Lect 10

3D hydrogen atom — Kepler problem

2D

+ 3D harmonic oscillator)

- A historically important problem. $V(r) = -e^2/r$

$\chi(r) = rR(r)$, that χ satisfies the radial Eq

$$\chi'' + \left[\frac{2m}{\hbar^2}\left(E + \frac{e^2}{r}\right) - \frac{l(l+1)}{r^2}\right]\chi = 0. \quad \text{and} \quad \chi(r) \xrightarrow{r\to 0} 0$$

QED scale unit: compton length $\frac{\hbar}{mc}$, energy $mc^2 = 0.5\,\text{Mev}$, velocity c

H-atom: electron bound state due to E-M interaction: $\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$

atomic length: Bohr radius $a = \frac{\hbar}{mc}\cdot\frac{1}{\alpha} = \frac{\hbar^2}{me^2} = 0.53\,\mathring{A}$

Ryderberg energy $E_{Ry} = mc^2 \cdot \alpha^2 = \frac{e^2}{a} = \frac{me^4}{\hbar^2} = 27.2\,\text{eV}$

velocity $v = \alpha c = e^2/\hbar$

$$\rightarrow \frac{d^2\chi}{dr^2} + \left[\left(\frac{2E/E_{Ry}}{a^2} + \frac{2}{ra}\right) - \frac{l(l+1)}{r^2}\right]\chi = 0$$

① The behavior of $\chi(r) \xrightarrow{r\to 0} r^{l+1}$ as analyzed in the last lecture.

② as $r\to\infty$, the leading contribution $\frac{2E/E_{Ry}}{a^2}$

$$\Rightarrow \chi \sim e^{-\sqrt{|2E/E_{Ry}|}\, r/a}, \quad \text{define } \beta = \sqrt{\frac{|2E|}{E_{Ry}}}\,\frac{1}{a}.$$

$$\sim e^{-\beta r}$$

- We define $\chi(r) = r^{l+1} e^{-\beta r} u(r)$ and find the equation that $u(r)$ satisfies.

$$\chi'(r) = (l+1)\, r^{l} e^{-\beta r} u(r) - \beta\, r^{l+1} e^{-\beta r} u(r) + r^{l+1} e^{-\beta r} u'(r)$$

$$\begin{aligned}\chi''(r) = {} & (l+1)l\, r^{l-1} e^{-\beta r} u(r) - \beta(l+1)\, r^{l} e^{-\beta r} u(r) + (l+1)\, r^{l} e^{-\beta r} u'(r) \\ & - \beta(l+1)\, r^{l} e^{-\beta r} u(r) + \beta^2 r^{l+1} e^{-\beta r} u(r) - \beta\, r^{l+1} e^{-\beta r} u'(r) \\ & + (l+1)\, r^{l} e^{-\beta r} u'(r) - \beta\, r^{l+1} e^{-\beta r} u'(r) + r^{l+1} e^{-\beta r} u''(r) \\ = {} & r^{l+1} e^{-\beta r} u''(r) + \left[2(l+1) - 2\beta r\right] r^{l} e^{-\beta r} u'(r) \\ & + \left[l(l+1) - 2\beta r(l+1) + \beta^2 r^2 \right] r^{l-1} e^{-\beta r} u(r)\end{aligned}$$

$$\Rightarrow \quad r u''(r) + \left[2(l+1) - 2\beta r\right] u'(r) - 2\left[(l+1)\beta - 1\right] u = 0$$

define $\xi = 2\beta r \quad \Rightarrow \quad \dfrac{du(r)}{dr} = \dfrac{du(\xi)}{d\xi} \cdot 2\beta$

$$\frac{d^2 u(r)}{d^2 r} = \frac{d^2 u(\xi)}{d\xi^2} (2\beta)^2$$

$$(2\beta)^2 r \frac{d^2 u(\xi)}{d\xi^2} + 2\beta\left[2(l+1) - 2\beta r\right] \frac{du(\xi)}{d\xi} - 2\left[(l+1)\beta - \frac{1}{a}\right] u(\xi) = 0$$

$$\xi \frac{d^2 u}{d\xi^2} + \left[2(l+1) - \xi\right] \frac{du(\xi)}{d\xi} - \left[(l+1) - \frac{1}{\beta a}\right] u(\xi) = 0$$

Compare with the confluent hyper-geometry Eq

$$\boxed{\xi \frac{d^2 u}{d\xi^2} + (\gamma - \xi) \frac{du}{d\xi} - \alpha u = 0, \quad \text{with} \quad \begin{aligned} \gamma &= 2(l+1) \\ \alpha &= l+1 - 1/\beta a. \end{aligned}}$$

Solution $\quad u = F(\alpha, \gamma, \xi) = 1 + \dfrac{\alpha}{\gamma}\xi + \dfrac{\alpha(\alpha+1)}{\gamma(\gamma+1)} \dfrac{\xi^2}{2!} + \cdots + \dfrac{\alpha(\alpha+1)\cdots(\alpha+n-1)}{\gamma(\gamma+1)\cdots(\gamma+n-1)} \dfrac{\xi^n}{n!} + \cdots$

$\longrightarrow e^{\xi}$ for generic values of α

but for the case $\alpha = -n_r$, $n_r = 0, 1, 2, \cdots$,

the above series ~~trancate~~ at the order of n_r

$$\Rightarrow F(-n_r, \gamma, \xi) = 1 + \frac{(-n_r)}{\gamma}\xi + \cdots + \frac{(-n_r)\cdots(-1)}{\gamma(\gamma+1)\cdots(\gamma+n-1)} \frac{\xi^{n_r}}{n_r!}$$

$$\alpha = l+1 - \frac{1}{\beta a} = -n_r \Rightarrow l+1+n_r = \frac{1}{\beta a} = n = 1,2,3\cdots$$

$$\Rightarrow E_n = -\frac{(\beta a)^2}{2} E_{Ry} = -\frac{1}{2n^2} E_{Ry}, \quad \boxed{n = 1,2,3,\cdots}.$$

degeneracy: $\left.\begin{array}{l} n_r = 0, 1, \cdots \; n-1 \\ l = n-1, \cdots \; 0 \end{array}\right\} \Rightarrow g = 1+3+\cdots 2n-1 = n^2$.

$$R_{n_r, l} \sim r^l e^{-\beta r} F(-n_r, 2l+2, 2\beta r), \quad \beta = \frac{1}{na}$$

$$\psi_{n,l,m}(r,\theta,\varphi) = R_{n,l}(r) Y_{lm}(\theta,\varphi)$$

$$R_{nl}(r) = \frac{2}{a^{3/2} n^2 (2l+1)!} \sqrt{\frac{(n+l)!}{(n-l-1)!}} \left(\frac{2r}{na}\right)^l e^{-\frac{r}{na}} F\left[-(n-1-l), 2l+2, \frac{2r}{na}\right]$$

Hydrogen wavefunction.

For example: $n=1$ $\quad R_{10} = \frac{2}{a^{3/2}} e^{-r/a}$

$n=2$ $\quad R_{20} = \frac{1}{\sqrt{2} a^{3/2}} \left(1 - \frac{r}{2a}\right) e^{-r/2a}$

$$R_{21} = \frac{1}{2\sqrt{6} a^{3/2}} \frac{r}{a} e^{-r/2a}$$

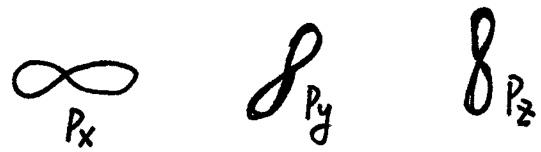
Why the degeneracy number is n^2? This cannot be explained by the rotation symmety itself. In fact. 3D Klepner problem has SO(4) sym- more conserved quantity — Runge-Lentz vector. (will be explained later)

① Exercise: Prove that if for a set of state with the same "l", $\psi_{n,l,m} = R_{n_r,l} Y_{lm}$, the sum of their ~~density~~ probility is isotropic. i.e.

$$\sum_{m=-l}^{l} Y_{lm}^*(\theta,\varphi)\, Y_{lm}(\theta,\varphi) = \text{const} = \frac{l+1}{4\pi}.$$

② angular distribution

p-orbit



$$Y_{11} = -\sqrt{\frac{3}{8\pi}}\,(x+iy)$$
$$Y_{10} = \sqrt{\frac{3}{4\pi}}\,z$$
$$Y_{1-1} = \sqrt{\frac{3}{8\pi}}\,(x-iy)$$

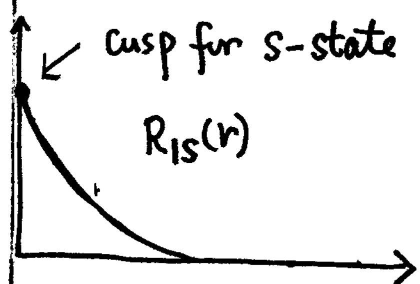
d-orbit $\quad d_{x^2-y^2} \quad d_{xy},\ d_{yz},\ d_{xz}$

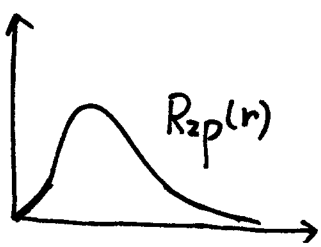
$d_{r^2-3z^2}$

$$Y_{2\pm2} = \frac{1}{2}\sqrt{15/8\pi}\,(x\pm iy)^2, \quad Y_{2,\pm1} = \mp\sqrt{15/8\pi}\,(x+iy)z,$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}}\,(2z^2-x^2-y^2)$$

③ radial ~~densi~~ wavefunction





....

3D harmonic oscillator $V(r) = \frac{1}{2} m\omega^2 r^2$, $\ell_0 = \sqrt{\frac{\hbar}{m\omega}}$

- Radial equation:

$$\begin{cases} \frac{d^2}{dr^2}\chi + \left[\frac{2m}{\hbar^2}\left(E - \frac{1}{2}m\omega^2 r^2\right) - \frac{\ell(\ell+1)}{r^2}\right]\chi = 0. \\ \chi = r R(r) \end{cases}$$

$$\frac{d^2}{dr^2}\chi + \left[\frac{2E/\hbar\omega}{\ell_0^2} - \frac{r^2}{\ell_0^4} - \frac{\ell(\ell+1)}{r^2}\right]\chi = 0$$

① behavior $\chi(r) \xrightarrow{r\to 0} r^{\ell+1}$ as before

② as $r \to +\infty$, $\chi(r) \sim e^{-\frac{r^2}{2\ell_0^2}}$

we define $\chi(r) = r^{\ell+1} e^{-\frac{r^2}{2\ell_0^2}} u(r)$.

no longer r-dependent!

- $$\to \frac{d^2u}{dr^2} + \underbrace{\left[\frac{2(\ell+1)}{r} - \frac{2r}{\ell_0^2}\right]}_{r\text{-dependent}}\frac{du}{dr} + \left[\frac{2E/\hbar\omega}{\ell_0^2} - \frac{2\ell+3}{\ell_0^2}\right]u = 0$$

then set $\xi = r^2/\ell_0^2$, $\Rightarrow \frac{du}{dr} = \frac{du}{d\xi}\frac{2r}{\ell_0^2}$, $\frac{d^2u}{dr^2} = \frac{d^2u}{d\xi^2}\left(\frac{2r}{\ell_0^2}\right)^2 + \frac{du}{d\xi}\frac{2}{\ell_0^2}$

$$\Rightarrow \frac{\xi}{\ell_0^2}\frac{d^2u}{d\xi^2} + \left[\frac{\ell+3/2}{\ell_0^2} - \frac{\xi}{\ell_0^2}\right]\frac{du}{d\xi} + \left[\frac{E/\hbar\omega}{2\ell_0^2} - \frac{\ell+3/2}{2\ell_0^2}\right]u = 0 \qquad = \frac{d^2u}{d\xi^2}\frac{4\xi}{\ell_0^2} + \frac{du}{d\xi}\frac{2}{\ell_0^2}$$

$$\to \xi\frac{d^2u}{d\xi^2} + \left[(\ell+3/2) - \xi\right]\frac{du}{d\xi} + \left[\frac{E/\hbar\omega}{2} - \frac{\ell+3/2}{2}\right]u = 0$$

Confluent hyper-geometry Eq, $\gamma = \ell + 3/2$

$$\alpha = \frac{1}{2}\left[E/\hbar\omega - (\ell + 3/2)\right]$$

$2\ell_0^2$ $2\ell_0^2$

- when $\alpha = -n_r$ integer, we have trancate polynomial solution $\Rightarrow$

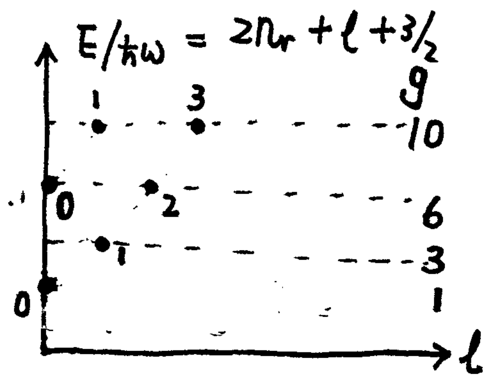
$$\frac{1}{2}\left[E/\hbar\omega - (\ell+3/2)\right] = n_r \Rightarrow E/\hbar\omega = 2n_r + \ell + 3/2 \quad \begin{pmatrix} n_r = 0, 1 \ldots \\ \ell = 0, 1, 2 \ldots \end{pmatrix}$$

$$\boxed{\begin{aligned} \psi_{n_r, lm}(r, \theta, \varphi) &= R_{n_r, l}(r)\, Y_{lm}(\theta, \varphi) \\ R_{n_r, l}(r) &= l_0^{-3/2} \left[\frac{2^{l+2-n_r}(2l+2n_r+1)!!}{\sqrt{\pi}\, n_r!\, [(2l+1)!!]^2} \right]^{1/2} \\ &\quad \times \left(\frac{r}{l_0}\right)^l e^{-\frac{r^2}{2l_0^2}} F\left[-n_r,\ l+3/2,\ \left(\frac{r}{l_0}\right)^2\right] \end{aligned}}$$

$$N = 2n_r + l \quad : \quad l = \begin{cases} 0, 2, \cdots N & \text{for } N \text{ is even} \\ 1, 3, \cdots N & \text{for } N \text{ is odd} \end{cases}$$

$$g = \begin{cases} \sum\limits_{\text{even}} (2l+1) \\ \sum\limits_{\text{odd}} (2l+1) \end{cases} = \frac{1}{2}(N+1)(N+2)$$

$$n_x + n_y + n_z = N \rightarrow g = \binom{N+2}{2}$$



§: 2D hydrogen atom

The 2D hydrogen atoms can be solved by slightly modifying the solution of the radial Eq of 3D case.

§ The 3D case : $\psi_{n_r,l,m}(r,\theta,\varphi) = R_{n_r,l}(r)\, Y_{lm}(\theta,\varphi)$

The radial Eq for $R_{n_r,l}(r)$ satisfies

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

normalization $\int_0^\infty R^*_{n_r,l}(r)\, R_{n_r',l}(r)\, r^2 dr = \delta_{n_r,n_r'}$

define $\chi_{n_r,l}(r) = r\, R_{n_r,l}(r) \Rightarrow$ effective 1D case

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

and $\int_0^\infty \chi^*_{n_r,l}(r)\, \chi_{n_r',l}(r)\, dr = \delta_{n_r n_r'}$

§ 2D: $\psi_{n_r,m}(r,\theta,\varphi) = R_{n_r,m}(r)\, e^{im\varphi}$

$$\left\{-\frac{\hbar^2}{2m}\left[\left(\frac{d^2}{dr^2}+\frac{d}{dr}\right)-\frac{|m|^2}{r^2}\right]+V(r)\right\} R_{n_r,m}(r) = E\, R_{n_r,m}(r)$$

normalization $\int_0^\infty R^*_{n_r,m}(r)\, R_{n_r',m}(r)\, r\, dr = \delta_{n_r n_r'}$

define $\chi_{n_r,m}(r) = r^{1/2} R_{n_r,m}(r)$

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

$$\int_0^\infty \chi^*_{n_r,m}(r)\, \chi_{n_r',m}(r)\, dr = \delta_{n_r n_r'}$$

Compare the Eqs of χ in 2D and 3D, $\Rightarrow$ we can related

$$\ell(\ell+1) \longleftrightarrow (m-1/2)(m+1/2),$$

i.e $\quad \ell = |m| - 1/2$.

for 3D:

$$E_n = -\frac{1}{2n^2} E_{Ry} \quad \text{with } n = n_r + \ell + 1$$

$\Rightarrow$ replace ℓ with $|m|-1/2$

2D $\quad n_{2D} = n_r + |m| + 1/2$, and $E_n^{2D} = -\frac{1}{2(n_r+|m|+1/2)^2} E_{Ry}$

$$\psi_{n_r,m}(r,\varphi) \sim e^{im\varphi} r^{|m|} e^{-r/(n_{2D}a)} F\left(-n_r, 2|m|+1, \frac{2r}{n_{2D}a}\right)$$

$n_{2D} = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots$

$g = 2n_{2D}$

degeneracy: $n_{2D} = 1/2 \Rightarrow n_r = m = 0$ $\quad$ 1

$3/2 \Rightarrow \left.\begin{matrix} n_r = 1 & m = 0 \\ n_r = 0 & m = \pm 1 \end{matrix}\right\}$ $\quad$ 3

$5/2 \Rightarrow \left.\begin{matrix} n_r = 2 & m = 0 \\ n_r = 1 & m = \pm 1 \\ n_r = 0 & m = \pm 2 \end{matrix}\right\}$ $\quad$ 5

The 2D hydrogen atom: the ground state energy is much lower $-2E_{Ry}$!

$$\left\{\begin{matrix} E_{2D} = -\frac{1}{2(n-1/2)^2} E_{Ry} \\ g = 2n-1 \end{matrix}\right. ; \quad \left\{\begin{matrix} E_{3D} = -\frac{1}{2n^2} E_{Ry} \\ g = n^2 \end{matrix}\right.$$