

### 3.4. The Radial Equation and Bound States

Once again the energy eigenfunctions for the central potential problem have simultaneous eigenfunctions of  $\vec{L}^2$  and  $L_z$  also ( $[H, \vec{L}^2] = 0 = [H, L_z] = [\vec{L}^2, L_z]$ )

$$\psi_{lm}(r, \theta, \varphi) = R(r) Y_l^m(\theta, \varphi),$$

with

$$\vec{L}^2 \psi_{lm} = \hbar^2 l(l+1) \psi_{lm}$$

$$L_z \psi_{lm} = m\hbar \psi_{lm}$$

and  $H \psi_{lm} = E \psi_{lm}$  reduces to the radial equation for  $R(r)$

$$0 = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \left( \frac{2m}{\hbar^2} (E - V(r)) - \frac{l(l+1)}{r^2} \right) R(r).$$

Before specifying the potential  $V(r)$ , let's discuss general properties of the radial eigenfunctions  $R(r)$ . If we assume that the force between the 2 particles decreases with their distance of separation,  $V(r) \rightarrow 0$  as  $r \rightarrow \infty$ , then asymptotically the radial equation becomes

$$\left( \frac{d^2}{dr^2} + \frac{2mE}{\hbar^2} \right) R(r) \sim 0 \text{ as } r \rightarrow \infty.$$

Hence for large  $r$  the eigenfunctions behave like

$$R(r) \sim f(r) e^{\pm \kappa r}$$

where  $\kappa = \sqrt{-\frac{2mE}{\hbar^2}}$  and  $f(r)$  is a function of  $r$  (like a power of  $r$ ) for which  $\frac{1}{f} \frac{df}{dr} \rightarrow 0$  as  $r \rightarrow \infty$ . This follows

from the radial equation again

$$\frac{dR}{dr} = \frac{f'}{f} R \pm \kappa R$$

$$\frac{d^2 R}{dr^2} = f'' e^{\pm \kappa r} \pm 2\kappa f' e^{\pm \kappa r} + \kappa^2 R$$

$$= \frac{f''}{f} R \pm 2\kappa \frac{f'}{f} R + \kappa^2 R$$

So

$$-\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{l(l+1)}{r^2} R + \frac{2mV(r)}{\hbar^2} R$$

$$= -\frac{f''}{f} R \mp 2\kappa \frac{f'}{f} R - \kappa^2 R - \frac{2}{r} \frac{f'}{f} R + \frac{2\kappa}{r} R + \frac{l(l+1)}{r^2} R + \frac{2mV}{\hbar^2} R$$

$$= -k^2 R$$

So as  $r \rightarrow \infty$  this yields

$$-\frac{f''}{f} + 2\kappa \frac{f'}{f} - \kappa^2 = -\kappa^2$$

$$\Rightarrow \frac{f'}{f} \sim 0 \text{ and hence } \frac{f''}{f} \sim 0 \text{ as } r \rightarrow \infty.$$

Further, we desire a  $R(r)$  that is square integrable. Thus as  $r \rightarrow \infty$ ,  $R(r)$  must decrease sufficiently quickly. Hence  $\kappa$  must be real. Thus we must have energy eigenvalues that are negative since

$$\kappa = \sqrt{\frac{-2mE}{\hbar^2}}. \text{ Since}$$

$V(r) \rightarrow 0$  as  $r \rightarrow \infty$ ,  $E < 0$  corresponds

to bound states of the 2 particles. The square integrable wavefunction describes a bound state. Thus we have asymptotically

$$R(r) \sim f(r) e^{-\kappa r} \quad \text{and} \quad \frac{d}{dr} \ln f \rightarrow 0 \text{ as } r \rightarrow \infty.$$

Next consider  $r$  close to the origin,  $r \rightarrow 0$ , if  $V(r)$  does not diverge as fast as  $\frac{1}{r^2}$  as  $r \rightarrow 0$ , then the radial equation close to the origin becomes

$$-\frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + l(l+1)R \sim 0 \text{ as } r \rightarrow 0.$$

This has two solutions

$$R \sim r^l \quad \text{or} \quad R \sim \frac{1}{r^{l+1}}$$

Again for the wavefunction to be well defined at the origin we exclude the  $\frac{1}{r^{l+1}}$  solution. Hence

as  $r \rightarrow 0$ ,  $R \sim r^l$ . Thus we can

write the radial wavefunction as

$$R(r) = u(r) r^l e^{-\lambda r}$$

where  $u(0)$  is a finite number and as  $r \rightarrow \infty$ ,  $u(r)$  grows at most like a power (i.e.  $\frac{u'}{u} \rightarrow 0$ ).

In practice we will fix the

behavior of  $u(r)$  at one extreme, say as  $r \rightarrow 0$ , then we will study the solution for  $u(r)$  when  $r \rightarrow \infty$ . In general we will find both  $e^{+kr}$  and  $e^{-kr}$  behavior for  $R$ , clearly unacceptable, since it will not be square integrable. Likewise if we fix only  $R \sim e^{-kr}$  as  $r \rightarrow \infty$ , then when we investigate these solutions at the origin we will find both  $R \sim r^2$  and  $\frac{1}{r^2}$  behavior, again unacceptable. Only for certain discrete values of  $k$  and hence the bound state energies will the unacceptable solutions disappear. They will search for those allowed values of  $k$  for which there is a solution which behaved like  $r^2$  as  $r \rightarrow 0$  and  $e^{-kr}$  as  $r \rightarrow \infty$ . That is, the square integrability of the wavefunction implies bound state energies.

With the above form for  $R(r)$ ,

$$R(r) = u(r) r^2 e^{-kr},$$

The Radial equation becomes

$$\frac{d^2}{dr^2} u(r) + 2 \left( \frac{l+1}{r} - \kappa \right) \frac{d}{dr} u(r)$$

$$- \left[ \frac{2(l+1)\kappa}{r} + \frac{2m}{\hbar^2} V(r) \right] u(r) = 0$$

### 3.5. The Hydrogen Atom

The hydrogen atom is a two body bound state composed of a proton of mass  $m_1 = 1.67 \times 10^{-27}$  kg ( $m_1 c^2 = 938$  MeV) and an electron of mass  $m_2 = 0.91 \times 10^{-30}$  kg ( $m_2 c^2 = 0.511$  MeV). The proton carries a positive charge  $e > 0$  while the electron has the opposite charge  $-e$ . The 2 particles are bound by the Coulomb potential

$$V(|\vec{r}_1 - \vec{r}_2|) = \frac{-e^2}{|\vec{r}_1 - \vec{r}_2|}$$

Hence the hydrogen atom potential is the form of the 2-body central potential we have been analyzing.