

RADIAL FUNCTION FOR LARGE R

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Shankar, R. (1994), *Principles of Quantum Mechanics*, Plenum Press. Chapter 12, Section 12.6.

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In solving the Schrödinger equation for spherically symmetric potentials, we found that we could reduce the problem to the equation

$$(0.1) \quad \left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + V(r) + \frac{l(l+1)\hbar^2}{2\mu r^2} \right] U_{El} = EU_{El}$$

where $U_{El}(r)$ is related to the radial function by

$$(0.2) \quad R_{El}(r) = \frac{U_{El}(r)}{r}$$

We've looked at some properties of U_{El} (which Griffiths calls u) for the hydrogen atom, but we can also try to extract some information about U_{El} in the more general case where we don't need to specify the potential V precisely. Here we'll examine what happens as $r \rightarrow \infty$.

By looking at 0.1, we can see that the centrifugal barrier term (the last term in the square brackets) disappears for large r , so the behaviour is determined by the nature of the potential V . We might think that, provided $V \xrightarrow[r \rightarrow \infty]{} 0$, we can just ignore the potential and solve the reduced equation

$$(0.3) \quad \frac{d^2 U_E}{dr^2} = -\frac{2\mu E}{\hbar^2} U_E$$

where we've dropped the subscript l since we're ignoring the centrifugal barrier, which is the only term in which l appears. In fact, this assumption proves to be faulty, in that the analysis is valid only if $V \rightarrow \frac{1}{r^a}$ where $a > 1$, or in other words, if $rV(r) \rightarrow 0$. To see why, we need to consider two cases: $E > 0$ (so that the particle can escape to infinity, since we're assuming $V \leq 0$ everywhere, and thus that E can take on any positive value); $E < 0$, so that the particle is bound, and there are discrete energy levels. Shakar treats the

$E > 0$ case so we'll look at the $E < 0$ case. In this case, 0.3 has the general solution

$$(0.4) \quad U_E = Ae^{-\kappa r} + Be^{\kappa r}$$

where

$$(0.5) \quad \kappa = \sqrt{-\frac{2\mu E}{\hbar^2}} = \sqrt{\frac{2\mu |E|}{\hbar^2}}$$

In the most general case, the constants A and B can be anything, subject to the usual constraint that the overall wave function is normalized. However, in order for this normalization to occur, we can't have the $e^{\kappa r}$ term, since that term blows up as $r \rightarrow \infty$. As we've seen in the specific example of the hydrogen atom, when we express the radial function as a series in powers of r , the series must terminate after a finite number of terms in order to keep the wave function finite, and it is this that results in the quantized energy levels. Although a direct link between the series solution and the form 0.4 isn't obvious, the net effect is that, when the energy has one of the allowed discrete values, the term $Be^{\kappa r}$ disappears from the asymptotic solution.

The form 0.4 is valid only under the restriction that $rV(r) \rightarrow 0$ for large r . To see why, suppose we write

$$(0.6) \quad U_E = f(r) e^{\pm \kappa r}$$

for some function f . If 0.4 is valid, then f should tend to a constant for large r . We can plug 0.6 into 0.1 and ignore the centrifugal term since we're looking only at large r . This gives

$$(0.7) \quad \frac{d^2 U_E}{dr^2} - \frac{2\mu}{\hbar^2} V U_E - \kappa^2 U_E = 0$$

Calculating the derivative, we have

$$(0.8) \quad \frac{dU_E}{dr} = (f' \pm \kappa f) e^{\pm \kappa r}$$

$$(0.9) \quad \frac{d^2 U_E}{dr^2} = (f'' \pm \kappa f' \pm \kappa f' + \kappa^2 f) e^{\pm \kappa r}$$

$$(0.10) \quad = (f'' \pm 2\kappa f' + \kappa^2 f) e^{\pm \kappa r}$$

Plugging this into 0.7 we get

$$(0.11) \quad f'' \pm 2\kappa f' - \frac{2\mu}{\hbar^2} V f = 0$$

At this point, Shankar assumes that f is slowly varying for large r , which seems reasonable, so we can disregard the second derivative, to get

$$(0.12) \quad f' = \mp \frac{\mu}{\kappa \hbar^2} V f$$

or

$$(0.13) \quad \frac{df}{f} = \mp \frac{\mu}{\kappa \hbar^2} V(r) dr$$

If we integrate this from some constant lower value r_0 up to an arbitrary large value r , we have

$$(0.14) \quad f(r) = f(r_0) \exp \left[\mp \frac{\mu}{\kappa \hbar^2} \int_{r_0}^r V(r') dr' \right]$$

The point now is that if $V(r) \rightarrow \frac{1}{r^a}$ with $a > 1$, then the integral of V will be an inverse power of r , and thus will go to zero as $r \rightarrow \infty$. In that case, the RHS of 0.14 does indeed tend to a constant as $r \rightarrow \infty$, and the asymptotic solution 0.4 is valid. However, if $V = -\frac{e^2}{r}$ (the Coulomb potential, as found in the hydrogen atom), then the integral of V is a logarithm and does not tend to zero for large r . In this case, we get

$$(0.15) \quad f(r) = f(r_0) \exp \left[\pm \frac{\mu e^2}{\kappa \hbar^2} \ln \frac{r}{r_0} \right]$$

$$(0.16) \quad = \left[r_0^{\mp \mu e^2 / \kappa \hbar^2} f(r_0) \right] r^{\pm \mu e^2 / \kappa \hbar^2}$$

The quantity in square brackets is a constant, but the last factor is a power of r which, for the positive exponent, continues to grow as $r \rightarrow \infty$. Thus the asymptotic solution 0.4 is valid only for potentials that fall off faster than $\frac{1}{r}$ for large r .

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