3D system

2017/4/4

Schrodinger equation in 3D

- in 3D system $$H = \frac{\mathbf{p}^2}{2\mu} + V(\mathbf{r})$$
- μ mass
- momentum operator in 3D

$$\mathbf{p} = \left(p_x, p_y, p_z\right) = \left(\frac{\hbar}{i}\frac{\partial}{\partial x}, \frac{\hbar}{i}\frac{\partial}{\partial y}, \frac{\hbar}{i}\frac{\partial}{\partial z}\right)$$

- Schrodinger equation

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\psi(x,y,z) + V(x,y,z)\psi(x,y,z) = E\psi(x,y,z)$$

Separable system

- The kinetic energy is additive

$$\mathbf{p}^2 = p_x^2 + p_y^2 + p_z^2$$

- if potential energy is additive

$$V(x,y,z) = V_1(x) + V_2(y) + V_3(z)$$

- motion in additive potential is separable
- In classical mechanics

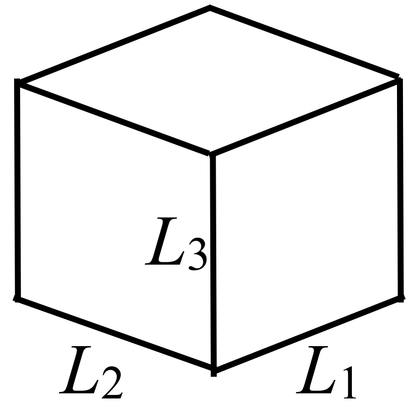
$$\mu \frac{d^2 x}{dt^2} = -\frac{\partial V_1(x)}{\partial x}$$

$$\mu \frac{d^2 y}{dt^2} = -\frac{\partial V_2(y)}{\partial y}$$

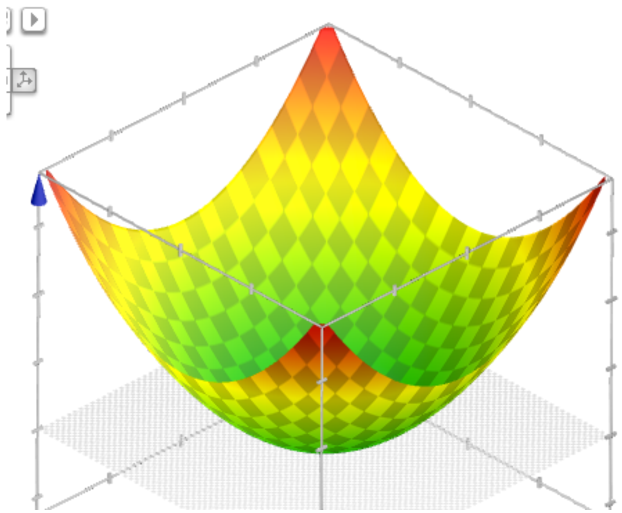
$$\mu \frac{d^2 z}{dt^2} = -\frac{\partial V_3(z)}{\partial z}$$

Examples

- particle in a infinite box of dimensions L_1, L_2 and L_3



- symmetric harmonic potential in 3D



$$V(x,y,z) = \frac{1}{2}m\omega^2 r^2 = \frac{1}{2}m\omega^2\left(x^2+y^2+z^2\right)$$

Separable system

- the eigenstate wavefunction

$$\psi(x,y,z) = u(x)v(y)w(z)$$

- for each coordinate variable

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}u(x) + V_1(x)u(x) = E_1 u(x)$$

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial y^2}v(y) + V_2(y)v(y) = E_2 v(y)$$

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial z^2}w(z) + V_3(z)w(z) = E_3 w(z)$$

- The eigenenergy is additive $E = E_1 + E_2 + E_3$

Central potential

- central potential problem

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

separable in spherical coordinate

- kinetic energy in spherical coordinate

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right] = -\frac{\hbar^2}{2\mu}\nabla^2$$

$$\nabla^2 \to \frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\left(\frac{\partial^2}{\partial \theta^2}+\cot\theta\frac{\partial}{\partial \theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right)$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

Easy way to memorize

$$\frac{\partial}{\partial x}=\frac{\partial r}{\partial x}\frac{\partial}{\partial r}+\frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta}+\frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}$$

$$\frac{\partial^2}{\partial x^2}=\frac{\partial}{\partial x}\left(\frac{\partial r}{\partial x}\frac{\partial}{\partial r}+\frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta}+\frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}\right)$$

$$=\left(\frac{\partial r}{\partial x}\right)^2\frac{\partial^2}{\partial r^2}+\left(\frac{\partial\theta}{\partial x}\right)^2\frac{\partial^2}{\partial\theta^2}+\left(\frac{\partial\phi}{\partial x}\right)^2\frac{\partial^2}{\partial\phi^2}+\frac{\partial^2 r}{\partial x^2}\frac{\partial}{\partial r}+\frac{\partial^2\theta}{\partial x^2}\frac{\partial}{\partial\theta}+\frac{\partial^2\phi}{\partial x^2}\frac{\partial}{\partial\phi}$$

$$+2\frac{\partial r}{\partial x}\frac{\partial\theta}{\partial x}\frac{\partial}{\partial r}\frac{\partial}{\partial\theta}+2\frac{\partial\theta}{\partial x}\frac{\partial\phi}{\partial x}\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi}+2\frac{\partial r}{\partial x}\frac{\partial\phi}{\partial x}\frac{\partial}{\partial r}\frac{\partial}{\partial\phi}$$

2nd derivative terms

$$\nabla^2=\left[\left(\frac{\partial r}{\partial x}\right)^2+\left(\frac{\partial r}{\partial y}\right)^2+\left(\frac{\partial r}{\partial z}\right)^2\right]\frac{\partial^2}{\partial r^2}+\left[\left(\frac{\partial\theta}{\partial x}\right)^2+\left(\frac{\partial\theta}{\partial y}\right)^2+\left(\frac{\partial\theta}{\partial z}\right)^2\right]\frac{\partial^2}{\partial\theta^2}+\left[\left(\frac{\partial\phi}{\partial x}\right)^2+\left(\frac{\partial\phi}{\partial y}\right)^2+\left(\frac{\partial\phi}{\partial z}\right)^2\right]\frac{\partial^2}{\partial\phi^2}$$

$$+\left[\frac{\partial^2 r}{\partial x^2}+\frac{\partial^2 r}{\partial y^2}+\frac{\partial^2 r}{\partial z^2}\right]\frac{\partial}{\partial r}+\left[\frac{\partial^2\theta}{\partial x^2}+\frac{\partial^2\theta}{\partial y^2}+\frac{\partial^2\theta}{\partial z^2}\right]\frac{\partial}{\partial\theta}+\left[\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}+\frac{\partial^2\phi}{\partial z^2}\right]\frac{\partial}{\partial\phi}$$

1st derivative terms

$$+2\left[\frac{\partial r}{\partial x}\frac{\partial\theta}{\partial x}+\frac{\partial r}{\partial y}\frac{\partial\theta}{\partial y}+\frac{\partial r}{\partial z}\frac{\partial\theta}{\partial z}\right]\frac{\partial}{\partial r}\frac{\partial}{\partial\theta}+2\left[\frac{\partial\theta}{\partial x}\frac{\partial\phi}{\partial x}+\frac{\partial\theta}{\partial y}\frac{\partial\phi}{\partial y}+\frac{\partial\theta}{\partial z}\frac{\partial\phi}{\partial z}\right]\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi}+2\left[\frac{\partial r}{\partial x}\frac{\partial\phi}{\partial x}+\frac{\partial r}{\partial y}\frac{\partial\phi}{\partial y}+\frac{\partial r}{\partial z}\frac{\partial\phi}{\partial z}\right]\frac{\partial}{\partial r}\frac{\partial}{\partial\phi}$$

cross terms =0

Jacobian

$$\frac{\partial r}{\partial x} = \sin\theta\cos\phi$$

$$\frac{\partial r}{\partial y} = \sin\theta\cos\phi$$

$$\frac{\partial r}{\partial z} = -\cos\theta$$

$$\frac{\partial \theta}{\partial x} = \frac{\cos\theta\cos\phi}{r}$$

$$\frac{\partial \theta}{\partial y} = \frac{\cos\theta\sin\phi}{r}$$

$$\frac{\partial \theta}{\partial z} = -\frac{\sin\theta}{r}$$

$$\frac{\partial \phi}{\partial x} = -\frac{\sin\phi}{r\sin\theta}$$

$$\frac{\partial \phi}{\partial y} = \frac{\cos\phi}{r\sin\theta}$$

$$\frac{\partial \phi}{\partial z} = 0$$

2nd derivative terms

$$\left(\frac{\partial r}{\partial x}\right)^2 + \left(\frac{\partial r}{\partial y}\right)^2 + \left(\frac{\partial r}{\partial z}\right)^2 = \sin^2\theta\cos^2\phi + \sin^2\theta\cos^2\phi + \cos^2\theta = 1$$

$$\left(\frac{\partial \theta}{\partial x}\right)^2 + \left(\frac{\partial \theta}{\partial y}\right)^2 + \left(\frac{\partial \theta}{\partial z}\right)^2 = \frac{\cos^2\theta\cos^2\phi}{r^2} + \frac{\cos^2\theta\sin^2\phi^2}{r} + \frac{\sin^2\theta}{r^2} = \frac{1}{r^2}$$

$$\left(\frac{\partial \phi}{\partial x}\right)^2 + \left(\frac{\partial \phi}{\partial y}\right)^2 + \left(\frac{\partial \phi}{\partial z}\right)^2 = \frac{\sin^2\phi}{r^2\sin^2\theta} + \frac{\cos^2\phi}{r^2\sin^2\theta} = \frac{1}{r^2\sin^2\theta}$$

cross terms

$$\frac{\partial r}{\partial x}\frac{\partial \theta}{\partial x} + \frac{\partial r}{\partial y}\frac{\partial \theta}{\partial y} + \frac{\partial r}{\partial z}\frac{\partial \theta}{\partial z} = \frac{\sin\theta\cos\theta\cos^2\phi}{r} + \frac{\sin\theta\cos\theta\sin^2\phi}{r} - \frac{\sin\theta\cos\theta}{r} = 0$$

$$\frac{\partial r}{\partial x}\frac{\partial \phi}{\partial x} + \frac{\partial r}{\partial y}\frac{\partial \phi}{\partial y} + \frac{\partial r}{\partial z}\frac{\partial \phi}{\partial z} = -\sin\theta\cos\phi\frac{\sin\phi}{r\sin\theta} + \sin\theta\cos\phi\frac{\cos\phi}{r\sin\theta} = 0$$

$$\frac{\partial \theta}{\partial x}\frac{\partial \phi}{\partial x} + \frac{\partial \theta}{\partial y}\frac{\partial \phi}{\partial y} + \frac{\partial \theta}{\partial z}\frac{\partial \phi}{\partial z} = \frac{\cos\theta\cos\phi}{r}\frac{\sin\phi}{r\sin\theta} + \frac{\cos\theta\sin\phi}{r}\frac{\cos\phi}{r\sin\theta} = 0$$

1st derivative terms

$$\frac{\partial^2 r}{\partial x^2} = \frac{y^2 + z^2}{r^2}$$

$$\frac{\partial^2 r}{\partial y^2} = \frac{x^2 + z^2}{r^2}$$

$$\frac{\partial^2 r}{\partial z^2} = \frac{x^2 + y^2}{r^2}$$

$$\frac{\partial^2 r}{\partial x^2} + \frac{\partial^2 r}{\partial y^2} + \frac{\partial^2 r}{\partial z^2} = \frac{2}{r}$$

$$\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} + \frac{\partial^2 \theta}{\partial z^2} = \frac{\cos\theta}{r^2 \sin\theta}$$

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0$$

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\cot\theta\frac{\partial}{\partial \theta}$$

$$= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{\hbar^2 r^2} L^2$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

Schrodinger equation

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\phi)+V(r)\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

radial part

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

$$=E\psi(r,\theta,\phi)$$

angular parts contain in this term

Separation of variables

- separation of variables

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

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

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

separation constant

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{2\mu r^2}{\hbar^2}(V-E)$$
$$+\frac{1}{Y\sin\theta}\left[\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]=0$$

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

Angular equation

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\phi^2}=-l(l+1)\sin^2\theta Y$$

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$$

$$\boxed{\frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+l(l+1)\sin^2\theta}+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=0$$

$$\frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+l(l+1)\sin^2\theta=m^2$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$$

φ equation

- equation for φ $$\frac{\partial^2 \Phi}{\partial \phi^2} = -m^2 \Phi$$

- boundary condition $$\Phi(\phi + 2\pi) = \Phi(\phi)$$

- solution $\Phi = e^{im\phi}$ $m = 0, \pm 1, \pm 2 \cdots$

θ equation

$$\sin\theta \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial\Theta}{\partial\theta}\right) + l(l+1)\sin^2\theta\Theta = m^2\Theta$$

- The solutions are special functions, called associated Legendre functions

$$\Theta(\theta) = P_l^m(\cos\theta)$$

Legendre polynomials

- Associated Legendre functions can be generated from Legendre polynomials *P_l*

$$P_l^m(x) = \left(1 - x^2\right)^{m/2} \left(\frac{d}{dx}\right)^m P_l(x) \qquad m > 0 \qquad P_l^{-m}(x) = P_l^m(x)$$

- Legendre polynomials are

$$P_l(x) = \frac{1}{2^l l!} \left(\frac{d}{dx}\right)^l \left(x^2 - 1\right)^l$$

called Rodrigues formula

limitations on *l* and *m*

- *l* should be non-negative integers $l = 0, 1, 2, \cdots$

- if $|m| > l$ $P_l^m(x) = 0$

- possible values of $m = -l, -l+1, \cdots, 0, \cdots l-1, l$

$$P_0 = 1$$

$$P_1 = x$$

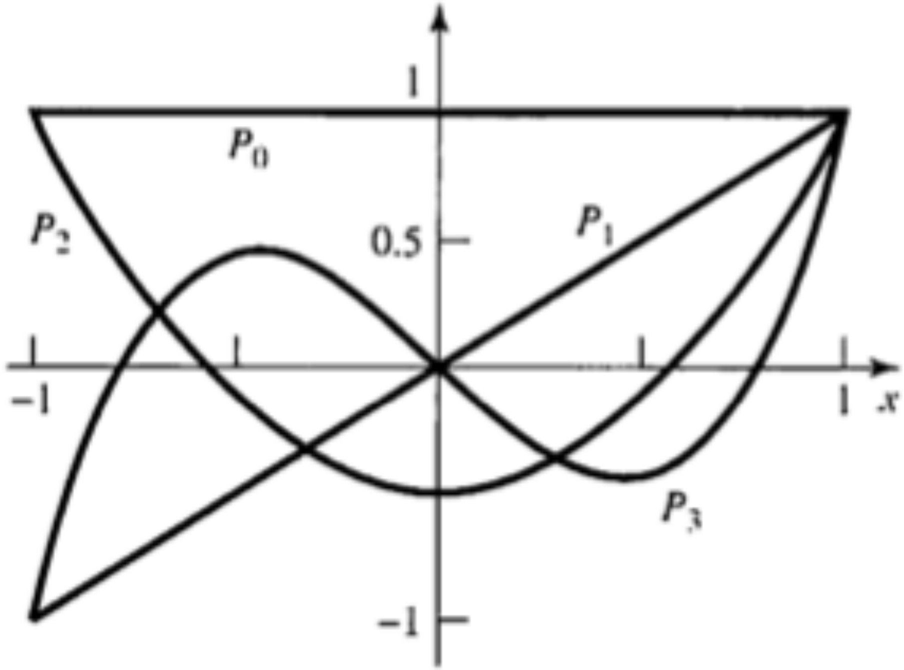
$$P_2 = \tfrac{1}{2}(3x^2 - 1)$$

$$P_3 = \tfrac{1}{2}(5x^3 - 3x)$$

$$P_4 = \tfrac{1}{8}(35x^4 - 30x^2 + 3)$$

$$P_5 = \tfrac{1}{8}(63x^5 - 70x^3 + 15x)$$

(a)



(b)

$$P_0^0 = 1$$

$$P_1^1 = \sin\theta$$

$$P_1^0 = \cos\theta$$

$$P_2^2 = 3\sin^2\theta$$

$$P_2^1 = 3\sin\theta\ \cos\theta$$

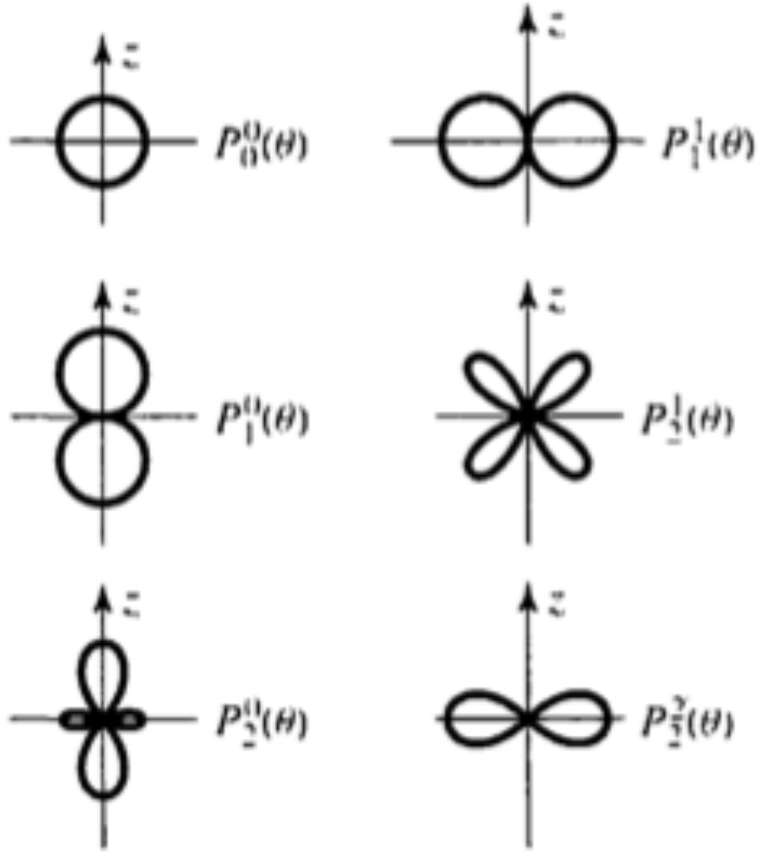
$$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$$

$$P_3^3 = 15\sin\theta(1-\cos^2\theta)$$

$$P_3^2 = 15\sin^2\theta\ \cos\theta$$

$$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$$

$$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$$



Spherical harmonics

- normalized wavefunctions *Y* are called spherical harmonics

$$\int |Y|^2 \sin\theta \, d\theta \, d\phi = 1$$

$$Y_{lm}(\theta,\phi) = (-1)^m \left[\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos\theta) e^{im\phi}$$

- *l*: azimuthal quantum number
- *m*:magnetic quantum number

Introduction of L

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{\hbar^2 r^2} L^2$$

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi} \qquad L_\pm = \hbar e^{\pm i\phi}\left(\pm\frac{\partial}{\partial \theta} + i\cot\theta\frac{\partial}{\partial \phi}\right)$$

$$L^2 = L_x^2 + L_y^2 + L_z^2 = L_+ L_- - \hbar L_z + L_z^2$$

$$L_+ L_- = \hbar^2 e^{i\phi}\left(\frac{\partial}{\partial \theta} + i\cot\theta\frac{\partial}{\partial \phi}\right) e^{-i\phi}\left(-\frac{\partial}{\partial \theta} + i\cot\theta\frac{\partial}{\partial \phi}\right)$$

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

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

$$= \hbar^2\left[-\frac{\partial^2}{\partial \theta^2} - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2} - \cot\theta\frac{\partial}{\partial \theta}\right]$$

Schrodinger equation

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\phi)+V(r)\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

radial part

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

angular parts contain in this term

Radial part

- use the eigenstate of L^2

$$L^2|l,m\rangle = l(l+1)\hbar^2|l,m\rangle \qquad L^2Y_{lm}(\theta,\phi) = l(l+1)\hbar^2Y_{lm}(\theta,\phi)$$

- separation of variables

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

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{l(l+1)}{r^2}\right]R_{nl}(r) + V(r)R_{nl}(r) = ER_{nl}(r)$$

Hydrogen atom

- attractive Coulomb potential

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

- Differential equation

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{l(l+1)}{r^2}\right]R_{nl}(r) - \frac{Ze^2}{4\pi\varepsilon_0 r}R_{nl}(r) = ER_{nl}(r)$$

$$\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{\hbar^2 l(l+1)}{2\mu r^2}\right)\right]R_{nl}(r) = 0$$

Scaling

- choose the scaling factor for length

$$E < 0 \qquad \frac{1}{x_0} = \frac{\sqrt{8\mu|E|}}{\hbar} = \frac{\sqrt{-8\mu E}}{\hbar}$$

- dimensionless length $\rho = \frac{r}{x_0} = \frac{\sqrt{-8\mu E}}{\hbar} r$

$$\left[\frac{1}{x_0^2}\frac{\partial^2}{\partial\rho^2} + \frac{1}{x_0^2}\frac{2}{\rho}\frac{\partial}{\partial\rho} + \frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 x_0\rho} - \frac{\hbar^2 l(l+1)}{2\mu x_0^2\rho^2}\right)\right]R(\rho) = 0$$

$$\left[\frac{\partial^2}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial}{\partial\rho} - \frac{1}{4} + \frac{2\mu}{\hbar^2}\frac{x_0 Ze^2}{4\pi\varepsilon_0\rho} - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0$$

$$\left[\frac{\partial^2}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial}{\partial\rho} - \frac{1}{4} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0$$

Characteristic length

- characteristic(eigen) length

$$\lambda = \frac{2\mu}{\hbar^2}\frac{x_0 Ze^2}{4\pi\varepsilon_0} = \frac{2\mu}{\hbar^2}\frac{Ze^2}{4\pi\varepsilon_0}\frac{\hbar}{\sqrt{-8\mu E}}$$

$$= \frac{Ze^2}{4\pi\varepsilon_0\hbar}\sqrt{\frac{\mu}{-2E}}$$

$$= Z\alpha\sqrt{\frac{\mu c^2}{-2E}}$$

$$x_0 = \frac{\hbar^2 4\pi\varepsilon_0\lambda}{2\mu Ze^2} = \frac{a_0\lambda}{2Z}$$

- fine structure constant

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 c\hbar} = \frac{1}{137}$$

asymptotic behavior

- when $\rho \to \infty$

$$\left[\frac{\partial^2}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial}{\partial\rho} - \frac{1}{4} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0$$

$$\longrightarrow \quad \left[\frac{\partial^2}{\partial\rho^2} - \frac{1}{4}\right]R(\rho) = 0$$

$$R(\rho) \to e^{-\rho/2}$$

- in general $R(\rho) = e^{-\rho/2}G(\rho)$

asymptotic behavior

- when $\rho \to 0$

$$\left[\frac{\partial^2}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial}{\partial\rho} - \frac{1}{4} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0$$

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

$$R(\rho) \propto \rho^s$$

$$s(s-1) + 2s - l(l+1) = 0 \qquad s(s+1) = l(l+1)$$

$s = l$ or $s = -l-1$

asymptotic behavior

- differential equation for G

$$\left[\frac{\partial^2}{\partial\rho^2}+\frac{2}{\rho}\frac{\partial}{\partial\rho}-\frac{1}{4}+\frac{\lambda}{\rho}-\frac{l(l+1)}{\rho^2}\right]e^{-\rho/2}G(\rho)$$

$$=e^{-\rho/2}\frac{\partial^2 G}{\partial\rho^2}-e^{-\rho/2}\frac{\partial G}{\partial\rho}+\frac{1}{4}e^{-\rho/2}G$$

$$+e^{-\rho/2}\frac{2}{\rho}\frac{\partial G}{\partial\rho}-e^{-\rho/2}\frac{1}{\rho}G+\left[-\frac{1}{4}+\frac{\lambda}{\rho}-\frac{l(l+1)}{\rho^2}\right]e^{-\rho/2}G$$

$$\frac{\partial^2 G}{\partial\rho^2}-\frac{\partial G}{\partial\rho}+\frac{2}{\rho}\frac{\partial G}{\partial\rho}-\frac{1}{\rho}G+\left[\frac{\lambda}{\rho}-\frac{l(l+1)}{\rho^2}\right]G=0$$

$$\frac{\partial^2 G}{\partial\rho^2}-\left(1-\frac{2}{\rho}\right)\frac{\partial G}{\partial\rho}+\left[\frac{\lambda-1}{\rho}-\frac{l(l+1)}{\rho^2}\right]G=0$$

asymptotic behavior

- owing to the behavior of R at small ρ

$$G(\rho) \propto \rho^l = \rho^l H(\rho)$$

$$\frac{\partial^2}{\partial\rho^2}\rho^l H(\rho) - \left(1-\frac{2}{\rho}\right)\frac{\partial}{\partial\rho}\rho^l H(\rho) + \left[\frac{\lambda-1}{\rho} - \frac{l(l+1)}{\rho^2}\right]\rho^l H(\rho) = 0$$

$$\rho^l \frac{\partial^2 H}{\partial\rho^2} + \frac{2l}{\rho}\rho^l \frac{\partial H}{\partial\rho} + \rho^l \frac{l(l-1)}{\rho^2} H - \left(1-\frac{2}{\rho}\right)\frac{\partial H}{\partial\rho} - \left(1-\frac{2}{\rho}\right)\frac{l}{\rho}\rho^l H + \left[\frac{\lambda-1}{\rho} - \frac{l(l+1)}{\rho^2}\right]\rho^l H = 0$$

$$\frac{\partial^2 H}{\partial\rho^2} + \left(\frac{2l+2}{\rho} - 1\right)\frac{\partial H}{\partial\rho} + \frac{\lambda-l-1}{\rho} H = 0$$

- We will take the similar approach with that in Chapter IV to discuss the possible eigenvalues

power series expansion

- Here we consider the approach of power series expansion for the differential equation

$$\frac{\partial^2 H}{\partial \rho^2} + \left(\frac{2l+2}{\rho} - 1 \right) \frac{\partial H}{\partial \rho} + \frac{\lambda - l - 1}{\rho} H = 0$$

- assuming $H(\rho) = \sum_k a_k \rho^k$

$$\frac{dH}{d\rho} = \sum_k k a_k \rho^{k-1} \qquad \frac{d^2 H}{d\rho^2} = \sum_k k(k-1) a_k \rho^{k-2}$$

$$\sum_k k(k-1) a_k \rho^{k-2} + \sum_k \left(\frac{2l+2}{\rho} - 1 \right) k a_k \rho^{k-1} + \frac{\lambda - l - 1}{\rho} \sum_k a_k \rho^k = 0$$

$$\sum_k \left[k(k-1) + k(2l+2) \right] a_k \rho^{k-2} + \sum_k (\lambda - l - 1 - k) a_k \rho^{k-1} = 0$$

recursion formula

- rearrange the order

$$\sum_k (k+1)(k+2l+2)a_{k+1}\rho^{k-1} + \sum_k (\lambda - l - 1 - k)a_k\rho^{k-1} = 0$$

- The coefficients

$$(k+1)(k+2l+2)a_{k+1} + (\lambda - l - 1 - k)a_k = 0$$

$$\frac{a_{k+1}}{a_k} = \frac{k+l+1-\lambda}{(k+1)(k+2l+2)}$$

recursion formula

- when *k* is large, it behaves as $\frac{a_{k+1}}{a_k} \to \frac{1}{k}$

$$a_k \approx \left(\frac{1}{k}\right)\left(\frac{1}{k-1}\right)\left(\frac{1}{k-2}\right)\cdots \simeq \frac{1}{k!}C$$

$$H(\rho) = \sum_k a_k \rho^k \simeq C \sum_k \frac{1}{k!}\rho^k = Ce^{\rho}$$

in general cases, $R(\rho) \simeq Ce^{\rho}e^{-\frac{\rho}{2}} = Ce^{\frac{\rho}{2}}$

diverges when ρ is large

termination of series

- we want a reasonable solution which is finite at infinite ρ $\quad a_k = 0$ for some k

$$k + l + 1 - \lambda = 0$$

- It restricts the value of λ

$$\lambda = k + l + 1 = n$$

- n is called principle quantum number
- some properties

$$\lambda = n = Z\alpha\sqrt{\frac{\mu c^2}{-2E}}$$

$$k \geq 0 \qquad\qquad n \geq l + 1$$

$$E = -\mu c^2 \frac{Z^2\alpha^2}{2n^2}$$

Numerical method-1

- another way of scaling, Bohr radius $a_0 = \frac{\hbar^2 4\pi\varepsilon_0}{\mu e^2}$
- rewrite the equation $\rho = \frac{r}{a_0}$

$$-\frac{\hbar^2}{2\mu}\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}\right]R_{nl}(r) - \frac{Ze^2}{4\pi\varepsilon_0 r}R_{nl}(r) = ER_{nl}(r)$$

$$\left[-\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{l(l+1)}{r^2}\right]R_{nl}(r) - \frac{2\mu Ze^2}{4\pi\varepsilon_0\hbar^2 r}R_{nl}(r) = \frac{2\mu}{\hbar^2}ER_{nl}(r)$$

$$\left[-\frac{\partial^2}{\partial\rho^2} - \frac{2}{\rho}\frac{\partial}{\partial\rho} - \frac{2Z}{\rho} + \frac{l(l+1)}{\rho^2}\right]R(\rho) = \frac{2\mu a_0^2}{\hbar^2}ER(\rho)$$

Numerical method-2

- normalization condition

$$\int \left|\rho R(\rho)\right|^2 d\rho = \int |f|^2 d\rho = 1 \qquad f = \rho R(\rho)$$

- The equation for *f*

$$-\frac{\partial^2}{\partial \rho^2} f(\rho) - \left[\frac{2Z}{\rho} - \frac{l(l+1)}{\rho^2}\right] f(\rho) = \lambda f(\rho)$$

$$\lambda = \frac{2\mu a_0^2}{\hbar^2} E = \frac{E}{R_y} \qquad R_y = \frac{\mu e^4}{8\varepsilon_0^2 h^2}$$

Numerical method-3

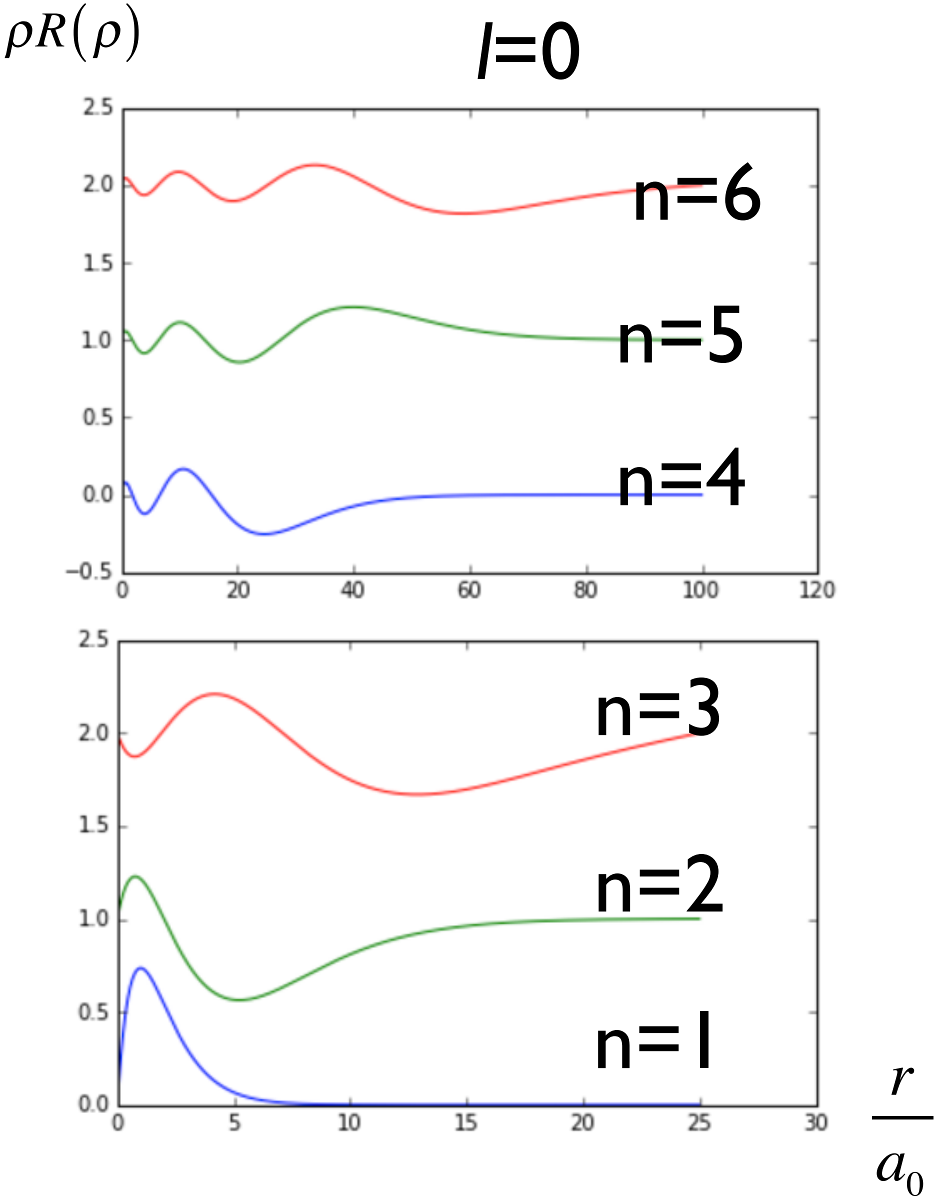
- Define the hermitian operator satisfying

$$\hat{O}|f\rangle = \lambda|f\rangle \qquad \hat{O} = -\frac{\partial^2}{\partial\rho^2} - \frac{2Z}{\rho} + \frac{l(l+1)}{\rho^2}$$

- If write the solution with a column vector with linearly spaced coordinate $\rho_{j+1} - \rho_j = \Delta\rho$

$$f(\rho) = \begin{pmatrix} \rho_1 R(\rho_1) \\ \rho_2 R(\rho_2) \\ \rho_3 R(\rho_3) \\ \vdots \\ \rho_N R(\rho_N) \end{pmatrix} \qquad \frac{d^2}{d\rho^2} = \frac{1}{(\Delta\rho)^2} \begin{pmatrix} -2 & 1 & 0 & & 0 \\ 1 & -2 & 1 & \cdots & 0 \\ 0 & 1 & -2 & & 0 \\ & \vdots & & \ddots & 1 \\ 0 & 0 & 0 & 1 & 2 \end{pmatrix}$$

Numerical method-4



eigenvalues

-0.99937578~ 1
-0.2499605 ~ 1/4
-0.10921206 ~1/9
-0.06246099 ~1/16
-0.03998396 ~1/25
-0.0277305 ~1/36
-0.01921007 ~1/49

mass difference

- the mass of a deutron(1p1n) is twice of a proton

- Eigenenergy and transition frequency scale as

$$\mu = \frac{mM}{m+M} = \frac{m}{1+\frac{m}{M}}$$

- small difference of transition energies for a deuterium(epn) and a hydrogen(ep)

Proton size puzzle

- to study the spectrum of a muonic hydrogen (μp)
- muon mass ~ 270 m_e
- a muon orbits much closer than an electron to the hydrogen nucleus, where it is consequently much more sensitive to the size of the proton.

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LETTERS

The size of the proton

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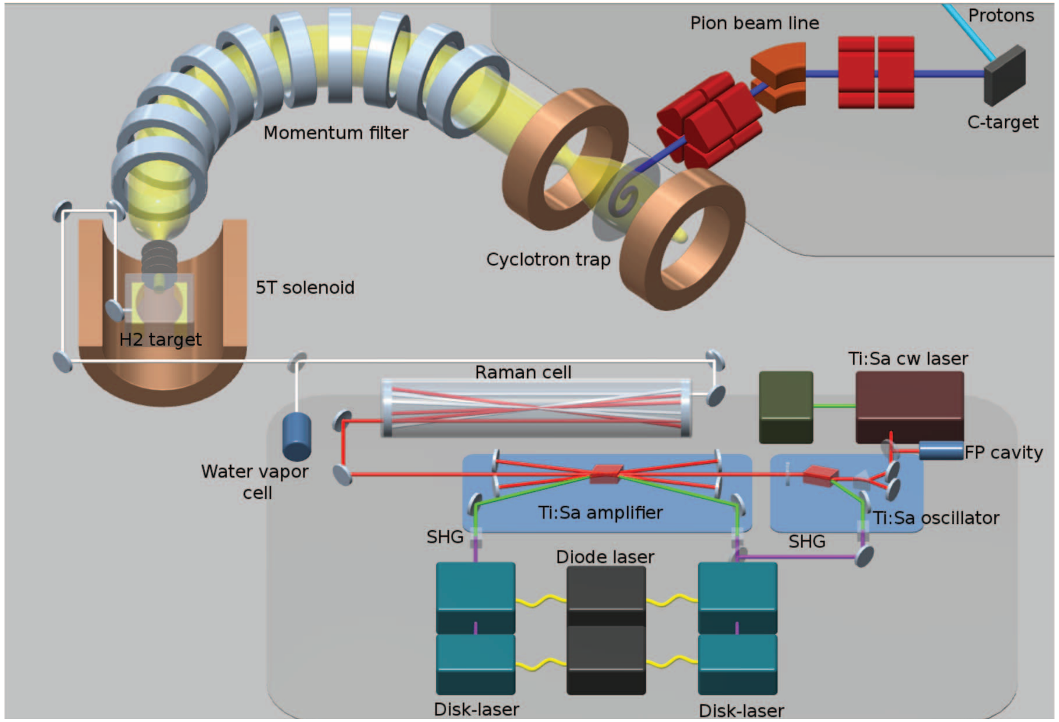


degeneracy

- energy only depends on n

$$n = k + l + 1$$

- since k is an integer, the number of possible k is n (from l=0, 1, ...n-1)
- for each l, there are $2l+1$ states (m=-l, ...l)
- total degeneracy

$$\sum_{l=0}^{n-1} 2l + 1 = n^2$$

ground state

- n=1, l=0

$$\frac{a_{k+1}}{a_k} = \frac{k+l}{(k+1)(k+2l+2)}$$

- only a_0 exists

radial

$$H(\rho) = 1$$

$$R(\rho) = e^{-\rho/2}$$

angular

$$Y_{00} = \text{cosntant}$$

1st excited state

- *n*=2, *l*=0

$$\frac{a_{k+1}}{a_k} = \frac{k+l-1}{(k+1)(k+2l+2)}$$

$$a_0 = 1$$

$$a_1 = -\frac{1}{2}$$

$$a_2 = 0$$

radial

$$H(\rho) = 1 - \frac{\rho}{2}$$

angular

$$Y_{00}$$

- *n*=2, *l*=1

radial

$$H(\rho) = 1$$

angular

$$Y_{11}, Y_{10}, Y_{1-1}$$

2nd excited state

- *n*=3, *l*=0

$$a_0 = 1$$
$$a_1 = -1$$
$$a_2 = \frac{1}{6}$$
$$a_3 = 0$$

$$\frac{a_{k+1}}{a_k} = \frac{k+l-2}{(k+1)(k+2l+2)}$$

radial $H(\rho) = 1 - \rho + \frac{\rho^2}{6}$

angular Y_{00}

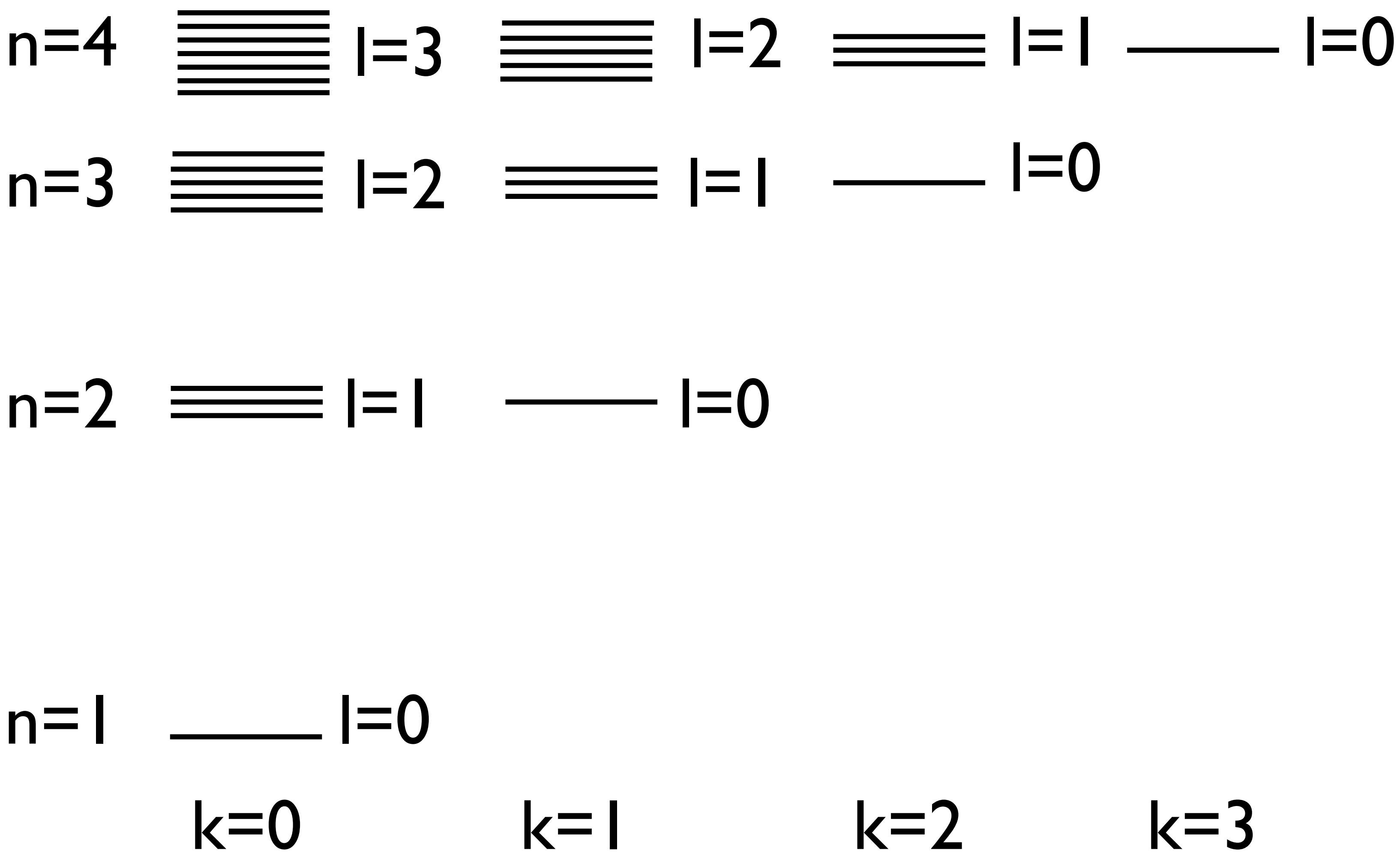
- *n*=3, *l*=1

$$a_0 = 1$$
$$a_1 = -\frac{1}{4}$$
$$a_2 = 0$$

radial $H(\rho) = 1 - \frac{\rho}{4}$

angular Y_{11}, Y_{10}, Y_{1-1}

spectrum



large degeneracy for 1/r potential

- To see this, consider a modification on potential such as

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2}{2\mu}\frac{g^2}{r^2} = V_0 + \frac{\hbar^2}{2\mu}\frac{g^2}{r^2}$$

- Schrodinger equation becomes

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right]\psi + \frac{1}{2\mu r^2}\left(L^2 + g^2\right)\psi + V_0(r)\psi = E\psi$$

effect of non 1/r potential

- eigenequation changes to

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{l^*\left(l^*+1\right)}{r^2}\right]R_{nl}\left(r\right)+V_0\left(r\right)R_{nl}\left(r\right)=ER_{nl}\left(r\right)$$

$$l^*\left(l^*+1\right)=l\left(l+1\right)+g^2$$

- energy degeneracy is lifted

$$E=-\mu c^2\frac{Z^2\alpha^2}{2n^2} \qquad n=k+l^*+1=k-\frac{1}{2}+\sqrt{\left(l+\frac{1}{2}\right)^2+g^2}$$

existence of a constant of motion

- The large degeneracy arises from the existence of an additional constant of motion except L^2
- The operator Lenz vector is defined by

$$\mathbf{A} = \frac{1}{2\mu\alpha}\left[\mathbf{L}\times\mathbf{p} - \mathbf{p}\times\mathbf{L}\right] + \frac{\mathbf{r}}{r} \qquad \left[H, \mathbf{A}\right] = 0$$

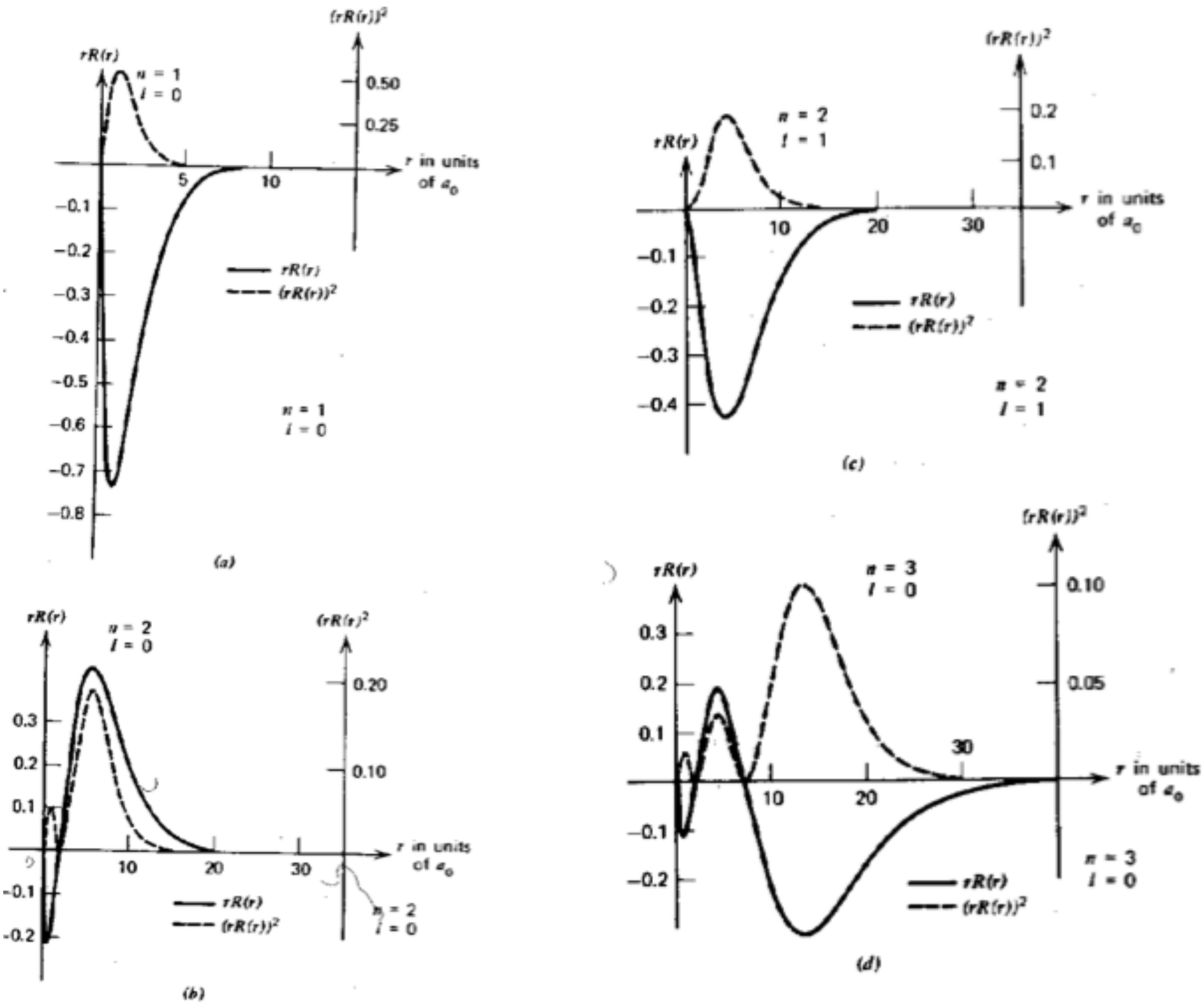
- Physical meaning of A: orientation of the elliptic orbit

associate Lagurre polynomials

- The radial eigenfunctions are called associate Lagurre polynomials

$$H(\rho) = L_{n-l-1}^{(2l+1)}(\rho)$$

$$L_n^{\alpha}(\rho) = \sum_{m=0} \begin{pmatrix} n+\alpha \\ n-m \end{pmatrix} \frac{(-\rho)^m}{m!}$$



rR(r)
(rR(r))²
n = 1
l = 0
0.50
0.25
5
10
r in units of a₀
−0.1
−0.2
−0.3
−0.4
−0.5
−0.6
−0.7
−0.8
rR(r)
(rR(r))²
n = 1
l = 0
(a)
rR(r)
n = 2
l = 0
(rR(r))²
0.20
0.10
0.3
0.2
0.1
10
20
30
r in units of a₀
-0.1
-0.2
rR(r)
(rR(r))²
n = 2
l = 0
(b)
(rR(r))²
rR(r)
n = 2
l = 1
0.2
0.1
10
20
30
r in units of a₀
−0.1
−0.2
−0.3
−0.4
rR(r)
(rR(r))²
n = 2
l = 1
(c)
(rR(r))²
rR(r)
n = 3
l = 0
0.10
0.05
0.3
0.2
0.1
30
10
20
r in units of a₀
−0.1
−0.2
n = 3
l = 0
rR(r)
(rR(r))²
(d)