Remark: when a particle has orbital and spin degrees of freedom, its total wave function is

$$\Psi_{n,l,m_l,m_s}(\vec{r}) = \psi_{n l m_l}(\vec{r})\,|s,m_s\rangle = R_{nl}(r)\,Y_{lm_l}(\theta,\phi)\,\underbrace{|s,m_s\rangle}_{\text{sometimes called } \chi}$$

here, the spin operator $\hat{\vec{S}}$ acts only on the spin part $|s,m_s\rangle$

the orbital operator $\hat{\vec{L}}$ acts only on the spatial part Y_{lm}

6.3.2 The free particle in spherical coordinates:

for a free particle $V(r)=0 \Rightarrow H = \frac{p^2}{2m} \Rightarrow E_k = \frac{\hbar^2 k^2}{2m}$,

where k is the wave number which varies continuously $\Rightarrow$ the energy spectrum of a free particle is infinitely degenerate as all the orientations of $\vec{k}$ in space correspond to the same energy

- for free particle the radial equation reads (7)

$$\frac{d^2u}{dr^2} - \frac{l(l+1)}{r^2}u + k^2 u = 0 \quad ; \text{ where } k_l^2(r) = \frac{2m}{\hbar^2}\left[E - \cancel{V(r)}^{\,0} - \frac{\hbar^2 l(l+1)}{2mr^2}\right]$$

$$= \frac{2mE}{\hbar^2} - \frac{l(l+1)}{r^2}$$

$$= k^2 - \frac{l(l+1)}{r^2}$$

where $k^2 = \frac{2mE}{\hbar^2}$

$\Downarrow$

let $kr = \rho \Rightarrow \frac{\partial}{\partial r} = \frac{\partial \rho}{\partial r}\frac{\partial}{\partial \rho} = k\frac{\partial}{\partial \rho}$

$$\Rightarrow \frac{\partial^2}{\partial r^2} = k^2 \frac{\partial^2}{\partial \rho^2}$$

$$\Rightarrow k^2 \frac{d^2u}{d\rho^2} - \frac{l(l+1)}{r^2}u + k^2 u = 0$$

divide by k^2 $\Rightarrow \frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u + u = 0$

$$\Rightarrow \frac{d^2u}{d\rho^2} + \left[1 - \frac{l(l+1)}{\rho^2}\right]u = 0 \quad \ldots\ldots (8)$$

spherical Bessel eq^n

let us write the last equation in terms of R ; $u(\rho) = \rho R(\rho)$

$$\Rightarrow \frac{d^2}{d\rho^2}(\rho R) + \left[1 - \frac{l(l+1)}{\rho^2}\right]\rho R = 0$$

; but $\frac{du}{d\rho} = \rho\frac{dR}{d\rho} + R$

$$\frac{d^2u}{d\rho^2} = \rho\frac{d^2R}{d\rho^2} + \frac{dR}{d\rho}\frac{d\rho}{d\rho} + \frac{dR}{d\rho}$$

$$= \rho\frac{d^2R}{d\rho^2} + 2\frac{dR}{d\rho}$$

$$\rho\frac{d^2R}{d\rho^2} + 2\frac{dR}{d\rho} + \left[1 - \frac{l(l+1)}{\rho^2}\right]\rho R = 0$$

divide by ρ

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[1 - \frac{l(l+1)}{\rho^2}\right]R = 0 \quad \text{---}(9)$$

- the general solution of the last Bessel eq^n is given by an independent Linear combination of the spherical Bessel functions $j_l(\rho)$ and the spherical Neumann functions $n_l(\rho)$

$$R(\rho) = A_l\, j_l(\rho) + B_l\, n_l(\rho) \quad \text{, where}$$

$$j_l(\rho) = (-\rho)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \frac{\sin\rho}{\rho} \quad \text{and} \quad n_l(\rho) = -(-\rho)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \frac{\cos\rho}{\rho}$$

the first few functions are

$$j_0(\rho) = \frac{\sin\rho}{\rho} \; ; \; j_1(\rho) = \frac{\sin\rho}{\rho^2} - \frac{\cos\rho}{\rho} \; ; \; j_2(\rho) = \left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\sin\rho - \frac{3\cos\rho}{\rho^2}$$

$$n_0(\rho) = -\frac{\cos\rho}{\rho} \; ; \; n_1(\rho) = -\frac{\cos\rho}{\rho^2} - \frac{\sin\rho}{\rho} \; ; \; n_2(\rho) = -\left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\cos\rho - \frac{3\sin\rho}{\rho^2}$$

now as $\rho \to 0$ $\quad j_l(\rho) \simeq \frac{2^l\, l!}{(2l+1)!}\rho^l$; by expanding $\frac{\sin\rho}{\rho}$ as a power series of ρ

finite as $\rho \to 0$ (acceptable)
(regular solution)

$$n_l(\rho) \simeq -\frac{(2l)!}{2^l l!}\frac{1}{\rho^{l+1}}$$ diverges as $\rho \longrightarrow 0$

(unacceptable)

(irregular solution)

so near the origin ($\rho \to 0$), only $j_l(\rho) = j_l(kr)$ contribute to the eigenfunctions of the free particle.

$$\psi_{nlm}(r,\theta,\phi) = j_l(kr)\, Y_{lm}(\theta,\phi) \;; \quad k^2 = \frac{2mE}{\hbar^2}$$

↳ continuous

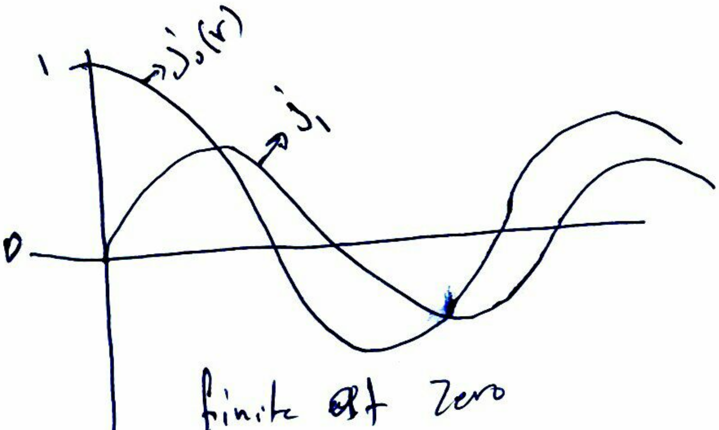
Now as $\rho \longrightarrow \infty$

$$j_l(\rho) \simeq \frac{1}{\rho}\sin\left(\rho - \frac{l\pi}{2}\right) \text{ and } n_l(\rho) \simeq -\frac{1}{\rho}\cos\left(\rho - \frac{l\pi}{2}\right)$$

so far away from the origin, both functions behave well

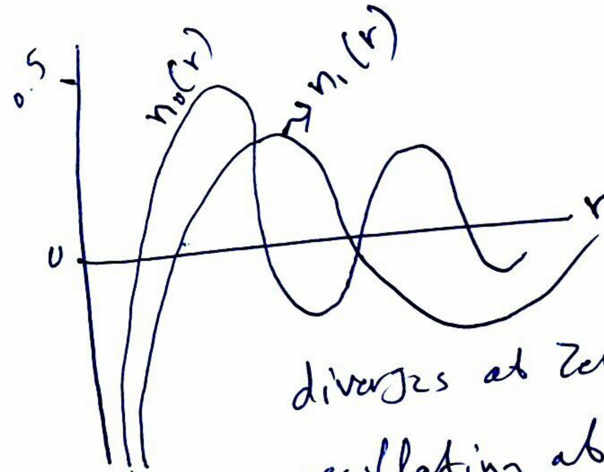
so we can take the general solution as ($\rho \to \infty$)

$$R(\rho) = A_l\, j_l(\rho) + B_l\, n_l(\rho) = A_l\, j_l(kr) + B_l\, n_l(kr)$$



finite at zero

oscillating at ∞



diverges at zero

oscillating at ∞

Notice that the amplitude of the wave functions becomes smaller as r increases. at large distances, the wavefunctions are represented by spherical waves.

- Remark: we have studied the free particle in both cartesian and spherical systems. whereas, the energy is given in both coordinates by the same expression $E = \frac{\hbar^2 k^2}{2m}$, the wavefunctions are given in Cartesian system by $e^{i\vec{k}\cdot\vec{r}}$ and in spherical system by spherical waves $j_l(kr)\, Y_{lm}(\theta,\phi)$.

we can however, show that both wave functions are equivalent. i.e we can generate plane waves from a linear combination of spherical waves that have the same k but different l and m values

$$e^{i\vec{k}\cdot\vec{r}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} a_{lm}\, j_l(kr)\, Y_{lm}(\theta,\phi)$$

for instance if $\vec{k}$ is along Z-axis ($m=0$), we have

$$e^{i\vec{k}\cdot\vec{r}} = e^{ikr\cos\theta} = \sum_{l=0}^{\infty} i^l (2l+1)\, j_l(kr)\, \underbrace{P_l(\cos\theta)}_{\text{Legender Polynomials (to be discussed Next)}}$$

where $Y_{l0}(\theta,\phi) \sim P_l(\cos\theta)$

- Note: if the incident wave is taken along the z-axis, then the wave function $e^{i\vec{k}\cdot\vec{r}}$ is completely symmetric under rotation about the Z-axis, i.e the wave function does not depend on $\phi \Rightarrow m=0 \Rightarrow Y_{l,0} \rightarrow P_l(\cos\theta)$

when $Y_{l0}(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}}\, P_l(\cos\theta)$