Central Potentials

The hamiltonian for a non-relativistic particle of mass m in a potential $V(\vec{r})$ is

$$H = \frac{\vec{P}^2}{2m} + V(\vec{r}). \tag{1}$$

If $V(\vec{r}) = V(r)$ depends only on the length $r = \|\vec{r}\| = (\vec{r}\cdot\vec{r})^{1/2}$, then we call $V(r)$ a central potential.

For a central potential $V(r)$, the hamiltonian (1)

$$H = \frac{P^2}{2m} + V(r) \tag{2}$$

is a scalar (i.e., invariant) under rotations, and so it commutes with the orbital angular-momentum operators $\vec{L}$ which generate rotations

$$[H, L_i] = 0 \quad \text{for } i = 1, 2, 3. \tag{3}$$

In this case, we may simultaneously diagonalize H, $\vec{L}^2$, and $L_3 = L_z$.

We know that the e-vecs of L^2 and L_3 are $|\ell, m\rangle$ with ℓ a non-negative integer and m an integer in the interval

$$-\ell \leq m \leq \ell. \tag{4}$$

We also know that $\vec{p}^{\,2}$ is simply related to $\vec{L}^2$ by (20) of the notes on orbital angular momentum (Noam)

$$\langle \vec{r} | \vec{p}^{\,2} | \psi \rangle = -\frac{\hbar^2}{r^2} \partial_r (r^2 \partial_r) \langle \vec{r} | \psi \rangle + \frac{1}{r^2} \langle \vec{r} | \vec{L}^2 | \psi \rangle. \tag{5}$$

The e-vecs of H, L^2, and L_3 may be labeled $|n, \ell, m\rangle$

$$H | n \ell m \rangle = E_{n\ell} | n \ell m \rangle \tag{6}$$

$$\vec{L}^2 | n \ell m \rangle = \hbar^2 \ell(\ell+1) | n \ell m \rangle \tag{7}$$

$$L_3 | n \ell m \rangle = \hbar m | n \ell m \rangle, \tag{8}$$

By (2, 5, 7), the energy equation (6) gives

$$E_{n\ell} \langle \vec{r} | n \ell m \rangle = \langle \vec{r} | H | n \ell m \rangle = \langle \vec{r} | \frac{\vec{p}^{\,2}}{2m} + V(r) | n \ell m \rangle$$

$$= -\frac{\hbar^2}{2mr^2} \partial_r (r^2 \partial_r) \langle \vec{r} | n \ell m \rangle + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} \langle \vec{r} | n \ell m \rangle$$

$$+ V(r) \langle \vec{r} | n \ell m \rangle. \tag{9}$$

Let $\langle \vec{r} \,|\, n\ell m \rangle = R_{n\ell}(r)\, Y_\ell^m(\theta,\phi)$

and recall (15) of the notes on orbital angular momentum (Noam)

$$\langle \vec{r} \,|\, \vec{L}^2 \,|\, n\ell m \rangle = -\hbar^2 \left[\frac{1}{\sin^2\theta} \partial_\phi^2 + \frac{1}{\sin\theta} \partial_\theta (\sin\theta\, \partial_\theta) \right] \langle \vec{r} \,|\, n\ell m \rangle. \tag{10}$$

Then the e-vec equations for $\vec{L}^2$ & L_3 (7&8) become

$$\langle \vec{r} \,|\, \vec{L}^2 \,|\, n\ell m \rangle = \hbar^2 \ell(\ell+1) \langle \vec{r} \,|\, n\ell m \rangle = \hbar^2 \ell(\ell+1) R_{n\ell}(r) Y_\ell^m(\theta,\phi)$$

$$= -\hbar^2 R_{n\ell}(r) \left[\frac{1}{\sin^2\theta} \partial_\phi^2 + \frac{1}{\sin\theta} \partial_\theta (\sin\theta\, \partial_\theta) \right] Y_\ell^m(\theta,\phi) \tag{11}$$

and by (10) of Noam

$$\langle \vec{r} \,|\, L_3 \,|\, n\ell m \rangle = \hbar m \langle \vec{r} \,|\, n\ell m \rangle = \hbar m R_{n\ell}(r) Y_\ell^m(\theta,\phi)$$

$$= \frac{\hbar}{i} \partial_\phi R_{n\ell}(r) Y_\ell^m(\theta,\phi). \tag{12}$$

The spherical harmonic $Y_\ell^m(\theta,\phi)$ thus must satisfy

$$-i\, \partial_\phi Y_\ell^m(\theta,\phi) = m\, Y_\ell^m(\theta,\phi) \tag{13}$$

and

$$-\frac{1}{\sin^2\theta} \partial_\phi^2 Y_\ell^m - \frac{1}{\sin\theta} \partial_\theta (\sin\theta\, \partial_\theta) Y_\ell^m = \ell(\ell+1) Y_\ell^m. \tag{14}$$

By (13), this last equation is

$$\frac{m^2}{\sin^2\theta} Y_\ell^m(\theta,\phi) - \frac{1}{\sin\theta}\, \partial_\theta(\sin\theta\, \partial_\theta)\, Y_\ell^m(\theta,\phi)$$
$$= \ell(\ell+1)\, Y_\ell^m(\theta,\phi) \qquad (15)$$

and it does not involve the variable ϕ.

The ϕ-dependence of $Y_\ell^m(\theta,\phi)$ is determined by (13) to be

$$Y_\ell^m(\theta,\phi) = \mathcal{P}_\ell^m(\theta)\, e^{im\phi} \qquad (16)$$

which satisfies (13) since

$$-i\,\partial_\phi\, \mathcal{P}_\ell^m(\theta)\, e^{im\phi} = m\, P_\ell^m(\theta)\, e^{im\phi}. \qquad (17)$$

For reasons of normalization and convention, the spherical harmonic Y_ℓ^m is

$$Y_\ell^m(\theta,\phi) = (-1)^m \sqrt{\left(\frac{2\ell+1}{4\pi}\right)\frac{(\ell-m)!}{(\ell+m)!}}\; P_\ell^m(\cos\theta)\, e^{im\phi} \qquad (18)$$

in which $$P_\ell^m(x) = (1-x^2)^{\frac{m}{2}}\, \frac{d^m}{dx^m}\, P_\ell(x) \qquad (19)$$

and

$P_\ell(x)$ is the Legendre polynomial

$$P_\ell(x) = \frac{(-1)^\ell}{2^\ell \ell!} \frac{d^\ell (1-x^2)^\ell}{dx^\ell} \qquad (20)$$

in which I used $x = \cos\theta$. The function $P_\ell^m(x)$ is the associated Legendre function.

The crazy factors in (18) ensure that the Y_ℓ^m are orthonormal

$$\delta_{\ell'\ell}\,\delta_{m'm} = \int_0^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta) \left[Y_{\ell'}^{m'}(\theta,\phi)\right]^* Y_\ell^m(\theta,\phi). \qquad (21)$$

The P_ℓ's are nice polynomials:

$$P_0(x) = 1, \qquad P_1(x) = x$$
$$P_2(x) = \tfrac{1}{2}(3x^2-1), \qquad P_3(x) = \tfrac{1}{2}(5x^3-3x). \qquad (22)$$

Even the Y_ℓ^m's are fairly simple

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}, \qquad Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta, \qquad Y_1^{\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$$
$$Y_2^0 = \sqrt{\frac{5}{16\pi}}\,(3\cos^2\theta - 1), \quad \text{etc.} \qquad (23)$$

So the θ,ϕ-dependence of the e-functions of a central potential are completely known & standardized.

With $\langle \vec{r} | n\ell m \rangle = \langle r\theta\phi | n\ell m \rangle = R_{n\ell}(r)\, Y_\ell^m(\theta,\phi)$, the energy equation (9) is

$$E_{n\ell} R_{n\ell}(r) Y_\ell^m = -\frac{\hbar^2}{2mr^2}\, \partial_r (r^2 R'_{n\ell}(r))\, Y_\ell^m + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} R_{n\ell}(r) Y_\ell^m + V(r) R_{n\ell}(r)\, Y_\ell^m \tag{24}$$

or since Y_ℓ^m is a common factor

$$E_{n\ell} R_{n\ell}(r) = -\frac{\hbar^2}{2mr^2} (r^2 R'_{n\ell})' + \left[\frac{\hbar^2 \ell(\ell+1)}{2mr^2} + V(r)\right] R_{n\ell} \tag{25}$$

in which

$$R'_{n\ell}(r) = \frac{d}{dr} R_{n\ell}(r). \tag{26}$$

It is not easy to solve (25). But exact solutions are known for some special potentials, such as

$$V(r) = -\frac{e^2}{r} \tag{27}$$

of the hydrogen atom.

Note that in (25) the brackets contain an effective potential

$$V_e(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}. \qquad (28)$$

If $V(r) = -e^2/r$, then the effective potential for $l = 0, 1$, and 2 looks like this:

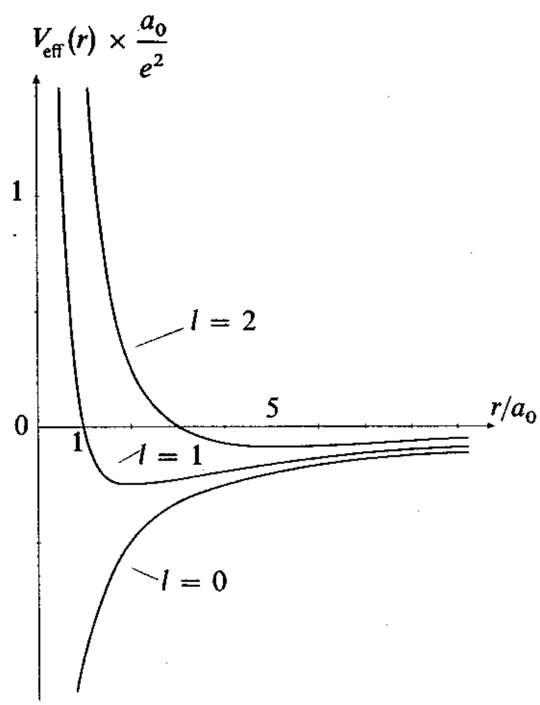

FIGURE 2

Shape of the effective potential $V_{eff}(r)$ for the first values of l in the case where $V(r) = -\frac{e^2}{r}$. When $l = 0$, $V_{eff}(r)$ is simply equal to $V(r)$. When l takes on the values 1, 2, etc., $V_{eff}(r)$ is obtained by adding to $V(r)$ the centrifugal potential $\frac{l(l+1)\hbar^2}{2\mu r^2}$, which approaches $+\infty$ when r approaches zero.

Clearly, only particles with $l = 0$ can get to $r = 0$.

The radial equation (25)

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\left(r^2 R'_{nl}\right)' + \left[\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right]R_{nl} = E_{nl}R_{nl} \tag{28}$$

simplifies because

$$\frac{1}{r^2}\left(r^2 R'\right)' = \frac{1}{r^2}\left(2rR' + r^2R''\right) = \frac{1}{r}\left(2R' + rR''\right)$$

$$= \frac{1}{r}\left(rR\right)''$$

$$= \frac{1}{r}\left(R + rR'\right)' = \frac{1}{r}\left(R' + R' + rR''\right)$$

$$= \frac{1}{r}\left(2R' + rR''\right), \tag{29}$$

So the radial equation is

$$-\frac{\hbar^2}{2m}\frac{1}{r}\left(rR_{nl}\right)'' + \left[V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}\right]R_{nl} = E_{nl}R_{nl}. \tag{30}$$

Most potentials $V(r)$ of interest behave more calmly than $l(l+1)/r^2$ for $l>0$ as $r \to 0$. So near $r=0$ the main terms in (30) are, for $l>0$,

$$-\frac{\hbar^2}{2m}\frac{1}{r}\left(rR_{nl}\right)'' + \frac{\hbar^2 l(l+1)}{2mr^2}R_{nl} = 0. \tag{31}$$

or $$r(rR_{n\ell})'' = \ell(\ell+1)R_{n\ell}. \tag{32}$$

Try $$R_{n\ell}(r) = r^s. \tag{33}$$

Then $$r(r\,r^s)'' = r(r^{s+1})'' = (s+1)r(r^s)'$$

$$= s(s+1)r^s = \ell(\ell+1)r^s \tag{34}$$

means $$s(s+1) = \ell(\ell+1) \tag{35}$$

or $$s = \ell \tag{36}$$

or $$s = -(\ell+1). \tag{37}$$

Choice (37) is too singular near $r=0$. So we conclude that as $r \to 0$

$$R_{n\ell}(r) \sim r^\ell \quad \text{for } \ell > 0. \tag{38}$$

The case $\ell=0$ depends upon the potential $V(r)$.

Most potentials of interest vanish as $r \to \infty$

$$\lim_{r\to\infty} V(r) = 0. \tag{39}$$

So as $r \to \infty$, the main terms in the radial equation (30) are

$$-\frac{\hbar^2}{2m}\frac{1}{r}(rR_{nl})'' = E_{nl}R_{nl}. \qquad (32)$$

or

$$(rR_{nl})'' = -\frac{2mE_{nl}}{\hbar^2}\, rR_{nl}. \qquad (33)$$

If $E_n < 0$, the two independent solutions are

$$rR_{nl}(r) = e^{\pm\sqrt{-\frac{2mE_{nl}}{\hbar^2}}\,r} \qquad (34)$$

of which only

$$rR_{nl}(r) = e^{-\sqrt{-2mE_{nl}}\,r/\hbar} \qquad (35a)$$

makes sense. If $E_n>0$, then $rR_{nl} \sim e^{\pm i\sqrt{2mE_{nl}}\,r/\hbar}$. (35b)

The function u defined by

$$R_{nl}(r) = \frac{u_{nl}(r)}{r} \qquad (36)$$

behaves as

$$u_{nl}(r) = \begin{cases} e^{-\sqrt{-2mE_{nl}}\,r/\hbar} & r\to\infty \\ r^{l+1}, \; l\geq 0, & r\to 0 \end{cases} \qquad (37)$$

The radial equation for $u = rR$ is

$$-\frac{\hbar^2}{2m} u''_{n\ell} + \left[V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} \right] u_{n\ell} = E_{n\ell} u_{n\ell} \,. \quad (38)$$

It describes a particle moving in one dimension in the effective potential

$$V_{ef}(r) = \begin{cases} V(r) + \dfrac{\hbar^2 \ell(\ell+1)}{2mr^2} & r > 0 \\ \infty & r < 0 \end{cases} \quad (39)$$

with boundary condition $u_{n\ell}(0) = 0$, (40)
at least for $\ell > 0$.

The behavior of $u_{n\ell}$ near $r=0$ for $\ell=0$ depends on $V(r)$. If $V(r) = -e^2/r$, then (38) for $\ell = 0$ is

$$-\frac{\hbar^2}{2m} u''_{n0} - \frac{e^2}{r} u_{n0} = E_{n0} u_{n0} \quad (41)$$

or near $r = 0$

$$-\frac{\hbar^2}{2m} u''_{n0} = \frac{e^2}{r} u_{n0} \,, \quad (42)$$

Let $u_{n0}(r) = c_1 r + c_2 r^2$. (43)

Then c_1 & c_2 must satisfy

$$-\frac{\hbar^2}{2m} 2 c_2 = \frac{e^2}{r} c_1 r = e^2 c_1 \qquad (44)$$

or

$$c_2 = -\frac{me^2}{\hbar^2} c_1 . \qquad (45)$$

Thus even for $l = 0$

$$u_{n0}(0) = 0 \qquad (46)$$

if $V(r) = -e^2/r$. So for the hydrogen atom, the asymptotic behavior is

$$\begin{cases} u_{nl}(r) \sim r^{l+1} & r \to 0 \qquad (47) \\ u_{nl}(r) \sim e^{-\sqrt{-2mE_{nl}}\, r/\hbar} & r \to \infty . \qquad (48) \end{cases}$$

The radial wave function R_{nl} goes as

$$R_{nl}(r) \sim r^l \quad \text{as } r \to 0 \qquad (49)$$

and as

$$R_{nl}(r) \sim e^{-\sqrt{-2mE_{nl}}\, r/\hbar} \qquad (50)$$

as $r \to \infty$. Eqs. (47-50) describe the salient behavior of u & R; polynomial factors are neglected in (48) & (50).