Week 5 - PHAS0004 ASU - Note

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Week 5 Hydrogen Atom Distribute.

Begin with TISE $-\hbar^2/2m \cdot d^2\psi(x)/dx^2 + V(x)\psi(x) = E\psi(x)$

$$V(x) = -e^2/4\pi\varepsilon_0 r$$

$\downarrow$ Convert to 3D. ①

$$-\hbar^2/2m \nabla^2 \psi(x,y,z) + V(x,y,z)\cdot\psi(x,y,z) = E\psi(x,y,z)$$

where $V(x,y,z) = -e^2/4\pi\varepsilon_0 \cdot \sqrt{x^2+y^2+z^2}$

☆ Idea of Eigenvalues : $\hat{p}\psi = a\psi$

$\underset{\text{Operators}}{\hat{p}}\ \underset{\text{Eigenfunction}}{\psi} = \underset{\text{Eigenvalue}}{a}\psi$

Ex. $\hat{p} = i\hbar\cdot\partial/\partial x$ Acting on $\psi = A\exp(ikx)$

$$i\hbar\cdot\partial/\partial x(A\exp(ikx)) = i\hbar\cdot Aik\exp(ikx)$$

$$= -A\hbar k\exp(ikx)$$

$$= -\hbar k\cdot\psi(x) = a\cdot\psi(x)$$

By operating on operation $\hat{p}$

$$\hat{p}\,\psi(x) = -\underbrace{\hbar k}_{\text{momentum}}\cdot\psi(x)$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z)+V(x,y,z)\cdot\psi(x,y,z)=E\psi(x,y,z)$$

$\downarrow$ ② Convert To eigen vector.

$\hat{H}\psi=E\psi$ where $\hat{H}=-\frac{\hbar^2}{2m}\nabla^2+V(x,y,z)$

$\downarrow$ ③ Spherical Coordinates

Ref: Introduction To quantum mechanics. – David Griffith.

Chap 4.1.1 Seperation Variables.

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

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

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

$$=\frac{1}{r^2}\cdot\left(2r\cdot\frac{\partial R}{\partial r}+\frac{\partial^2 R}{\partial r^2}\cdot r^2\right)Y+\frac{1}{r^2\sin\theta}\left(\cos\theta\cdot\frac{\partial Y}{\partial\theta}+\frac{\partial^2 Y}{\partial\theta^2}\sin\theta\right)R$$

$$+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\cdot R$$

$$=\left(\frac{2}{r}\frac{\partial R}{\partial r}+\frac{\partial^2 R}{\partial r^2}\right)Y+\left[\frac{1}{r^2}\cdot\cot\theta\cdot\frac{\partial Y}{\partial\theta}+\frac{1}{r^2}\cdot\frac{\partial^2 Y}{\partial\theta^2}+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right]\cdot R$$

TISE: $-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\cdot\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial R}{\partial r}\right)Y+\frac{1}{r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\cdot\frac{\partial Y}{\partial\theta}\right)R+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)R\right]$
$+VRY=ERY$

$\downarrow$ devide RY. Multiply $-2mr^2/\hbar^2$

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

★ only depend on r, ★ only depend on θ

each must be constant

$= $ Set as $l(l+1)$ $l \in \mathbb{Z}^*$. $= -l(l+1)$

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

★ Repeat Seperation $Y = \Theta(\theta)\,\Phi(\phi)$

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

only θ again, Assume $= m^2$ only ϕ $= -m^2$

$\downarrow$

$$\sin\theta\cdot\frac{d}{d\theta}\left(\sin\theta\cdot\frac{d\Theta}{d\theta}\right) + [l(l+1)\sin^2\theta - m^2]\Theta = 0$$

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

Legendre Formula:

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

Table 4.1: Some associated Legendre functions, $P_l^m(\cos\theta)$.

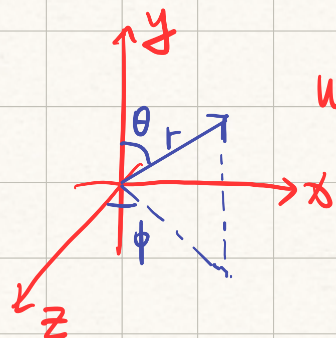
$P_1^1 = \sin\theta$	$P_3^3 = 15\sin\theta(1-\cos^2\theta)$
$P_1^0 = \cos\theta$	$P_3^2 = 15\sin^2\theta\cos\theta$
$P_2^2 = 3\sin^2\theta$	$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$
$P_2^1 = 3\sin\theta\cos\theta$	$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$
$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$	

(Griffith. P127 Table 4.1)

$\downarrow$

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \Rightarrow \Phi(\phi) = \exp(im\phi)$$

★ In polar coordinates.



when $\phi + 2\pi$. $\hat{r}$ no change

$$\Phi(\phi+2\pi) = \Phi(\phi)$$

$$\exp(im(\phi+2\pi)) = \exp(im\phi)$$

$$i\sin(m(\phi+2\pi)) = i\sin(m\phi)$$

$$\Rightarrow m \in \mathbb{Z} = 0, \pm1, \pm2 \cdots$$

Summary: ①. Seperation to function with $\Theta(\theta)$ $\Phi(\phi)$ $R(r)$

② Define $l(l+1)$ and $-l(l+1)$ where $l>0$

③ Define $m \in \mathbb{Z} = 0, \pm 1, \pm 2 \cdots$

④ Use Legender Polinomial $P_l^m(\cos\theta)$

☆ P_l^m if $|m|>l$ $P_l^m = 0$

$\Rightarrow l = 0, 1, 2 \cdots$ $m = -l, -l+1, \cdots -1, 0, 1, \cdots l-1, l$

Final Steps! ⑤ Normalize function

$$\int |\psi|^2 \cdot r^2 \sin\theta \, dr \, d\theta \, d\phi = \underbrace{\int |R|^2 \cdot r^2 \, dr}_{1} \cdot \underbrace{\int |Y|^2 \sin\theta \, d\theta \, d\phi}_{1} = 1$$

Y part : Several Math Stepts Even not include in this book

Table 4.2: The first few spherical harmonics, $Y_l^m(\theta, \phi)$.

$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$	$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$	$Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta \cos\theta e^{\pm 2i\phi}$
$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta e^{\pm i\phi}$	$Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\phi} P_l^m(\cos\theta),$$

(Griffith. P128 Table 4.2)

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

Solusion Conneet with $V(r)$

Finally $\psi = Y_l^m(\theta, \phi) \cdot R(r)$

Chap 4.1.3 Radiation Method. (only focus on $R(r)$)

☆ $Y(\theta, \phi)$ will be same for all spherically symmetric V

$$\partial/\partial r\,(r^2 \partial R/\partial r)\,1/R + (E-V)\frac{2mr^2}{\hbar^2} = l(l+1)R$$

★ Set $u(r) = r \cdot R(r)$

$R = u/r \qquad dR/dr = [r(du/dr) - u]/r^2 \qquad d/dr\,[r^2(dR/dr)] = r\,d^2u/dr^2$

Finally $-\hbar^2/2m \cdot d^2u/dr^2 + [V + \hbar^2/2m \cdot \frac{l(l+1)}{r^2}]u = Eu$

★ 1D Schd. Equation : $-\hbar^2/2m \cdot \partial^2\psi/\partial x^2 + V \cdot \psi = E\psi$

Normalize.

Further Step Require Specific $V(r)$.

difference only $V \rightarrow V + \underbrace{\hbar^2/2m \cdot \frac{l(l+1)}{r^2}}$

Centrifugal Term

Hydrogen Atom : $V(r) = -e^2/4\pi\varepsilon_0 \cdot 1/r$

$$-\hbar^2/2m \cdot d^2u/dr^2 + [-e^2/4\pi\varepsilon_0 r + \hbar^2/2m \cdot \frac{l(l+1)}{r^2}]u = Eu$$

$$-d^2u/dr^2 + [-\frac{e^2 2m}{4\pi\varepsilon_0 r\hbar^2} + \frac{l(l+1)}{r^2}]u = \frac{2mE}{\hbar^2} \cdot u$$

★ In bound State $E<0$ Set $k = \sqrt{-2mE}/\hbar$

$$[+\frac{e^2 2m}{4\pi\varepsilon_0 r\hbar^2} - \frac{l(l+1)}{r^2} + k^2]u = d^2u/dr^2$$

$$[\frac{e^2 m}{2\pi\varepsilon_0 r\hbar^2 \cdot k^2} - \frac{l(l+1)}{r^2 k^2} + 1]u = d^2u/dr^2 \cdot 1/k^2$$

Try Set $\rho = kr$, $q = \frac{me^2}{2\pi\varepsilon_0\hbar^2 k}$

$$[-q/\rho + \frac{l(l+1)}{\rho^2} + 1]u = d^2u/d\rho^2$$

☆ Try asymptotic $\rho\to\infty$ $\rho\to 0$

$d^2u/d\rho^2 = u$ $d^2u/d\rho^2 = \frac{l(l+1)}{\rho}\cdot u$

$\Rightarrow u = A\exp(-\rho) + \underbrace{B\exp(\rho)}_{\text{explode}}$ $\Rightarrow u(\rho) = C\cdot\rho^{l+1} + \underbrace{D\rho^{-l}}_{\text{explode}}$ ☆

$u \sim A\exp(-\rho)$ when faraway $u(\rho) \sim C\rho^{l+1}$ when close.

$u(\rho) = \exp(-\rho)\cdot\rho^{l+1}$. Sth function or Constant.

Set $u(\rho) = \exp(-\rho)\cdot\rho^{l+1}\cdot v(\rho)$ $\downarrow$ back to origion.

$$\rho\cdot d^2v/d\rho^2 + 2(l+1-\rho)\cdot dv/d\rho + [q-2(l+1)]v = 0.$$

☆ Assume $v = \sum_0^\infty a_j\rho^j$

$$dv/d\rho = \sum_0^\infty a_j\rho^{j-1}\cdot j = \sum_0^\infty (j+1)a_{j+1}\rho^j$$

$$d^2v/d\rho^2 = \sum_0^\infty j(j+1)a_{j+1}\rho^{j-1}$$

$$\sum_{j=0}^{\infty}\left\{\rho\cdot j(j+1)\cdot a_{j+1}\rho^{j-1} + 2(l+1-\rho)\cdot(j+1)\cdot a_{j+1}\rho^j + [q-2l-2]\cdot a_j\rho^j\right\} = 0$$

$\downarrow$

☆ $\frac{\sum a_{j+1}\rho^j}{\sum a_j\rho^j} = a_{j+1}$

$$j\cdot(j+1)\,a_{j+1} + 2(l+1)(j+1)\,a_{j+1} - 2j\,a_j + [q - 2(l+1)]\,a_j = 0$$

Finally $a_{j+1} = \left\{\dfrac{2(j+l+1)-q}{(j+1)(j+2l+2)}\right\} a_j$

For Large j (relate with $\rho\uparrow\uparrow$) $a_{j+1} \approx \dfrac{2j}{j^2} = 2/j$

$\Rightarrow a_j = 2^j/j! \cdot A$

★ In text book $j(j+1)$
$j+1$ part only prepare for Taylor Expansion

Trace back to $v(\rho) = A\cdot\sum_0^\infty 2^j/j!\,\rho^j$
$= Ae^{2\rho}$

$\Rightarrow u(\rho) = Ae^{\rho}\rho^{l+1}$ X Blows up at $l\uparrow\uparrow$

Function of a must Terminate at Some point : $a_{j_{max}+1} = 0$

$2(\underbrace{j_{max}+l+1}_{\text{define as } n}) - q = 0$

$q = 2n$

★ n so called priciple quantum number

For $E = -\hbar^2 k^2/2m = -me^4/8\pi^2\varepsilon_0\hbar^2 q^2$

$= -\left[\dfrac{m}{2\hbar^2}\left(\dfrac{e^2}{4\pi\varepsilon_0}\right)^2\right]\dfrac{1}{n^2} = E_1/n^2$ with $n = 1,2,3\ldots$

★ For $n=1$ $E_1 = -13.6\,eV$ Binding Energy

And r for $n=1 \Rightarrow 4\pi\varepsilon_0\hbar^2/me^2 = 0.529 \times 10^{-10}m$ — Bohr radius

Summary

0. Focus on $R(r)$ part in $\psi = R(r) \cdot Y(\theta, \phi)$ $\overset{l(l+1)}{=}$
2. Set $u(r)$ Split Centrifugal Terms.
3. Set k, $p = kr$, q to simplify
4. Approach by $p \to \infty / 0$ ☆ p Assume $=$ solution of $P(0) \cdot P(\infty) \cdot V(p)$
5. ☆ Assume $V(p) = \sum_{0}^{\infty} a_j p^j$
6. Try anylaysis on $j \to \infty \Rightarrow$ Blows Up.
7. Set terminate point $n = (j_{max} + 1 + l)$

Further Step. Add $Y(r, \phi)$ Back

As we can see, $R(r)$ related to (n, l) Y on (l, m)

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) \cdot Y_l^m(\theta, \phi)$$

$$= 1/r \, p^{l+1} \exp(-p) \, V(p) \cdot Y_l^m(\theta, \phi)$$

☆ define $p = kr$ + $q = 2n = 2/ak$ for $a = 4\pi\varepsilon_0\hbar^2/me^2$

$\Rightarrow p = (1/na) r = r/na$

Ex. $\psi_{100}(r,\theta,\phi) = \underbrace{R_{10}(r)}\cdot \underbrace{Y_0^0(\theta,\phi)}$

[☆] $a_0/a \exp(-r/a)$

Constant Value : $1/\sqrt{4\pi}$

$\int R^2(r)\cdot dr = 1$ ← a_0 : sth. Constant.

$\Rightarrow \psi_{100}(r,\theta,\phi) = 1/\sqrt{\pi a^3} \exp(-r/a)$

vanish to $2/\sqrt{a}$

$R_{10} = 2/\sqrt{2a}\cdot \exp(-r/a)$

[☆] : $R_{10}(r) = 1/r\,(r/a)^1 \exp(-r/a)\cdot \underbrace{V(-r/a)}$

$V(-r/a) = \sum_0^j \sum a_j (r/a)^j$

where terminate at

$(j_{max} = n-l-1) = 0$

only a_0 exsist.

$= a_0/a \cdot \exp(-r/a)$

[why l, m define as angular / magnetic number ?]

$\hat{L} = -i\hbar\cdot(\hat{r}\times\nabla)$

$\hat{L}(Y_l^m(\theta,\phi)) = \hbar^2[\underbrace{l(l+1)}]\cdot Y_l^m$

Angular momentum

$\hat{L}_z = -i\hbar(\hat{r}\times\nabla_z)$

$\hat{L}_z \Phi_m = \hbar \underbrace{m} \Phi(\phi)$

Angular momentum in z

$n > l \geq |m|$

$n = 1, 2 \cdots \infty$

$l = 0, 1, 2 \cdots (n-1)$

$m = 0, \pm 1, \pm 2 \cdots \pm l$