THE CLASSICAL TO QUANTUM TRANSITION
by
P. S. Signell

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Acknowledgments

A. Boundary Conditions on a Free Wave
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Title: The Classical to Quantum Transition

Author: P. S. Signell, Dept. of Physics, Michigan State University

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Input Skills:
1. Vocabulary: motion from potential energy curves (MISN-0-22), satellite orbit calculations (MISN-0-102), Coulomb’s law (MISN-0-114), atomic hydrogen Bohr formula (MISN-0-215), discrete atomic levels (MISN-0-216), deBroglie waves (MISN-0-240), wave equation solutions (MISN-0-201), quantum probability density (from wave function (MISN-0-240), harmonic oscillator potential energy function (MISN-0-25).

Output Skills (Knowledge):

K1. Starting with Newton’s Second Law and the Coulombic interaction, derive the classically-predicted relation between the hydrogen atom’s energy and radius. Use the ground state energy of the atom to find the Bohr radius.

K2. Describe the failure(s) of the classical orbital model of the atom.

K3. Demonstrate the classical particle mechanics would not be expected to be correct for the hydrogen atom.

K4. Recite the rules for construction of the full Schrodinger Equation. Illustrate the rules by writing down the Schrodinger Equation for a given potential energy function.

K5. Draw the wave function for the first excited state of a free particle between impenetrable walls and show that it satisfies the Schrodinger Equation and appropriate boundary conditions. Determine its energy.

K6. Describe in words and diagram how energy quantization is produced by the Schrodinger Equation plus boundary conditions.

K7. Explain why the zeros of a rising-exponential-coefficient plot show a system’s allowed energies.
1. Introduction and Overview

The goal here is to understand how the classical Bohr model of the atom failed and to develop its successor, the Schrödinger Equation. To these ends we first examine the failure of the classical orbital model in some detail, while picking up useful ideas and terminology. We then determine a criterion for introducing necessary changes in the theory and use it to construct the Schrödinger Equation for potential-less regions of space. After a quick application to see how the new theory overcomes the problems associated with its predecessor, we move on to the full Schrödinger Equation with forces. Solutions are obtained for the simple harmonic oscillator.

2. Classical Attempt and Failure

2a. Similarities: Electron-Proton, Earth-Sun Systems. As a first attempt to determine the basis of atomic structure one would certainly try to capitalize on the similarities between the earth-sun system and the hydrogen atom, that simplest of all atomic systems. In this atom, the central proton is almost 2,000 times heavier than the electron, which means that to a very good approximation the proton’s position can be taken to be the center of mass of the atom. In this respect, it is similar to the earth-sun system. Furthermore, the force keeping the electron bound to the proton in the hydrogen atom is just the Coulombic interaction, an inverse square law, again as in the earth-sun system:

\[ F_{ep} = -\left(\frac{e^2}{4\pi\varepsilon_0}\right)\left(\frac{1}{r^2}\right)\hat{r} = -(1.44 \text{ eV nm})\left(\frac{1}{r^2}\right)\hat{r} \quad (1) \]

\[ F_{ES} = -(\gamma M_E M_S)\left(\frac{1}{r^2}\right)\hat{r} = -(4.95 \times 10^{-72} \text{ eV nm})\left(\frac{1}{r^2}\right)\hat{r} \quad (2) \]

Thus the forces for the earth-sun and electron-proton systems differ only by their (constant) strength factors.

2b. Orbital Radius From System Energy. If the hydrogen atom’s electron obeys Newton’s Second Law, just as does the earth as it orbits the sun, then the electron should traverse an orbit similar to the earth’s but reduced in size. What size would that be? Since we experimentally know the energy of the ground state of the hydrogen atom, \( E_0 = -13.6 \text{ eV} \), a good method for finding the radius would be to obtain it from that energy. In the earth-sun system, assuming a circular orbit, one can easily relate the radius and energy by combining Newton’s Second Law for centripetal acceleration with the Law of Universal Gravitation,

\[ M_E v_E^2/r_0 = \gamma M_E M_S/r_0^2, \quad (3) \]

eliminate the velocity in the energy expression

\[ E_0 = \frac{1}{2} M_E v_E^2 - \gamma M_E M_S/r_0 \]

and substituting for the \( (M_E v^2) \) term gives

\[ r_0 = -\left(\frac{\gamma M_E M_S}{2E_0}\right). \quad (4) \]

Since the energy of a bound object like the earth is negative we can write:

\[ r_0 = \frac{(\gamma M_E M_S)}{2|E_0|} \]

The relation of \( r_0 \) and \( E_0 \) to the earth’s potential energy \( V(r) \) is illustrated in Fig. 1. To find the radius of the electron’s presumed orbit in the hydrogen atom, we need only compare equations (1) and (2) for the two force laws, then alter Eq. (4) to make it an energy-radius relation for the electron-proton system:

\[ r_0 = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\left(\frac{1}{2|E_0|}\right). \quad (5) \]

With \( E_0 = -13.6 \text{ eV} \), \( r_0 \) (H ground state) = 0.053 nm. This \( r_0 \) is called the Bohr radius. It was first calculated by A. Bohr, using a somewhat different method.\(^4\)

\(^1\)See “Two-Body Kinematics and Dynamics” (MISN-0-45).
\(^2\)See “Hydrogen-like Energy Levels” (MISN-0-215) and “Transitions and Spectral Analysis” (MISN-0-216).
\(^3\)See “Potential Energy and Motion: Potential Curves, Turning Points” (MISN-0-22).
\(^4\)The notation \( r_0 \) for the Bohr radius is somewhat misleading since \( n = 1 \) for that state. It is traditional, however, to use zero as a subscript on all ground state quantities.
2c. Erroneous Prediction: Synchrotron Radiation. There are two major problems associated with the classical orbital model of the hydrogen atom, problems which did not arise in the application to the solar system. The first is related to the very large centripetal acceleration of the electron in the hydrogen atom, some 1025 times that of the earth in its orbital motion. Classical electromagnetic theory predicts, and experiment confirms, that all charged particles emit electromagnetic energy when macroscopically accelerated. Such light emitted by circularly orbiting charged particles is called synchrotron radiation because it is a constant fact of life for those using synchrotrons, devices in which beams of electrons travel in circular evacuated tubes. In order to make up for the electrons’ continual loss of energy by synchrotron radiation, energy must be constantly fed to the particles. In the ground state of the hydrogen atom, contrary to what happens in a synchrotron, the electron does not emit synchrotron radiation. In fact, no loss of energy of any kind has ever been observed for a hydrogen atom ground state electron.

2d. Erroneous Prediction: Continuous Energies and Radii. A second problem associated with the orbital atomic model is that classical orbits can be at any negative energy and hence at any radius. However, it is well established experimentally that in the hydrogen atom only those energies occur which satisfy the Bohr formula:

\[ E_n = -\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{2\hbar^2 n^2}; \]

This discrete set of allowed energies implies a discrete set of allowed orbits. For circular orbits, one straightforwardly finds the allowed radii to be:

\[ r_n = n^2 r_0; \quad n = 1, 2, 3, \ldots \]

where \( r_0 \) is the Bohr radius. Every hydrogen atom is found to have exactly the same discrete set of energies, and they are not changed as a result of collisions. This is in sharp contrast to the binary gravitational systems such as the Earth and the sun, Mars and the sun, etc.

2e. Summary of the Classical Orbital Models Problems. One can summarize the two erroneous predictions of the classical orbital model as saying that an electron in the ground state of the hydrogen atom would lose energy by synchrotron radiation and thus quickly and continuously spiral in toward the proton. This predicted quick collapse of the hydrogen atom does not, in fact, take place; the ground state is completely stable and so the classical orbital model is wrong.

3. The Schrödinger Equation for \( V=0 \)

3a. Wave Properties of Electron May Be Important. One might expect that since the hydrogen atom Bohr radius is so extremely small, it might be comparable to the deBroglie wavelength of the electron. If that is true, then one would expect the wave properties of the electron to be important and classical particle mechanics would certainly fail to describe the electron in the hydrogen atom.\(^6\)

3b. Wavelength of Electron: Larger Than Bohr Radius. It is easy to compute the deBroglie wavelength of the hydrogen atom ground state electron. If the wavelength is small compared to the Bohr radius then classical mechanics should describe the situation well. If fact, however, the wavelength so computed turns out to be larger than the Bohr radius! It is then obvious\(^7\) that wave properties are important and the question becomes one of how to set up a new mechanics which builds-in the deBroglie wave properties and yet reduces to the classical description when the wavelength is small compared to the size of the interaction region.

3c. Example of a Wave Function. For sound waves or waves on a string, the one-dimensional spatial dependence of standing waves is usually written:\(^8\)

\[ \psi(x) = A\sin(2\pi x/\lambda). \quad (6) \]

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\(^5\)See “Transitions and Spectral Analysis” (MISN-0-216).

\(^6\)See “The Time-Dependent Schrödinger Equation: Derivation of Newton’s Second Law” (MISN-0-248), wherein Newton’s Second Law is found to be the first term in a power series, the next term of which is computed and examined. Thus the relationship of quantum and classical mechanics is made precise.

\(^7\)See “deBroglie Waves” (MISN-0-240).

\(^8\)See “Wave Equations and Solutions” (MISN-0-201).
We will assume that standing waves, not traveling waves, are appropriate to the case of a bound state, where the bound particle stays in the region around the force center.

3d. deBroglie’s Relation to Schrödinger Equation. Taking the second derivative of \( \psi \) with respect to \( x \) and applying deBroglie’s relation between momentum and wavelength, we get:

\[
\frac{d^2 \psi(x)}{dx^2} = -\frac{p^2}{\hbar^2} \psi(x).
\]

For any spatial point \( x \) where the potential energy function for the particle, \( V(x) \), is zero Eq. (7) becomes:

\[
-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = E \psi; \quad V(x) = 0.
\]

and \( E \) is the particle’s total energy. Eq. (8) is the equation Schrödinger found for a particle at any point where \( V = 0 \).

3e. Rules for Constructing the Schrödinger Equation. We have made a plausible argument for Eq. (8) but quantum mechanics is more general than classical mechanics and so cannot be derived from it. Quantum mechanics, and the Schrödinger equation in particular, arises from a set of rules from which one can properly derive both classical and quantum effects. Here are the rules by which the Schrödinger equation is usually constructed for a single particle in a potential \( V \):

(i) Write down the classical energy equation,

\[
E = \frac{p^2}{2m} + V.
\]

(ii) Multiply on the right by the wave function \( \psi(x) \),

\[
E \psi = \frac{p^2}{2m} \psi + V \psi;
\]

where \( \psi \) is to be determined later, and;

(iii) Replace each component of the momentum by the corresponding momentum derivative operator:

\[
p_x = -i\hbar \frac{d}{dx},
\]

\[
p_y = -i\hbar \frac{d}{dy},
\]

\[
p_z = -i\hbar \frac{d}{dz}.
\]

For our one-dimensional \( x \)-axis case, with zero potential, the above three rules immediately reproduce Eq. (8).

We must now examine methods of solving Eq. (8) for cases of interest, and especially see if it solves the problems encountered by the classical orbital model of the atom.

4. Limited Free Motion: Quantization

4a. Impenetrable Walls. A very crude model that exhibits some of the features of bound states is shown in Fig. 2, where a particle is constrained to one-dimensional motion in the interval \(-a < x < a\) by impenetrable walls at its boundaries. The fact that the walls are impenetrable means that \( \psi(x) \) is zero inside them, since \( |\psi|^2 \) is the particle’s probability density and the probability of finding the particle inside the impenetrable walls is presumably zero.

4b. Boundary Conditions At Walls. The wave function \( \psi(x) \) must be point-wise continuous, so we have the boundary conditions on the wave function in the free region:

\[
\psi(\pm a) = 0.
\]

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\[9\] Sometimes written \( U(x) \).

\[10\] See “deBroglie Waves” (MISN-0-240), “The Uncertainty Principle” (MISN-0-241) and “Exponential Quantum Decay Through a Barrier” (MISN-0-250).

\[11\] Justification for the continuity of \( \psi(x) \) involves replacing the walls by finite repulsive potentials and then letting them become infinite.

**Figure 2.** Rudimentary model of a bound state; for illustrating quantization of energy.
4c. Schrödinger Equation General Solution in Free Region.

The general solution to the Schrödinger Eq. (8) in the free region between the walls of Fig. 2 is easily verified by differentiation to be:

$$\psi_k(x) = A(k) \sin kx + B(k) \cos kx,$$

where $k \equiv \sqrt{2m|E|/\hbar}$.

4d. Apply the Boundary Conditions. There are two integration constants, $A$ and $B$, because of the second derivative in the Schrödinger equation: at any given energy these two constants are determined by the boundary conditions, Eq. (11). One can go through algebraic manipulations (Appendix A) or merely draw sine and cosine waves between the walls which obey the boundary conditions, as illustrated in Fig. 3.

The wave functions are:

$$\psi_1(x) = \frac{1}{\sqrt{a}} \cos \left(\frac{\pi x}{2a}\right);$$
$$\psi_2(x) = \frac{1}{\sqrt{a}} \sin \left(\frac{2\pi x}{2a}\right);$$
$$\psi_3(x) = \frac{1}{\sqrt{a}} \cos \left(\frac{3\pi x}{2a}\right);$$

etc., where the factors $(1/\sqrt{a})$ come from the requirement that the wave functions be normalized. This means that the wave functions contain a multiplying factor such that the total probability of finding the particle in the interval $-a < x < a$ is 100%:

$$1.00 = \int_{-a}^{+a} p_n(x) \, dx = \int_{-a}^{+a} |\psi_n(x)|^2 \, dx.$$  

4e. Energy is Quantized. Comparing equations (12) and (13), one sees that the energies are restricted to the values:

$$E_n = \frac{\hbar^2 \pi^2 n^2}{8ma^2}; n = 1, 2, 3, \ldots$$

The energy is said to be quantized, meaning that it is restricted to a set of discrete values.\(^{12}\)

5. Quantization From Realistic Forces

5a. Concept of Cut-Off Radius. How can we apply our Schrödinger Eq. (8), valid only where the potential energy is zero, to the real world with forces which produce bound states? Fortunately, realistic forces generally become negligibly small beyond some finite radius from the force center. An arbitrarily-drawn example is shown in Fig. 4. We can make the good approximation of setting the potential equal to zero beyond a cut-off radius $r_c$, and then use our $V = 0$ Schrödinger equation in the outside region.

5b. Central Forces. Most interesting forces are central forces, spherically symmetric about their force centers. We will consider one such force, using its force center as origin and not worrying about its shape inside $r_c$. If you want, you can picture the force as the Coulombic one between the electron and the proton for a hydrogen atom in its ground state. A reasonable value for the cut-off radius might be 20 Bohr radii. That is, 20 times the classical turning point radius for energy $E_0$.

\(^{12}\)The only way one can make a new wave function for Fig. 3 is by inserting at least a half more oscillation into one of the wave functions. This results in quantized wave function curvatures, hence quantized wave function second derivatives, hence quantized energies.
5c. The Schrödinger Equation in Three Dimensions. Our previous Schrödinger equation was in one dimension, but realistic forces are, of course, in a three-dimensional world. Following the three rules given in Section 2, we get:

\[ E\psi(x, y, z) = -\frac{\hbar^2}{2m} \left( \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) \psi(x, y, z), \quad V = 0; \quad (15) \]

written in the abbreviated form:

\[ E\psi = -\frac{\hbar^2}{2m} \nabla^2 \psi. \quad (16) \]

5d. The Radial Wave Equation. In spherical coordinates the Schrödinger equation becomes\(^\text{13}\) (Appendix B):

\[ E u(r) = -\frac{\hbar^2}{2m} \frac{d^2 u(r)}{dt^2}, \quad V(r) = 0, \quad (17) \]

where \( u(r) \) is called the radial wave function. So that the solution to Eq. (17) is also a solution to the original Eq. (16) we have to require \( u(r) \) to vanish at the origin:\(^\text{14}\)

\[ u(0) = 0. \quad (18) \]

5e. The Radial Probability Density. The radial probability density \( P(r) \) is obtained from the radial wave function \( u(r) \) in the usual manner:

\[ P(r) = |u(r)|^2. \]

This means that the probability of finding the particle between spherical shells of radius \( r_1 \) and \( r_2 \) is:

\[ P(r_1 < r < r_2) = \int_{r_1}^{r_2} P(r) \, dr = \int_{r_1}^{r_2} |u(r)|^2 \, dr. \]

The normalization integral becomes:

\[ 1.00 = \int_0^\infty |u(r)|^2 \, dr, \]

with a lower limit which differs from that in the one-dimensional case.

\(^{13}\)The rest of the discussion in this section is restricted to states of zero angular momentum, not a significant restriction for present purposes.

\(^{14}\)Not to be explained further here, except that otherwise the \( \nabla^2 \) operator in the right side of Eq. (16) would produce a delta function which could not be matched on the left side of the equation.

5f. Integration Constants For the Radial Equation Solutions. Since our radial Schrödinger Eq. (17) still contains a second derivative we would expect to have two integration constants in the solution, one determined by the boundary condition at the origin, Eq. (18), and the other determined by some other boundary condition. The integration constants would, in general, be different at each energy.

5g. Bound State Solution Beyond Cut-Off Radius. Bound states have negative energies so it is convenient to define

\[ \kappa \equiv \sqrt{-2mE/\hbar} = \sqrt{2m|E|/\hbar}, \]

and put our radial Schrödinger Eq. (17) into the form:

\[ \frac{d^2 u(r)}{dr^2} = \kappa^2 u(r); \quad E < 0, V(r) = 0. \quad (20) \]

The solution to Eq. (20) can be seen by inspection (taking the derivatives mentally) to be:

\[ u(r) = A(\kappa) e^{\kappa r} + B(\kappa) e^{-\kappa r}; \quad E < 0, V(r) = 0. \quad (21) \]

As noted, this is the solution for all negative energies and for all continuously-connected space points outside the range of the potential.

5h. Boundary Conditions Lead to Discrete States. The probability that the particle would be found to be outside the cut-off radius is:

\[ P(r_c < r < \infty) = \int_{r_c}^\infty |u(r)|^2 \, dr = \int_{r_c}^\infty |A(\kappa) e^{\kappa r} + B(\kappa) e^{-\kappa r}|^2 \, dr. \]

which is infinite because of the exponentially rising term. This is an obvious absurdity since most of the probability should be within the range...
of the force, and especially since the total probability of being somewhere in all of space must be unity! The wave function (21) is said to be unnormalizable for non-zero values for $A$ since these do not permit the particle to have merely 100% probability of being somewhere in all of space. The only way in which the radial wave function (21) can represent a bound state of a physical system is for $A(\kappa)$ to be zero. This, then, constitutes the second boundary condition necessary to completely specify the wave function everywhere. In general, no matter what potential is used, $A(\kappa)$ is some function determined by the nature of the force in the region $0 < r < r_c$. Suppose that for some particular force $A(\kappa)$ has the functional form shown in Fig. 5.\textsuperscript{15} These are a discrete set, so the bound-state solutions are at those values of $\kappa$ where $A(\kappa) = 0$, labeled $\kappa_1, \kappa_2, \ldots$, in the figure. The bound states produced by the Schrödinger equation are discrete regardless of what force is present.

Acknowledgments

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A. Boundary Conditions on a Free Wave

We begin with the free-particle solutions, Eq. (12):

$$\psi_k(x) = A(k) \sin kx + B(k) \sin kx,$$

and apply the impenetrable-walls simultaneous boundary conditions

$$\psi(\pm a) = 0.$$ 

These two conditions yield, respectively;

$$0 = A(k) \sin ka + B(k) \cos ka,$$

$$0 = -A(k) \sin ka + B(k) \cos ka.$$ 

How can we make both equations be satisfied simultaneously? There are four minimum possibilities:

(i) $A(k) = B(k) = 0$,

(ii) $A(k) = \cos ka = 0$,

(iii) $B(k) = \sin ka = 0$,

(iv) $\sin ka = \cos ka = 0$.

The first of these can be immediately eliminated because it results in $\psi = 0$ everywhere, and the fourth is impossible to satisfy. The two possibilities are left:

(i) $A = 0$ and $\cos ka = 0$ hence $ka = \frac{n\pi}{2}; n = 1, 3, 5, \ldots$

(ii) $B = 0$ and $\sin ka = 0$ hence $ka = \frac{n\pi}{2}; n = 2, 4, 6, \ldots$

In general, then, $k = \frac{n\pi}{2}; n = 1, 2, 3, \ldots$. Substituting these combinations into Eq. (12) produces the allowed wave functions of Eq. (13).

B. Laplacian In Spherical Coordinates

Ba. Laplacian in Spherical Coordinates. By judicious use of:\textsuperscript{16}

$$\begin{align*}
x &= r \sin \theta \cos \phi \\
y &= r \sin \theta \sin \phi \\
z &= r \cos \theta,
\end{align*}$$

one can derive the equality:\textsuperscript{17}

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r^2 \frac{\partial}{\partial r}} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta \frac{\partial}{\partial \theta}} \left( \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta \frac{\partial}{\partial \phi^2}} \right).$$

\textsuperscript{15}See “Numerical Solution of the Schrödinger Equation for the Hydrogen Atom” (MISN-0-245), in which is developed the computer algorithm used to generate Fig. 5 of the present unit.

\textsuperscript{16}See, for example, Methods of Theoretical Physics, P. M. Morse and H. Feshbach, McGraw-Hill, NY (1953).

\textsuperscript{17}Note the change of notation for the derivatives, to agree with common usage, from that used in Eq. (15). There is no operational distinction between the two notations for the case at hand, where the coordinate components are entirely independent of each other.
Bb. The Radial Equation. By the method of separation of coordinates, one finds the solutions to be of the form:\(^{18}\)

\[ \psi_{n\ell m}(r, \theta, \varphi) = R_{n \ell}(r)Y_{\ell m}(\theta, \varphi) \]

where

\[ Y_{\ell m}(\theta, \varphi) \equiv \sqrt{\frac{(\ell + 1)/2}{(\ell + m)!}} P_{\ell}^m(\cos \theta) \frac{1}{\sqrt{2 \pi}} e^{im\varphi} \]

\[ P_{\ell}^m = \frac{(1 - z^2)^{m/2}}{2^\ell \ell!} \frac{d^{m+\ell}}{dz^{m+\ell}} (z^2 - 1)^\ell; \]

where: \( m, \ell = 0, 1, 2, \ldots; m \leq \ell \). If one defines

\[ u_{n\ell}(r) \equiv rR_{n\ell}(r), \]

then the equation for \( u_{n\ell}(r) \) for a potential \( V(r) \) is:

\[
\left( -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\ell(\ell + 1)\hbar^2}{2mr^2} + V(r) \right) u_{n\ell}(r) = E_n u_{n\ell}(r).
\]

The second term in the brackets is the quantum-mechanical equivalent of the classical angular-motion kinetic-energy term.\(^{19}\)

Bc. The Boundary Condition at the Origin. The boundary condition at the origin is determined by an unusual property of the Laplacian operator when acting on an inverse-radius function. To see this, suppose the radial wave function approaches a constant as the radius approaches zero:

\[ \lim_{r \to 0} u(r) \to a. \quad (22) \]

The full wave function approaches that constant divided by the radius:

\[ \lim_{r \to 0} \psi(r) \to \frac{a}{r}. \]

In the full Schrödinger equation, then, one has, where this approximation is valid:

\[
\nabla^2 \psi = \nabla^2 \frac{a}{r} = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \left( \frac{a}{r} \right) = 0, \quad (23)
\]

except at the origin.

If one integrates the function \( \left( \nabla^2 \frac{a}{r} \right) \) throughout a volume including the origin, the result is:\(^{20}\)

\[
\int \left( \nabla^2 \frac{a}{r} \right) dV = -4\pi a,
\]

regardless of the size of the volume. This independence of the size of the volume is logical in view of equation (23). Thus the radius of the volume can be shrunk to zero and the answer \((-4\pi a)\) remains.

None of the other terms in our Schrödinger equation are capable of generating such an anomalous function in the neighborhood of the origin, so the equation cannot be satisfied unless the constant in Eq. (22) is zero:

\[ \lim_{r \to 0} u(r) \to 0. \]

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\(^{18}\)See, for example, *Methods of Theoretical Physics*, P. M. Morse and H. Feshbach, McGraw-Hill, NY (1953).

\(^{19}\)See “Derivation of the Constants of the Motion for Central Forces” (MISN-0-58).

\(^{20}\)Use the divergence theorem to convert the integrand to an integral over a spherical surface.