20190514 Ch4 particle dynamics in 3D

Monday, May 13, 2019 9:59 AM

Notice: quiz III at 5/28, covering ch3, allowing 3 pages A4 formula sheet
final exam 6/10, covering all materials. allowing 4 pages of above

for a particle of mass m in an infinitely deep spherical potential well

$V(r) = \begin{cases} 0, & r<a \\ +\infty, & r \geq a \end{cases}$, find the eigen energy and eigen-wave function for the bound state, $\boxed{l=0}$ case.

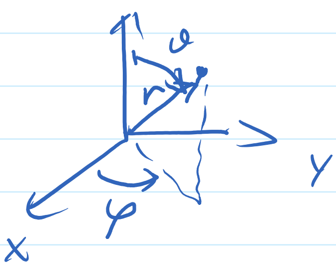
- recap particle dynamics in 3D

introduce 3D coordinate
introduce state. ket. wavefunctions in 3D
$\psi(x,y,z)$

introduce probability distribution. $\longleftrightarrow$ 1D case.
introduce degeneracy ☆

§1. wavefunction in spherical coordinates.

$\vec{r} = (x, y, z) \longleftrightarrow (r, \theta, \varphi)$



H_0 in freespace

$$H = \frac{\vec{P}^2}{2m} = \frac{P_x^2 + P_y^2 + P_z^2}{2m} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

in spherical coordinate scalar 标量

$$\vec{P} = -i\hbar\vec{\nabla} = -i\hbar\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

$$\vec{\nabla} \cdot f = \frac{\partial f}{\partial r}\hat{r} + \frac{1}{r}\frac{\partial f}{\partial \theta}\hat{\theta} + \frac{1}{r\sin\theta}\frac{\partial f}{\partial \varphi}\hat{\varphi}$$

$$\vec{P}^2 = -\hbar^2\vec{\nabla}^2$$

$$\vec{p}^{\,2} = -\hbar^2 \nabla^2$$

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

$$H = \frac{\vec{p}^{\,2}}{2m} = -\frac{\hbar^2}{2m}\vec{\nabla}^2$$

$$H|\psi\rangle \xrightarrow{\text{spherical}} -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) - \frac{\hbar^2}{2mr^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right)$$

angular momentum

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

$$\boxed{H_0 = \underbrace{\frac{p_r^2}{2m}}_{\text{radial 经向}} + \underbrace{\frac{\vec{L}^2}{2mr^2}}_{\text{angular 角向}}} \quad , \quad p_r^2 = -\hbar^2 \frac{1}{r^2}\left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}\right)$$

- central potential 中心势

$$V = V(r)$$

$$+V = \frac{p_r^2}{2m} + \frac{\vec{L}^2}{2mr^2} + V(r).$$

H depending on ① momentum along radial direction
② radial "position" $-r$
③ angular momentum $\vec{L}$

because $V = V(r) \neq V(\theta, \varphi)$, so there is a symmetry of the Hamiltonian along angular position coordinate.

to see the structure of H, then we calculate commuters with operaters.

$[H, \vec{L}^2] = 0 \longrightarrow H, \vec{L}^2$ share the same eigenstates.

$[H, L_z] = 0$ H, L_z share ✓ ✓ ✓

the eigen state $\psi(r,\theta,\varphi) = \underline{\underline{R(r)}}\, \Phi(\theta,\varphi)$

$\Phi(\theta,\varphi) = Y_l^m(\theta,\varphi)$

let's show this is true that $\psi(r,\theta,\varphi) = R(r)\Phi(\theta,\varphi)$.

trying solve the eigen equation

$$H\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + r^2(V(r)-E)\psi = \frac{\vec{L}^2}{2m}\psi$$

if we set $\psi = R(r)\Phi(\theta,\varphi)$

and devide ψ on both sides

$$-\frac{\hbar^2}{2m}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)\frac{1}{R} + r^2(V(r)-E) = \frac{\frac{\vec{L}^2}{2m}\Phi(\theta,\varphi)}{\Phi(\theta,\varphi)} = C$$

separation of variable 分离变量

$\Phi(\theta,\varphi) = Y_l^m(\theta,\varphi)$ spherical harmonics

$\vec{L}^2 Y_l^m(\theta,\varphi) = \underline{\hbar^2 l(l+1)}\cdot Y_l^m(\theta,\varphi)$ 填空题 fill-in-the-blank

$$C = \frac{\hbar^2}{2m}l(l+1)$$

plug it back to radial equation, and we arrive to

$$-\frac{\hbar^2}{2m}\underbrace{\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)} + r^2(V(r)-E)R - \frac{\hbar^2}{2m}l(l+1)R = 0$$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) = 2r\frac{\partial R}{\partial r} + r^2\frac{\partial^2 R}{\partial r^2}.$$

introduce a new radial function $u(r)$

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

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) = \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\left(\frac{u}{r}\right)\right) = \frac{\partial}{\partial r}\left(r^2\frac{u'}{r} - u\right)$$

$u' = \frac{\partial u}{\partial r}$

$$= \frac{\partial}{\partial r}(ru' - u) = \cancel{u'} + ru'' - \cancel{u'} = ru'' = r\frac{\partial^2 u}{\partial r^2}.$$

$$= \frac{\partial}{\partial r}(ru' - u) = \cancel{u'} + ru'' - \cancel{u'} = ru'' = r\frac{\partial^2 u}{\partial r^2}.$$

$$\boxed{\Rightarrow \quad -\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial r^2} + \left[\frac{l(l+1)}{2mr^2}\hbar^2 + V(r)\right]u(r) = E\,u(r).}$$

effective schrödinger's equation for $u(r)$.

probability around (r, θ, φ)

$$|\psi|^2 r^2 dr \sin\theta \, d\theta \, d\varphi \; \underset{\psi = R(r) Y_l^m(\theta,\varphi)}{=\!=\!=} \; |R(r)|^2 r^2 dr \, |Y_l^m|^2 \sin\theta \, d\theta \, d\varphi$$

$$R = \frac{u}{r} \qquad = |u|^2 dr \; |Y_l^m(\theta,\varphi)|^2 \sin\theta \, d\theta \, d\varphi.$$

$\Rightarrow$ $u(r)$ is sufficient to act like a one dimensional wavefunction along r.

$r \in [0, \infty)$

vs. for normal one-dimensional $x \in (-\infty, \infty)$

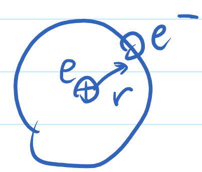
effective Schödinger's - equation

$$H_r = H_{0,r} + V_{eff,r}$$

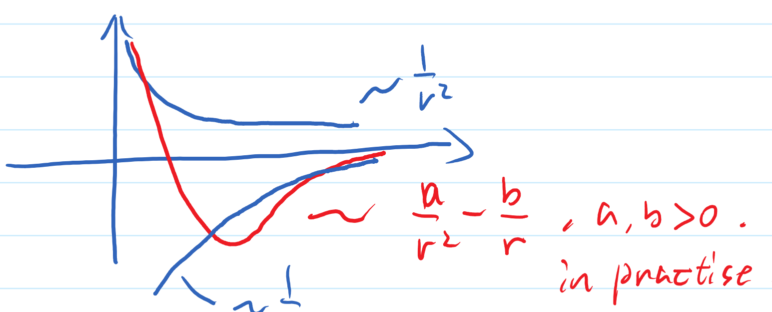
$$= \frac{p_r^2}{2m} + \underbrace{\left[\hbar^2 \frac{l(l+1)}{2mr^2} + V(r)\right]}_{V_{eff}} = \frac{p_r^2}{2m} + V_{eff}.$$

if we have $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$

Coulomb potential



V_{eff} ? sketch



$\frac{\hbar^2}{2mr^2} l(l+1) \longrightarrow$ centrifugal potential

离心势

- properties of $u(r)$.

$\psi(r,\theta,\varphi)$ as a wave function.

continues
finite
square integreble.
single value.

$R(r) = \frac{u(r)}{r}$, R shares the same property as wavefunc

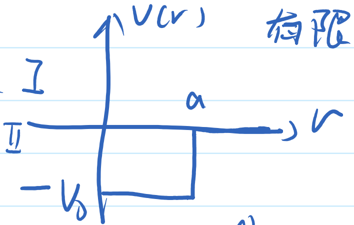
$$\Rightarrow \boxed{\lim_{r\to 0} u(r) \to 0}$$

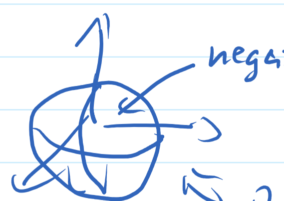
as we show $|u(r)|^2 dr$ represents probability,
we also need $\lim_{r\to\infty} |u(r)| \to 0$.

example 1. Spherical square well. (finite case) 有限深球势阱

$$V(r) = \begin{cases} -V_0, & r<a, \text{section I} \\ 0, & r>a, \text{section II} \end{cases}$$

$V_0 > 0$.





schrödinger's equation becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial r^2} + \left(\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right)u(r) = Eu(r)$$

solve for the ground bound state. $l=0$, $E<0$.

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial r^2} + V(r)u(r) = Eu(r)$$

one dimensional finite depth square well.

section I: $-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial r^2} - V_0 u(r) = Eu(r) \Rightarrow$

section II $-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial r^2} = Eu(r)$.

section I $\frac{\partial^2 u}{\partial r^2} + \frac{2m}{\hbar^2}(V_0+E)u = 0$.

section I $\quad \frac{\partial^2 u}{\partial r^2} + \frac{2m}{\hbar^2}(V_0 + E)\, u = 0.$

define $\quad k^2 = \frac{2m}{\hbar^2}(V_0 + E) \quad \begin{cases} -V_0 < E < 0 \\ V_0 + E \ \text{positive.} \end{cases}$

$$\frac{\partial^2 u}{\partial r^2} + k^2 u = 0$$

$\left.\begin{array}{l} u = A \sin kr + C \cos kr. \\ \text{we need } \lim_{r\to 0} u \to 0, \quad C = 0 \end{array}\right\} \Rightarrow u = A \sin kr, \ r < a.$

section II $\quad \frac{\partial^2 u}{\partial r^2} + \frac{2m}{\hbar^2} E\, u = 0, \qquad E < 0.$

define $\quad \alpha^2 = -\frac{2mE}{\hbar^2}$

$$u = B\, e^{-\alpha r}, \quad r > a$$

$$\Rightarrow \ u(r) = \begin{cases} A \sin kr, & r < a \\ B e^{-\alpha r}, & r > a \end{cases}$$

$$\int_0^\infty |u(r)|^2 dr = 1 \Rightarrow \int_0^a A^2 \sin^2 kr\, dr + \int_a^\infty B^2 e^{-2\alpha r} dr = 1$$

continuous $\quad A \sin ka = B e^{-\alpha a}$

choose A and B, so that

$$u(r) = \begin{cases} N \frac{\sin kr}{\sin ka}, & r < a \\ N e^{-\alpha(r-a)}, & r > a. \end{cases}$$

N : normalization factor. $\quad N = \frac{1}{\sqrt{\int_0^a \frac{\sin^2 kr}{\sin^2 ka} dr + \int_a^{+\infty} e^{-2\alpha(r-a)} dr}}$

for the full eigenstate, we have

$$\psi(r, \theta, \varphi) = \frac{u(r)}{r} Y_l^m(\theta, \varphi)$$

$\begin{cases} l = 0 : \\ m = 0 \end{cases} \quad Y_0^0(\theta, \varphi) = \frac{1}{2}\sqrt{\frac{1}{\pi}}$

final answer : $\quad \psi(r, \theta, \varphi) = \begin{cases} N \frac{\sin kr}{\sin ka} \cdot \frac{1}{r} \cdot \frac{1}{\sqrt{4\pi}}, & r < a \\ \underline{N e^{-\alpha(r-a)}} \cdot \frac{1}{\ldots}, & r > a. \end{cases}$

$$N\frac{e^{-\alpha(r-a)}}{r}\cdot\frac{1}{\sqrt{4\pi}},\quad r>a.$$

N as above.

$$Y_0^0(\theta,\varphi)=\frac{1}{2}\sqrt{\frac{1}{\pi}},$$

$$\begin{cases} Y_1^{-1}=\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{-i\varphi}, \quad Y_1^1=\frac{-1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{i\varphi}, \\ Y_1^0=\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta. \end{cases}$$

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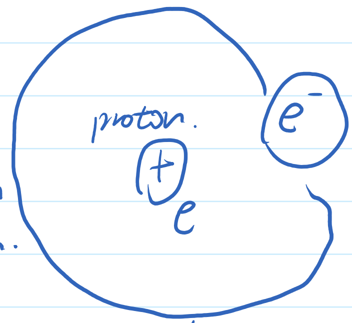
§2 Hydrogen atom.



try to solve for eigen wavefunction and eigen energy of a H-atom.

we ignore spin for e^- and proton for now.

$$H=\frac{P_{proton}^2}{2m_{proton}}+\frac{P_e^2}{2m_e}-\frac{e^2}{4\pi\varepsilon_0|\vec{r}_e-\vec{r}_{proton}|}$$

apply techniques from classical mechanics.

define $\underline{\vec{r}=\vec{r}_e-\vec{r}_p}$ $\leftarrow$ relative position betwee e^- and proton.

$$\mu=\frac{m_e m_p}{m_e+m_p} \leftarrow \text{reduced mass}$$

$$\vec{p}=\frac{m_p\vec{P}_e-m_e\vec{P}_p}{m_p+m_e},\quad \vec{P}_0=\vec{P}_e+\vec{P}_p,\quad M=m_e+m_p.$$

$$\Rightarrow\quad H=\frac{\vec{P}_0^{\,2}}{2M}+\frac{\vec{p}^{\,2}}{2\mu}-\frac{e^2}{4\pi\varepsilon_0|\vec{r}|}$$

$\Rightarrow$ in the center of mass frame 质心坐标.

$$H = \frac{\vec{p}^2}{2\mu} - \underbrace{\frac{e^2}{4\pi\varepsilon_0 |\vec{r}|}}_{V(r)}$$

we can apply the separation between radial and angular to the Hamiltonian.

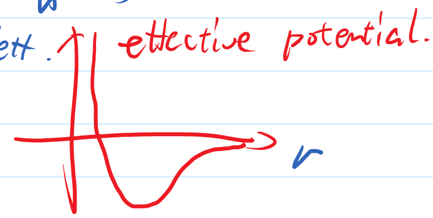
$$\mu = \frac{m_e m_p}{m_e + m_p} \xrightarrow{m_p \sim 1836\, m_e} \mu = \frac{m_e}{1 + \frac{m_e}{m_p}} \simeq m_e$$

$$\Rightarrow \begin{cases} -\frac{\hbar^2}{2\mu} \vec{\nabla}^2 \psi - \frac{e^2}{4\pi\varepsilon_0 r} \psi = E\psi . \\ \psi(r,\theta,\varphi) = R(r)\, Y_l^m(\theta,\varphi) = \frac{u(r)}{r} Y_l^m(\theta,\varphi) . \end{cases}$$

we apply effective Schrödinger's equation of $u(r)$

$$\Longrightarrow \left(-\frac{\partial^2}{\partial r^2} + \frac{l(l+1)}{r^2} - \frac{2\mu e^2}{4\pi\varepsilon_0 \hbar^2} \frac{1}{r} + \frac{2\mu |E|}{\hbar^2} \right) u(r) = 0 .$$

Q: if we need a bound state, what do we need for E?

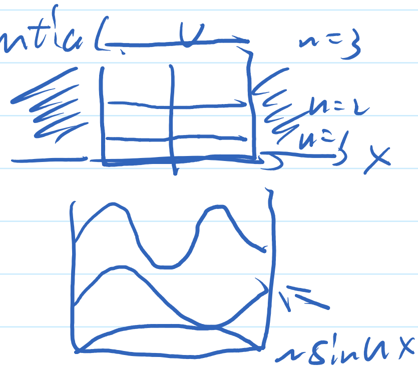


A: $E < 0$.

$$V_{eff}: \quad -\frac{e^2}{4\pi\varepsilon_0 r} + \hbar^2 \frac{l(l+1)}{r^2} .$$

how is the eigen energy spacing for bound states?

① we have 1-D infinitely deep potential



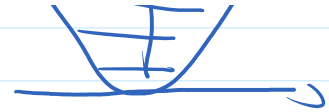
$$V = \begin{cases} +\infty, & x > a \text{ or } x < -a \\ 0, & -a < x < a . \end{cases}$$

$E_n \sim$ a. $E_n \propto n$
b. $E_n \propto n^2$ ✓
c. $E_n \propto n^3$

② 1-D harmonic oscillator

$V = \frac{1}{2} m\omega^2 x^2$

(2) 1-D harmonic oscillator



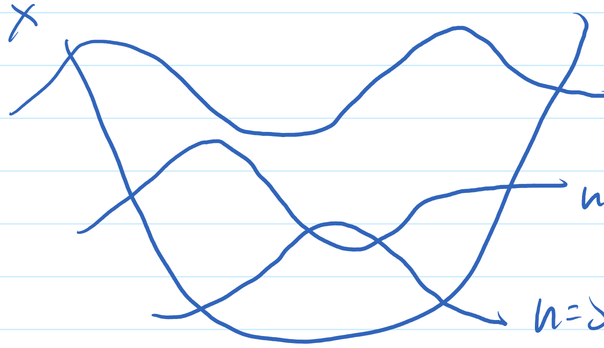
$V=\frac{1}{2}m\omega^2 x^2$,

E_n. a. $E_n \propto n+\frac{1}{2}$ ✓

b. n^2 ✗

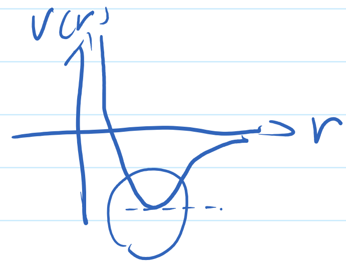
c. n^3 ✗

$E_n=\hbar\omega(n+\frac{1}{2}), n=0,1,2,\cdots$



③ H-atom

$$V_{eff}=-\frac{e^2}{4\pi\epsilon_0 r}+\frac{\hbar^2 l(l+1)}{2mr^2}$$



ask minimum of V_{eff}?

$V_{eff}'=0 \Rightarrow r_{min}$

then expand V_{eff} around r_{min}

$$V_{eff}=V_{min}+\frac{1}{2}kr^2+\frac{1}{2}\eta r^3+\cdots$$

even more relaxed than the harmonic oscillator.

$$E_n\propto -\frac{1}{n^2}$$

$$\left(-\frac{\partial^2}{\partial r^2}+\frac{l(l+1)}{r^2}-\frac{2\mu e^2}{4\pi\epsilon_0\hbar^2}\frac{1}{r}+\frac{2\mu|E|}{\hbar^2}\right)u(r)=0$$

first is to redine the coordinates

$\left(\frac{\epsilon}{2}\right)^2=\frac{2\mu|E|}{\hbar^2}$, let $\begin{cases} x=r\epsilon, & \epsilon \text{ in unit of } \frac{1}{[r]} \\ x \text{ is unitless.} \end{cases}$

$$\Rightarrow \frac{d^2u}{dx^2}+\left[-\frac{1}{4}+\frac{2\mu e^2}{4\pi\epsilon_0\hbar^2}\frac{1}{\epsilon x}-\frac{l(l+1)}{x^2}\right]u=0.$$

$\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$ ~ unit of length. effective Bohr radius.

$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$, $a_0' = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$, let $\boxed{\lambda = \frac{2}{a_0' \epsilon}}$ ~ unitless

$$\frac{d^2u}{dx} + \left[-\frac{1}{4} + \frac{\lambda}{x} - \frac{l(l+1)}{x^2}\right]u = 0.$$

$\lim_{x\to 0} u = 0$, $\lim_{x\to\infty} u = 0$.

method: asymptotic

let $x \to 0$, dominant part is $-\frac{l(l+1)}{x^2}$

$$\frac{\partial^2 u}{\partial x^2} - \frac{l(l+1)}{x^2}u = 0 \longrightarrow u \xrightarrow{x\to 0} x^{l+1}$$

$x \to \infty$, dominant part is $-\frac{1}{4}$

$$\frac{\partial^2 u}{\partial x^2} - \frac{1}{4}u = 0 \longrightarrow u \xrightarrow{x\to\infty} e^{-x/2}$$

$$u = \underbrace{e^{-x/2}\, x^{l+1}}_{\text{asymptotic part}}\, F(x)$$

asymptotic part 渐近的 ← polynomial 多项式

$\Rightarrow$ $xF'' + (2l+2-x)F' - (l+1-\lambda)F = 0.$

define $F = \sum_i C_i x^i \Rightarrow$ formular between different orders of C_i

$\Rightarrow (i+1)\cdot(2l+2+i)C_{i+1} = (l+1-\lambda+i)C_i.$

$\Rightarrow$ need to truncate at certain i

we have $\lambda = l+1+i \geq l$

$\lambda = \frac{2}{a_0' \epsilon} = l+1+i = n$ as integer

$\lambda = \frac{}{a_0' \epsilon} = l+1+2 = n$ as integer

$\Rightarrow$ with $\begin{cases} \left(\frac{\epsilon}{2}\right)^2 = \frac{2\mu|E|}{\hbar^2} \\ \epsilon = \frac{2}{n a_0'} \end{cases}$ $\Rightarrow$ $|E| = \frac{\hbar^2}{2\mu a_0'^2} \cdot \frac{1}{n^2}$

$E<0$ for bound state.

we have $\boxed{E_n = -\frac{\hbar^2}{2\mu a_0'^2} \cdot \frac{1}{n^2}}$

$n \geq l+1$, or $l \leq n-1$

$l = 0, 1, 2, \cdots, n-1$ for H-atom.

n: primary quantum number

choice of l depends on n.

$E_n \propto -\frac{1}{n^2}$, nothing to do with l, so for each n, there are $l = 0 \sim n-1$ different states, so it's n-fold degenerate so far.

choice of n, $\underset{\underset{0 \sim n-1}{\uparrow}}{l}$, $\underset{\underset{-l \sim +l}{\uparrow}}{m}$

$\Rightarrow$ for a given n, overall degeneracy is

$$\sum_{l=0}^{n-1} \sum_{m=-l}^{+l} = \underline{\sum_{l=0}^{n-1} 2l+1} = n(n-1)+n = n^2.$$

$\psi = \frac{u(r)}{r} Y_l^m(\theta,\varphi) \Leftarrow u(x) = e^{-x/2} x^{l+1} F(x)$

$$\begin{cases} \psi(r,\theta,\varphi) = \sqrt{\left(\frac{2}{n a_0'}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}}\ \underline{e^{-\frac{r}{n a_0'}}}\ \underline{\left(\frac{2r}{n a_0'}\right)^l}\ \underline{F_{nl}\left(\frac{2r}{n a_0'}\right)}\ \underline{Y_l^m(\theta,\varphi)} \\ a_0' = \frac{4\pi\varepsilon_0 \hbar^2}{\mu e^2}, \quad \mu = \frac{m_e m_p}{m_e + m_p}. \end{cases}$$

$a_0' = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$, $\mu = \frac{m_e m_p}{m_e + m_p}$.

Bohr radius $0.5\,\mathring{A} \sim 5\times10^{-11}\,m$

$E = -\frac{\hbar^2}{2\mu a_0'^2}\cdot\frac{1}{n^2}$, quantum number n, l, m.