(Lecture 9) Wave Mechanics : Hydrogen Atom

1. The Two-Body Problem

- 원자 내의 핵과 전자(Two-Body)의 운동에 대한 파동방정식

  particle 1 의 위치 (x_1, y_1, z_1)

  particle 2 의 위치 (x_2, y_2, z_2)

  Two-body wave function $\Psi(\vec{r}_1, \vec{r}_2)$ *or* $\Psi(x_1, y_1, z_1; x_2, y_2, z_2)$

(意味) $\Psi^*(\vec{r}_1, \vec{r}_2)\Psi(\vec{r}_1, \vec{r}_2)d\tau_1 d\tau_2$

= 입자 1 이 위치 $\vec{r}_1$ 주변의 volume $d\tau_1$ 내에 존재하며 (and) 입자 2 가 위치 $\vec{r}_2$ 주변의 volume $d\tau_2$ 내에 존재할 확률.

($d\tau_1 = dx_1\, dy_1\, dz_1$, $d\tau_2 = dx_2\, dy_2\, dz_2$ volume element)

입자 1 의 운동에너지 operator $-\dfrac{\hbar^2}{2m_1}\vec{\nabla}_1^2$ *i.e.* $-\dfrac{\hbar^2}{2m_1}\left(\dfrac{\partial^2}{\partial x_1^2} + \dfrac{\partial^2}{\partial y_1^2} + \dfrac{\partial^2}{\partial z_1^2}\right)$

입자 2 의 운동에너지 operator $-\dfrac{\hbar^2}{2m_2}\vec{\nabla}_2^2$

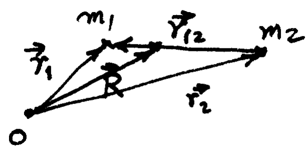
두 입자 간의 위치에너지 = 두 입자 간의 상호작용(interaction) 즉, 힘에 대응되는 potential energy는 입자 간 거리 r_{12}에만 의존하는 경우가 대부분 :

$$V = V(r_{12}) = V(|\vec{r}_1 - \vec{r}_2|)$$

- Schrődinger Eq. :

$$\left[-\frac{\hbar^2}{2m_1}\vec{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\vec{\nabla}_2^2 + V(r_{12})\right]\Psi(\vec{r}_1, \vec{r}_2) = E\Psi(\vec{r}_1, \vec{r}_2) \qquad (1)$$

좌표계 변환 $(\vec{r}_1, \vec{r}_2) \rightarrow (\vec{R}, \vec{r}_{12})$



$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} \qquad (\,C.M.\ \ coordinate) \qquad (2)$$

$$\vec{r}_{12} = \vec{r}_1 - \vec{r}_2 \qquad (\,relative\ \ coordinate) \qquad (3)$$

을 이용하면, $-\frac{\hbar^2}{2m_1}\vec{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\vec{\nabla}_2^2 = -\frac{\hbar^2}{2M}\vec{\nabla}_{CM}^2 - \frac{\hbar^2}{2\mu}\vec{\nabla}_{rel}^2$ (4)

여기서, $M = m_1 + m_2$, $\mu = \frac{m_1 m_2}{m_1 + m_2}$ 이고

$$\vec{\nabla}_{CM}^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}, \qquad \vec{R} \equiv (X, Y, Z)$$

$$\vec{\nabla}_{rel}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \qquad \vec{r}_{12} \equiv (x, y, z)$$

또한 $\Psi(\vec{r}_1, \vec{r}_2) = \Psi(\vec{R}, \vec{r}_{12}) = \psi_{CM}(\vec{R})\psi_{rel}(\vec{r}_{12})$ 로 표현하면

(1), (4)를 이용하여

$$-\frac{\hbar^2}{2M}\vec{\nabla}_{CM}^2 \psi_{CM}(\vec{R}) = E_{CM}\psi_{CM}(\vec{R}) \qquad (5)$$

$$-\frac{\hbar^2}{2\mu}\vec{\nabla}_{rel}^2 \psi_{rel}(\vec{r}_{12}) + V(r_{12})\psi_{rel}(\vec{r}_{12}) = E_{rel}\psi_{rel}(\vec{r}_{12}) \qquad (6)$$

로 (5), (6) 식으로 분리가 가능함.

또한 $E = E_{CM} + E_{rel}$

↑ ↑

C.M. motion 의 에너지 — relative motion 의 에너지

(物理的 상황)

→ CM motion : energy E_{CM}

수소원자 spectrum : electron 의 核에 대한 relative motion에 대한 energy 준위 구조.

← ψ_{rel}, E_{rel}

(5)식의 solution : $E_{CM} \geq 0$ 일때만 가능.

$$\psi_{CM}(\vec{R}) = const \times \exp i(k_x X + k_y Y + k_z Z) = const \times \exp i(\vec{k} \cdot \vec{R})$$

여기서 $k^2 \hbar^2 = 2ME_{CM}$

원자의 내부 구조 : ψ_{rel}, E_{rel} 에 관련 ← $V(r_{12})$ 에 기인.

2. The Schrődinger's Equation in Spherical Coordinates

Major interaction between the electron and the proton in the hydrogen atom : Electrostatic Coulomb potential

$$V(r_{12}) = V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

Other minor interactions :

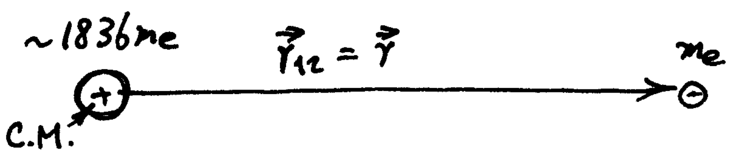
i) magnetic moment of electron in the magnetic field generated by the orbital motion

ii) relativistic effect

iii) spin (intrinsic spin)

iv) quantum-electrodynamic effect

v) magnetic moment of electron interacting with the nuclear magnetic moment



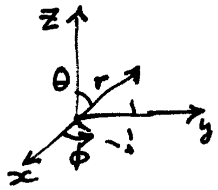
(x, y, z) Cartesian coordinate $V(x,y,z) = -\frac{Ze^2}{4\pi\varepsilon_0} \cdot \frac{1}{\sqrt{x^2+y^2+z^2}}$

$$\hat{T} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right), \qquad \mu = \frac{m_p m_e}{m_p + m_e} \cong m_e$$

(r, θ, ϕ) Spherical coordinate system

↑ spherically symmetric potential V=V(r) 이므로.

$$\begin{cases} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{cases}$$



By changing the Laplacian operator,

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}. \qquad (1)$$

- Total wave function $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$

(1)에 대입하여 정리하면

$$\begin{aligned}&\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}(E-V)R = \\ &\quad -\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = C(const)\end{aligned} \qquad (2)$$

$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$ 으로 두면

$$-\frac{1}{\Theta}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-C\sin^2\theta=\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=-m^2\ (let) \qquad (3)$$

$-m^2$ 으로 두는 이유 :

$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} < 0$ 이면 periodic solution for Φ,

> 0 이면 exponential solution for Φ.

ϕ는 0 와 2π 가 일치하므로 periodic solution 이 필요.

$\rightarrow \quad \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2 \quad \rightarrow \quad \Phi(\phi) = \exp(im\phi) \quad or \quad \exp(-im\phi)$

single-value $\Phi(\phi)$를 위해서는 $\Phi(\phi)=\Phi(\phi+2\pi)$로부터

$\exp(im\phi) = \exp(im(\phi+2\pi)) = \exp(im\phi)\cdot\exp(i2\pi m)$ or m=정수.

General solution : $\Phi(\phi) = A\exp(im\phi) + B\exp(-im\phi)$

m = positive or negative integer 이면

{exp($im\phi$), exp($-im\phi$)}는 { exp($im\phi$) }와 동일.

Θ-equation : $\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+(C\sin^2\theta-m^2)\Theta=0$

change of variables $\xi = \cos\theta$

$$\frac{d}{d\xi}\left((1-\xi^2)\frac{d\Theta}{d\xi}\right)+[C-\frac{m^2}{1-\xi^2}]\Theta=0 \qquad (4)$$

simplest solution for $m = 0$, $C = l(l+1)$ $(l = 0, 1, 2, \ldots)$

$$(4) \rightarrow \quad (1-\xi^2)\frac{d^2 P_l(\xi)}{d\xi^2} - 2\xi\frac{dP_l(\xi)}{d\xi} = -l(l+1)P_l(\xi) \tag{5}$$

Legendre differential equation

$P_l(\xi) = P_l(\cos\theta)$: Legendre polynomials

$l = 0$: $\Theta_0(\mathrm{m}=0) = P_0(\cos\theta) = 1$

$l = 1$: $\Theta_1(\mathrm{m}=0) = P_1(\cos\theta) = \cos\theta$

$l = 2$: $\Theta_2(\mathrm{m}=0) = P_2(\cos\theta) = 3\cos^2\theta - 1$ etc.

solution for non-zero m : associated Legendre polynomials(functions)

$$P_{lm}(\xi) = (1-\xi^2)^{m/2}\frac{d^m P_l(\xi)}{d\xi^m} = \Theta_{lm}(\theta) \tag{6}$$

Spherical harmonic functions : $Y_{lm}(\theta,\phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$

$$Y_{00} = \frac{1}{\sqrt{4\pi}},$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta \qquad Y_{1\pm1} = \sqrt{\frac{3}{8\pi}}\sin\theta\exp(\pm i\phi),$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \qquad Y_{2\pm1} = \sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta\exp(\pm i\phi)$$

$$Y_{2\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\exp(\pm 2i\phi),$$

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}\cdot\frac{(l-m)!}{(l+m)!}}\,P_{lm}(\cos\theta)\exp(im\phi) \tag{7}$$

where

$$P_{lm}(\cos\theta) = \frac{(-1)^m}{2^l l!}(1-\cos^2\theta)^{m/2}\frac{d^{l+m}}{d(\cos\theta)^{l+m}}(\cos^2\theta - 1)^l, \quad -l \le m \le +l \tag{8}$$

cf. The continental convention differs by sign for odd-m.

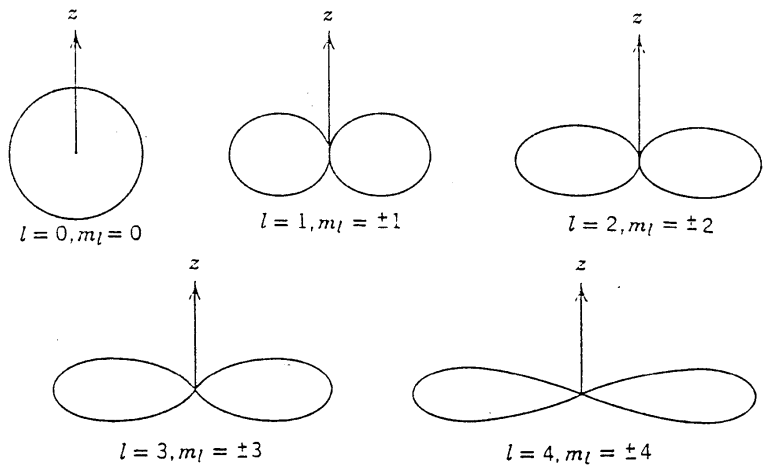


Figure 7-9 Polar diagrams of the directional dependence of the one-electron probability densities for $l = 0, 1, 2, 3, 4$; $m_l = \pm l$.

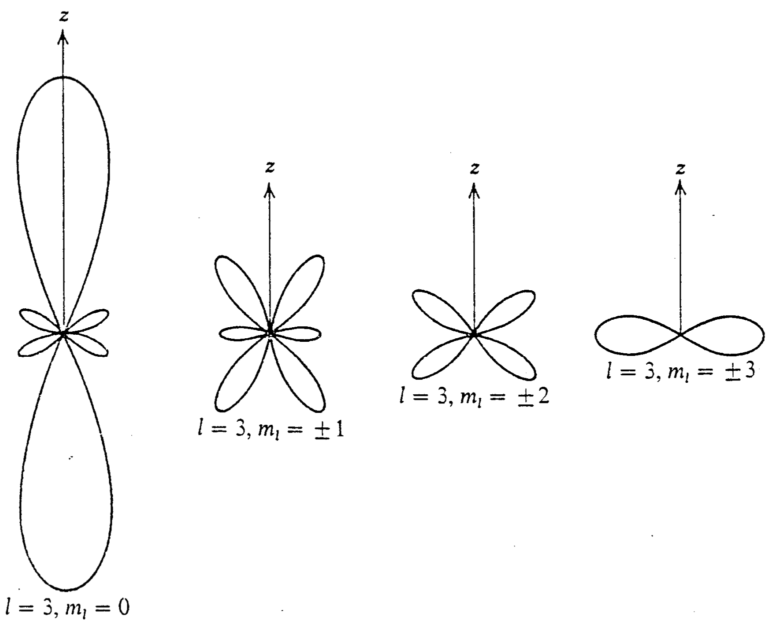


Figure 7-8 Polar diagrams of the directional dependence of the one-electron atom probability densities for $l = 3$; $m_l = 0, \pm 1, \pm 2, \pm 3$.

- Radial part of the wave equation :

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left(E-V-\frac{l(l+1)\hbar^2}{2\mu r^2}\right)R=0 \qquad (9)$$

$R(r)=\dfrac{u(r)}{r}$ 의 변형이 쉬운 해로 귀결됨.

$$\frac{d^2u(r)}{dr^2}+\frac{2\mu}{\hbar^2}\left(E-V(r)-\frac{l(l+1)\hbar^2}{2\mu r^2}\right)u(r)=0 \qquad (10)$$

(9), (10) : radial wave equation
(10)식은 1 차원 wave equation 과 유사.
Remind the Kepler problem in classical mechanics where the Hamiltonian is

$$H=\frac{p_r^2}{2m}+\frac{p_\theta^2}{2mr^2}+V(r) \quad \text{in } (r,\theta) \text{ coordinates.}$$

(10)식과 비교하면, $p_\theta^2=L^2=l(l+1)\hbar^2$

Hydrogen problem : $V(r)=-\dfrac{Ze^2}{4\pi\varepsilon_0 r}$

HO problem 의 경우와 유사한 과정으로 해를 구함 :

i) $r\to\infty$: $\dfrac{d^2u}{dr^2}+\dfrac{2\mu E}{\hbar^2}u=0$, $u\to exp(-\alpha r), exp(+\alpha r)$; $\alpha^2=-\dfrac{2\mu E}{\hbar^2}$ (E<0)

$exp(+\alpha r)$은 발산하므로 $u(r)\to exp(-\alpha r)$

ii) $r\to 0$: const. coeff. = $\dfrac{2\mu E}{\hbar^2}$, $1/r$ 관련항 = $\dfrac{2\mu}{\hbar^2}V(r)$에 비해

$1/r^2$ 관련항이 우세 → $\dfrac{d^2u}{dr^2}-\dfrac{l(l+1)}{r^2}u=0$

$u(r)=r^c(1+a_1r+a_2r^2+\cdots)$ 형의 해

lowest order term r^c 의 만족 : $c(c-1)r^{c-2}-l(l+1)r^{c-2}=0$

$c=l+1$ or $-l$

$r\to 0$: $u(r)\propto \; r^{l+1} \; or \; r^{-l}$

r^{-l} 은 r=0 주변에서 발산. r^{l+1} 채택.

따라서 $u(r)=r^{l+1}\exp(-\alpha r)F(r)$

F(r) 은 power series 형태이므로 HO 문제풀이에서처럼 수렴을 위해 truncation 조건을 구하면

$$E_n=-\frac{Ze^2}{4\pi\varepsilon_0}\cdot\frac{1}{2a_0}\cdot\frac{1}{n^2}, \qquad a_0=\frac{4\pi\varepsilon_0\hbar^2}{Ze^2\mu} \text{ (Bohr radius)}$$

이며, $n > l$ 인 integer (또는 $l \leq n$-1).

→ Bohr formula와 동일. m_e 대신 reduced mass μ.

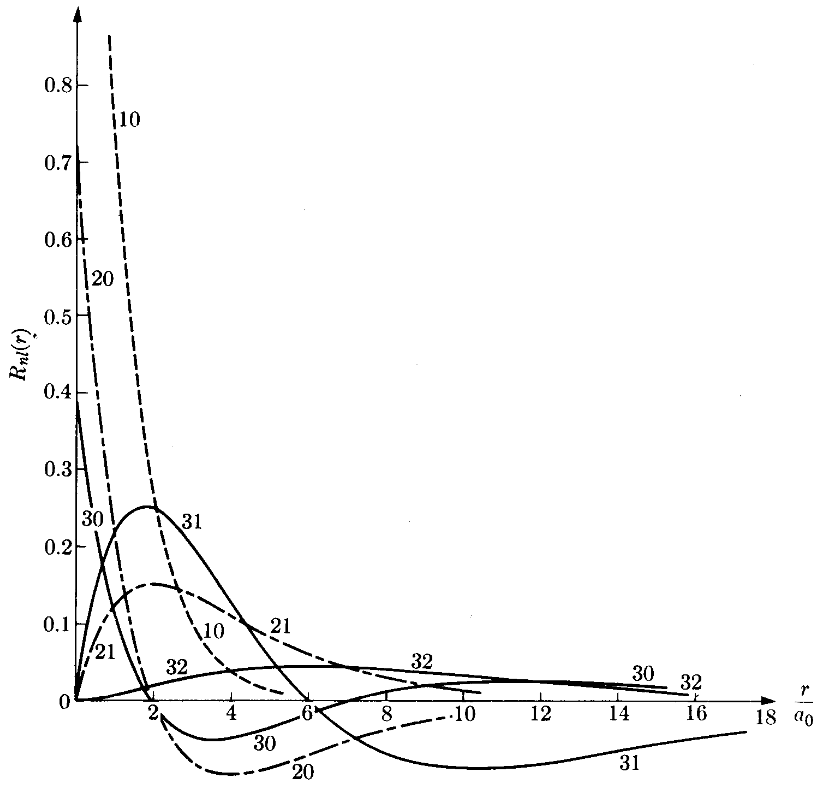


Fig. 7–4 The radial wave functions R_{nl} $(r)$for hydrogenic atoms for n = 1, 2, 3. Each curve is labeled with two integers, representing the corresponding n and l values. Note the effect of the centrifugal force in "pushing out" the wave function from the center of the atom. Note also that the functions have $n - l - 1$ nodes.

- Total wave function :

$$\Psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\phi) \quad or \quad \frac{u_{nl}(r)}{r}Y_{lm}(\theta,\phi)$$

Normalization : $\int \Psi^*\Psi d\tau = \iiint \Psi^*\Psi\ r^2 \sin\theta dr d\theta d\phi = 1$

By normalizing the radial and the spherical part, respectively,

$$\iint Y_{lm}^*(\theta,\phi)Y_{lm}(\theta,\phi)\sin\theta d\theta d\phi = 1 \quad \text{and}$$

$$\int_0^\infty R_{nl}^*(r)R_{nl}(r)r^2 dr = 1 \ \text{ 또는 } \ \int_0^\infty u_{nl}^*(r)u_{nl}(r)dr = 1.$$

Spherical harmonic function 은 이미 규격화되어 있으므로 radial wave function 을 규격화하여 상수를 결정함.

- Quantum numbers :

  n = 1, 2, 3, … principal quantum number (주양자수 主量子數)

  l = 0, 1, 2, … orbital angular momentum quantum number (궤도각운동량 양자수 軌道角運動量 量子數)

  m = -l, -l+1, …, l-1, l magnetic substate quantum number (자기부준위 양자수 磁氣副準位 量子數)

  l = 0, 1, 2, …에 따른 상태를 각각 s-, p-, d-, f-, … state 라 함.

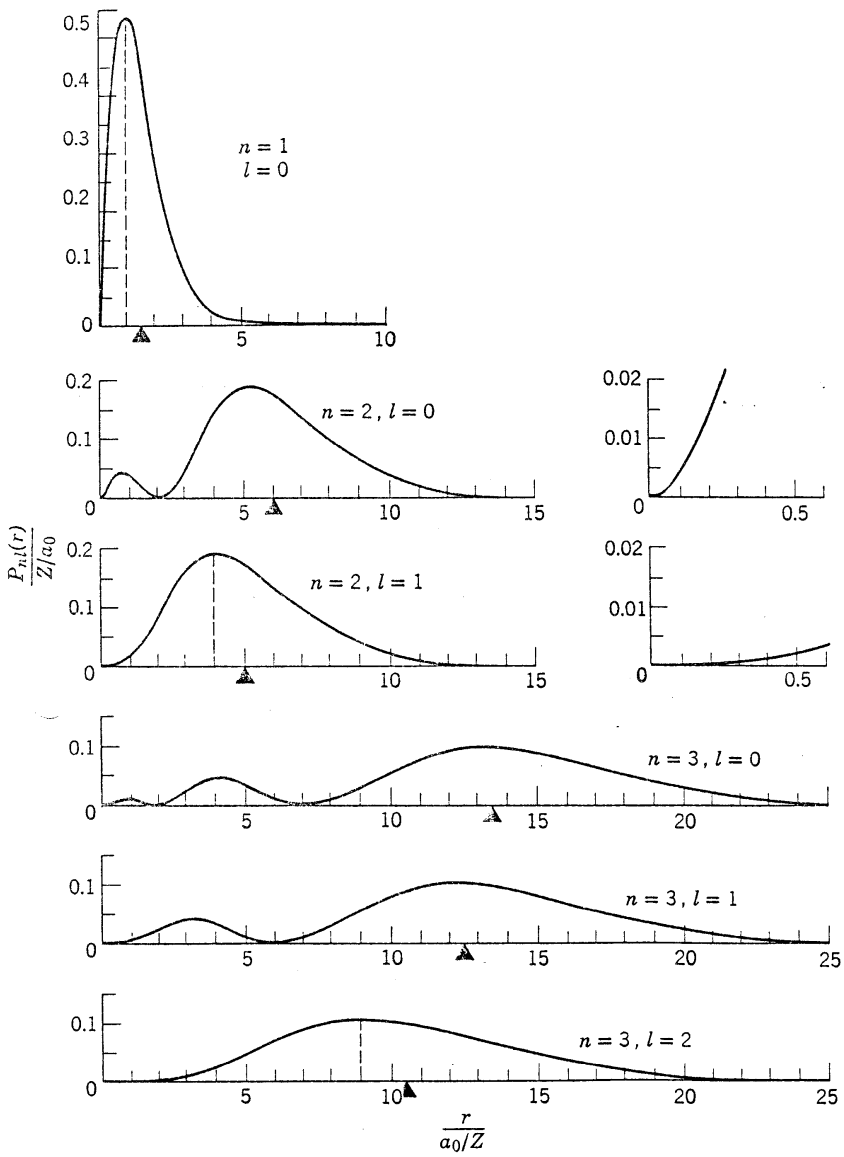


Figure 7-5 The radial probability density for the electron in a one-electron atom for n = 1, 2, 3 and the values of l shown. The triangle on each abscissa indicates the value of $\overline{r_{nl}}$ as given by (7-29). For $n = 2$ the plots are redrawn with abscissa and ordinate scales expanded by a factor of 10 to show the behavior of $P_{nl}(r)$ near the origin. Note that in the three cases for which $l = l_{max} = n - 1$ the maximum of $P_{nl}(r)$ occurs at $r_{Bohr} = n^2 a_0/Z$, which is indicated by the location of the dashed line.

3. Orbital Angular Momentum

- Classical mechanics : central force $\rightarrow V = V(r)$

  $\rightarrow$ conservation of orbital angular momentum $\vec{L} = \vec{r} \times \vec{p}$

  Quantum mechanics : orbital momentum operator

$$\hat{p} = -i\hbar\vec{\nabla} \text{ 로부터 } \quad \hat{L} = -i\hbar(\vec{r} \times \vec{\nabla}) \qquad (1)$$

Cartesian coordinates

$$\begin{aligned} \hat{L}_x &= -i\hbar\,(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}), \\ \hat{L}_y &= -i\hbar\,(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}), \\ \hat{L}_z &= -i\hbar\,(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}). \end{aligned} \qquad (2)$$

$\rightarrow$ Changing to the spherical coordinate system

$$\begin{aligned} \hat{L}_x &= +i\hbar\,(\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}), \\ \hat{L}_y &= -i\hbar\,(\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}), \\ \hat{L}_z &= -i\hbar\,\frac{\partial}{\partial\phi}. \end{aligned} \qquad (3)$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \qquad (4)$$

- Eigenvalues and eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$:

$$\hat{L}^2\psi_{nlm} = -\hbar^2 R_{nl}\underbrace{\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_{lm}}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y_{lm}}{\partial\phi^2}\right]}_{-l(l+1)Y_{lm}}$$

$$= \hbar^2 l(l+1)R_{nl}Y_{lm} = \hbar^2 l(l+1)\psi_{nlm}$$

$\rightarrow$ $\hat{L}^2$ eigenfunctions : $Y_{lm}(\theta,\phi)$, eigenvalues : $\hbar^2 l(l+1)$

또한 $\hat{L}_z\psi_{nlm} = R_{nl}(r)\Theta_{lm}(\theta)\left(-i\hbar\frac{d\Phi_m(\phi)}{d\phi}\right) = m\hbar R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi) = m\hbar\psi_{nlm}$

→ $\hat{L}_z$ eigenfunctions : $Y_{lm}(\theta,\phi)$ 또는 $e^{im\phi}$, eigenvalues $m\hbar$

m : magnetic (substate) quantum number = quantum number of the z-component of the orbital angular momentum

For a given l-state, $-l \leq m \leq +l$ ($2l+1$ possible states!)

$\hat{L}_x$, $\hat{L}_y$ 의 eigenstate 가 아니므로 eigenvalue 는 결정적이지 않음.

z-축의 선정 : 구대칭 상태 (spherical symmetric state)

즉, s-state(l=0) : $Y_{lm}(\theta,\phi) = Y_{00}(\theta,\phi) = const$ 의 경우는 상관 없음.

방향성이 존재하는 상태 : p, d, f, …states (l≠0)의 경우

$|Y_{lm}(\theta,\phi)|^2$ 의 plot 이용.

z-축은 구대칭 상태의 symmetry 축에 해당.

l : orbital angular momentum quantum number

- Parity of the state $\psi_{nlm}(\vec{r})$:

Definition --- positive(even) parity $\psi(-\vec{r}) = \psi(\vec{r})$

negative(odd) parity $\psi(-\vec{r}) = -\psi(\vec{r})$

$\vec{r} = (r, \theta, \phi) \quad \rightarrow \quad -\vec{r} = (r, \pi-\theta, \phi+\pi)$

$\psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\theta,\phi)$ 이므로 parity 는 $Y_{lm}(\theta,\phi)$ 에 의해 결정됨.

→ Angular dependency of the wave function

$Y_{lm}(\pi-\theta,\phi+\pi) = (-1)^l Y_{lm}(\theta,\phi)$ 이므로 parity = $(-1)^l$.

Bibliography :

(Basic)

1. R.H. Dicke and J.P. Wittke, Introduction to Quantum Mechanics, Reading, Addison-Wesley Publishing Company, Inc., 1960
2. P.T. Matthews, Introduction to Quantum Mechanics, New York, McGraw-Hill Publishing Company, 1963
3. R.L. White, Basic Quantum Mechanics, New York, McGraw-Hill Publishing Company, 1966

4. H.E. White, Introduction to Atomic Spectra, Singapore,McGraw-Hill International Inc., 1934

(Intermediate)

5. R. Eisberg and R. Resnick, Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles, 2nd Ed., New York, John Wiley & Sons Inc., 1974, 1985
6. A. Messiah, Quantum Mechanics, Vol. I, II, Amsterdam, North-Holland Publishing Company, 1962
7. J.J. Sakurai, Modern Quantum Mechanics, Menlo Park, The Benjamin/ Cummings Publishing Company, Inc., 1985
8. E.U. Condon and G.H. Shortley, The Theory of Atomic Spectra, Cambridge, The University Press, 1935, 1951