# Normalization conditions for 3D wave function

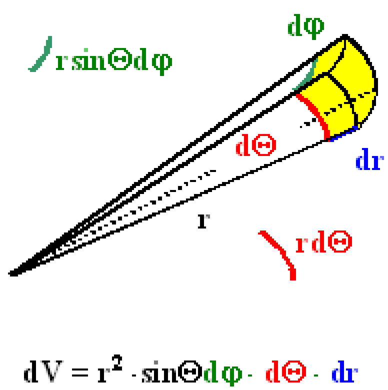
$$\iiint \psi^*(x,y,z)\psi(x,y,z)\,dxdydz = 1$$

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

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

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

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




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

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

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

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

# The hydrogen atom I (Text 8.2)

The central potential for hydrogen atom is the Coulomb potential:

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

Radial Schrodinger equation becomes:

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \left[-\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} + \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}\right]u = Eu$$

Introduce variable

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

$$\rho = \kappa r$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \left[-\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} + \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}\right]u = Eu \Rightarrow -\frac{\hbar^2}{2\mu}\kappa^2\frac{d^2u}{d\rho^2} + \left[-\frac{\kappa}{4\pi\varepsilon_0}\frac{Ze^2}{\rho} + \frac{\hbar^2}{2\mu}\frac{\kappa^2\ell(\ell+1)}{\rho^2}\right]u = Eu$$

$$\Rightarrow \frac{d^2u}{d\rho^2} - \frac{2\mu}{\hbar^2\kappa^2}\left[-\frac{\kappa}{4\pi\varepsilon_0}\frac{Ze^2}{\rho} + \frac{\hbar^2}{2\mu}\frac{\kappa^2\ell(\ell+1)}{\rho^2}\right]u = \underbrace{-\frac{2\mu}{\hbar^2\kappa^2}Eu}_{=u}$$

$$\Rightarrow \frac{d^2u}{d\rho^2} = \left(1 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{2\mu}{\kappa\hbar^2}\frac{1}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right)u$$

$$\Rightarrow \frac{d^2u}{d\rho^2} = \left(1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right)u \qquad \rho_0 = \frac{\mu Ze^2}{2\pi\varepsilon_0\hbar^2\kappa}$$

# The energy spectrum I (Text 8.2)

Asymptotic behaviors:

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

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

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

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

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

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

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

Solution:

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

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

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

$\therefore$ 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 $\rho \to \infty$, the differential equation becomes

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

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

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

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

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

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

Solution:

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

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

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

$\therefore$ 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):

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

# The energy spectrum III (Text 8.3)

Series solution:

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

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

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

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

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

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

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

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

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

# 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.

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

Let $n = \ell+1+j_{max}$ $\qquad n = 1,2,3,......$

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

With $\rho_0 = \dfrac{Z\mu e^2}{2\pi\varepsilon_0 \kappa\hbar^2}$

$$\therefore \frac{Z\mu e^2}{2\pi\varepsilon_0 \kappa\hbar^2} = 2n \Rightarrow \kappa = \frac{Z\mu e^2}{4\pi\varepsilon_0 n\hbar^2}$$

$$E = -\frac{\hbar^2\kappa^2}{2\mu} = -\frac{Z^2\mu e^4}{32\pi^2\varepsilon_0{}^2\hbar^2}\cdot\frac{1}{n^2} = -13.6\text{eV}\,\frac{1}{n^2} \quad (\text{for } Z=1)$$

—— Same result as Bohr model.

# The energy spectrum VI (Text 8.3)

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

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

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

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

| n | $\ell$ | 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!