

Normalization conditions for 3D wave function

$$\iiint \psi^*(x, y, z) \psi(x, y, z) dx dy dz = 1$$

$$\Rightarrow \int_0^{2\pi} \int_0^\pi \int_0^\infty \psi^*(r, \theta, \phi) \psi(r, \theta, \phi) r^2 \sin \theta dr d\theta d\phi = 1$$

$$\Rightarrow \int_0^{2\pi} \int_0^\pi \int_0^\infty [R_{n\ell}(r) Y_{\ell m}(\theta, \phi)]^* [R_{n\ell}(r) Y_{\ell m}(\theta, \phi)] r^2 \sin \theta dr d\theta d\phi = 1$$

$$\Rightarrow \int_0^{2\pi} \int_0^\pi Y_{\ell m}^*(\theta, \phi) Y_{\ell m}(\theta, \phi) \sin \theta d\theta d\phi \int_0^\infty R_{n\ell}^*(r) R_{n\ell}(r) r^2 dr = 1$$

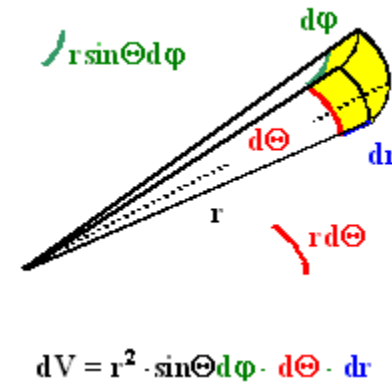
$$\Rightarrow \begin{cases} \int_0^{2\pi} \int_0^\pi Y_{\ell m}^*(\theta, \phi) Y_{\ell m}(\theta, \phi) \sin \theta d\theta d\phi = 1 \\ \int_0^\infty R_{n\ell}^*(r) R_{n\ell}(r) r^2 dr = 1 \end{cases}$$

With $R = \frac{u}{r}$

$$\int_0^\infty R_{n\ell}^*(r) R_{n\ell}(r) r^2 dr = 1 \Rightarrow \int_0^\infty u_{n\ell}^*(r) u_{n\ell}(r) dr = 1$$

For the normalization to be possible, we also know $R \rightarrow 0$ at least as fast as $\frac{1}{r}$ as $r \rightarrow \infty$

$$\therefore u(\infty) = 0$$



The hydrogen atom I (Text 8.2)

The central potential for hydrogen atom is the Coulomb potential:

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$$

Radial Schrodinger equation becomes :

$$-\frac{\hbar^2}{2\mu} \frac{d^2 u}{dr^2} + \left[-\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} + \frac{\hbar^2}{2\mu} \frac{\ell(\ell+1)}{r^2} \right] u = Eu$$

Introduce variable

$$\kappa = \frac{\sqrt{-2\mu E}}{\hbar} \quad (E < 0)$$

$$\rho = \kappa r$$

$$\begin{aligned} -\frac{\hbar^2}{2\mu} \frac{d^2 u}{dr^2} + \left[-\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} + \frac{\hbar^2}{2\mu} \frac{\ell(\ell+1)}{r^2} \right] u = Eu &\Rightarrow -\frac{\hbar^2}{2\mu} \kappa^2 \frac{d^2 u}{d\rho^2} + \left[-\frac{\kappa}{4\pi\epsilon_0} \frac{Ze^2}{\rho} + \frac{\hbar^2}{2\mu} \frac{\kappa^2 \ell(\ell+1)}{\rho^2} \right] u = Eu \\ &\Rightarrow \frac{d^2 u}{d\rho^2} - \frac{2\mu}{\hbar^2 \kappa^2} \left[-\frac{\kappa}{4\pi\epsilon_0} \frac{Ze^2}{\rho} + \frac{\hbar^2}{2\mu} \frac{\kappa^2 \ell(\ell+1)}{\rho^2} \right] u = \underbrace{-\frac{2\mu}{\hbar^2 \kappa^2} Eu}_{=u} \\ &\Rightarrow \frac{d^2 u}{d\rho^2} = \left(1 - \frac{Ze^2}{4\pi\epsilon_0} \frac{2\mu}{\kappa \hbar^2} \frac{1}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right) u \\ &\Rightarrow \frac{d^2 u}{d\rho^2} = \left(1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right) u \quad \rho_0 = \frac{\mu Ze^2}{2\pi\epsilon_0 \hbar^2 \kappa} \end{aligned}$$

The energy spectrum I (Text 8.2)

Asymptotic behaviors:

As $\rho \rightarrow \infty$, the differential equation becomes

$$\frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right] u \rightarrow \frac{d^2 u}{d\rho^2} = u$$

$$\therefore u = Ae^{\rho} + Be^{-\rho}$$

For finite u as $\rho \rightarrow \infty$, $A = 0$.

i.e. $u(r) \sim e^{-\rho}$ as $\rho \rightarrow \infty$.

Now consider $\rho \rightarrow 0$, the differential equation becomes

$$\frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right] u \rightarrow \frac{d^2 u}{d\rho^2} = \frac{d^2 u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u$$

Solution :

$$u = C\rho^{\ell+1} + D\rho^{-\ell}$$

For finite u as $\rho \rightarrow 0$, $D = 0$.

i.e. $u(r) \sim \rho^{\ell+1}$ as $\rho \rightarrow 0$.

$\therefore$ The radial wave function must be in the form $u(r) = \rho^{\ell+1} e^{-\rho} v(\rho)$

The energy spectrum II (Text 8.3)

Asymptotic behaviors:

As $\rho \rightarrow \infty$, the differential equation becomes

$$\frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right] u \rightarrow \frac{d^2 u}{d\rho^2} = u$$

$$\therefore u = Ae^{\rho} + Be^{-\rho}$$

For finite u as $\rho \rightarrow \infty$, $A = 0$.

i.e. $u(r) \sim e^{-\rho}$ as $\rho \rightarrow \infty$.

Now consider $\rho \rightarrow 0$, the differential equation becomes

$$\frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right] u \rightarrow \frac{d^2 u}{d\rho^2} = \frac{d^2 u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u$$

Solution :

$$u = C\rho^{\ell+1} + D\rho^{-\ell}$$

For finite u as $\rho \rightarrow 0$, $D = 0$.

i.e. $u(r) \sim \rho^{\ell+1}$ as $\rho \rightarrow 0$.

$\therefore$ The radial wave function must be in the form $u(r) = \rho^{\ell+1} e^{-\rho} v(\rho)$

Substitute this back to the original differential equation, we have (hand out) :

$$\rho \frac{d^2 v}{d\rho^2} + 2(\ell+1-\rho) \frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)]v = 0$$

The energy spectrum III (Text 8.3)

Series solution:

$$\text{Let } v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

$$\therefore \frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j'=0}^{\infty} (j'+1) c_{j'+1} \rho^{j'} \quad (j' = j-1) = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j$$

$$\frac{d^2 v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1}$$

$$\rho \frac{d^2 v}{d\rho^2} + 2(\ell+1-\rho) \frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)]v = 0$$

$$\Rightarrow \rho \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1} + 2(\ell+1-\rho) \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j + [\rho_0 - 2(\ell+1)] \sum_{j=0}^{\infty} c_j \rho^j = 0$$

$$\Rightarrow j(j+1) c_{j+1} + 2(\ell+1)(j+1) c_{j+1} - 2j c_j + [\rho_0 - 2(\ell+1)] c_j = 0$$

$$\Rightarrow j(j+1) c_{j+1} + 2(\ell+1)(j+1) c_{j+1} = 2j c_j - [\rho_0 - 2(\ell+1)] c_j$$

$$\Rightarrow c_{j+1} = \frac{2(\ell+1+j) - \rho_0}{j(j+1) + 2(\ell+1)(j+1)} c_j$$

$$\Rightarrow c_{j+1} = \frac{2(\ell+1+j) - \rho_0}{(j+2\ell+2)(j+1)} c_j$$

The energy spectrum IV (Text 8.3)

Termination of series $\Rightarrow$ Quantization of energy level (compare with the case of simple harmonic potential):

Note that for large j ,

$$c_{j+1} = \frac{2(\ell+1+j) - \rho_0}{(j+2\ell+2)(j+1)} c_j \approx \frac{2j}{j^2} c_j = \frac{2}{j} c_j$$

This is the same recurrence relationship for $e^{2\rho}$

Since $u = e^{-\rho} \rho^{\ell+1} v$, u will become $e^{\rho} \rho^{\ell+1}$ if we let v becomes an infinite series.

This mean we have to let $c_j = 0$ at some $j = j_{\max} + 1$ so that v is a finite series.

$$\text{i.e. } 2(\ell+1+j_{\max}) - \rho_0 = 0$$

$$\text{Let } n = \ell+1+j_{\max} \quad n = 1, 2, 3, \dots$$

$$\therefore 2n - \rho_0 = 0 \Rightarrow \rho_0 = 2n$$

$$\text{With } \rho_0 = \frac{Z\mu e^2}{2\pi\epsilon_0 \kappa \hbar^2}$$

$$\therefore \frac{Z\mu e^2}{2\pi\epsilon_0 \kappa \hbar^2} = 2n \Rightarrow \kappa = \frac{Z\mu e^2}{4\pi\epsilon_0 n \hbar^2}$$

$$E = -\frac{\hbar^2 \kappa^2}{2\mu} = -\frac{Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \cdot \frac{1}{n^2} = -13.6 \text{eV} \frac{1}{n^2} \quad (\text{for } Z=1)$$

———— Same result as Bohr model.

The energy spectrum VI (Text 8.3)

Since $n = j_{\max} + \ell + 1 \Rightarrow j_{\max} = n - \ell - 1$

$$j_{\max} \geq 0 \Rightarrow n - \ell - 1 \geq 0$$

$$\Rightarrow \ell \leq n-1$$

So we now have three quantum numbers, n , ℓ , and m to label the orbital of an atom.

n	ℓ	Degeneracy
1	0(s)	1
2	0(s), 1(p)	1+3=4
3	0(s), 1(p), 2(d)	1+3+5=9
4	0(s), 1(p), 2(d),3(f)	1+3+5+7 =16

← Actual degeneracy is double of this value!

1 H																	2 He				
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne				
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar				
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr				
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe				
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn				
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Uun												

■ hydrogen

■ alkali metals

■ alkali earth metals

■ transition metals

■ poor metals

■ nonmetals

■ noble gases

■ rare earth metals

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr