) is the Bessel function of the second kind, and which in the region \( r = 0 \) is dominated by the terms

\[
y_1 \left( \sqrt{2Za} / a_0 \right) \propto 1 / r - \frac{2Z}{a_0} \ln r + \ldots.
\]

The first observation is that the divergent solution fails to satisfy the cusp condition. The reason is that the divergent function is not a solution of the original physical problem, but corresponds to the system whose potential is

\[
V_{\text{div}}(r) = -\frac{Z}{4\pi \epsilon r} - \frac{\hbar^2}{2m} 4\pi r \delta(r).
\]

As previously, the divergent solution must be rejected on physical grounds.

There is an addition problem with the divergent solution in this case. The divergent solution in this case yields a divergent total energy, \( E_1 = -\infty \). Considering just the Coulomb energy, we find that its average values diverges,

\[
-\frac{1}{2} \int_0^\infty dr r |\psi(r)|^2 = -\infty.
\]

Another divergence comes from the delta potential \( V(r) \approx -\delta(r) \). The kinetic energy cancels the divergence due to the delta potential but not that due to the Coulomb interactions and, as a consequence, the total energy diverges.

6. Conclusion

We conclude that a divergent wavefunction, even if it is square-integrable, is not a solution of the particle in a box model. This means that the property of square-integrability is insufficient condition of physical eligibility. Instead, the physical aspects of the system must be taken into account. The divergence requires some physical cause. We identify this cause as the delta like attractive potential \( V(r) \approx -\delta(r) \). This potential, however, lends little physical interpretation and is best regarded as a mathematical curiosity; first, because of its unusual functional form; and second, because it yields the average potential energy that diverges. These observations lead to the conclusion that the presence of a divergence in a wavefunction, although an interesting feature, is highly unlikely from physical point of view.

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