ch # 6 3-D Problems in Spherical Coordinates.

6.3

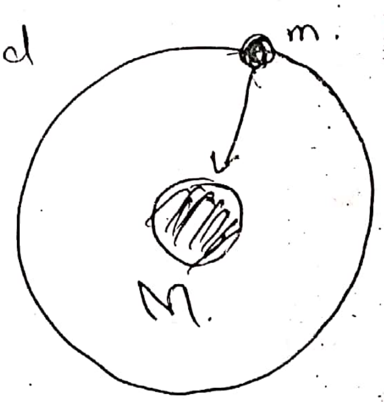
Central Potential:

Here we study the Schrodinger wave equ for a Particle of Mass "m", moving in a spherically symmetric Potential

$$V(\bar{r}) = V(r)$$

which is also known as the Central Potential.

Let a body of mass "m" is moving in a sphere, a force which is always directed towards or away from a fixed Point is called a central force. So $V(r)$ be the potential produced by a Central force, where "r" is the radius Vector.



The motion of a particle in this Potential is described by a time-independent Schrodinger wave equ.

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi = E\psi$$

where "μ" is the reduced mass of the system.

$$\mu = \frac{mM}{m+M}$$

So in above equ. the Hamiltonian of the system is.

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + V(r).$$

In spherical polar coordinates, the Hamiltonian can be expressed as.

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\phi^2}\right] + V(r)$$

$$= -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right] - \frac{\hbar^2}{2\mu}\frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + V(r)$$

$$\hat{H} = \frac{-\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right] + \frac{L^2(\theta,\phi)}{2\mu r^2}\Bigg] + V(r)$$

where.

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

So the Schrodinger equ is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \frac{L^2(\theta,\phi)}{r^2\hbar^2}\psi - \frac{2\mu}{\hbar^2}\left[V-E\right]\psi = 0$$

solve by separating the variables, with quantum numbers n, l and m.

$$\psi = R_{nl}(r)\, F_{lm}(\theta,\phi)$$

$$\Rightarrow \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)F - \frac{R}{r^2\hbar^2}L^2F - \frac{2\mu}{\hbar^2}(V-E)RF =$$

divide by RF, we get.

$$\frac{1}{Rr^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{1}{r^2\hbar^2F}L^2F - \frac{2\mu}{\hbar^2}(V-E) = 0.$$

multiply by r^2

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2\mu r^2}{\hbar^2}(V-E) = \frac{1}{\hbar^2}\frac{L^2F}{F}$$

Both sides of the above equ can be set equal to a constant

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2\mu r^2}{\hbar^2}(V-E) = C.$$

called Radial equation.

and

$$\frac{1}{\hbar^2 F} L^2 F = c, \quad \text{— Angular Equation.}$$

From this, we get.

$$L^2 F(\theta,\phi) = c\hbar^2 F(\theta,\phi).$$

i.e. F is an eigenfunction of L^2 with eigenvalue $c\hbar^2$.. But we know that the eigenvalues of L^2 are $\ell(\ell+1)\hbar^2$, where $\ell = 0, 1, 2, 3, \ldots$, so we have.

$$\therefore \quad C = \ell(\ell+1)$$

The eigenfunctions of L^2 are the spherical harmonics, so.

$$Y_{\ell m}(\theta,\phi) = C_{\ell m} P_{\ell m}(\cos\theta)\, e^{im\phi}$$

$$= C_{\ell m}(1-\xi^2)^{m/2} \frac{d^m}{d\xi^m} P_\ell(\xi)\, e^{im\phi}$$

where $\xi = \cos\theta$

$$m = -\ell, \ldots, \ell$$

$\Rightarrow$

$$F(\theta,\phi) = Y_{\ell m}(\theta,\phi)$$

Hence the angular part is simply the spherical Harmonics.

So now try to solve the Radial Part,

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2\mu r^2}{\hbar^2}(V-E) = C$$

where $C = \ell(\ell+1)$, therefore

$$\cancel{\frac{1}{R}}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2\mu r^2}{\hbar^2}(V-E)R = \ell(\ell+1)R$$

Let us define $R(r) = \dfrac{u(r)}{r}$

So

$$\frac{d}{dr}\left[r^2\left(-\frac{u}{r^2} + \frac{1}{r}\frac{du}{dr}\right)\right] - \frac{2\mu r^2}{\hbar^2}(V-E)\frac{u}{r}$$

$$-\ell(\ell+1)\frac{u}{r} = 0$$

$$\frac{d}{dr}\left[-u + r\frac{du}{dr}\right] - \frac{2\mu r^2}{\hbar^2}(V-E)\frac{u}{r}$$

$$\cancel{-\frac{du}{dr}} + r\frac{d^2u}{dr^2} + \cancel{\frac{du}{dr}} \qquad -\ell(\ell+1)\frac{u}{r} = 0$$

or

$$r\frac{d^2u}{dr^2} - \frac{2\mu r^2}{\hbar^2}(V-E)\frac{u}{r} - \ell(\ell+1)\frac{u}{r} = 0$$

$$\frac{d^2u}{dr^2} + \frac{2\mu}{\hbar^2}(E-V)u - \frac{\ell(\ell+1)}{r^2}u = 0$$

or

$$\frac{d^2u}{dr^2} + \frac{2\mu}{\hbar^2}\left(E - V_{eff}\right)u = 0$$

where $V_{eff} = V + \frac{\hbar^2}{2\mu} \cdot \frac{l(l+1)}{r^2}$ is the effective potential which is the sum of given potential V and a constant centrifugal or repulsive potential

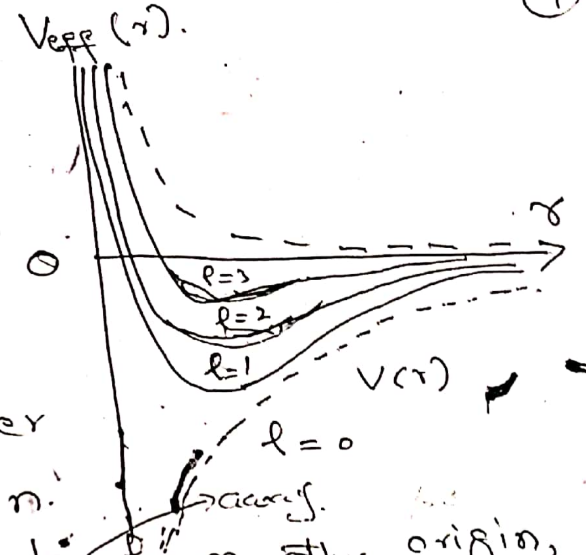
$$\frac{\hbar^2}{2\mu} \frac{l(l+1)}{r^2}$$

when $l = 0$, $V_{eff} = V$.

In case of atoms, $V(r)$ is the Coulomb potential resulting from the attractive forces between the electrons and nucleus.

For the eigenvalue eqn. to describe the ground states, the potential $V(r)$ must be attractive because $\frac{l(l+1)\hbar^2}{2\mu r^2}$ is repulsive.

Figure shows that, as "l" increases, the depth of the V_{eff} decreases and and its minimum moves farther away from the origin.

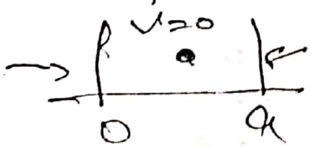


The farther the particle from the origin, the less bound it will be. This is due to the fact that as the particle angular momentum increases, the particle becomes less and less bound.

The spherical square well Potential

Free particle in spherical ~~Coordinates~~

Consider an example of an infinite spherical well as:



$$V(r) = \begin{cases} 0, & \text{if } r<a, \quad 0<r<a \\ \infty, & \text{if } r>a. \quad 0>r>a \end{cases}$$

The wavefn is zero outside the well

For the inside of the well, the radial equation is (where $V=0$)

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2}(E-V)u - \frac{\ell(\ell+1)}{r^2}u = 0.$$

So $V = 0$ inside the well

therefore

$$\frac{d^2u}{dr^2} + \left[\frac{2mE}{\hbar^2} - \frac{\ell(\ell+1)}{r^2}\right]u = 0$$

$$\frac{d^2u}{dr^2} = \left[\frac{\ell(\ell+1)}{r^2} - k_1^2\right]u.$$

where $k_1 = \frac{\sqrt{2mE}}{\hbar}$

The boundary conditions are

$\rho > r >$

$$u(a) = 0.$$

For the simple case, when $\ell = 0$

$\rho < r <$

$$\frac{d^2u}{dr^2} = -k_1^2 u.$$

$$\frac{d^2u}{dr^2} + k_1^2 u = 0.$$

The Sol. is

$$u(r) = A\sin(k_1 r) + B\cos(k_1 r)$$

As. $$R(r) = \frac{u(r)}{r}$$

therefore

$$R(r) = A\frac{\sin(k_1 r)}{r} + B\frac{\cos(k_1 r)}{r}$$

As. $r \to 0$, $\frac{\cos(k_1 r)}{r}$ is divergent
↓
undefine sol.

So we set $B = 0$. ~~an~~ then

$$r R_{nl}(r) = A\sin(k_1 r)$$

At $r \to a$ $r R_{nl}(a) = U_{nl}(a) = 0$

So at ~~and~~ $r = a$

$$A\sin(k_1 a) = 0$$

$$k_1 a = n\pi \Rightarrow k_1 = \frac{n\pi}{a}$$

Hence

$$k_1^2 = \frac{2mE}{\hbar^2}$$

the allowed eigenenergies are.

$$E_{nl} = \frac{\hbar^2 k_1^2}{2m}$$

$$E_{nl} = \frac{\hbar^2}{2m}\left(\frac{n^2\pi^2}{a^2}\right)$$

$$E_{n0} = \frac{n^2 \pi^2 \hbar^2}{2 m a^2} \quad (n = 1, 2, 3, \ldots)$$

The normalization of $U_{nl}(r)$ implies that

$$A = \sqrt{\frac{2}{a}}$$

Therefore the total wavefn ψ with quantum numbers n, l, m is in this case.

$$\psi_{nlm} = R_{nl}(r)\, F_{lm}(\theta, \phi).$$

for $l = 0,\ m = 0$

$$\psi_{n00} = R_{n0}(r)\, Y_{00}(\theta, \phi).$$

As $R_{nl}(r) = A \sin (kr)$

$$R_{n0}(r) = \sqrt{\frac{2}{a}}\, \frac{\sin (k_1 r)}{r} \longrightarrow \text{Putting } k_1 \text{ value}$$

$$= \sqrt{\frac{2}{a}}\, \frac{\sin (n\pi r/a)}{r}$$

$$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$

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Hence.

$$\psi_{n00} = \frac{1}{\sqrt{2\pi a}} \frac{\sin\left(\frac{n\pi r}{a}\right)}{r}$$

One can notice that the stationary state are specified by three quantum numbers, n, l, m : i-e

$$\psi_{nlm}(r, \theta, \phi)$$

Now for $l \neq 0$, the Radial equ is

$$\frac{d^2u}{dr^2} = \left[\frac{l(l+1)}{r^2} - k_1^2\right]u$$

The general solution of this equ is

$$\boxed{U_{nl}(r) = Ar\, J_l(k_1 r) + Br\, N_l(k_1 r)}$$

where $J_l(x)$ is the spherical Bessel function of order l, and $N_l(x)$ is spherical Neumann function of order l.

The $J_\ell(x)$ and $N_\ell(x)$ can be written as

$$J_\ell(x) = (-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\sin x}{x}$$

and

$$N_\ell(x) = -(-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\cos x}{x}$$

Note that the Bessel functions are finite at the origin (As $x \to 0$ — first boundary Condi) but Neumann fns. are divergent at the origin. Therefore we set $B=0$, since

$$U_{n\ell}(r) = A\, r\, J_\ell(K_1 r)$$

and $U_{n\ell}(r) = r R_{n\ell}(r)$.

So.

$$R_{n\ell}(r) = A J_\ell(K_1 r)$$

for 2nd boundary Condition

at $r=a$, $R_{n\ell}(a) = 0$.

This means that K_1 must be taken in such a way that

$$J_\ell(K_1 a) = 0.$$