

Infinite-Rydberg Limit of the Hydrogen Atom: The Lowest-Energy Unbound States

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The radial wavefunctions of the hydrogen atom have an interesting mathematical behavior in the limit of infinite n , which is the infinite Rydberg limit. Finding the limiting functions corresponds to solving the radial Schrödinger equation for $E = 0$. Frobenius expansion gives two solutions, each of which is a convergent expansion, but neither is square-integrable. For bound states, the second Frobenius solution is discarded because a relation between the solutions at $r = 0$ is violated and the square-integrable solution survives. We can't rule out either of the $E = 0$ solutions on the same grounds, which highlights the fact that half the mathematical solutions for the energies $E < 0$ have been artificially wiped away. We have lived without a probability interpretation for all the unbound-state wave functions, so I conjecture here that there may be physical significance to the non-integrable wave functions at $E < 0$ that are ignored in textbooks.

1. Introduction

For the hydrogen atom problem in quantum mechanics, the complete solution to the time-independent Schrödinger equation is given by a discrete set of square-normalized wave functions for any energy lower than 0 (bound states), and a continuum of non-normalizable wave functions for unbound states. Interestingly, the bound-state energy levels accumulate to an infinite density near $E = 0$, leading one to ask what wave functions are associated with the $E = 0$ limit. That is the question to be addressed in this paper.

2. Derivation of Radial Wave Functions

For the hydrogen problem in quantum mechanics, consider the bound-state stationary solution to the Schrödinger equation:

$$\Psi(r, \theta, \varphi) = \frac{u(r)}{r} Y_l^m(\theta, \varphi) \quad (1)$$

where r is radius from the proton, θ and φ are spherical polar coordinates, and $Y_l^m(\theta, \varphi)$ are spherical-harmonic functions. Henceforth we assume zero angular momentum, so $l = m = 0$ and $Y_0^0 = 1$. For this case, the radial wave function $u(r)$ in the hydrogen Coulomb potential is given by the following [1]:

$$\frac{a}{2} \frac{d^2 u}{dr^2} + \frac{u}{r} = E u \quad (2)$$

where a is the Bohr radius $4\pi\epsilon_0\hbar^2/me^2$, and e and m are the electron's charge and mass.

The energy eigenvalues E_n are proportional to $-1/n^2$. That much is commonplace, but here is something new. In the infinite-Rydberg limit, $n \rightarrow \infty$, so $E = 0$. For that case Eq. (2) becomes

$$\frac{a}{2} \frac{d^2 u}{dr^2} + \frac{u}{r} = 0. \quad (3)$$

To simplify the algebra, I now define x as the radius in units of half the Bohr radius, i.e. $x = 2r/a$. Defining $u'' = d^2 u / dx^2$, Eq. (3) then becomes

$$u'' + \frac{u}{x} = 0. \quad (4)$$

The Frobenius method [2] suffices to find the two linearly independent solutions to Eq. (4).

The first solution, $u_1(x)$, is obtained through the expansion

$$u_1(x) = x^q \sum_{k=0}^{\infty} b_k x^k. \quad (5)$$

Here q satisfies the indicial equation $q^2 - q = 0$, hence $q = 0$ or 1 . The first solution is obtained from the case $q = 1$: Substitution of Eq. (5) into Eq. (4) yields the recursion relation

$$b_{k+1} = -\frac{b_k}{(k+1)(k+2)}. \quad (6)$$

In computing the solution u_1 , one can either use the recursion as given by Eq. (6) or obtain the explicit result

$$b_k = (-1)^k \frac{b_0}{k!(k+1)!}. \quad (7)$$

Henceforth, I select $b_0 = 1$ in anticipation of being unable to select its value via square normalization of Ψ over all space.

Because the roots of the indicial equation are separated by an integer, the second solution of Eq. (4) (with $q = 0$) is given by [2]

$$u_2(x) = \ln x \cdot u_1(x) + \sum_{k=0}^{\infty} c_k x^k. \quad (8)$$

Substituting Eq. (8) into Eq. (4) and noting that the logarithmic terms cancel because they are multiplied by $u_1'' + u_1/x$, one has:

$$\frac{2 u_1'}{x} - \frac{2 u_1}{x^2} + \sum_{k=0}^{\infty} c_k k(k-1) x^{k-2} + \sum_{k=0}^{\infty} c_k x^{k-1} = 0. \quad (9)$$

This equation is used to solve for the coefficients c_k . The following conditions emerge:

$$c_0 = -b_0 = -1 \quad (10a)$$

$$c_{k+1} = -\frac{1}{k+1} [c_k + (2k-1)b_k]. \quad (10b)$$

In summary, the two radial wave functions for $E=0$ and zero angular momentum are $\Psi_i(x) = u_i(x)/x$, for $i=1,2$ and $x = 2r/a$. Here,

$$u_1(x) = \sum_{k=0}^{\infty} b_k x^{k+1} \quad (11)$$

where b_k are given by Eq. (7) with $b_0 = 1$. Also,

$$u_2(x) = \ln x \cdot u_1(x) + \sum_{k=0}^{\infty} c_k x^k \quad (12)$$

where c_k are given by Eq. (10).

3. Behavior of Radial Wave Functions

A Matlab program was used to generate the radial wave functions derived in the previous section, and Figs. 1 and 2 below.

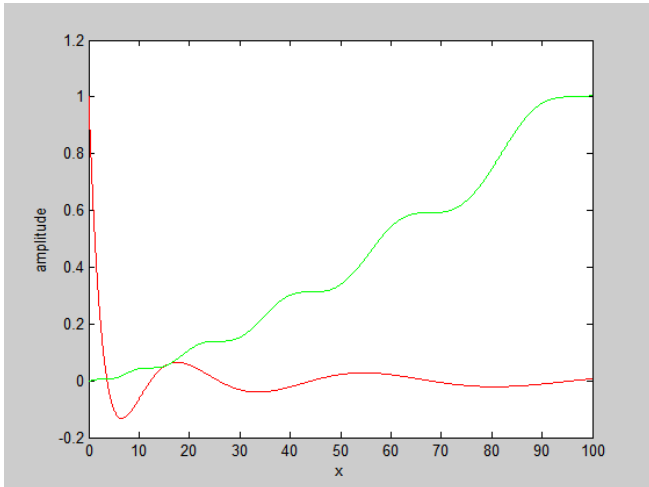


Fig. 1. Plot of the 1st Frobenius zero- E radial function $u_1(x)$ (red curve) and the integral from 0 to x of $|u_1|^2$ (green curve). Here, x is the radius in units of half the Bohr radius $a/2$.

Fig. 1 shows the function $\psi_1(x)$. There is actually a black curve in the plot, but the red curve hides it because expansion to 40 and 60 terms is indistinguishable for $x < 100$. The series converges very fast.

In Fig. 1, the green curve does not seem to be asymptoting to a constant value. This makes it unlikely that the wavefunction is square-integrable, in which case it could not be a probability amplitude. This wavefunction is a very interesting one, because it is at the feather edge between the bound states (which are square-integrable) and the unbound ones (which are sine waves over all space, and hence not square-integrable). Is it the lowest-energy unbound state or the highest-energy bound state? Because ψ_1 is not square-integrable over all space, it is legitimate to classify it as unbound, and anyway the bound states are defined as denumerable whereas the $E=0$ state is not in the denumerable set.

The same general remarks apply to the second Frobenius solution $u_2(x)$ shown in Fig. 2. That solution, whose expansion also converges rapidly, is also not square integrable, but I did not plot

the cumulative integral because it grows too rapidly for graceful graphical representation. Also, it should be noted that u_2 has a logarithmic singularity at 0 (truncated in the plot), which still allows computation of the cumulative integral.

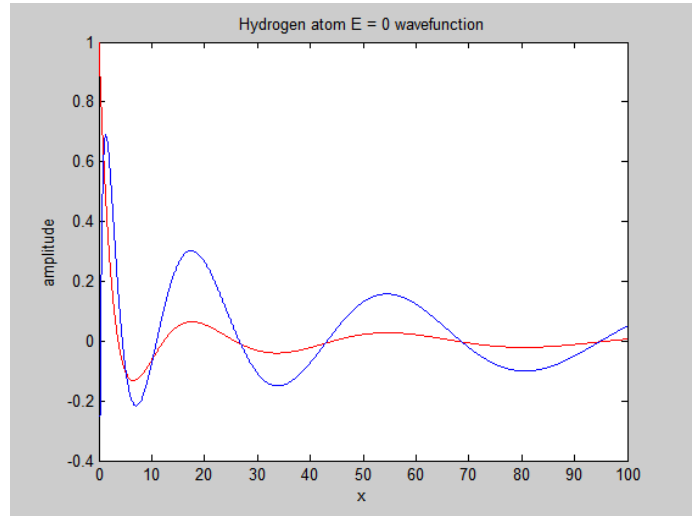


Fig. 2. Plot of the two Frobenius zero- E radial functions $u_1(x)$ (red curve) and $u_2(x)$ (blue curve).

It should also be noted that, unlike both bound and unbound-state wave functions, both of the $E=0$ wave functions are associated with a zero temporal frequency (because $E=0=\omega$). The wave functions $\psi(r,t)$ are truly static, with no time variation.

4. Conclusion

After looking at the two $E=0$ radial eigenfunctions, it is natural to ask: Why do textbooks derive only one radial eigenfunction u_1 for each $E < 0$ state? The answer is implicit in Exercise 10.1 of [1], which rules out the other solution u_2 because, in conjunction with u_1 , it violates self-adjointness of the Hamiltonian at $x=0$ via $u_1(0) u_2'(0) \neq u_2(0) u_1'(0)$. By itself this condition does not pick out which of the two rival solutions is allowed. The question of square-integrability is not mentioned, yet it must be the tie-breaker: Only the familiar u_1 must be square-integrable, hence interpretable as a probability amplitude.

Our $E=0$ solutions also fail Merzbacher's condition, but because neither is square-integrable, it is not clear how to select one over the other. The $E=0$ situation highlights the fact that half the mathematical solutions for the energies $E < 0$ have been artificially wiped away. We have lived without a probability interpretation for all the unbound-state wave functions, so I conjecture here that there may be some physical significance to the non-integrable wave functions at $E < 0$ that are automatically ignored in textbooks. Further study of these eigenfunctions, albeit an academic exercise, could lead to valuable physical insights for all the energy states of the hydrogen-atom problem.

References

- [1] E. Merzbacher, **Quantum Mechanics**, pp. 186-199 (Wiley, 1961).
- [2] E. Kreyszig, **Advanced Engineering Mathematics**, 2nd Ed., pp. 168-177 (Wiley, 1967).