

Central Potentials

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

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

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)

$$H = \frac{\vec{p}^2}{2m} + V(r) \quad (2)$$

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

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

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

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

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

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

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

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

$$H |n, l, m\rangle = E_n |n, l, m\rangle \tag{6}$$

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

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

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

$$\begin{aligned} E_n \langle \vec{r} | n, l, m \rangle &= \langle \vec{r} | H | n, l, m \rangle = \langle \vec{r} | \frac{\vec{p}^2}{2m} + V(r) | n, l, m \rangle \\ &= -\frac{\hbar^2}{2m r^2} \partial_r (r^2 \partial_r) \langle \vec{r} | n, l, m \rangle + \frac{\hbar^2 l(l+1)}{2m r^2} \langle \vec{r} | n, l, m \rangle \\ &\quad + V(r) \langle \vec{r} | n, l, m \rangle. \end{aligned} \tag{9}$$

$$\text{Let } \langle \vec{r} | n l m \rangle = R_{nl}(r) Y_l^m(\theta, \phi)$$

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

$$\langle \vec{r} | \vec{L}^2 | n l m \rangle = -\hbar^2 \left[\frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) \right] \langle \vec{r} | n l m \rangle \quad (10)$$

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

$$\begin{aligned} \langle \vec{r} | \vec{L}^2 | n l m \rangle &= \hbar^2 l(l+1) \langle \vec{r} | n l m \rangle = \hbar^2 l(l+1) R_{nl}(r) Y_l^m(\theta, \phi) \\ &= -\hbar^2 R_{nl}(r) \left[\frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) \right] Y_l^m(\theta, \phi) \end{aligned} \quad (11)$$

and by (10) of Noam

$$\begin{aligned} \langle \vec{r} | L_3 | n l m \rangle &= \hbar m \langle \vec{r} | n l m \rangle = \hbar m R_{nl}(r) Y_l^m(\theta, \phi) \\ &= \frac{\hbar}{i} \frac{\partial}{\partial \phi} R_{nl}(r) Y_l^m(\theta, \phi), \end{aligned} \quad (12)$$

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

$$-i \frac{\partial}{\partial \phi} Y_l^m(\theta, \phi) = m Y_l^m(\theta, \phi) \quad (13)$$

and

$$-\frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} Y_l^m - \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) Y_l^m = l(l+1) Y_l^m \quad (14)$$

By (13), this last equation is

$$\frac{m^2}{\sin^2 \theta} Y_e^m(\theta, \phi) - \frac{1}{\sin \theta} \partial_\theta (\sin \theta \partial_\theta) Y_e^m(\theta, \phi) = l(l+1) Y_e^m(\theta, \phi) \quad (15)$$

and it does not involve the variable ϕ .

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

$$Y_e^m(\theta, \phi) = P_e^m(\theta) e^{im\phi} \quad (16)$$

which satisfies (13) since

$$-i \partial_\phi P_e^m(\theta) e^{im\phi} = m P_e^m(\theta) e^{im\phi} \quad (17)$$

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

$$Y_e^m(\theta, \phi) = (-1)^m \sqrt{\left(\frac{2l+1}{4\pi}\right) \frac{(l-m)!}{(l+m)!}} P_e^m(\cos \theta) e^{im\phi} \quad (18)$$

in which

$$P_e^m(x) = (1-x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} P_e(x) \quad (19)$$

and

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

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

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

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

The P_ℓ 's are nice polynomials:

$$P_0(x) = 1, \quad P_1(x) = x \quad (22)$$

$$P_2(x) = \frac{1}{2}(3x^2 - 1), \quad P_3(x) = \frac{1}{2}(5x^3 - 3x).$$

Even the Y_ℓ^m 's are fairly simple

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}, \quad Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta, \quad Y_1^{\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi} \quad (23)$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1), \quad \text{etc.}$$

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

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

$$E_{nl} R_{nl}(r) Y_l^m = -\frac{\hbar^2}{2m r^2} \partial_r (r^2 R'_{nl}(r)) Y_l^m + \frac{\hbar^2}{2m r^2} l(l+1) R_{nl}(r) Y_l^m + V(r) R_{nl}(r) Y_l^m \quad (24)$$

or since Y_l^m is a common factor

$$E_{nl} R_{nl}(r) = -\frac{\hbar^2}{2m r^2} (r^2 R'_{nl})' + \left[\frac{\hbar^2 l(l+1)}{2m r^2} + V(r) \right] R_{nl} \quad (25)$$

in which

$$R'_{nl}(r) = \frac{d}{dr} R_{nl}(r). \quad (26)$$

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

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

of the hydrogen atom.

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

$$V_e(r) = V(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} \quad (28)$$

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

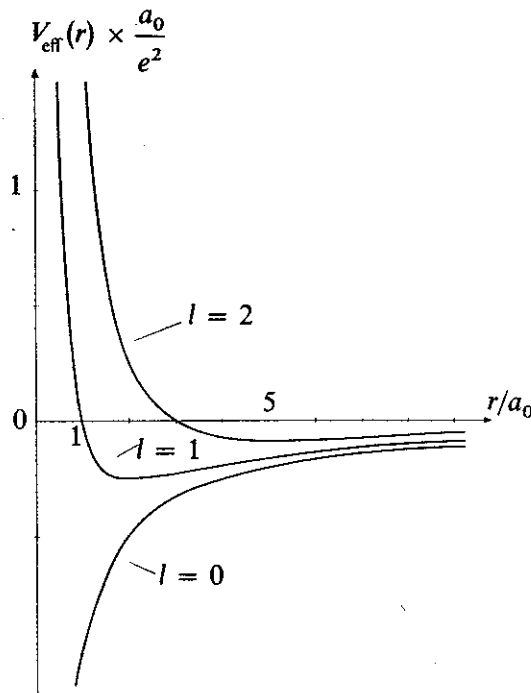


FIGURE 2

Shape of the effective potential $V_{\text{eff}}(r)$ for the first values of l in the case where $V(r) = -\frac{e^2}{r}$. When $l = 0$, $V_{\text{eff}}(r)$ is simply equal to $V(r)$. When l takes on the values 1, 2, etc., $V_{\text{eff}}(r)$ 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)

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

simplifies because

$$\begin{aligned} \frac{1}{r^2} (r^2 R')' &= \frac{1}{r^2} (2r R' + r^2 R'') = \frac{1}{r} (2R' + r R'') \\ &= \frac{1}{r} (r R)'' \\ &= \frac{1}{r} (R + r R')' = \frac{1}{r} (R' + R' + r R'') \\ &= \frac{1}{r} (2R' + r R''), \end{aligned} \quad (29)$$

So the radial equation is

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

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

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

$$\text{or } r(r R_{nl})'' = l(l+1) R_{nl} \quad (32)$$

$$\text{Try } R_{nl}(r) = r^s \quad (33)$$

$$\begin{aligned} \text{Then } r(r r^s)'' &= r(r^{s+1})'' = (s+1)r(r^s)' \\ &= s(s+1)r^s = l(l+1)r^s \end{aligned} \quad (34)$$

means

$$s(s+1) = l(l+1) \quad (35)$$

or

$$s = l \quad (36)$$

$$\text{or } s = -(l+1) \quad (37)$$

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

$$R_{nl}(r) \sim r^l \quad \text{for } l > 0. \quad (38)$$

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

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

$$\lim_{r \rightarrow \infty} V(r) = 0. \quad (39)$$

So as $r \rightarrow \infty$, the main terms in the

radial equations (30) are

$$-\frac{\hbar^2}{2m} \frac{1}{r} (r R_{nl})'' = E_n R_{nl} \quad (32)$$

or

$$(r R_{nl})'' = -\frac{2mE_n}{\hbar^2} r R_{nl} \quad (33)$$

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

$$r R_{nl}(r) = e^{\pm \sqrt{-\frac{2mE_n}{\hbar^2}} r} \quad (34)$$

of which only

$$r R_{nl}(r) = e^{-\sqrt{-2mE_n} r/\hbar} \quad (35a)$$

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

The function u defined by

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

behaves as

$$u_{nl}(r) = \begin{cases} e^{-\sqrt{-2mE_n} r/\hbar} & r \rightarrow \infty \\ r^{l+1} & , l > 0, r \rightarrow 0 \end{cases} \quad (37)$$

The radial equation for $u = rR$ is

$$-\frac{\hbar^2}{2m} u_{nl}'' + \left[V(r) + \frac{\hbar^2 l(l+1)}{2m r^2} \right] u_{nl} = E_{nl} u_{nl} \quad (38)$$

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

$$V_{\text{eff}}(r) = \begin{cases} V(r) + \frac{\hbar^2 l(l+1)}{2m r^2} & r > 0 \\ \infty & r < 0 \end{cases} \quad (39)$$

with boundary condition $u_{nl}(0) = 0$, (40)
at least for $l > 0$.

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

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

or near $r=0$

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

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

Then c_1 & c_2 must satisfy

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

or

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

Thus when for $l=0$

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

If $V(r) = -e^2/r$, so for the hydrogen atom, the asymptotic behavior is

$$\left\{ \begin{array}{l} u_{nl}(r) \sim r^{l+1} \quad r \rightarrow 0 \quad (47) \\ u_{nl}(r) \sim e^{-\sqrt{-2mE_{nl}} r/\hbar} \quad r \rightarrow \infty \quad (48) \end{array} \right.$$

The radial wave function R_{nl} goes as

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

and as

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

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