

lec 11. 3D hydrogen atom - Kepler problem

- A historically important problem. $V(r) = -\frac{e^2}{r}$ (3D harmonic oscillator)

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

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

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 $a = \frac{\hbar}{mc} \cdot \frac{1}{\alpha} = \frac{\hbar^2}{me^2} = 0.53 \text{ \AA}$

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

velocity $v = \alpha c = \frac{e^2}{\hbar}$

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

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

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

$\Rightarrow \chi \sim e^{-\sqrt{|2E/E_{Ry}|} r/a}$, 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.

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

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

$$\Rightarrow r u''(r) + [2(\ell+1) - 2\beta r] u'(r) - 2[(\ell+1)\beta - 1] u = 0$$

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

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

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

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

Compare with the confluent hyper-geometry Eq

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

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

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

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

the above series ~~truncates~~ truncate at the order of n_r

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

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

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

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

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

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

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

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 symmetry itself. In fact, 3D Kepler problem has $SO(4)$ sym. more conserved quantity — Runge-Lenz vector. (will be explained later)

① Exercise: Prove that if for a set of state with the same l , $\psi_{n,l,m} = R_{n,l} Y_{l,m}$,

the sum of their density probability is isotropic. i.e.

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

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② angular distribution

p-orbit



$$Y_{11} = -\sqrt{\frac{3}{8\pi}} (x+iy)$$

d-orbit

$$dx^2-y^2$$

$$dr^2-3z^2$$

$$dxy, dyz, dxz$$

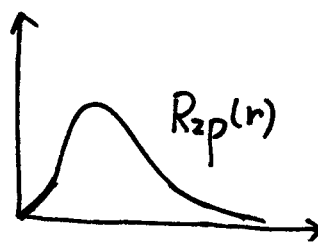
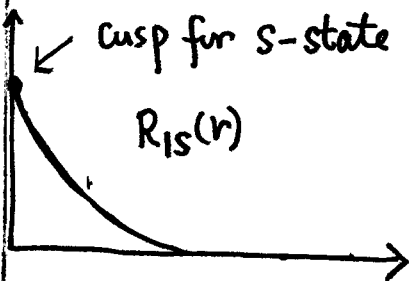
$$Y_{10} = \sqrt{\frac{3}{4\pi}} z$$

$$Y_{1-1} = \sqrt{\frac{3}{8\pi}} (x-iy)$$

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

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

③ radial ~~densi~~ wavefunction



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

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Radial equation: $\frac{d^2}{dr^2} \chi + \left[\frac{2m}{\hbar^2} (E - \frac{1}{2} m \omega^2 r^2) - \frac{l(l+1)}{r^2} \right] \chi = 0$.

$\chi = r R(r)$

$$\frac{d^2}{dr^2} \chi + \left[\frac{2E/\hbar\omega}{l_0^2} - \frac{r^2}{l_0^4} - \frac{l(l+1)}{r^2} \right] \chi = 0$$

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

② as $r \rightarrow +\infty$, $\chi(r) \sim e^{-\frac{r^2}{2l_0^2}}$

We define $\chi(r) = r^{l+1} e^{-\frac{r^2}{2l_0^2}} u(r)$.

no longer r -dependent!

$$\rightarrow \frac{d^2 u}{dr^2} + \underbrace{\left[\frac{2(l+1)}{r} - \frac{2r}{l_0^2} \right]}_{r\text{-dependent}} \frac{du}{dr} + \left[\frac{2E/\hbar\omega}{l_0^2} - \frac{2l+3}{l_0^2} \right] u = 0$$

then set $\xi = r^2/l_0^2$, $\Rightarrow \frac{du}{dr} = \frac{du}{d\xi} \frac{2r}{l_0^2}$, $\frac{d^2 u}{dr^2} = \frac{d^2 u}{d\xi^2} \left(\frac{2r}{l_0^2}\right)^2 + \frac{du}{d\xi} \frac{2}{l_0^2}$

$$\Rightarrow \frac{\xi}{l_0^2} \frac{d^2 u}{d\xi^2} + \left[\frac{l+3/2}{l_0^2} - \frac{\xi}{l_0^2} \right] \frac{du}{d\xi} + \left[\frac{E/\hbar\omega}{2l_0^2} - \frac{l+3/2}{2l_0^2} \right] u = 0 = \frac{d^2 u}{d\xi^2} \frac{4\xi}{l_0^2} + \frac{du}{d\xi} \frac{2}{l_0^2}$$

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

Confluent hyper-geometry Eq,

$$\gamma = l + 3/2$$

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

$2l_0^2$

$2l_0^2$

When $\alpha = -N_r$ integer, we have truncate polynomial solution \Rightarrow

$$\frac{1}{2} \left[\frac{E/\hbar\omega}{2} - (l+3/2) \right] = N_r \Rightarrow E/\hbar\omega = 2N_r + l + 3/2 \quad (N_r = 0, 1, \dots, l = 0, 1, 2, \dots)$$

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

$$R_{n_r, l}(r) = l_0^{-3/2} \left[\frac{2^{l+2-n_r} (2l+2n_r+1)!!}{\sqrt{\pi} n_r! [(2l+1)!!]^2} \right]^{1/2}$$

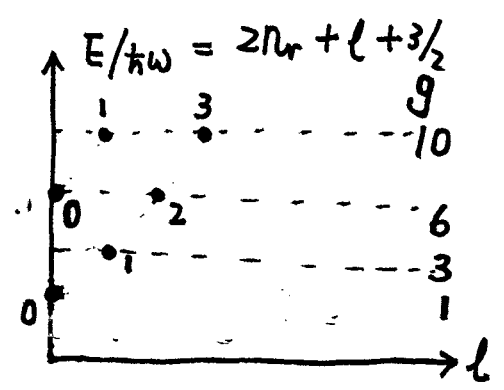
$$\times \left(\frac{r}{l_0}\right)^l e^{-\frac{r^2}{2l_0^2}} F\left[-n_r, l+3/2, \left(\frac{r}{l_0}\right)^2\right]$$

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

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

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



§

2D

hydrogen atom

①

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

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

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

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

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

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 $\int_0^\infty \chi_{n,r,l}^*(r) \chi_{n',r',l}(r) dr = \delta_{n,r,n'}$

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

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

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

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

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

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

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

$$l(l+1) \leftrightarrow (m-1/2)(m+1/2),$$

i.e $l = |m| - 1/2.$

for 3D:

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

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

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

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

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

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

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

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

$$g = 2n_{2D}$$

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

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