Applied Statistical Mechanics

Lecture Note - 3

Quantum Mechanics – Applications and Atomic Structures

Jeong Won Kang

Department of Chemical Engineering

Korea University

Subjects

- Three Basic Types of Motions (single particle)
  - Translational Motions
  - Vibrational Motions
  - Rotational Motions
- Atomic Structures
  - Electronic Structures of Atoms
  - One-electron atom / Many-electron atom

Free Translational Motion

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

OR

$$H\psi = E\psi$$

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

Solutions

$$\psi_k = Ae^{ikx} + Be^{-ikx} \qquad E_k = \frac{k^2\hbar^2}{2m}$$

- All values of energies are possible (all values of k)
- Momentum $e^{ikx} \rightarrow p_x = +k\hbar \qquad e^{-ikx} \rightarrow p_x = -k\hbar$
- Position → See next page

Probability Density

B = 0

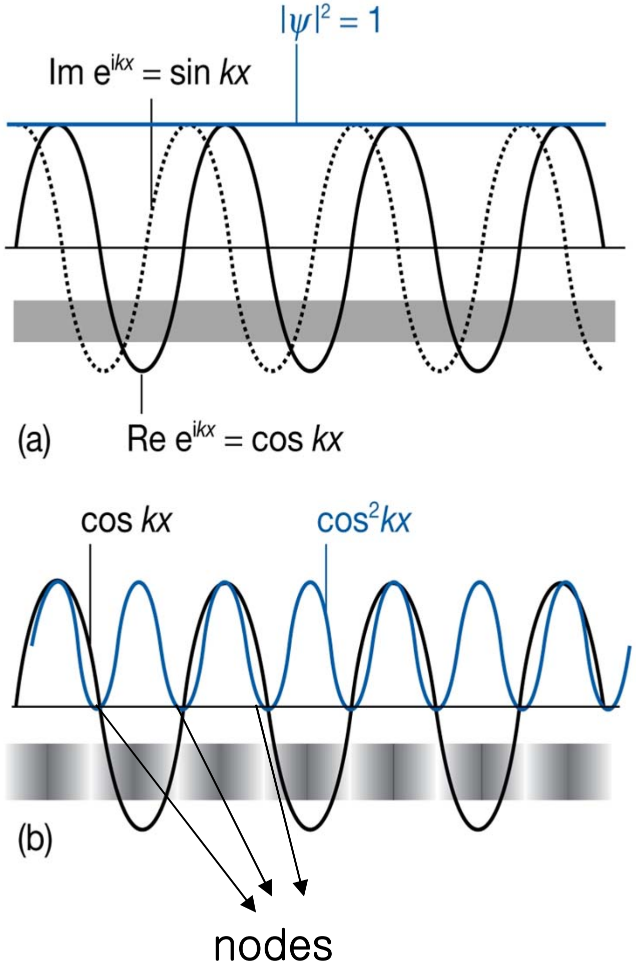
$$\psi = Ae^{ikx} \qquad |\psi|^2 = |A|^2$$

A = 0

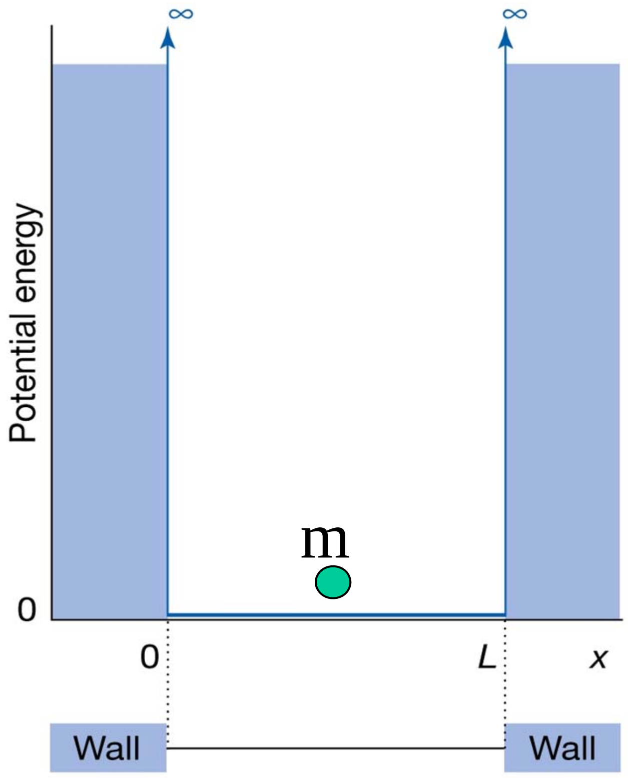
$$\psi = Be^{-ikx} \qquad |\psi|^2 = |B|^2$$

A = B

$$\psi = 2A\cos kx \qquad |\psi|^2 = 4|A|\cos^2 kx$$



A particle in a box



Consider a particle of mass *m* is confined between two walls

$$V = 0 \quad \text{for} \quad 0 < x < L$$

$$V = \infty \quad \text{for} \quad x = 0 \;\text{ and } x = L$$

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi}$$

$$\boxed{\psi_k = C\sin kx + D\cos kx \quad E_k = \frac{k^2\hbar^2}{2m}}$$

All the same solution as the free particle but with *different boundary condition*

A particle in a box

- Applying boundary condition

$$\psi_k = C\sin kx + D\cos kx$$

$$\psi(x=0)=0 \longrightarrow D=0$$

$$\psi(x=L)=0 \longrightarrow C\sin kL = 0 \longrightarrow kL = n\pi$$

$$\psi_n(x) = C\sin(n\pi x/L) \quad \mathrm{n}=1,2,3,\ldots \longrightarrow$$

n cannot be zero

- Normalization

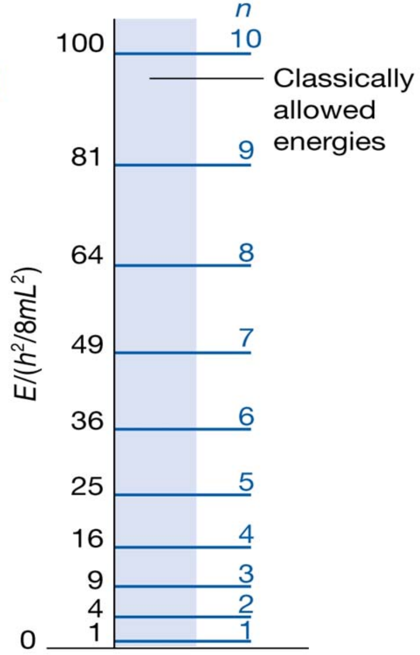
$$\int_0^L \psi_n{}^2 dx = C^2\int_0^L \sin^2(n\pi x/L)dx = \frac{C^2L}{2} = 1$$

$$C = \left(\frac{2}{L}\right)^{1/2} \qquad \psi_n(x) = \left(\frac{2}{L}\right)^{1/2}\sin(n\pi x/L) \quad \mathrm{n}=1,2,3,\ldots \qquad E_n = \frac{n^2h^2}{8mL}$$

A particle in a box
- Properties of the solutions

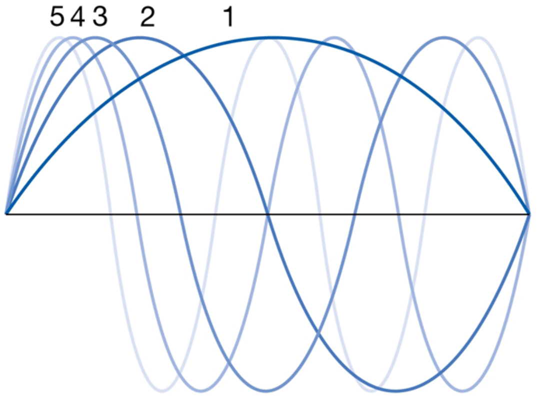
- ***n*** : Quantum number (allowable state)

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin(n\pi x/L) \quad \mathrm{n} = 1,2,3,...$$



- Momentum

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin(n\pi x/L) = \frac{1}{2i}\left(\frac{2}{L}\right)^{1/2} (e^{ikx} \text{-} e^{\text{-}ikx}) \quad k = \frac{n\pi}{L}$$



$$e^{ikx} \rightarrow p_x = +k\hbar$$

Probability : 1/2

$$e^{-ikx} \rightarrow p_x = -k\hbar$$

Probability : 1/2

A particle in a box
- Properties of the solutions

- ***n*** cannot be zero (*n* = *1,2,3,…*)
  - Lowest energy of a particle (zero-point energy)
  - If a particle is confined in a finite region (particle's location is not indefinite), momentum cannot be zero

$$E_1 = \frac{h^2}{8mL}$$

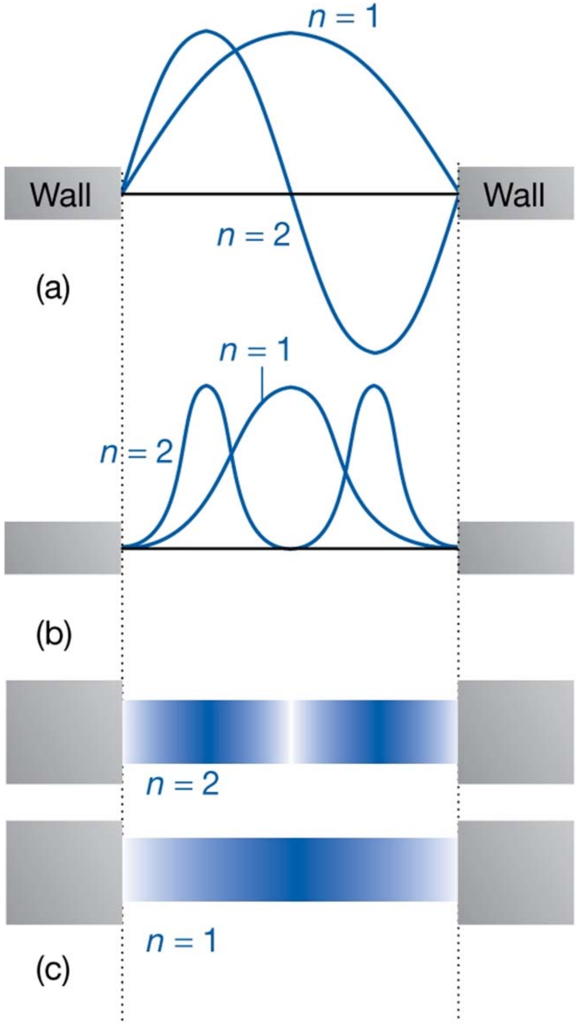
- If the wave function is to be zero at walls, but smooth, continuous and not zero everywhere, the it must be curved → *possession of kinetic energy*

Wave function and probability density

$$\psi^2(x) = \left(\frac{2}{L}\right)\sin^2(n\pi x / L)$$

With n→∞, more uniform distribution:
corresponds to classical prediction

"*correspondence principle*"



Orthogonality and bracket notation

Orthogonality

$$\boxed{\int \psi_n^* \psi_{n'} d\tau = 0}$$

⟶ *Wave functions corresponding to different energies are orthogonal*

Dirac Bracket Notation

$$\int \psi_n^* \psi_{n'} d\tau = \langle n | n' \rangle = 0 \qquad (n \neq n')$$

$$\langle n | n' \rangle = 0 \qquad \langle n | n \rangle = 1$$

<n| “BRA”

|n’> “KET”

$$\langle n | n' \rangle = \delta_{nn'} \longrightarrow \text{Kronecker delta}$$

Orthonormal

=Orthogonal + Normalized

Motion in two dimension

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)=E\psi$$ →

$$\psi(x,y)=X(x)Y(y)$$ →

Separation of Variables

$$-\frac{\hbar^2}{2m}\frac{d^2Y}{dx^2}=E_Y Y$$

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2}=E_X X$$

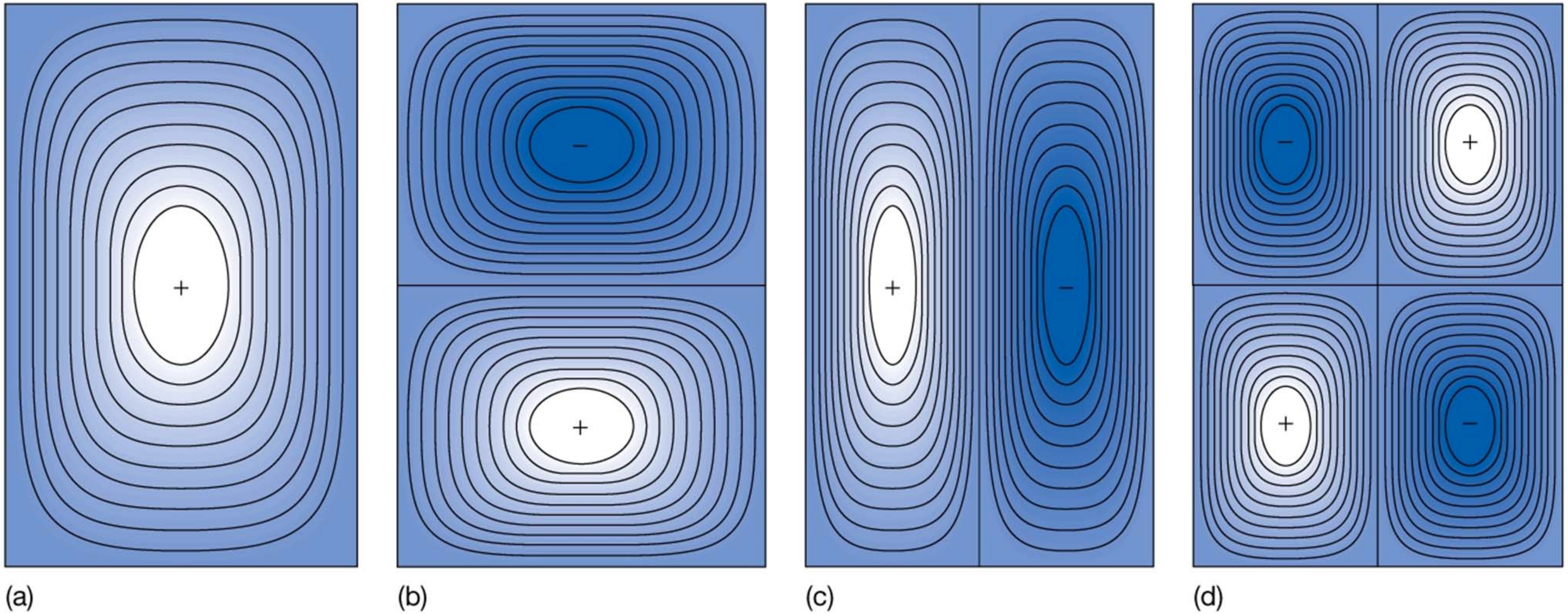
$$E=E_X+E_Y$$

Solution

$$X_{n_1}(x)=\left(\frac{2}{L_1}\right)^{1/2}\sin\frac{n_1\pi x}{L_1}\qquad Y_{n_2}(y)=\left(\frac{2}{L_2}\right)^{1/2}\sin\frac{n_2\pi y}{L_2}$$

$$\psi_{n_1,n_2}(x,y)=\left(\frac{2}{L_1}\right)^{1/2}\left(\frac{2}{L_2}\right)^{1/2}\sin\frac{n_1\pi x}{L_1}\sin\frac{n_2\pi y}{L_2}\qquad E_{n_1,n_2}=\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}\right)\frac{h^2}{2m}$$

The wave functions for a particle confined to a rectangular surface



$n_1 = 1, n_2 = 1$ $n_1 = 1, n_2 = 2$ $n_1 = 2, n_2 = 1$ $n_1 = 2, n_2 = 2$

Degeneracy

- Degenerate :
  - ☐ Two or more wave functions correspond to the same energy
  - ☐ If $L_1 = L_2$ then

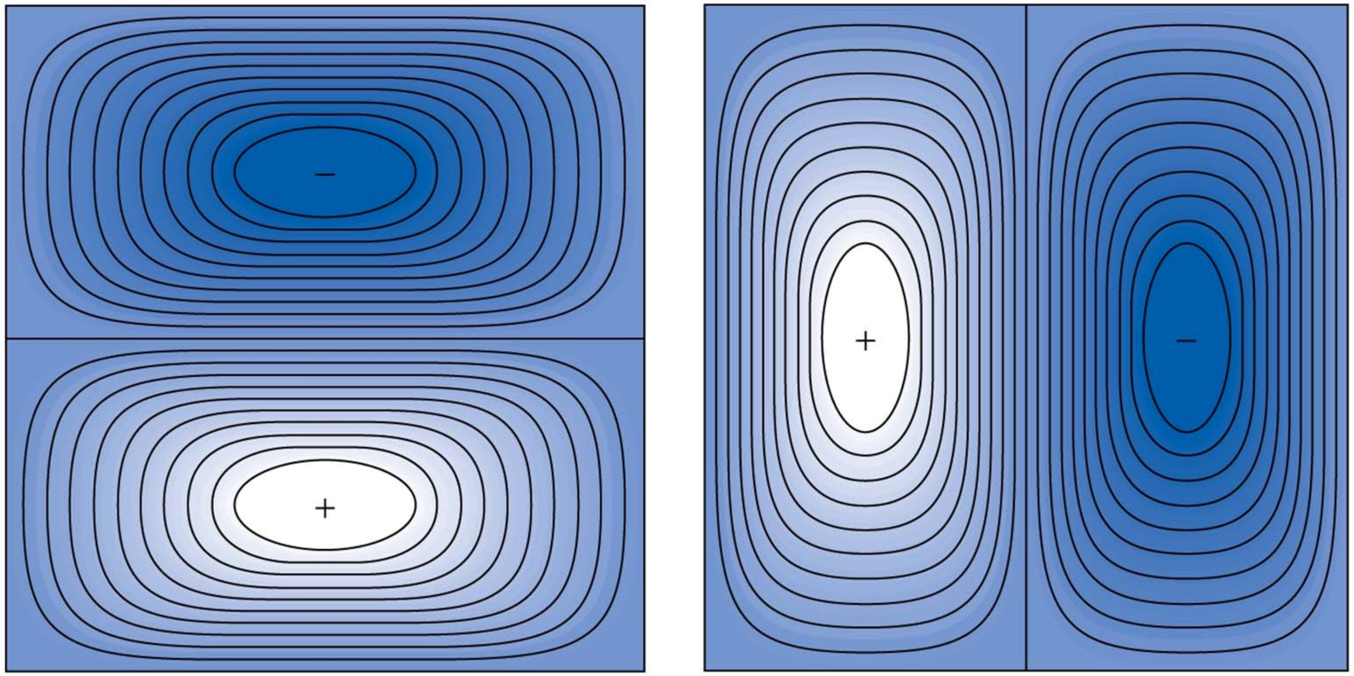
$$\psi_{1,2}(x,y) = \left(\frac{2}{L}\right)\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L}$$

$$\psi_{2,1}(x,y) = \left(\frac{2}{L}\right)\sin\frac{2\pi x}{L}\sin\frac{\pi y}{L}$$

$$\boxed{\begin{aligned} E_{1,2} &= \frac{5h^2}{8mL^2} \\ E_{2,1} &= \frac{5h^2}{8mL^2} \end{aligned}} \longrightarrow$$

the same energy with different wave functions

Degeneracy



$$\psi_{1,2}(x,y) = \left(\frac{2}{L}\right)\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L} \qquad \psi_{2,1}(x,y) = \left(\frac{2}{L}\right)\sin\frac{2\pi x}{L}\sin\frac{\pi y}{L}$$

if $L_1 \neq L_2$, the wave functions are not degenerate

$\longrightarrow$ The degeneracy can be traced to *the symmetry of the system*

Motion in three dimension

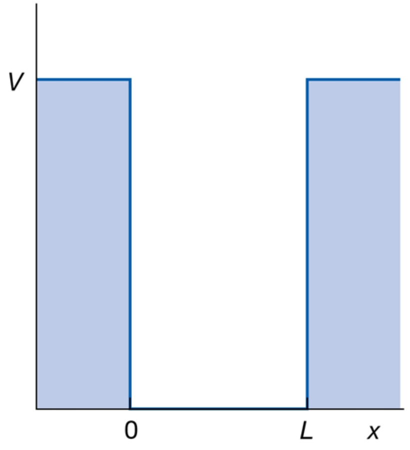
$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)=E\psi$$

Solution

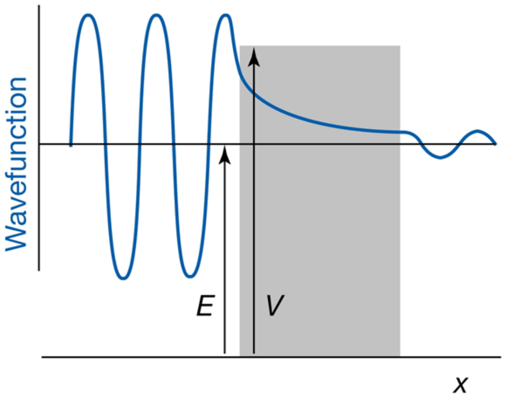
$$\psi_{n_1,n_2,n_3}(x,y,z)=\left(\frac{2}{L_1}\right)^{1/2}\left(\frac{2}{L_2}\right)^{1/2}\left(\frac{2}{L_3}\right)^{1/2}\sin\frac{n_1\pi x}{L_1}\sin\frac{n_2\pi y}{L_2}\sin\frac{n_3\pi y}{L_3}$$

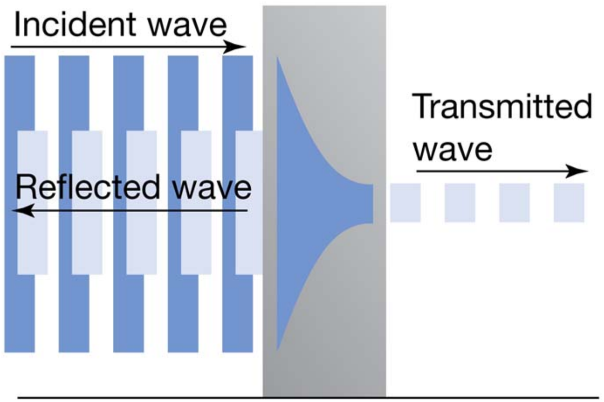
$$E_{n_1,n_2,n_3}=\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}+\frac{n_3^2}{L_3^2}\right)\frac{h^2}{2m}$$

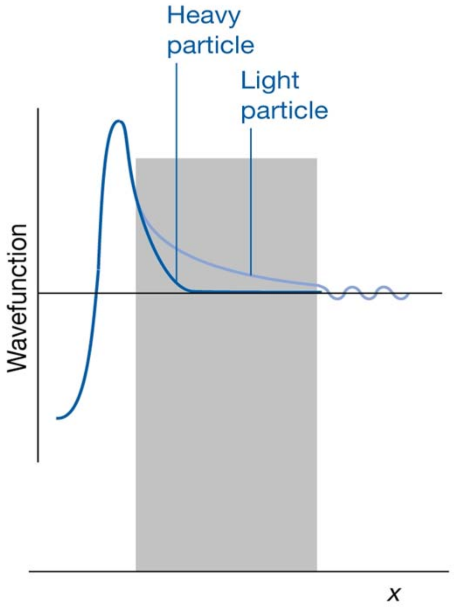
Tunneling



- **If the potential energy of a particle does not rise to infinity when it is in the wall of the container and E < V , the wave function does not decay to zero**
- **The particle might be found outside the container (leakage by penetration through forbidden zone)**

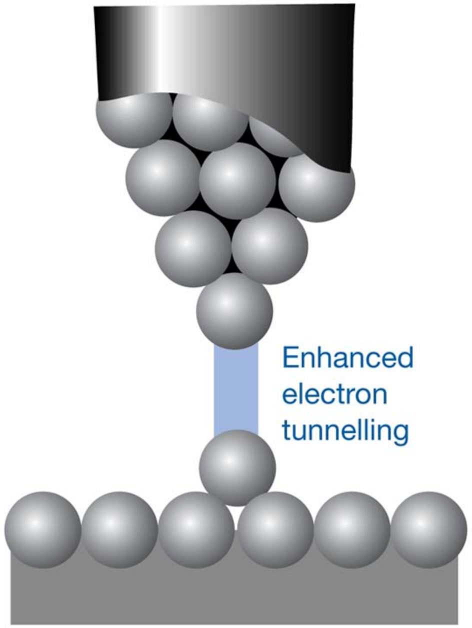


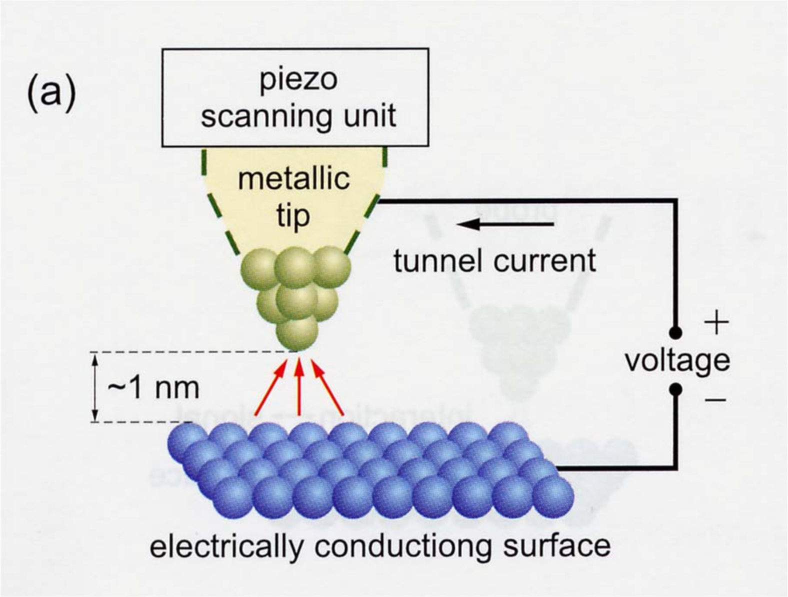


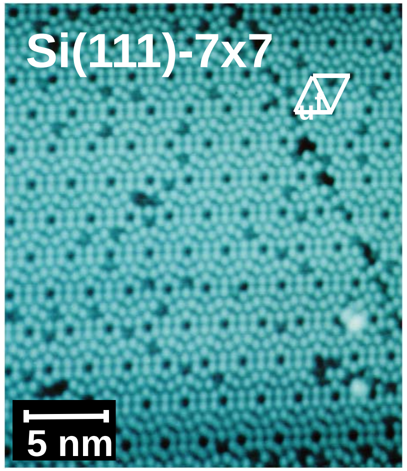


Use of tunneling

- STM (Scanning Tunneling Microscopy)







Vibrational Motion

- Harmonic Motion

$$F = -kx$$

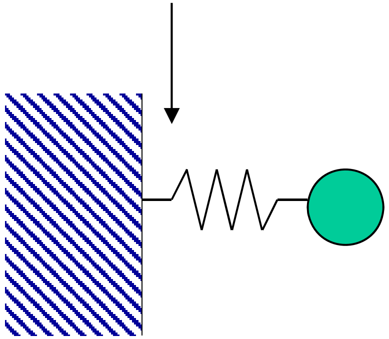
- Potential Energy

$$V = \frac{1}{2}kx^2$$

- Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2 = E\psi$$

k : force constant



reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Solutions

Wave Functions

$$\psi_v = N_v H_v(y) e^{-y^2/2} \qquad \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4} \qquad y = \frac{x}{\alpha}$$

Energy Levels

$$E_v = (v + \frac{1}{2})\hbar\omega \qquad \omega = \left(\frac{k}{m}\right)^{1/2} \qquad v = 0,1,2,\ldots$$

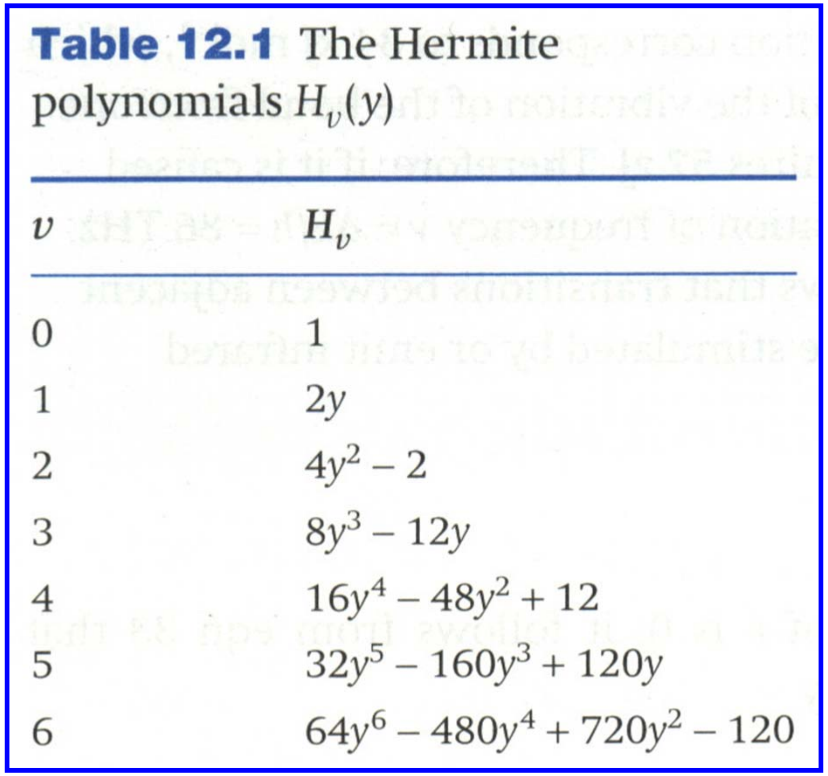


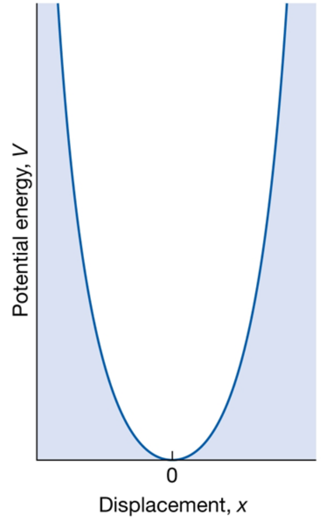
Table 12.1 The Hermite polynomials $H_v(y)$

v	H_v
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$

Energy Levels

Potential energy

$$V = \frac{1}{2}kx^2$$



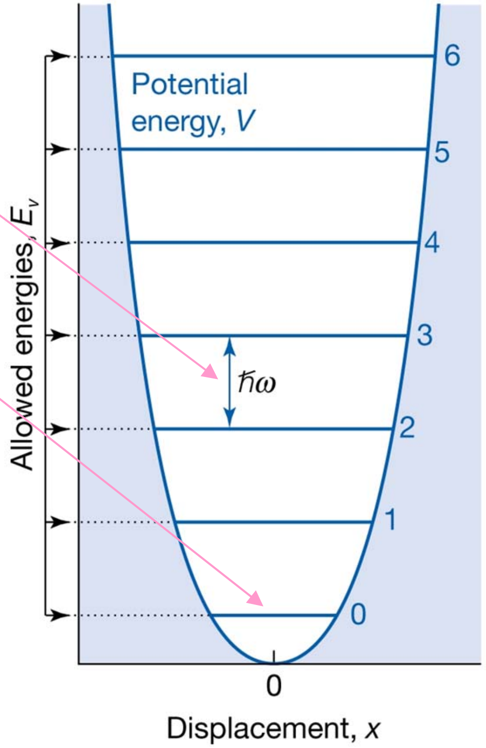
$$E_v = (v + \frac{1}{2})\hbar\omega \qquad \omega = \left(\frac{k}{m}\right)^{1/2} \qquad v = 0,1,2,...$$

Quantization of energy : comes from B.C

$$\psi_v = 0 \quad \text{at} \quad x = \pm\infty$$

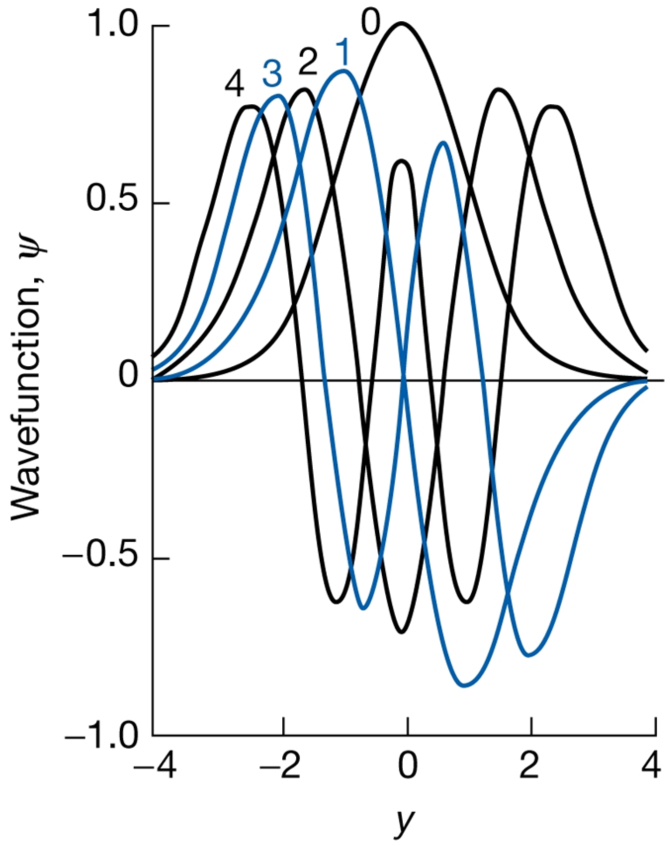
$$E_{v+1} - E_v = \hbar\omega$$

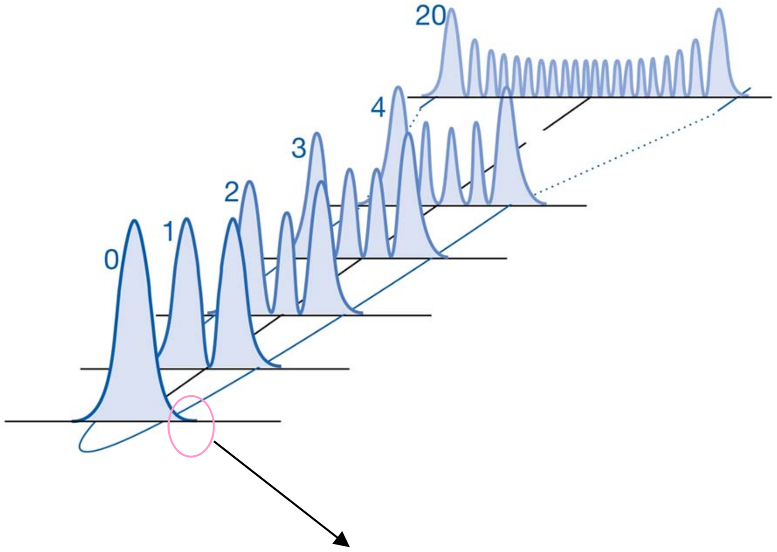
$$E_0 = \frac{1}{2}\hbar\omega$$



Reason for zero-point energy → the particle is confined : position is not uncertain, momentum cannot be zero

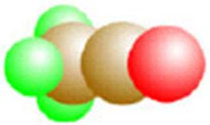
Wave functions





Quantum tunneling

The properties of oscillators



- Expectation values

$$\langle \Omega \rangle = \langle v | \hat{\Omega} | v \rangle = \int_{-\infty}^{\infty} \psi_v^* \hat{\Omega} \psi_v \, dx$$

- Mean displacement and mean square displacement

$$\langle x \rangle = 0 \qquad \langle x^2 \rangle = (v + \frac{1}{2}) \frac{\hbar}{(mk)^{1/2}}$$

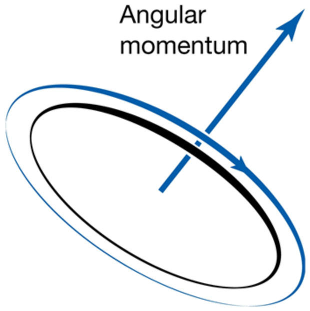
- Mean potential energy and mean kinetic energy

$$\langle V \rangle = \left\langle \frac{1}{2} kx^2 \right\rangle = \frac{1}{2}(v + \frac{1}{2}) \frac{\hbar}{(mk)^{1/2}} \longrightarrow \langle V \rangle = \frac{1}{2} E_v \qquad \langle E_K \rangle = \frac{1}{2} E_v$$

- Virial Theorem
  - If the potential energy of a paticle has the form $V=ax^b$, then its mean potential and kinetic energies are related by

$$2\langle E_K \rangle = b\langle V \rangle$$

Rotation in Two Dimensions : Particles on a ring

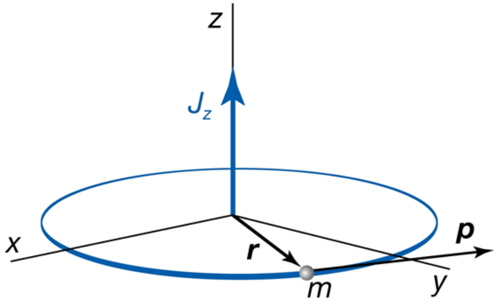


- A Rotational motion can be described by its angular momentum J
  - **J** : vector
  - Rate at which a particle circulates
  - Direction : the axis of rotation

$$J = I\omega$$

I : moment of inertial $I = mr^2$

ω : angular velocity



- A particle of mass m constrained to move in a circular path of radius r in xy-plane
  - V = 0 everywhere
  - Total Energy = Kinetic Energy

$$E = p^2 / 2m$$

$$J_z = \pm pr$$

$$E = \frac{J_z^2}{2I}$$

Rotation in Two Dimension

Schrödinger eqn.

$$\frac{d^2\psi}{d\phi^2} = \frac{2IE}{\hbar^2}\psi$$

B.C

$$\psi_{m_l}(\phi + 2\pi) = \psi_{m_l}(\phi)$$

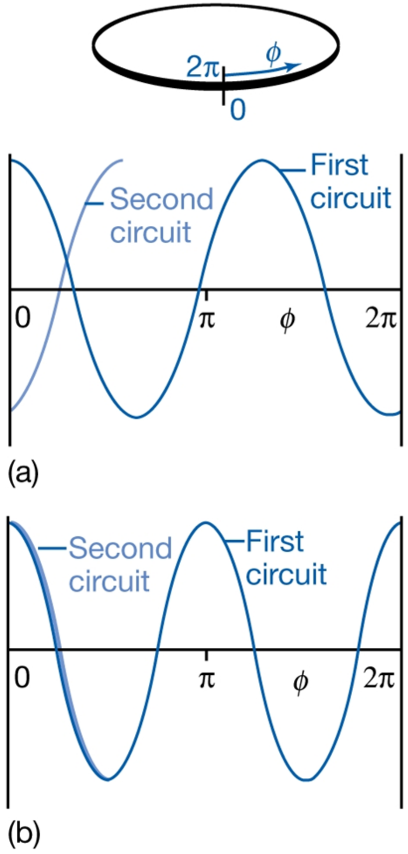
Wave Functions

$$\psi_{m_l}(\phi) = \frac{e^{im_l\phi}}{(2\pi)^{1/2}} \qquad m_l = 0, \pm 1, \pm 2, \ldots$$

Energy Levels

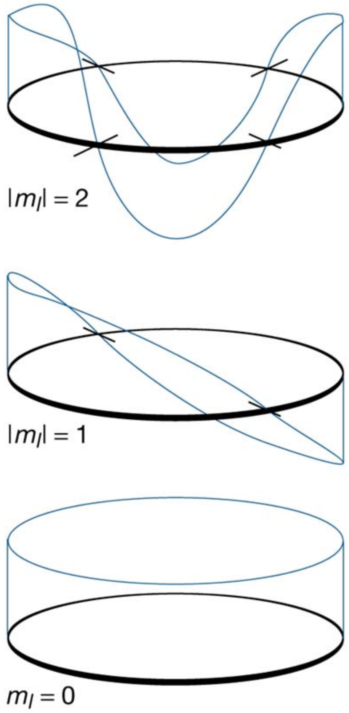
$$E_{m_l} = \frac{J_z^2}{2I} = \frac{m_l^2\hbar^2}{2I}$$

The wave function have to be single-valued

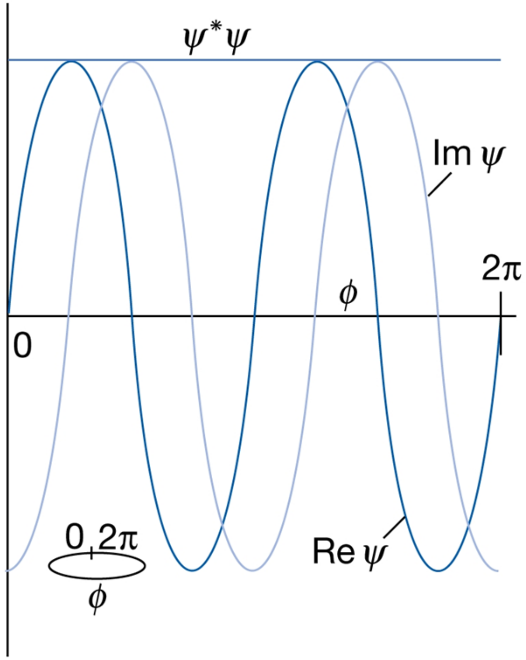


Wave functions

- States are doubly degenerate except for $m_l = 0$



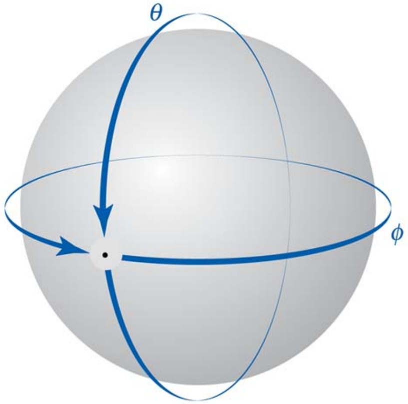
The real parts of wave functions

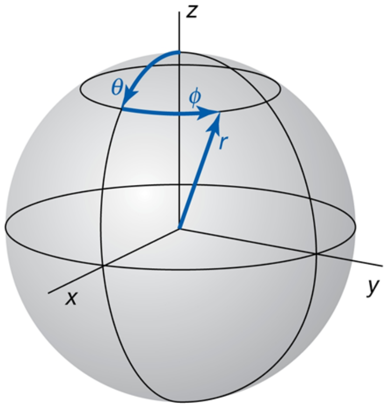


Rotation in Three dimension

- A particle of mass *m* free to move anywhere on the 3D surface or a sphere

- Colatitude (여위도) : θ
- Azimuth (방위각) : ϕ





Rotation in Three dimension

Schrödinger eqn.

$$-\frac{\hbar}{2m}\nabla^2\psi = E\psi$$

Wave Functions

$Y_{l,m_l}(\theta,\phi)$:spherical harmonics

$l = 0,1,2,,...$ $\quad m_l = l, l-1, l-2,...,-l$

Energy Levels

$$E = l(l+1)\frac{\hbar}{2I}$$

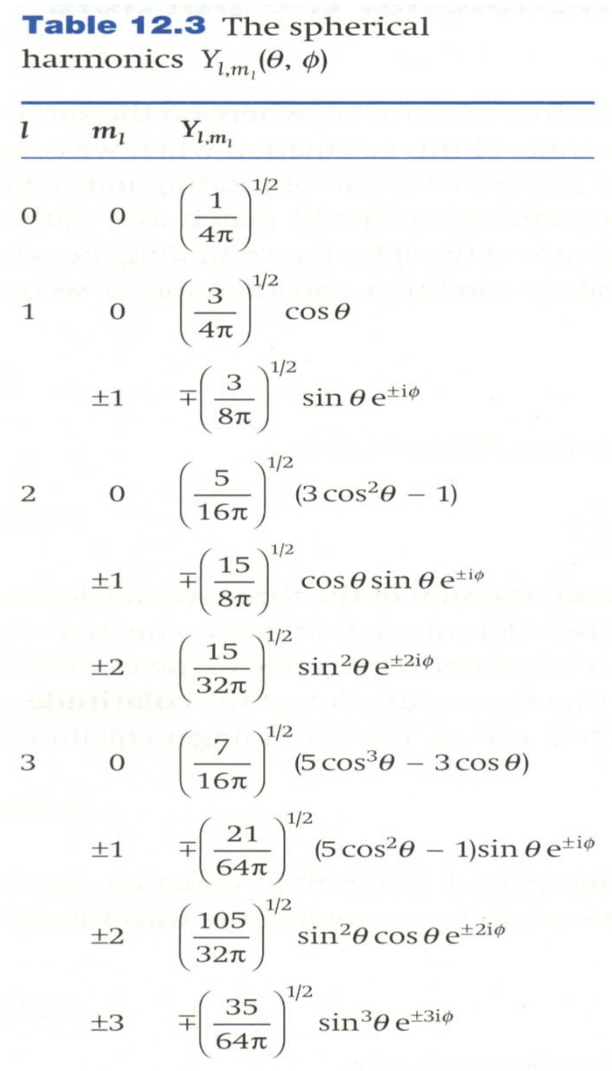
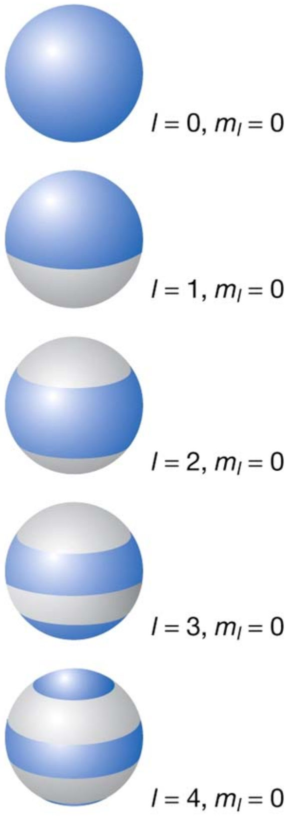


Table 12.3 The spherical harmonics $Y_{l,m_l}(\theta,\phi)$

l	m_l	Y_{l,m_l}
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\, e^{\pm i\phi}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta - 3\cos\theta)$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta - 1)\sin\theta\, e^{\pm i\phi}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\, e^{\pm 3i\phi}$

Wave functions



Location of angular nodes

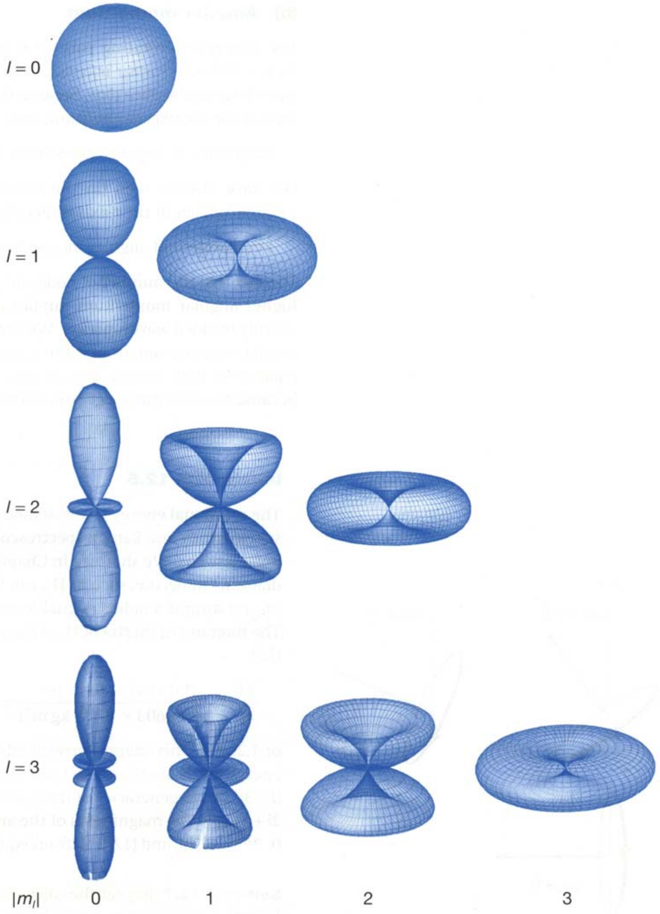
***(2l + 1)* fold degeneracy**

Orbital momentum quantum number

$$l = 0,1,2,,...$$

Magnetic Quantum number

$$m_l = l, l-1, l-2, ..., -l$$



Wave functions

Angular Momentum

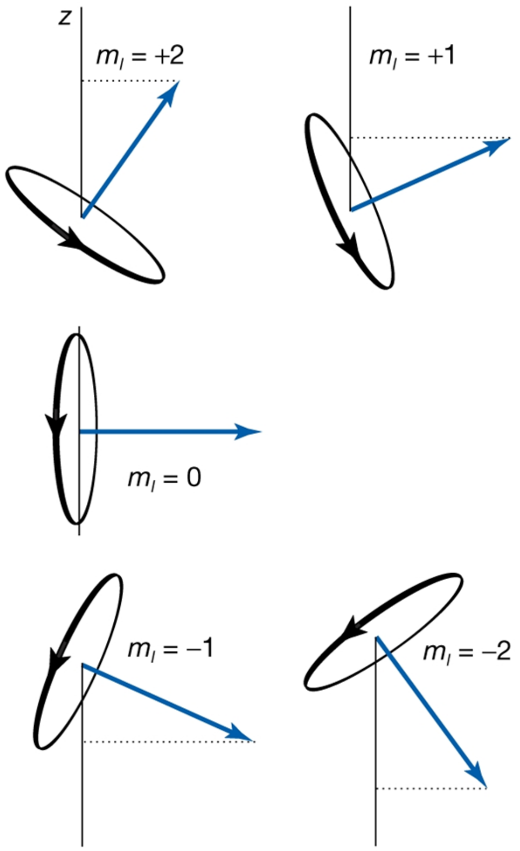
- The energy of a rotating particle
  - ☐ Classically, $E = \dfrac{J^2}{2I}$
  - ☐ Quantum mechanical

$$E = l(l+1)\frac{\hbar^2}{2I} \qquad l = 0,1,2,...$$

- Angular Momentum
  - ☐ Magnitude of angular momentum $= \{l(l+1)\}h^{1/2}$
  - ☐ Z-component of angular momentum $= m_l\hbar$

Space Quantization

- The orientation of rotating body is quantized : rotating body may not take up an arbitrary orientation with respect to some specified axis



Space Quantization

Angular momentum L (l_x, l_y, l_z)

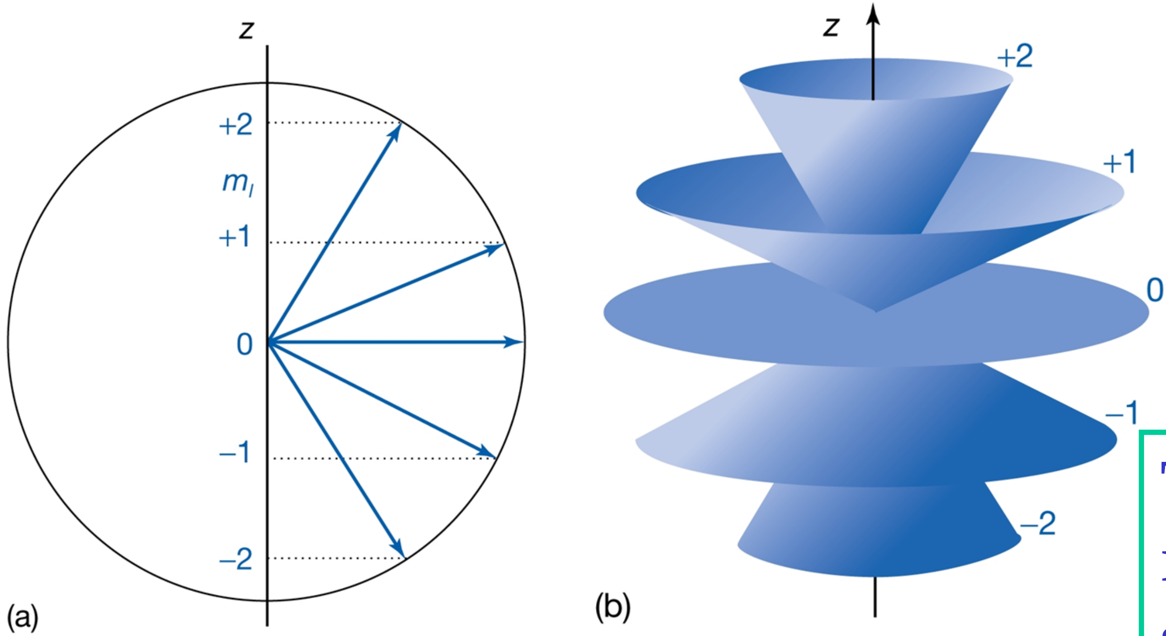
$$l_x = h/2\pi i\ \{-\sin\phi(\partial/\partial\theta)\ -\cot\theta\ \cos\phi(\partial/\partial\varphi)\}$$

$$l_y = h/2\pi i\ \{\cos\phi(\partial/\partial\theta)\ -\cot\theta\ \sin\phi(\partial/\partial\varphi)\}$$

$$l_y = h/2\pi i\ (\partial/\partial\varphi)$$

- The vector model
  - **l_x, l_y, l_z do not commute with each other. (l_x, l_y, l_z are complementary observables)**
  - **uncertainty principle forbids the simultaneous, exact specification of more than one component (unless l=0).**
  - **-If l_z is known, impossible to ascribe values to l_x, l_y.**

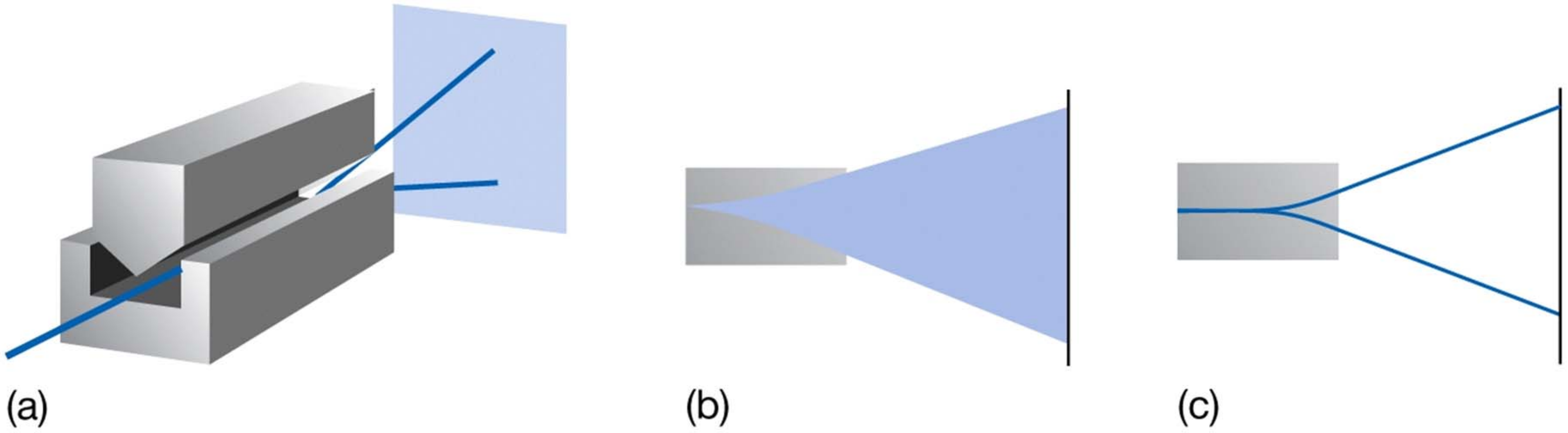
The Vector Model



The vector representing the state of angular momentum lies with its tip on any point on the mouth of the cone.

Experiment of Stern-Gerlach

- Otto Stern and Walther Gerlach (1921)
  - ☐ Shot a beam of silver atoms through an inhomogeneous magnetic field
  - ☐ Evidence of space quantization

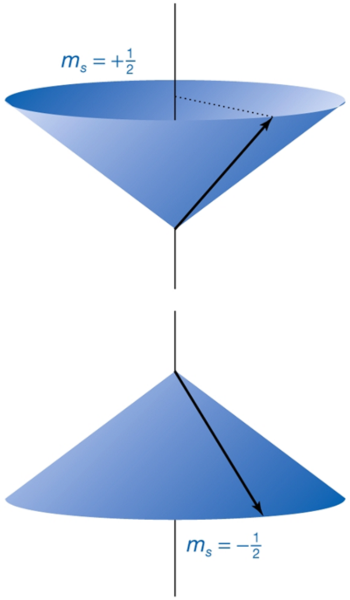


The classically expected result

The Observed outcoming using silver atoms

Spin

- Stern and Gerlach
  - observed two bands using silver atoms (2)
  - The result conflicts with prediction : *(2l+1)* orientation (*l* must be an integer)
- Angular momentum due to the motion of the electron about its own axis : spin
- Spin magnetic number : m_s
  - $m_s = s, s\text{-}1, \ldots, \text{-}s$
  - Spin angular momentum $= \left(\frac{3}{4}\right)^{1/2}\hbar = 0.866\hbar$
- Electron spin
  - s = ½
  - Only two states



Fermions and Bosons

- Electrons : s=1/2
- Photons : s=1

Fermions

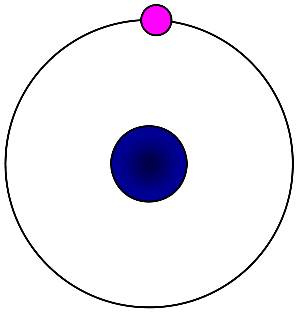
Particles with half-integral spin (s=1/2)
Elementary particles that constitute matters →Electrons, nucleus

Bosons

Particles with integral spin (s=0,1,…)
Responsible for the forces that binds fermions →Photons

Atomic Structure
and Atomic Spectra

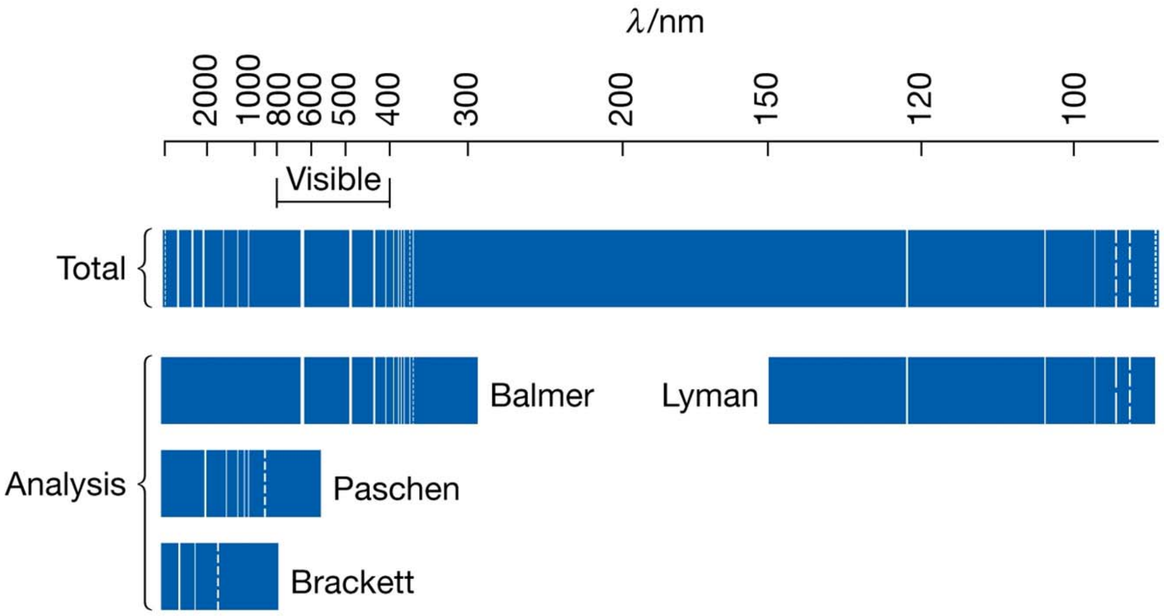
Topics



- Electronic Structure of Atoms
  - One Electron Atom : hydrogen atom
  - Many-Electron Atom (polyelectronic atom)
- Spectroscopy
  - Experimental Technique to determine electronic structure of atoms.
  - Spectrum
    - Intensity vs. frequency (ν), wavelength (λ), wave number (ν/c)

Structure and Spectra of Hydrogen Atoms

- Electric discharge is passed through gaseous hydrogen , H_2 molecules and H atoms emit lights of discrete frequencies



Spectra of hydrogenic atoms

- Balmer, Lyman and Paschen Series (J. Rydberg)
  - $n_1 = 1$ (Lyman)
  - $n_1 = 2$ (Balmer)
  - $n_1 = 3$ (Paschen)
  - $n_2 = n_1 + 1, n_1 + 2, \ldots$
  - $R_H = 109667\ \text{cm}^{-1}$ (Rydberg constant)

$$\tilde{\nu} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

- Ritz combination principle
  - The wave number of any spectral line is the difference between two terms

$$T_n = \frac{R_H}{n^2} \qquad \tilde{\nu} = T_1 - T_2$$

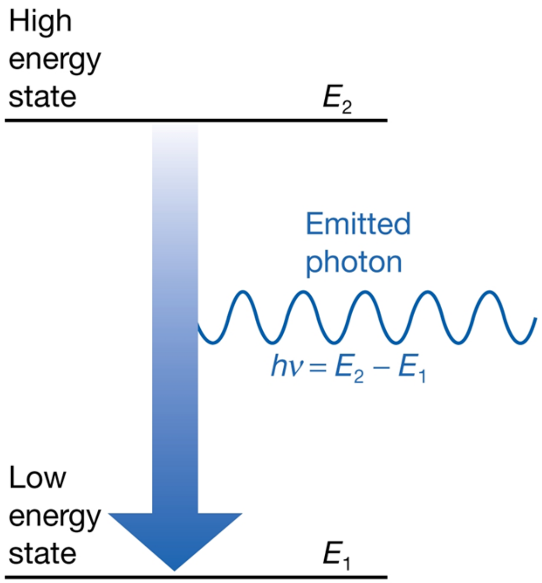
The wave lengths can be correlated by two integers
→ Two different states

Spectra of hydrogenic atoms

- Ritz combination principle
  - Transition of one energy level to another level with emission of energy as photon
- Bohr frequency condition

$$\Delta E = h\nu = hcT_1 - hcT_2$$

원자에서 방출되거나 흡수된 electromagnetic radiation 은 주어진 특정 양자수로 제한된다.
따라서 원자들은 몇 가지 주어진 상태만을 가질 수 있음을 알 수 있다.
남은 문제는 양자역학을 이용하여 허용된 에너지 레벨을 구하는 것이다.



The Structure of Hydrogenic Atoms

- Coulombic potential between an electron and hydrogen atom (Z : atomic number , nucleus charge = Ze)

$$V = -\frac{Ze^2}{4\pi e_0 r}$$

- Hamiltonian of an electron + a nucleus

$$H = \hat{E}_{K,electron} + \hat{E}_{K,nucleus} + V = -\frac{\hbar^2}{2m_e}\underset{\substack{\downarrow \\ \text{Electron} \\ \text{coordinate}}}{\nabla_e^2} - \frac{\hbar^2}{2m_N}\underset{\substack{\downarrow \\ \text{Nucleus} \\ \text{coordinate}}}{\nabla_N^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

Separation of Internal motion

- Full Schrödinger equation must be separated into two equations
  - Atom as a whole through the space
  - Motion of electron around the nucleus
- Separation of relative motion of electron from the motion of atom as a whole (Justification 13.1)

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N} \approx \frac{1}{m_e}$$

The Schrödinger Equation

$$H\psi = E\psi \longrightarrow -\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

Separation of Variable :
Energy is centrosymmetric
Energy is not affeced by
angular component (Y)
(Justification 13.2)

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

$$\Lambda^2 Y = -l(l+1)Y \longrightarrow$$

Y : All the same equation as in Chap.12
(Section 12.7, the particle on a sphere)
Spherical Harmonics

$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2R}{dr^2} + \frac{2}{R}\frac{dR}{dr}\right) - V_{eff}R = ER \longrightarrow$$

R : Radial Wave Equation
New solution required

$$V_{eff} = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

The Radial Solutions

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$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2R}{dr^2}+\frac{2}{R}\frac{dR}{dr}\right)-V_{eff}R=ER$$

Solution

$$R(r)=(\text{polynomial in r})\times(\text{decaying exponential in r})$$

Reduced distance $\rho=\frac{2Zr}{a_0}$

Bohr Radius $a_0=\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$

Allowed Energies

$$E_n=-\frac{Z^2\mu e^4}{32\pi^2 e_0^2\hbar^2 n^2} \quad \text{with} \quad n=1,2,3...$$

Associated Laguerre polynomials

Radial Solution

$$R_{n,l}(r)=N_{n,l}\left(\frac{\rho}{n}\right)^l L_{n,l}(\rho)e^{-\rho/2n}$$

Hydrogenic Radial Wavefunctions

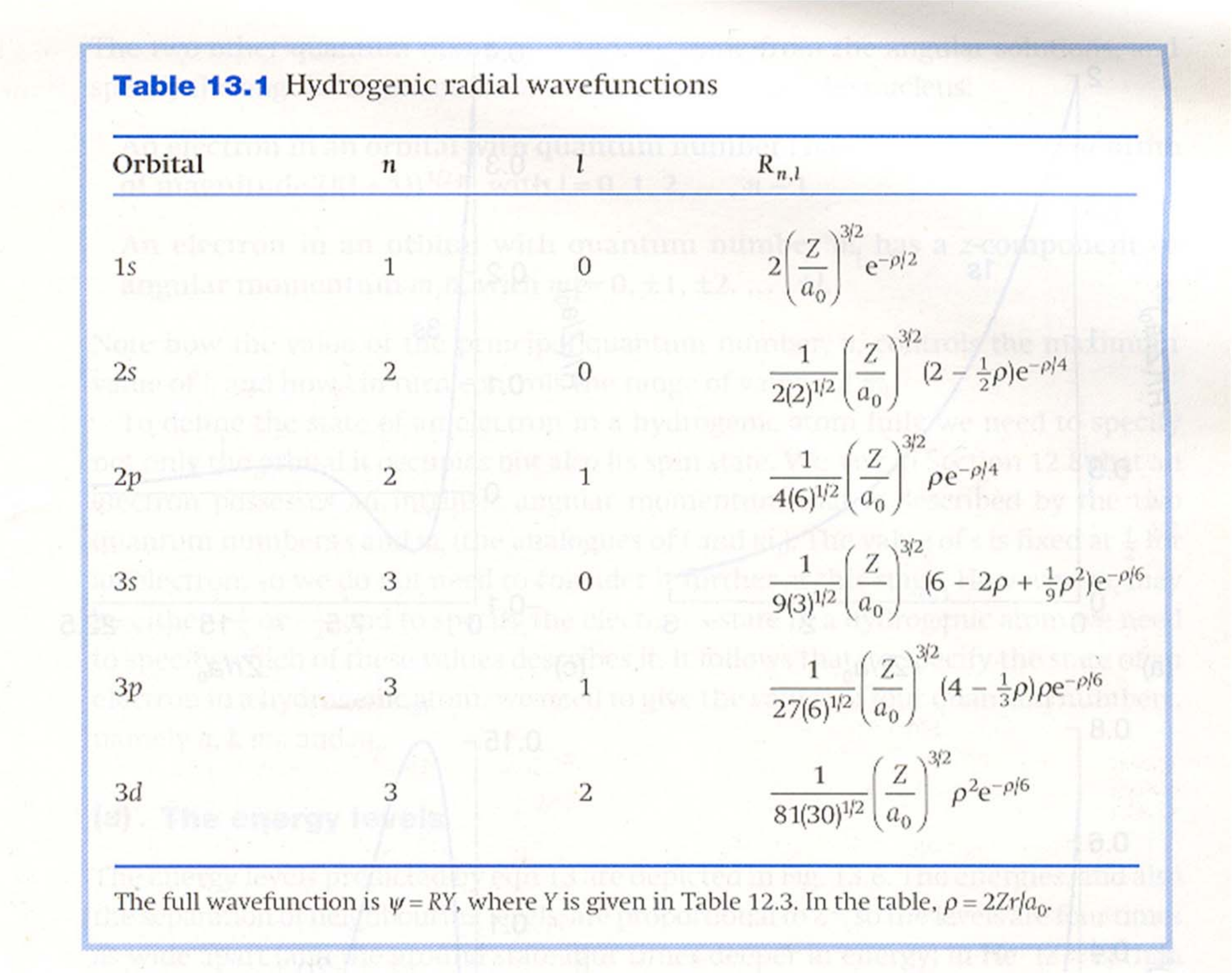
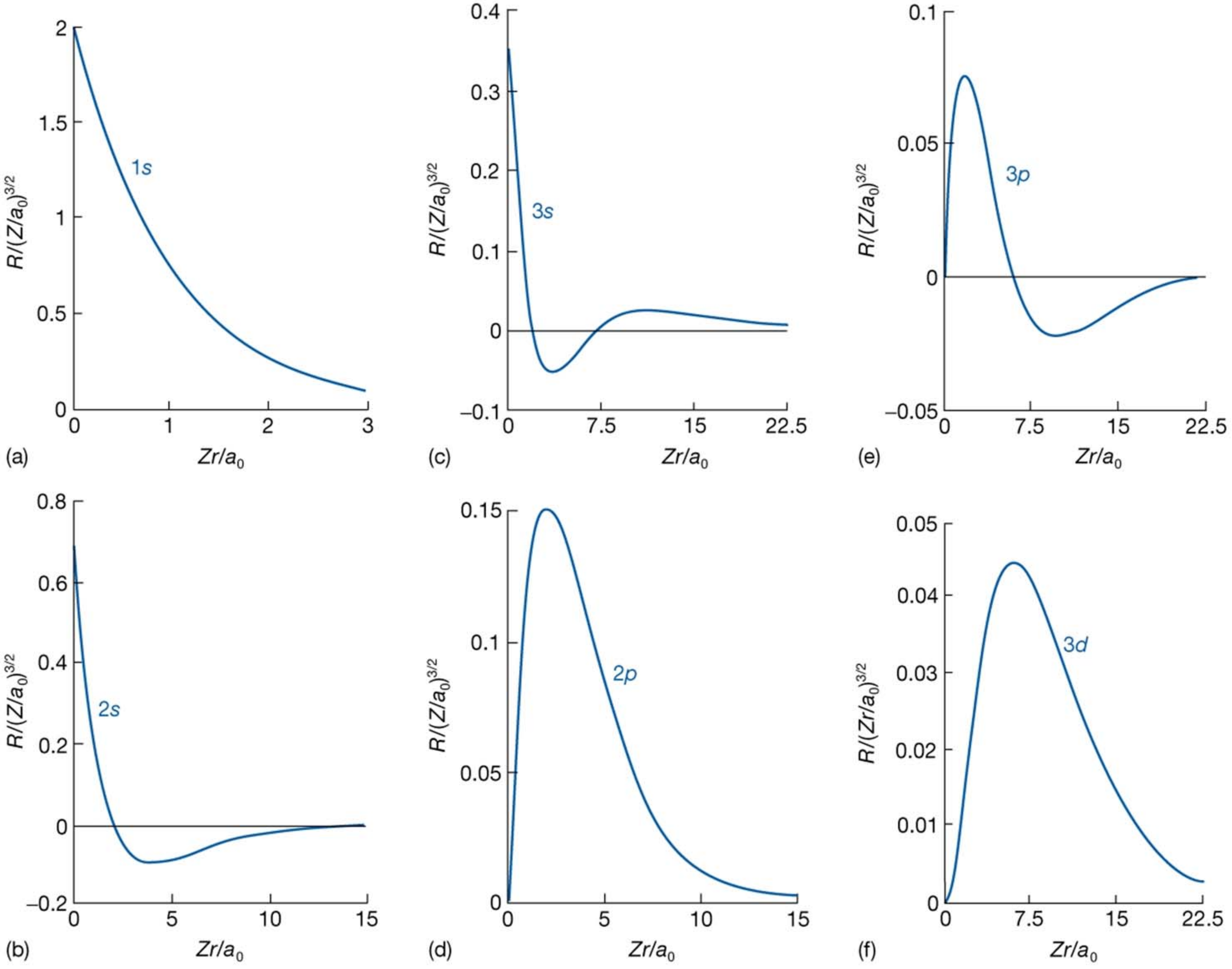


Table 13.1 Hydrogenic radial wavefunctions

Orbital	n	l	$R_{n,l}$
1*s*	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$
2*s*	2	0	$\frac{1}{2(2)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} (2 - \frac{1}{2}\rho)e^{-\rho/4}$
2*p*	2	1	$\frac{1}{4(6)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/4}$
3*s*	3	0	$\frac{1}{9(3)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} (6 - 2\rho + \frac{1}{9}\rho^2)e^{-\rho/6}$
3*p*	3	1	$\frac{1}{27(6)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} (4 - \frac{1}{3}\rho)\rho e^{-\rho/6}$
3*d*	3	2	$\frac{1}{81(30)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/6}$

The full wavefunction is $\psi = RY$, where Y is given in Table 12.3. In the table, $\rho = 2Zr/a_0$.

The Radial Solutions



Atomic Orbital and Their Energies

- Quantum numbers n, l, m_l

  - ☐ n : Principal quantum number (n=1,2,3,…) ⟶ Shell
    - Determines the energies of the electron

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 e_0^2 \hbar^2 n^2} \quad \text{with} \quad n = 1,2,3...$$

  - ☐ an electron with quantum number *l* has angluar momentum ⟶ Sub Shell

$$\{l(l+1)\}^{1/2}\hbar \ \text{ with } \ l = 0,1,..,n-1$$

  - ☐ An electron with quantum number m_l has z-component of angular momentum

$$m_l\hbar \quad \text{with} \quad m_l = 0,\pm1,\pm2,...,\pm l$$

The energy levels

- Bound / Unbound State
  - Bound State : negative energy
  - Unbound State : positive energy (not quantized)
- Ryberg const. for hydrogen atom

$$hcR_H = -\frac{\mu_H e^4}{32\pi^2 e_0^2 \hbar^2}$$

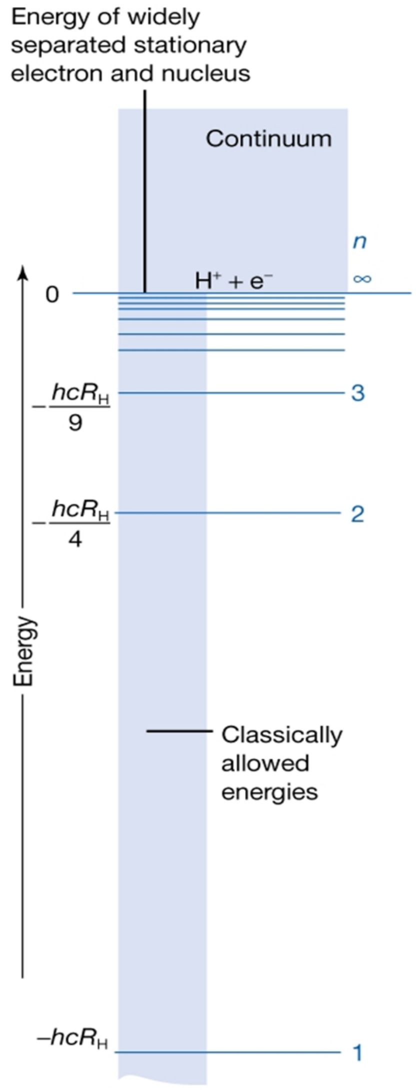
- Ionization energy
  - Mininum energy required to remove an electron form the ground state

Energy of hydrogen at ground state n=1

$$E_1 = -hcR_H = \frac{\mu_H e^4}{32\pi^2 e_0^2 \hbar^2}$$

Ionization Energy

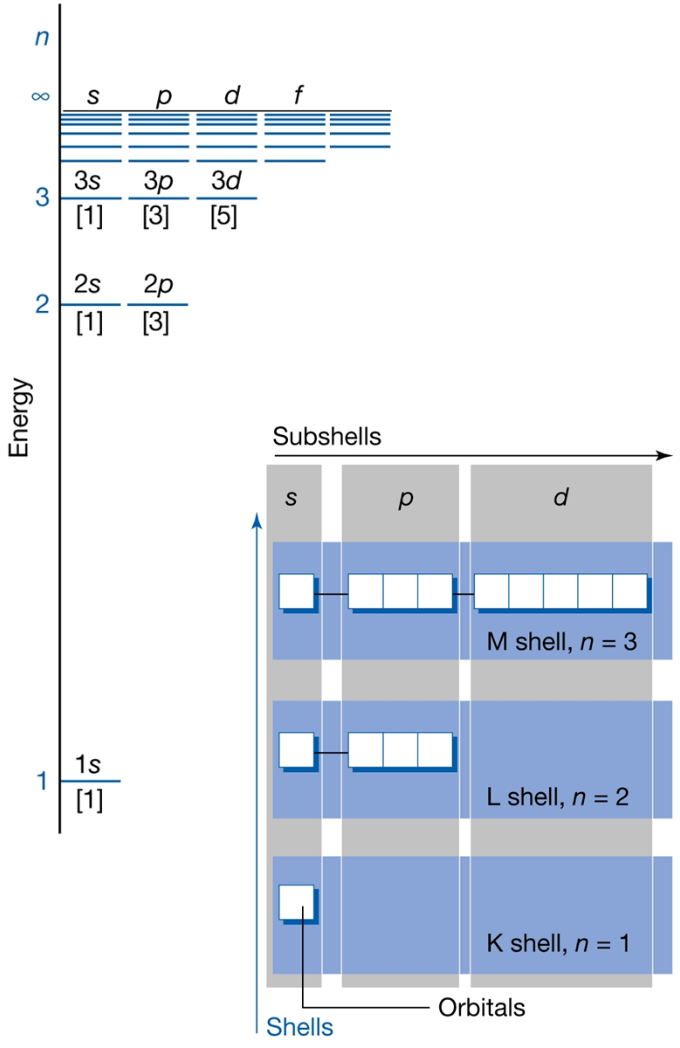
$$I = hcR_H$$



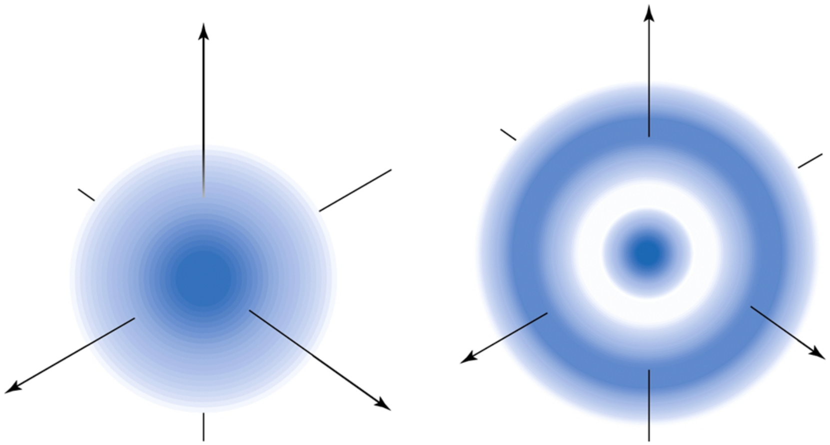
Shells and Subshells

- Shell
  - n = 1 (K), 2 (L), 3 (M), 4(N)
- Subshell (l=0,…. , n-1)
  - l = 0 (s), 1 (p), 2 (d), 3(f), 4(g), 5 (h), 6 (i)
- Examples
  - n = 1
    - l = 0 → only 1s (1)
  - n = 2
    - l = 0, 1 → 2s (1) , 2p (3)
  - n = 3
    - l = 0, 1, 2 → 3s (1), 3p (3), 3d (5)
- number of orbitals in n_{th} shell : n^2
- *n^2 –f old degenerate*

m_l s are limited to the value -l,..,0, …+l



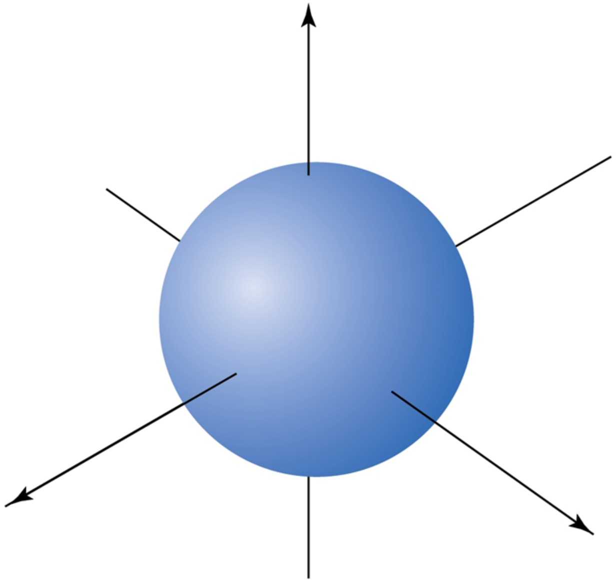
Ways to depicting probability density



(a) 1*s*

(b) 2*s*

Electron densities
(Density Shading)



Boundary surface
(within 90 % of electron probability)

Radial Nodes

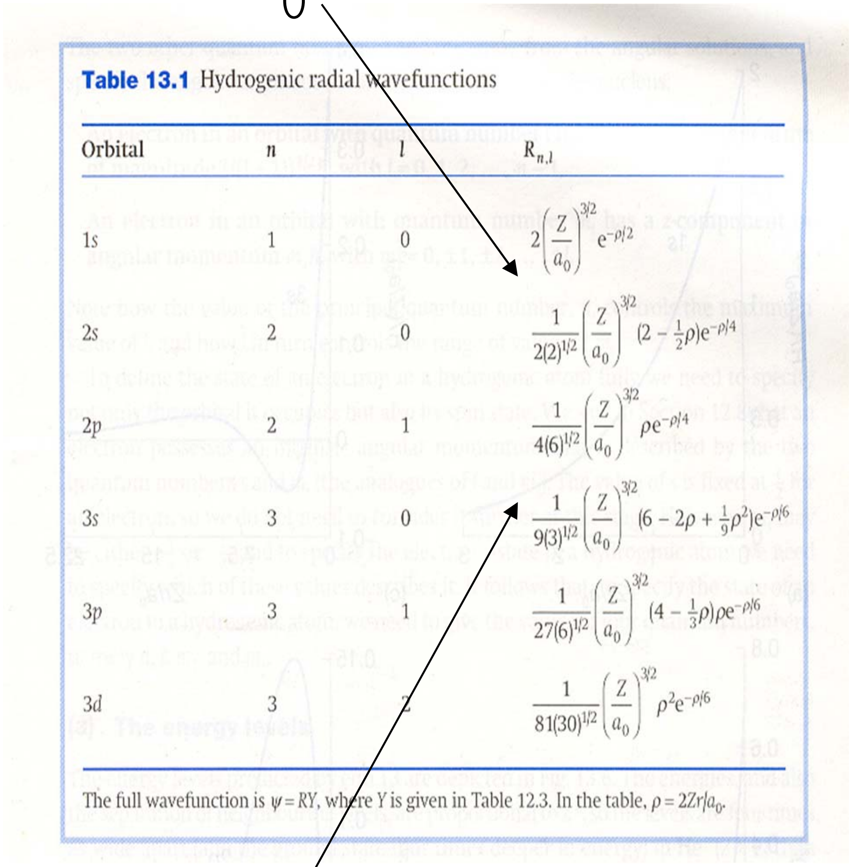
- Wave function becomes zero (*R(r) = 0*)
  - ☐ For 2s orbital :

$$r = 2a_0 / Z$$

  - ☐ For 3s orbital :

$$r = 1.90a_0 / Z \qquad r = 7.10a_0 / Z$$

0



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2p	2	1	$\frac{1}{4(6)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/4}$
3s	3	0	$\frac{1}{9(3)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} (6-2\rho+\frac{1}{9}\rho^2)e^{-\rho/6}$
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The full wavefunction is $\psi = RY$, where Y is given in Table 12.3. In the table, $\rho = 2Zr/a_0$.

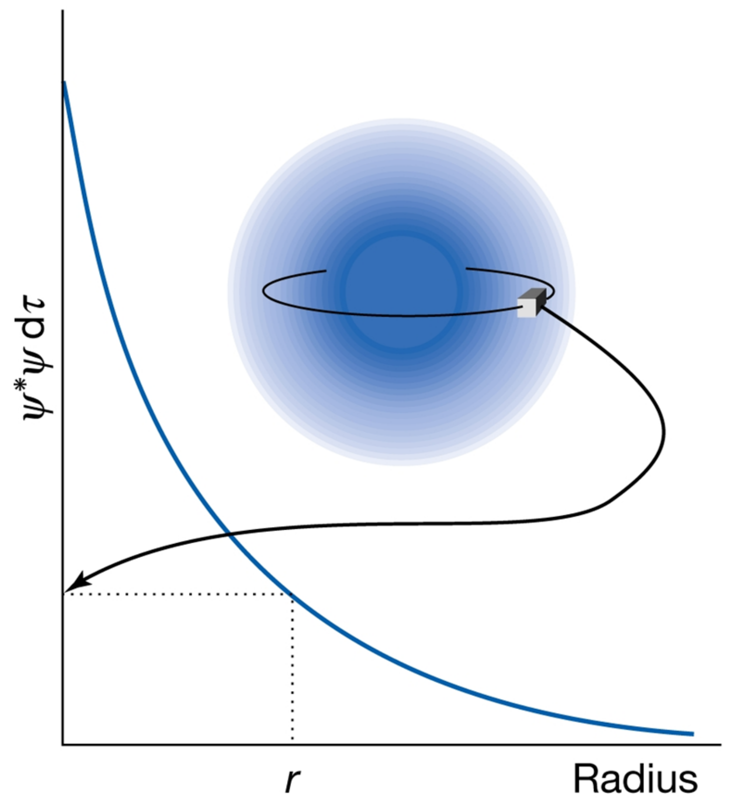
0

Radial Distribution Function

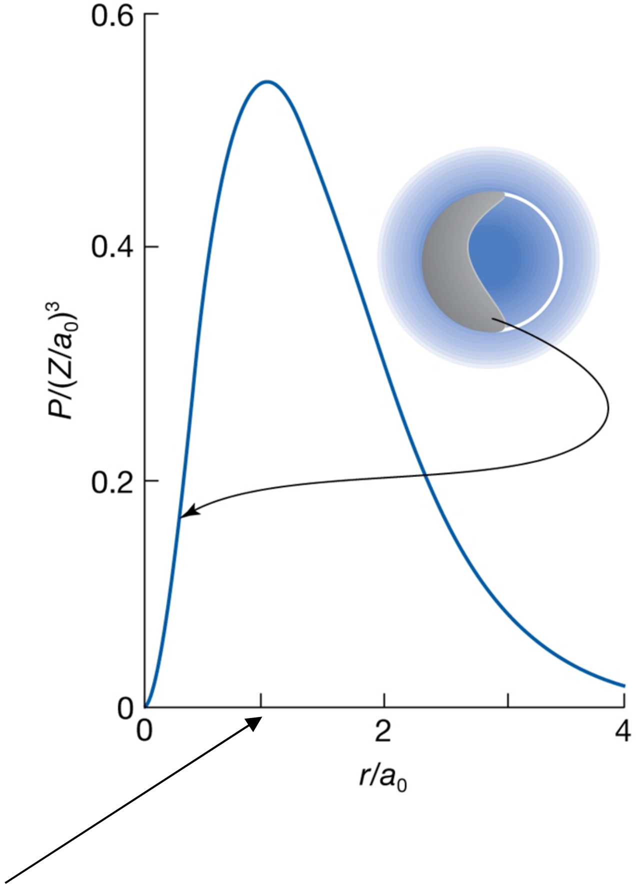
- Wave Function $|\psi|^2$
  - probability of finding an electron in any region
- Probability Density (1s) $|\psi|^2 \propto e^{-2Zr/a_0}$
- Probability at any radius r = *P (r) dr* $P(r) = 4\pi r^2 \psi^2$
- Radial Wave Function : *R(r)* $P(r) = r^2 R(r)^2$
- Radial Distribution Function : *P(r)*
  - *dr* 을 곱하면 확률이 된다.
  - 1s orbital 에 대하여 ,

$$P(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0}$$

Radial Distribution Function



Wave function



Radial Distribution Function

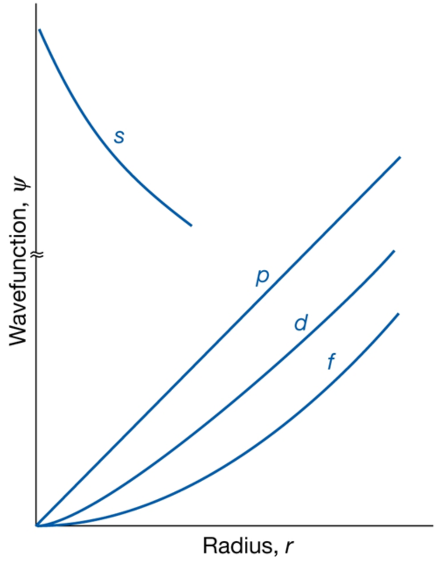
Bohr radius

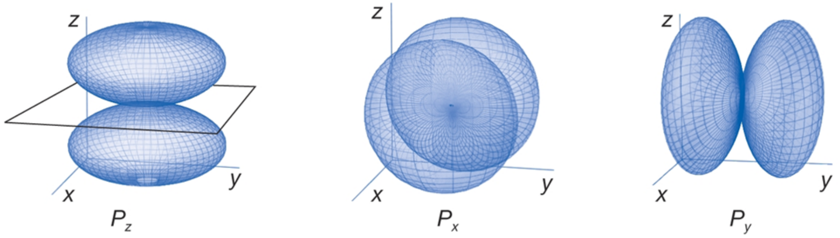
p-Orbital

- Nonzero angular momentum
  - $l > 0$

$$\psi \propto r^{l}$$

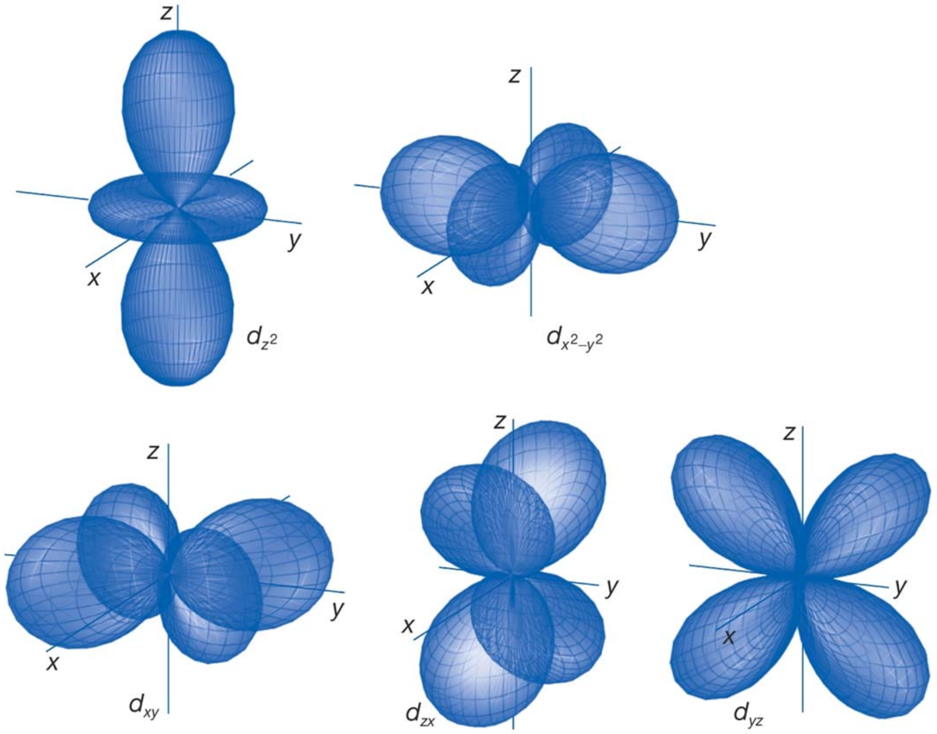
- p-orbital
  - $l = 1$
    - $m_l = 0$ $\qquad \psi_{p_z}$
    - $m_l = +1$ $\qquad \psi_{p_x}$
    - $m_l = -1$ $\qquad \psi_{p_y}$





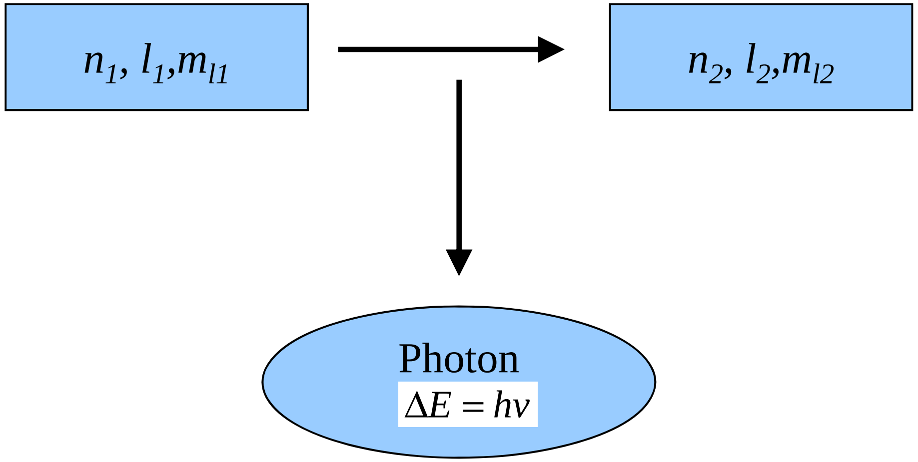
D-orbital

- $n = 3$
  - $l = 2$
  - $m_l = +2, +1, 0,1,2$



Spectroscopic transitions and Selection rules

- Transition (change of state)



$n_1,\ l_1, m_{l1}$

$n_2,\ l_2, m_{l2}$

Photon

$\Delta E = h\nu$

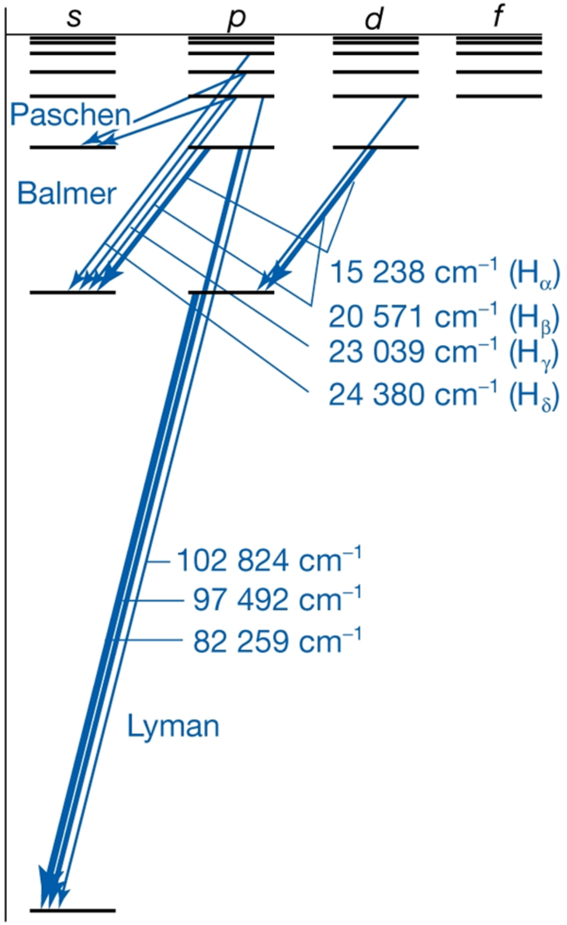
$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 e_0^2 \hbar^2 n^2} \quad \text{with} \quad n = 1,2,3\ldots$$

- All possible transitions are not permissible
  - Photon has intrinsic spin angular momentum : s = 1
  - d orbital *(l=2)* → s orbital *(l=0)* (X) forbidden
    - Photon cannot carry away enough angular momentum

Selection rule for hydrogenic atoms

- Selection rule
  - ☐ Allowed $\Delta l = \pm 1$ $\Delta m_l = 0, \pm 1$
  - ☐ Forbidden

- Grotrian diagram



Structures of Many-Electron Atoms

- The Schrödinger equation for many electron-atoms
    - Highly complicated
    - All electrons interact with one another
    - Even for helium, approximations are required
- Approaches
    - Simple approach based on H atom
        - Orbital Approximation
    - Numerical computation technique
        - Hartree Fock self consistent field (SCF) orbital

Pauli exclusion principle

- Quantum numbers
  - Principal quantum number : n
  - Orbital quantum number : l
  - Magnetic quantum number : m_l
  - Spin quantum number : m_s
- Two electrons in atomic structure can never have all four quantum numbers in common
- All four quantum number → "Occupied"

Penetration and Shielding

- Unlike hydrogenic atoms 2s and 2p orbitals are not degenerate in many-electron atoms
  - electrons in s orbitals generally lie lower energy than p orbital
  - electrons in many-electron atoms experiences repulsion form all other electrons → shielding
- Effective nuclear charge, shielding constant

$$Z_{eff} = Z - \sigma$$

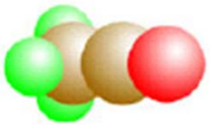
Z_{eff} : effective nuclear charge

σ : shielding constant

Penetration and Shielding

- An *s* electrons has a greater “**penetration**” through inner shell than *p* electrons
- Energies of electrons in the same shell
  - $s < p < d < f$
- Valence electrons
  - electrons in the outer most shell of an atom in its ground state
  - largely responsible for chemical bonds

The building-up principle

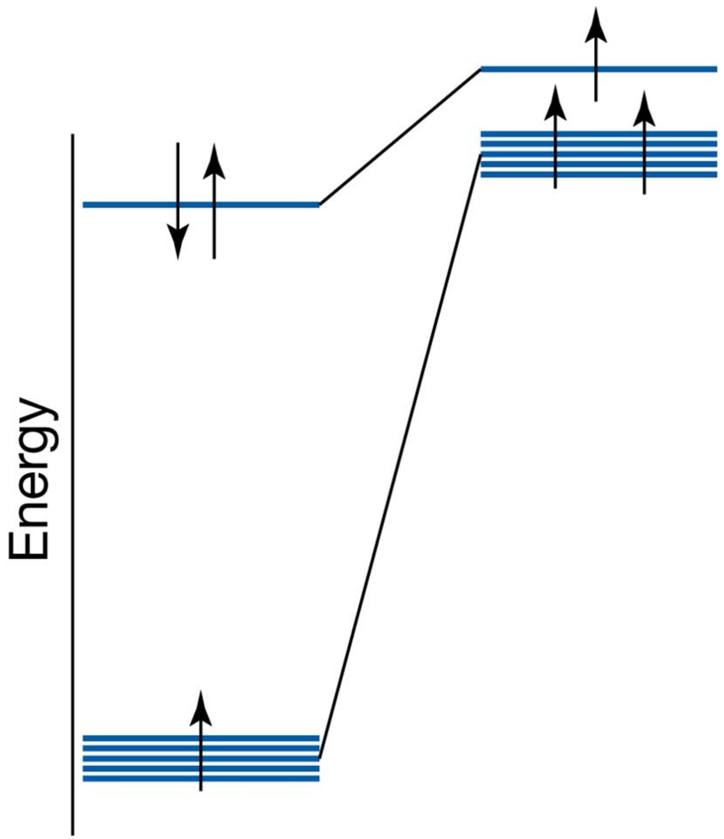


- The building-up principle (Aufbau principle)
  - The order of occupation of electrons
  - *1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s*
  - There are complicating effects arising from electron-electron repulsion (when the orbitals have very similar energies)
- Electrons occupy different orbitals of a given subshell before doubly occupying any one of them
  - Example : Carbon
    - $1s^2\ 2s^2\ 2p^2 \rightarrow 1s^2\ 2s^2\ 2p_x^1 2p_y^1$ (O) $1s^2\ 2s^2\ 2p_x^2$ (X)
- *Hund's* maximum multiplicity principle
  - An atom in its ground state adopts configuration with the greatest number of unpaired electrons

↑↑ favorable ↑↓ unfavorable

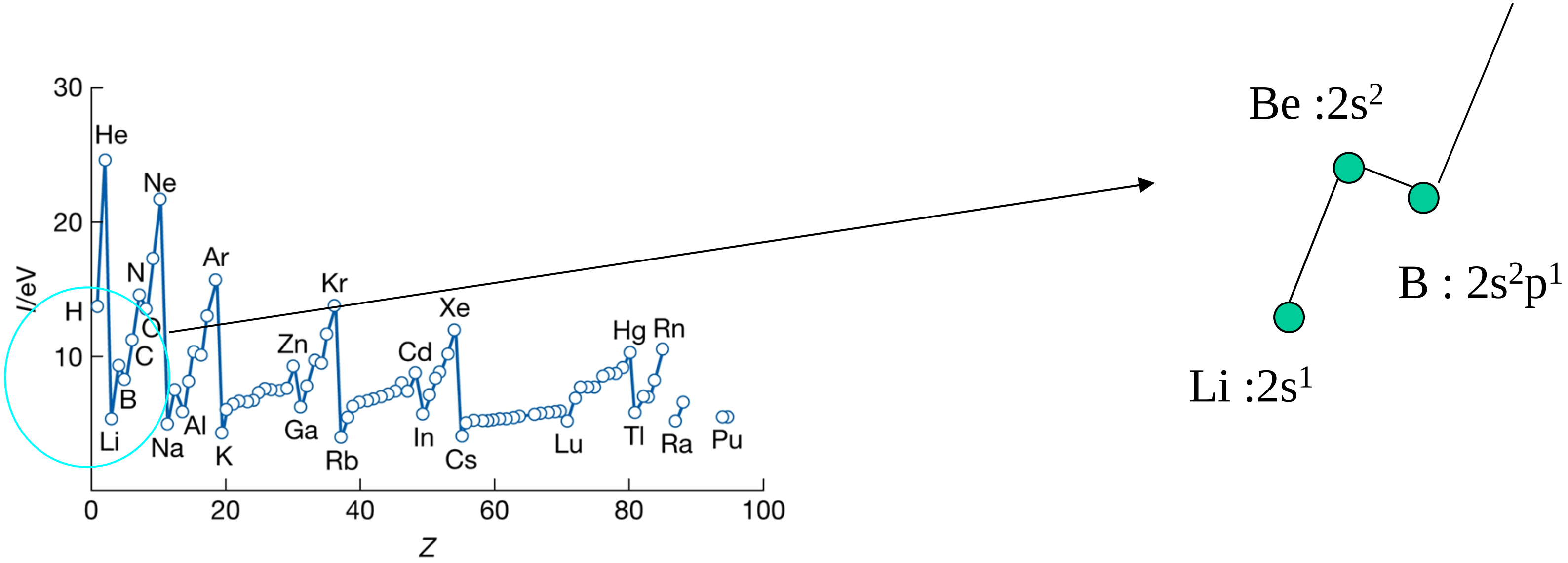
3d and 4s orbital

- Sc atom (*Z=21*)
  - [Ar]3d$_3$
  - [Ar]3d$_2$4s$_1$
  - [Ar]3d$_1$4s$_2$
- 3d has lower energy than 4s orbital
- 3d repulsion is much higher than 4s (average distance from nucleus is smaller in 3d)



Ionization energy

- Ionization energy
  - ☐ I_1 : The minimum energy required to remove an electron from many-electron atom in the gas phase
  - ☐ I_2 : The minimum energy required to remove a second electron from many-electron atom in the gas phase



Self-consistent field orbital

- Potential energy of electrons

$$V = -\sum_{i} \frac{Ze^2}{4\pi e \varepsilon_o r_i} + \boxed{\frac{1}{2}\sum_{i,j}{}^{'} \frac{e^2}{4\pi e \varepsilon_o r_{ij}}}$$

- Central difficulty → presence of electron-electron interaction
  - ☐ Analytical solution is hopeless
  - ☐ Numerical techniques are available
    - → Hartree-Fock Self-consistent field (SCF) procedure (HF method)

Schrödinger equation for Neon Atom
$1s^2 2s^2 2p^6$, 2p electrons

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$$-\frac{\hbar^2}{2m_e}\nabla_1^2\psi_{2p}(r_1) \longrightarrow$$

Kinetic energy of electron

$$-\frac{Ze^2}{4\pi\varepsilon_o r_1}\psi_{2p}(r_1) \longrightarrow$$

Potential energy (electron – nucleus)

$$+\frac{e^2}{2\pi\varepsilon_o}\left\{\sum_i\int\frac{\psi_i(r_2)^*\psi_i(r_2)}{r_{12}}d\tau_2\right\}\psi_{2p}(r_1) \longrightarrow$$

Columbic operator
(electron – electron charge density)

$$-\frac{e^2}{4\pi\varepsilon_o}\left\{\sum_i\int\frac{\psi_i(r_2)^*\psi_{2p}(r_2)}{r_{12}}d\tau_2\right\}\psi_i(r_1) \longrightarrow$$

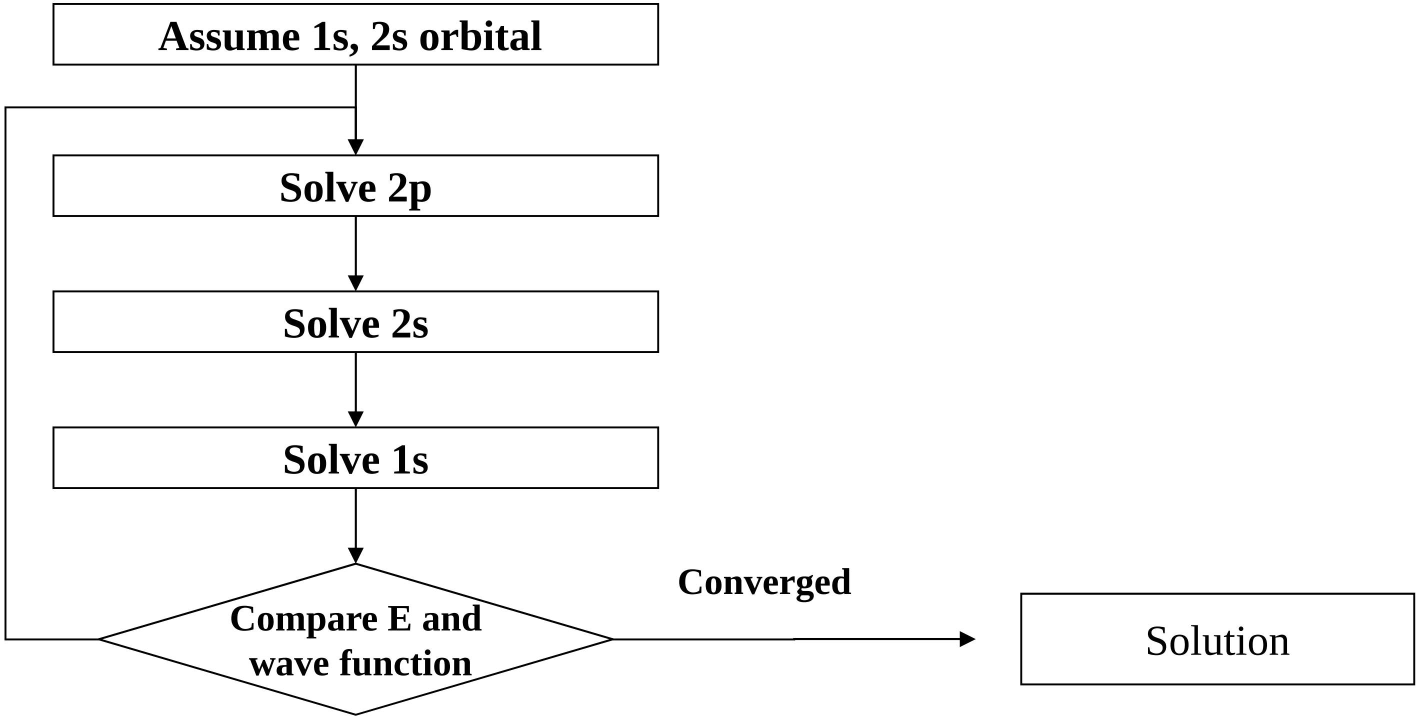
Exchange operator
(Spin correlation effect)

$$=E_{2p}\psi_{2p}(r_1)$$

Sum over orbitals (1s, 2s)

HF Procedure

- There is no hope solving previous eqn. analytically
- Alternative procedure (numerical solution)



Assume 1s, 2s orbital

Solve 2p

Solve 2s

Solve 1s

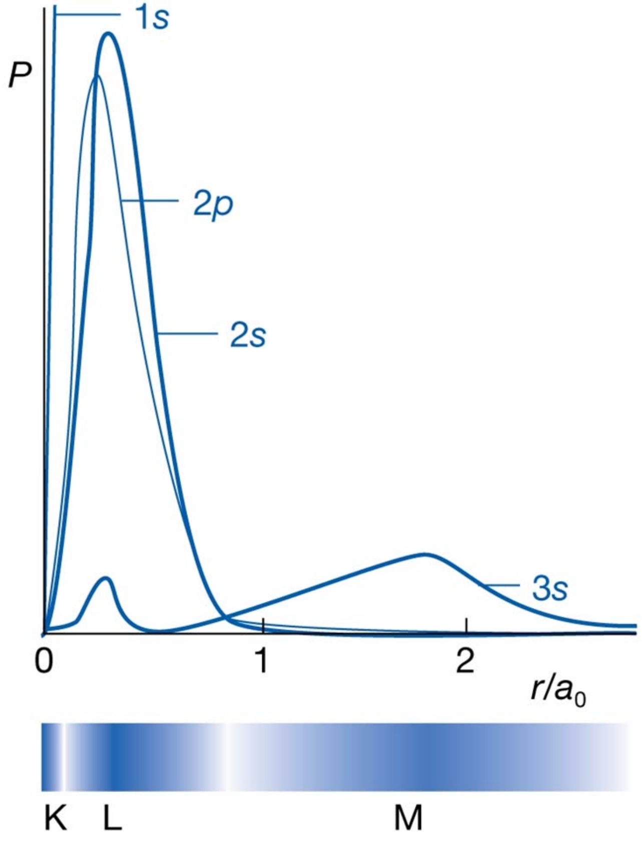
Compare E and wave function

Converged

Solution

Example

- Orbitals of Na using SCF calculation



Quiz

- What is a degeneracy ?
- Explain four quantum number.
- Why transition between two states are not always allowed ?
- Explain difficulties of solving Schrödinger equations for many-electron atoms.