

-III.)

Finally, The Schrödinger equation for the relative motion wavefunction can be studied (denote ∇_r^2 by ∇^2 now)

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(|\vec{r}|) \right] \psi(\vec{r}) = E \psi(\vec{r})$$

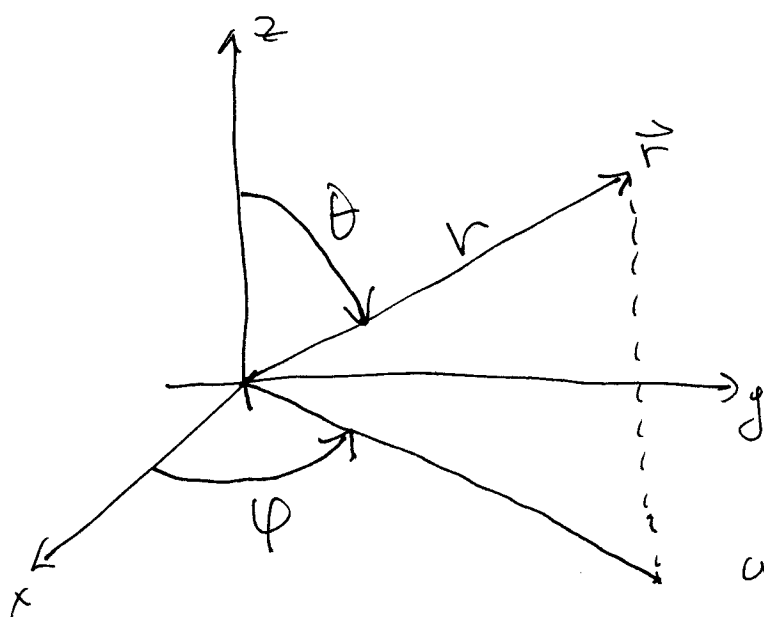
This is just the Schrödinger equation for a particle of mass m moving in the central potential $V = V(|\vec{r}|)$.

A.)

Spherical Polar Coordinates and Separation of Variables

Since the interaction of the (relative) particle with the potential ~~of only~~ depends of the magnitude $|\vec{r}|$ of the position coordinate we can imagine that the motion in the other directions with $|\vec{r}|$ fixed should separate from the $|\vec{r}|$ radial motion. This is readily seen by using spherical polar coordinates:

iii. A.)



$$x = r \sin \theta \cos \varphi$$

$$y = r \sin \theta \sin \varphi$$

$$z = r \cos \theta$$

$$0 \leq \theta \leq \pi$$

$$0 \leq \varphi \leq 2\pi$$

$$\text{and } r^2 = x^2 + y^2 + z^2.$$

The Laplacian ∇^2 in spherical polar coordinates is

$$\begin{aligned} \nabla^2 = & \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \\ & + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \\ & + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \end{aligned}$$

In spherical polar coordinates

$$V = V(|\vec{r}|) = V(r).$$

Hence we try to solve Schrödinger's eq. by separation of variables

III.A.) Ansatz: $\psi(\vec{r}) = R(r) Y(\theta, \varphi)$

Plug into Sch.-eq.:

$$\left(-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) \right) Y(\theta, \varphi)$$

$$+ \frac{R(r)}{r^2} \left(-\frac{\hbar^2}{2m} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] Y(\theta, \varphi) \right)$$

$$+ [V(r) R(r)] Y(\theta, \varphi) = E R(r) Y(\theta, \varphi)$$

So multiply by r^2 and $\div R Y$

$\Rightarrow$

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

$$= -\frac{1}{Y(\theta, \varphi) \sin^2 \theta} \left(-\frac{\hbar^2}{2m} \right) \left[\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} Y(\theta, \varphi) \right) + \frac{\partial^2}{\partial \varphi^2} Y(\theta, \varphi) \right]$$

function
of r only
 $\equiv -\frac{\hbar^2}{2m} \lambda$
(= separation constant)

function of (θ, φ) only

$$= -\frac{\hbar^2}{2m} \lambda \quad (= \text{separation constant})$$

III A) Thus we have separated the equations

1) The Radial Equation:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} R(r) \right)$$

$$+ \left[\frac{2m}{\hbar^2} (E - V(r)) - \frac{\lambda}{r^2} \right] R(r) = 0$$

2) The angular equation:

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} Y(\theta, \varphi) \right) + \lambda \sin^2 \theta Y(\theta, \varphi) + \frac{\partial^2}{\partial \varphi^2} Y(\theta, \varphi) = 0$$

Since the φ -derivative is isolated in the Δ equation, we can try separation of angular variables

Ansatz:

$$Y(\theta, \varphi) = A \Theta(\cos \theta) \Phi(\varphi)$$

where $A = \text{constant}$ which will be used to later normalize $Y(\theta, \varphi)$.

III. A) Plugging into the ∇^2 equation and dividing by $\Psi(\theta, \varphi) \Rightarrow$

$$\frac{1}{\Psi(\cos \theta)} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \Psi(\cos \theta) \right) + \lambda \sin^2 \theta \Psi(\cos \theta) \right]$$

function
of θ only
 $\equiv L = (\text{separation constant})$

$$= - \frac{1}{\Phi(\varphi)} \frac{d^2}{d\varphi^2} \Phi(\varphi)$$

function of φ only
 $\equiv L (= \text{separation constant})$

Thus we have separated the angular equation

1) Polar angular equation:

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \Psi(\cos \theta) \right) + \left(\lambda - \frac{L}{\sin^2 \theta} \right) \Psi(\cos \theta) = 0$$

2) Azimuthal angular equation:

$$\frac{d^2}{d\varphi^2} \Phi(\varphi) + L \Phi(\varphi) = 0$$

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-III. A) We can immediately solve the azimuthal eq.

$$\Phi(\varphi) = \begin{cases} A e^{i\sqrt{\nu}\varphi} + B e^{-i\sqrt{\nu}\varphi} & , \nu \neq 0 \\ A' + B'\varphi & , \nu = 0. \end{cases}$$

We must now impose our continuity conditions on the wavefunction,

$\Phi(\varphi)$ and $\frac{d\Phi(\varphi)}{d\varphi}$ are continuous throughout

the domain $0 \leq \varphi \leq 2\pi$. In particular after rotation by 2π (requiring single valuedness) we are back to the same point in space, so $\Phi(0) = \Phi(2\pi)$.

For $\nu \neq 0 \Rightarrow \sqrt{\nu} = m$, an integer

For $\nu = 0 \Rightarrow B' = 0$. Thus all

cases and solutions can be written as

$$\Phi_m(\varphi) = A e^{im\varphi}, \quad m = 0, \pm 1, \pm 2, \dots$$

- III A) The polar angle equation with $\nu = m^2$ -198-
 now becomes

$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta} \Theta(\cos\theta) \right) + \left(\lambda - \frac{m^2}{\sin^2\theta} \right) \Theta(\cos\theta) = 0$$

Define $\xi \equiv \cos\theta$ so that as $0 \leq \theta \leq \pi$
 ξ ranges $-1 \leq \xi \leq +1$.

$$\text{So } \frac{d}{d\theta} = \frac{d\xi}{d\theta} \frac{d}{d\xi} = -\sin\theta \frac{d}{d\xi} \quad \text{and}$$

$$\begin{aligned} & \frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta} \Theta(\cos\theta) \right) \\ &= \frac{1}{\sin\theta} \left(-\sin\theta \frac{d}{d\xi} \right) \left(-\sin^2\theta \frac{d}{d\xi} \Theta(\xi) \right) \\ &= \frac{d}{d\xi} \left[\sin^2\theta \frac{d}{d\xi} \Theta(\xi) \right] \\ &= \frac{d}{d\xi} \left[(1-\xi^2) \frac{d\Theta(\xi)}{d\xi} \right]. \end{aligned}$$

→ The Polar angle eq. becomes

$$\frac{d}{d\xi} \left[(1-\xi^2) \frac{d\Theta(\xi)}{d\xi} \right] + \left(\lambda - \frac{m^2}{1-\xi^2} \right) \Theta(\xi) = 0$$

Sketch of Solution:

- III A) 1) Notice as $\xi \rightarrow \pm 1$, the last term $\frac{-m}{1-\xi^2} \oplus$ is singular! we can eliminate this singularity by defining

$$\oplus(\xi) \equiv (1-\xi^2)^{\frac{|m|}{2}} P(\xi)$$

Plugging this into the Polar eq. we find (eventually) an equation for $P(\xi)$:

$$(1-\xi^2) \frac{d^2}{d\xi^2} P(\xi) - 2(|m|+1)\xi \frac{d}{d\xi} P(\xi) + (\underbrace{\lambda - m^2 - |m|}_{= (\lambda - |m|(|m|+1))}) P(\xi) = 0$$

2) This equation is satisfied by

$$P(\xi) \equiv \frac{d^{|m|}}{d\xi^{|m|}} P(\xi)$$

with $P(\xi)$ obeying the differential equation for $m=0$:

$$(1-\xi^2) \frac{d^2 P(\xi)}{d\xi^2} - 2\xi \frac{dP(\xi)}{d\xi} + \lambda P(\xi) = 0$$

- III A) Thus we find for the range $-1 \leq \xi \leq 1$ -200-

$$\Theta(\xi) = (1-\xi^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{d\xi^{|m|}} P(\xi)$$

where $P(\xi)$ obeys the equation

$$(1-\xi^2) \frac{d^2}{d\xi^2} P(\xi) - 2\xi \frac{d}{d\xi} P(\xi) + \lambda P(\xi) = 0$$

That is

$$\frac{d}{d\xi} \left[(1-\xi^2) \frac{d}{d\xi} P(\xi) \right] + \lambda P(\xi) = 0$$

This is just Legendre's Equation for $P(\xi)$

It has well behaved solutions in the region $-1 \leq \xi \leq +1$, including the end points $\xi = \pm 1$, only if the separation constant λ has the discrete values

$$\lambda = l(l+1), \quad l = 0, 1, 2, \dots$$

The resulting solutions $P_l(\xi)$ are then polynomials in ξ , called the Legendre polynomials

- III A)

$$P_\ell(\xi) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{d\xi^\ell} (\xi^2 - 1)^\ell$$

Sketch of Solution:

1) Ansatz: Power Series Solution

$$P(\xi) = \sum_{L=0}^{\infty} a_L \xi^L$$

Substitute into Legendre eq. $\Rightarrow$ recursion relation for a_L

$$1) \quad 2a_2 = -\lambda a_0$$

$$2) \quad 6a_3 = (2-\lambda)a_1$$

$$3) \quad L \geq 2 : (L+1)(L+2)a_{L+2} = [L(L+1) - \lambda]a_L$$

2) Suppose $\lambda \neq \ell(\ell+1)$, $\ell=0, 1, 2, \dots$

$$\frac{a_{L+2}}{a_L} = \frac{L(L+1) - \lambda}{(L+1)(L+2)} \xrightarrow{L \rightarrow \infty} 1$$

So as $\xi \rightarrow 1$, the series will diverge like

$$\frac{1}{(1-\xi^2)} = \sum_{L=0}^{\infty} (-1)^L (\xi^2)^L \text{ Since this}$$

III A) $\frac{a_{L+2}}{a_L} \rightarrow 1$ for all L . This implies the

$\Theta(\xi)$ diverges like

$$\Theta(\xi) \sim \frac{1}{(1-\xi^2)^{l+\frac{1}{2}}}$$

But the wavefunction Ψ is to be finite over the whole domain $0 \leq \theta \leq \pi$, that is $-1 \leq \xi \leq 1$.

Thus λ must be some integer

$$\lambda = l(l+1) \quad l=0,1,2,\dots$$

Then the power series for $P(\xi)$ terminates after $L=l$,

$$\frac{a_{L+2}}{a_L} = \frac{L(L+1) - l(l+1)}{(L+1)(L+2)},$$

so for $L \geq l$, $a_{L+2} = 0$. The $P(\xi)$

are polynomials of order l , the Legendre polynomials.

Since $\Theta(\xi)$ is proportional to the

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-III A) l th derivative of $P(z)$, it vanishes unless $|m| \leq l$. Hence each value of l allows $2l+1$ values of m , running from $-l$ to $+l$.

So with $\lambda = l(l+1)$, the recursion relation becomes

$$a_{L+2} = \frac{-(l-L)(L+l+1)}{(L+1)(L+2)} a_L$$

and all even powers are related to a_0 and all odd powers are related to a_1 . Further if l is even then the series terminates and we have $a_1 = 0, a_0 \neq 0$ and $P_l(z) = P_l(-z)$

If $l = \text{odd}$ then the odd series terminates and we put $a_0 = 0, a_1 \neq 0$ and $P_l(-z) = -P_l(z)$.

So consider the even and odd series. We can solve the above recursion formula to yield:

III A.)

a) $l = 2n$; $N = 1, 2, \dots, n$; $n = 1, 2, \dots$

$$a_{2N} = (-1)^N \frac{(2n+2N)!}{(2N)!(n+N)!(n-N)!} a_0$$

b) $l = 2n+1$; $n = 0, 1, 2, \dots$; $N = 1, 2, \dots, n$

$$a_{2N+1} = (-1)^N \frac{(2n+2N+2)!}{(n+N+1)!(n-N)!(2N+1)!} a_1$$

Thus we obtain the Legendre Polynomials $P_l(\xi)$:

a) For $l = 2n$, $n = 0, 1, 2, \dots$

$$P_l(\xi) = a_0 \sum_{\substack{N=0 \\ (l=2n)}}^n (-1)^N \frac{(2n+2N)!}{(2N)!(n+N)!(n-N)!} \xi^{2N}$$

b) For $l = 2n+1$, $n = 0, 1, 2, \dots$

$$P_l(\xi) = a_1 \sum_{\substack{N=0 \\ (l=2n+1)}}^n (-1)^N \frac{(2n+2N+2)!}{(2N+1)!(n+N+1)!(n-N)!} \xi^{2N+1}$$

III A)

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By Convention :
$$a_0 \equiv \frac{(-1)^n}{2^{2n}} \quad ; \quad a_1 \equiv \frac{(-1)^n}{2^{2n+1}}$$

Hence the first few Legendre Poly. are

$$P_0(z) = 1$$

$$P_1(z) = z$$

$$P_2(z) = \frac{1}{2}(3z^2 - 1)$$

$$P_3(z) = \frac{1}{2}(5z^3 - 3z)$$

$\vdots$

Properties of Legendre Polynomials :

1) $P_l(z)$ is real

$$2) P_l(-z) = (-1)^l P_l(z)$$

3) $P_l(z)$ is a polynomial in z of degree l .

$$4) P_l(\pm 1) = (\pm 1)^l$$

- III A) 5) The Rodrigues Formula:

$$P_l(z) = \frac{1}{2^l l!} \frac{d^l}{dz^l} (z^2 - 1)^l$$

6) Orthogonality:

$$\int_{-1}^{+1} dz P_l(z) P_{l'}(z) = \frac{2}{2l+1} \delta_{ll'}$$

7) Generating Function:

$$Z(s) = \sum_{l=0}^{\infty} s^l P_l(z) = \frac{1}{\sqrt{1-2zs+s^2}}$$

So

$$l! P_l(z) = \left. \frac{\partial^l}{\partial s^l} Z(s) \right|_{s=0}$$

Thus using the Legendre polynomials, we have solutions to the polar angular equation. These are most easily expressed in terms of the

III A) Associated Legendre Functions

$P_l^m(z)$ for $l=0,1,2,\dots$ and $m=-l, -l+1, \dots, 0, +1, +2, \dots, +l$

$$P_l^m(z) \equiv (1-z^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{dz^{|m|}} P_l(z)$$

Hence the polar angle eigenfunctions

$\Theta(z)$ are given by the associated Legendre functions

$$\Theta_{lm}(z) = P_l^m(z)$$

The properties of $P_l^m(z)$ follow from those of $P_l(z)$

1) $P_l^m(z)$ is real

$$2) P_l^m(-z) = (-1)^{l+|m|} P_l^m(z)$$

$$3) P_l^m(z) = P_l^{-m}(z)$$

$$4) P_l^0(z) = P_l(z)$$

- III A) 5) Rodrigues Formula

$$P_l^m(z) = \frac{(-1)^{|m|} (l+|m|)!}{2^l l! (l-|m|)!} (1-z^2)^{-\frac{|m|}{2}} \frac{d^{l-|m|}}{dz^{l-|m|}} (z^2-1)^l$$

6) Generating Function: Differentiate the generating function for $P_l(z)$ $|m|$ times w.r.t z and multiply by $(1-z^2)^{\frac{|m|}{2}}$ yields

$$\sum_{l=|m|}^{\infty} P_l^m(z) s^l = \frac{(2|m|)! (1-z^2)^{\frac{|m|}{2}} s^{|m|}}{2^{|m|} (|m|)! (1-2zs+s^2)^{|m|+\frac{1}{2}}}$$

7) Orthogonality:

$$\int_{-1}^{+1} dz P_l^m(z) P_{l'}^m(z) = \frac{2}{2l+1} \frac{(l+|m|)!}{(l-|m|)!} \delta_{ll'}$$

8) Low Order Associated Legendre Functions:

$$\begin{array}{l|l} P_l^0(z) = P_l(z) & P_2^1(z) = 3z\sqrt{1-z^2} \\ P_1^1(z) = \sqrt{1-z^2} & P_2^2(z) = 3(1-z^2) \\ & \vdots \end{array}$$

III A)

Putting this all back together, the angular eigenfunctions are given by

$Y(\theta, \varphi) = A P_l(\cos\theta) \Phi(\varphi)$ and are labelled by the (l, m) integers

$$Y_l^m(\theta, \varphi) = A_{lm} P_l^m(\cos\theta) e^{+im\varphi}$$

with $l=0, 1, 2, \dots$ and $m=-l, -(l-1), \dots, 0, 1, 2, \dots, l$

Recall from page -196- the (polar & azimuthal) angular eigenvalue equations:

$$\begin{aligned} 1) \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) - \frac{m^2}{\sin^2\theta} \right] Y_l^m(\theta, \varphi) \\ = -l(l+1) Y_l^m(\theta, \varphi) \end{aligned}$$

$$\begin{aligned} 2) -i \frac{\partial}{\partial\varphi} Y_l^m(\theta, \varphi) &= m Y_l^m(\theta, \varphi) \\ \Rightarrow \left(\frac{\partial^2}{\partial\varphi^2} + m^2 \right) Y_l^m(\theta, \varphi) &= 0. \end{aligned}$$

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- III A) Choosing the normalization constant A_{lm} as

$$A_{lm} \equiv (-1)^{\frac{|m|+m}{2}} \left[\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2}$$

The $Y_l^m(\theta, \varphi)$ are called Spherical Harmonics

Their properties are given by those of P_l^m and $e^{im\varphi}$:

1) Orthogonality

$$\int_{4\pi} d\Omega Y_l^{m*}(\theta, \varphi) Y_{l'}^{m'}(\theta, \varphi) = \delta_{ll'} \delta_{mm'}$$

where the solid angle integration is given by

$$\int_{4\pi} d\Omega \equiv \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin\theta$$

$$\left(= \int_0^{2\pi} d\varphi \int_{-1}^{+1} d\zeta \right)$$

$\zeta = \cos\theta$

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- III A) 2) Low Order Spherical Harmonics:

$$Y_0^0(\theta, \varphi) = \frac{1}{\sqrt{4\pi}}$$

$$Y_1^{\pm 1}(\theta, \varphi) = \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\varphi}$$

$$Y_1^0(\theta, \varphi) = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$Y_2^{\pm 2}(\theta, \varphi) = \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{\pm 2i\varphi}$$

$$Y_2^{\pm 1}(\theta, \varphi) = \mp \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{\pm i\varphi}$$

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

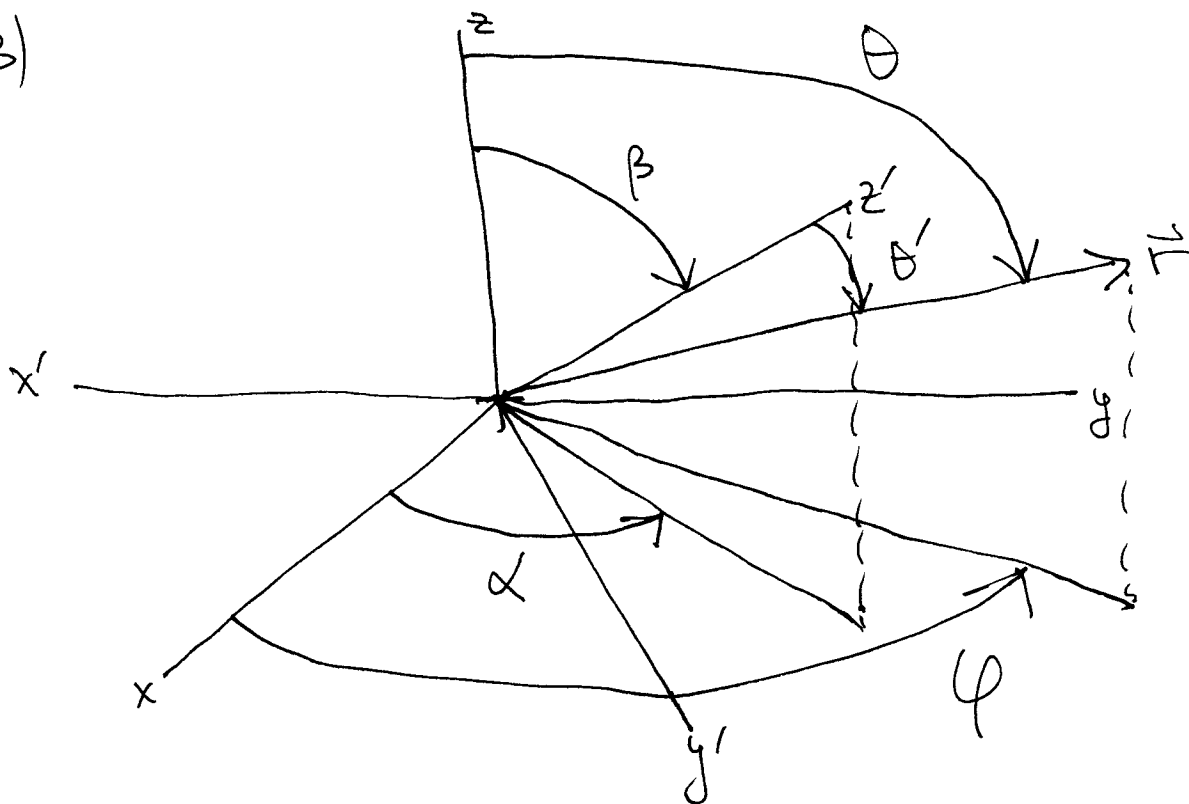
⋮

3) (Advanced Property) Addition Theorem
For Spherical Harmonics

$$P_l(\cos\theta') = \frac{4\pi}{2l+1} \sum_{m=-l}^{+l} Y_l^{m*}(\beta, \alpha) Y_l^m(\theta, \varphi)$$

with the angles $\alpha, \beta, \theta, \varphi, \theta'$ given by

- III A) 3)



Finally, the energy eigenfunction for a particle of mass m moving in a central potential $V=V(r)$ is

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

where $R(r)$ obeys the radial equation:

- III. A)

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

III. B) The Radial Equation:

This equation simplifies by a change of variables: Let

$$R(r) = \frac{1}{r} u(r)$$

$$\text{Then } \frac{dR}{dr} = \left[r \frac{du}{dr} - u \right] \frac{1}{r^2}$$

$$\frac{d}{dr} \left[r^2 \frac{dR}{dr} \right] = r \frac{d^2 u}{dr^2}$$

Hence the Radial Equation becomes

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

III.B.) This radial equation looks like a one-dimensional Schrödinger equation with the effective potential

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$$

containing an extra piece called the centrifugal term $\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$. It tends to throw the particle outward - away from the origin just as the "centrifugal" (pseudo-) force in classical mechanics!

Now recall the normalization of the wavefunction

$$1 = \int d^3r |\psi_{lm}(\vec{r})|^2$$

$$= \int_{r=0}^{\infty} dr r^2 |R|^2 \underbrace{\int_{4\pi} d\Omega |Y_{lm}|^2}_{=1}$$

$$= \int_{r=0}^{\infty} dr r^2 |R|^2 = \int_{r=0}^{\infty} dr |u(r)|^2$$

- III B) Hence our normalization condition reduces to -215-

$$1 = \int_{r=0}^{\infty} dr |\psi(r)|^2$$

Next, the potential must be specified.

c) The Hydrogen Atom

The Hydrogen atom is a two body bound state composed of a proton of mass $m_1 = 1.7 \times 10^{-28} \text{ Kg}$ ($m_1 c^2 = 938 \text{ MeV}$) and an electron of mass $m_2 = 9.1 \times 10^{-31} \text{ Kg}$ ($m_2 c^2 = 0.511 \text{ MeV}$). The proton carries positive charge $e > 0$ and the electron has opposite charge $-e$. The 2 particles are bound by the Coulomb potential (in SI units)

$$V(|\vec{r}_1 - \vec{r}_2|) = - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

which in spherical polar coordinates is given by

$$V(r) = - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$