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

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

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

$$R_{El}(r)=\frac{U_{El}(r)}{r} \tag{2}$$

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 $r\to\infty$.

By looking at 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 $V\underset{r\to\infty}{\longrightarrow}0$, we can just ignore the potential and solve the reduced equation

$$\frac{d^2U_E}{dr^2}=-\frac{2\mu E}{\hbar^2}U_E \tag{3}$$

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 $V\to\frac{1}{r^a}$ where $a>1$, or in other words, if $rV(r)\to 0$. To see why, we need to consider two cases: $E>0$ (so that the particle can escape to infinity, since we're assuming $V\le 0$ 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, 3 has the general solution

$$U_E = Ae^{-\kappa r} + Be^{\kappa r} \tag{4}$$

where

$$\kappa = \sqrt{-\frac{2\mu E}{\hbar^2}} = \sqrt{\frac{2\mu |E|}{\hbar^2}} \tag{5}$$

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 terms blows up as $r \to \infty$. 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 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 4 is valid only under the restriction that $rV(r) \to 0$ for large r. To see why, suppose we write

$$U_E = f(r)\, e^{\pm\kappa r} \tag{6}$$

for some function f. If 4 is valid, then f should tend to a constant for large r. We can plug 6 into 1 and ignore the centrifugal term since we're looking only at large r. This gives

$$\frac{d^2U_E}{dr^2} - \frac{2\mu}{\hbar^2} V U_E - \kappa^2 U_E = 0 \tag{7}$$

Calculating the derivative, we have

$$\frac{dU_E}{dr} = \left(f' \pm \kappa f\right) e^{\pm\kappa r} \tag{8}$$

$$\frac{d^2U_E}{dr^2} = \left(f'' \pm \kappa f' \pm \kappa f' + \kappa^2 f\right) e^{\pm\kappa r} \tag{9}$$

$$= \left(f'' \pm 2\kappa f' + \kappa^2 f\right) e^{\pm\kappa r} \tag{10}$$

Plugging this into 7 we get

$$f'' \pm 2\kappa f' - \frac{2\mu}{\hbar^2} V f = 0 \tag{11}$$

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

$$f' = \mp \frac{\mu}{\kappa\hbar^2} V f \tag{12}$$

or

$$\frac{df}{f} = \mp \frac{\mu}{\kappa\hbar^2} V(r)\; dr \tag{13}$$

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

$$f(r) = f(r_0) \exp\left[\mp \frac{\mu}{\kappa\hbar^2} \int_{r_0}^{r} V(r')\, dr'\right] \tag{14}$$

The point now is that if $V(r) \to \frac{1}{r^a}$ with $a > 1$, then the integral of V will be an inverse power of r, and thus will go to zero as $r \to \infty$. In that case, the RHS of 14 does indeed tend to a constant as $r \to \infty$, and the asymptotic solution 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

$$\begin{aligned} f(r) &= f(r_0) \exp\left[\pm \frac{\mu e^2}{\kappa\hbar^2} \ln \frac{r}{r_0}\right] && (15) \\ &= \left[r_0^{\mp\mu e^2/\kappa\hbar^2} f(r_0)\right] r^{\pm\mu e^2/\kappa\hbar^2} && (16) \end{aligned}$$

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 $r \to \infty$. Thus the asymptotic solution 4 is valid only for potentials that fall off faster than $\frac{1}{r}$ for large r.

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