Chem 212

What is quantum mechanics?

Every object has both characteristics of particle and wave

countable and discrete

spreads all over the space (simultaneously) and shows interference

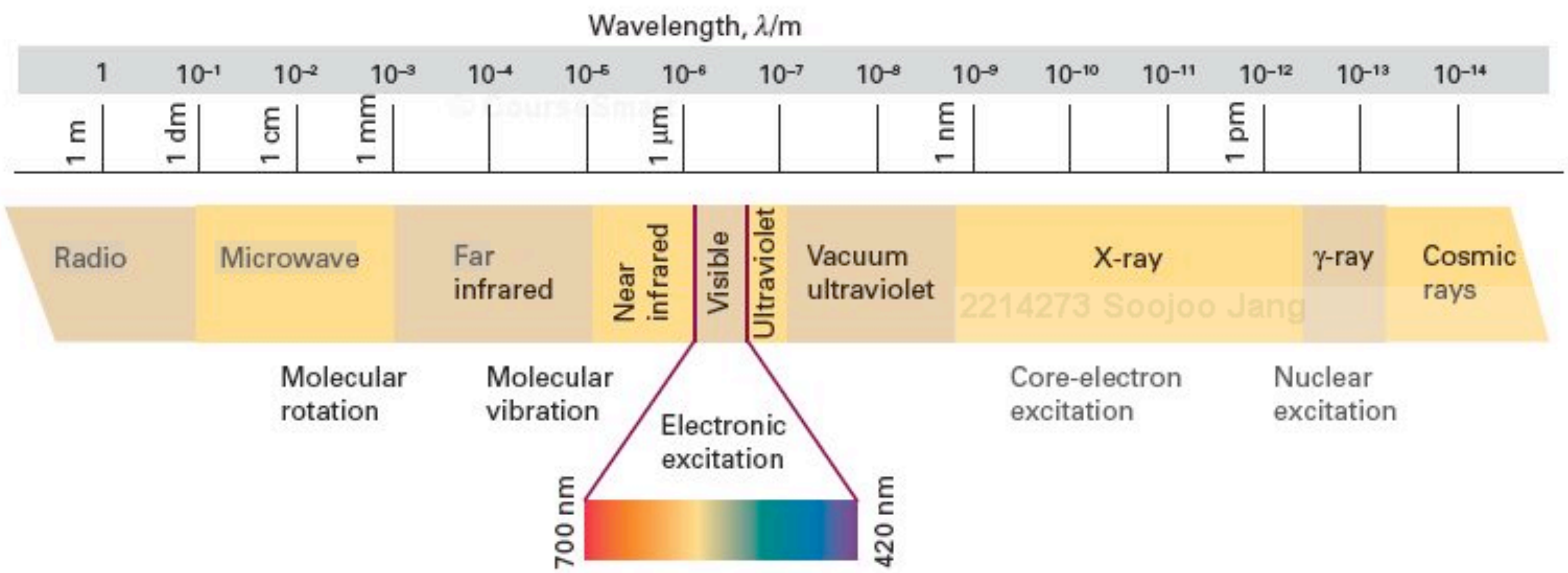
Experimental evidences

- Blackbody radiation
- Photoelectric effect
- Heat capacity of solid

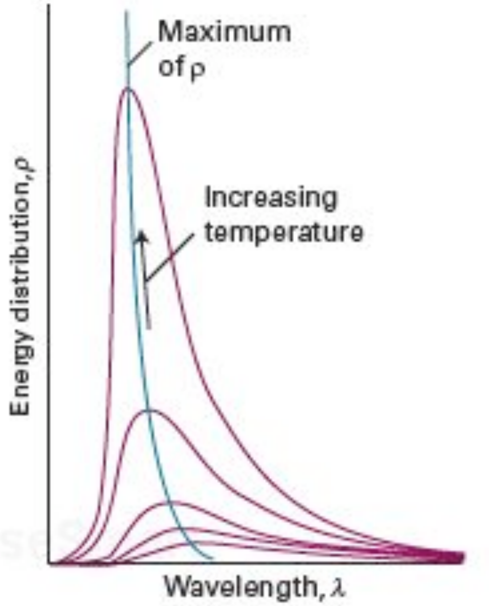
Light is an electro-magnetic wave.

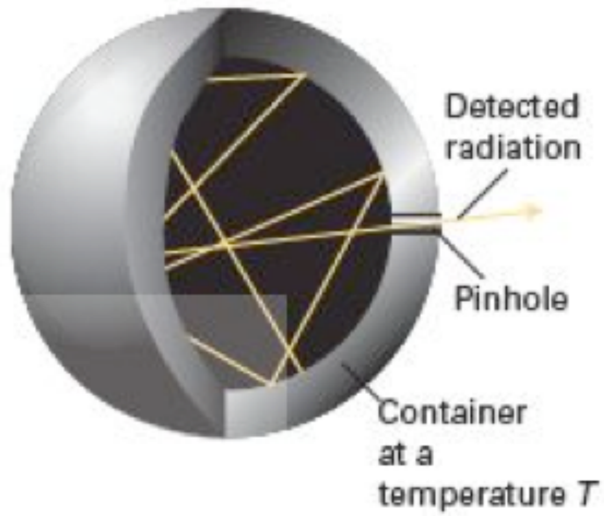
$$c = \lambda \nu \qquad \tilde{\nu} = 1/\lambda$$

$$c = 2.998 \times 10^{8} m s^{-1}$$



Black Body Radiation





Planck Distribution: $$\rho(\lambda) = \frac{8\pi hc}{\lambda^5(e^{hc/(\lambda k_B T)} - 1)}$$

Derived based on the assumption that $E = nh\nu, \quad n = 0, 1, \ldots$

$\text{Planck's constant} : h = 6.626 \times 10^{-34}\ \text{Js}$

Heat capacity of monoatomic solid

Dulong and Petit's law (valid for any monoatomic solid at high temp.)

$$U_m = N_A \cdot 3k_BT$$
$$C_{V,m} = \left(\frac{\partial U_m}{\partial T}\right)_V = 3R = 24.9\ \mathrm{JK^{-1}mol^{-1}}$$

Einstein's formula:

$$U_m = \frac{3N_A h\nu}{e^{h\nu/(k_BT)} - 1}$$
$$C_{V,m} = 3R\left(\frac{h\nu}{k_BT}\right)^2 \frac{e^{h\nu/(k_BT)}}{(e^{h\nu/(k_BT)} - 1)^2}$$

$$E_{osc} = nh\nu, \quad n = 0, 1, 2, \ldots$$

Debye: more realistic distribution of oscillator energies

Photoelectric Effect: $$\frac{1}{2}m_e v^2 = h\nu - \Phi$$

(Particle nature of light)

de Broglie - any particle has wave characteristics

$$\lambda = \frac{h}{p}$$

(Experimental evidence: Davisson and Germer, diffraction of electron from a nickel crystal)

(Time independent) Schrödinger Equation

$$\hat{H}\psi(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Examples:

Particle in 1-D Box: $-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x), 0 < x < L$

$$(\psi(x) = 0 \quad x \leq 0 \text{ or } x \geq 0)$$

Harmonic Oscillator: $-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi(x) = E\psi(x)$

General Expression in 3-D Spherical Coordinate System:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi(r,\theta,\phi) + V(r,\theta,\phi)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi(r,\theta,\phi)+V(r,\theta,\phi)\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

Free rotation in three dimension: r is fixed at R and $\psi(r,\theta,\phi)\rightarrow\psi(\theta,\phi)$

$$-\frac{\hbar^2}{2m}\left(\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{R^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi(\theta,\phi)=E\psi(\theta,\phi)$$

$$\psi(\theta,\phi)=\Theta(\theta)\Phi(\phi)$$

$$-\frac{\hbar^2}{2m}\left(\frac{\Phi(\phi)}{R^2\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta(\theta)}{d\theta}+\frac{\Theta(\theta)}{R^2\sin^2\theta}\frac{d^2\Phi(\phi)}{d\phi^2}\right)=E\Theta(\theta)\Phi(\phi)$$

$$\frac{d^2\Phi(\phi)}{d\phi^2}=-m^2\Phi(\phi) \qquad m=0,\pm1,\pm2,\ldots$$

$$-\frac{\hbar^2}{2mR^2}\left(\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta(\theta)}{d\theta}-\frac{m^2}{R^2\sin^2\theta}\Theta(\theta)\right)=E\Theta(\theta)$$

$$-\frac{\hbar^2}{2mR^2}\left(\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta(\theta)}{d\theta}-\frac{m^2}{R^2\sin^2\theta}\Theta(\theta)\right)=E\Theta(\theta)$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta(\theta)\right)+\left(\frac{2IE}{\hbar^2}-\frac{m^2}{\sin^2\theta}\right)\Theta(\theta)=0$$

$$\Theta(\theta)=P_l^{|m|}(\cos\theta)$$ Associated Legendre Polynomial

$$\frac{2IE}{\hbar^2}=l(l+1), l=0,1,2,\ldots, l\geq|m|$$

$$Y_{lm}(\theta,\phi)=N_{lm}P_l^{|m|}(\cos\theta)e^{im\phi}$$

Associated Legendre Polynomial

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{\partial}{\partial\theta}P_l^{|m|}(\cos\theta)\right)+\left(l(l+1)-\frac{m^2}{\sin^2\theta}\right)P_l^{|m|}(\cos\theta)=0$$

$$l=0,1,2\ldots;l\geq|m|$$

Spherical Harmonics

$$Y_{lm}(\theta,\phi)=N_{lm}P_l^{|m|}(\cos\theta)e^{im\phi}$$

This is an eigenfunction of the total angular momentum:

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

and the angular momentum along the z-axis:

$$\hat{L}_z=\frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

Associated Legendre Polynomial

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{\partial}{\partial\theta}P_l^{|m|}(\cos\theta)\right)+\left(l(l+1)-\frac{m^2}{\sin^2\theta}\right)P_l^{|m|}(\cos\theta)=0$$

$$l=0,1,2\ldots;l\geq|m|$$

What are corresponding eigenvalues?

$$Y_{lm}(\theta,\phi)=N_{lm}P_l^{|m|}(\cos\theta)e^{im\phi}$$

$$\hat{L}^2Y_{lm}(\theta,\phi)=-\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}Y_{lm}(\theta,\phi)=\boxed{\hbar^2 l(l+1)}Y_{lm}(\theta,\phi)$$

$$\hat{L}_z=\frac{\hbar}{i}\frac{\partial}{\partial\phi}Y_{lm}(\theta,\phi)=\boxed{m\hbar}Y_{lm}(\theta,\phi)$$

(Time independent) Schrödinger Equation

$$\hat{H}\psi(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

General Expression in 3-D Spherical Coordinate System:

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$\longrightarrow \quad -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\psi(\mathbf{r}) + \frac{\hat{L}^2}{mr^2}\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

If $V(\mathbf{r}) = V(r)$ (independent of θ and ϕ)

$\psi(\mathbf{r}) = R(r)Y_{lm}(\theta,\phi)$ simplifies the problem.

For hydrogen-like atom,

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{Ze^2}{4\pi\epsilon_0|\mathbf{r}_e - \mathbf{r}_N|} = -\frac{\hbar^2}{2M}\nabla_{cm}^2 - \frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

↑

Free motion of center of mass of the atom

For internal state of the hydrogen-like atom,

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hat{L}^2}{\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\psi(\mathbf{r}) = R(r)Y_{lm}(\theta,\phi)$$

$$\hat{H}R(r)Y_{lm}(\theta,\phi) = \left(-\frac{\hbar^2}{2\mu}\frac{Y_{lm}(\theta,\phi)}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{\hbar^2 l(l+1)Y_{lm}(\theta,\phi)}{2\mu r^2} - \frac{Ze^2 Y_{lm}(\theta,\phi)}{4\pi\epsilon_0 r}\right)R(r) = ER(r)Y_{lm}(\theta,\phi)$$

For hydrogen-like atom,

$$\psi(\mathbf{r}) = R(r)Y_{lm}(\theta, \phi)$$

$$\frac{d}{dr^2} rR(r) + \left(-\frac{l(l+1)}{r^2} + \frac{2\mu E}{\hbar^2} + \frac{2\mu Z e^2}{4\pi\epsilon_0 \hbar^2 r}\right) rR(r) = 0$$

$$\rho = \alpha r$$

$$\frac{d^2}{d\rho^2}\left(\rho R(\rho/\alpha)\right) + \left(-\frac{l(l+1)}{\rho^2} + \frac{2\mu E}{\hbar^2 \alpha^2} + \frac{2\mu Z e^2}{4\pi\epsilon_0 \hbar^2 \alpha}\frac{1}{\rho}\right)\left(\rho R(\rho/\alpha)\right) = 0$$

$$\alpha = \frac{2\mu Z e^2}{4\pi\epsilon_0 \hbar^2} = \frac{2Z}{a} \qquad a = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2}$$

For hydrogen-like atom,

$$\psi(\mathbf{r}) = R(r)Y_{lm}(\theta,\phi)$$

$$\rho = \alpha r$$

$$\frac{d^2}{d\rho^2}(\rho R(\rho/\alpha)) + \left(-\frac{l(l+1)}{\rho^2} + \frac{2\mu E}{\hbar^2\alpha^2} + \frac{2\mu Ze^2}{4\pi\epsilon_0\hbar^2\alpha}\frac{1}{\rho}\right)(\rho R(\rho/\alpha)) = 0$$

$$\alpha = \frac{2\mu Ze^2}{4\pi\epsilon_0\hbar^2} = \frac{2Z}{a}$$

$$a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

Solution of the above differential equation satisfying the boundary conditions exist only when

$$\frac{2\mu E}{\hbar^2\alpha^2} = -\frac{1}{4n^2}, n = 1, 2, 3, \ldots \text{ and } n \geq l+1$$

For hydrogen-like atom,

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

$$\rho = \alpha r$$

$$\frac{d^2}{d\rho^2}(\rho R_{nl}(\rho/\alpha)) + \left(-\frac{l(l+1)}{\rho^2} - \frac{1}{4n^2} + \frac{1}{\rho}\right)(\rho R_{nl}(\rho/\alpha)) = 0$$

$$\alpha = \frac{2\mu Z e^2}{4\pi\epsilon_0\hbar^2} = \frac{2Z}{a} \qquad a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

$$\frac{2\mu E}{\hbar^2\alpha^2} = -\frac{1}{4n^2}, n = 1,2,3,\ldots \text{ and } n \geq l+1$$

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right)\psi_{nlm}(\mathbf{r}) = E_n\psi_{nlm}(\mathbf{r})$$

$$E_n = \boxed{-\frac{\hbar^2\alpha^2}{8\mu}\frac{1}{n^2} = -\frac{\mu Z^2 e^4}{8h^2\epsilon_0^2}\frac{1}{n^2} = -\frac{Z^2 R_\mu}{n^2}hc} \qquad R_\mu = \frac{\mu e^4}{8\epsilon_0^2 h^3 c}$$

For hydrogen atom,

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta,\phi) \qquad \rho = \alpha r$$

$$E_n = -\frac{R_H}{n^2}hc \qquad R_H = \frac{\mu_H e^4}{8\epsilon_0^2 h^3 c} = \frac{\mu_H}{m_e}R_\infty, \; R_\infty = \frac{m_e e^4}{8\epsilon_0^2 h^3 c}$$

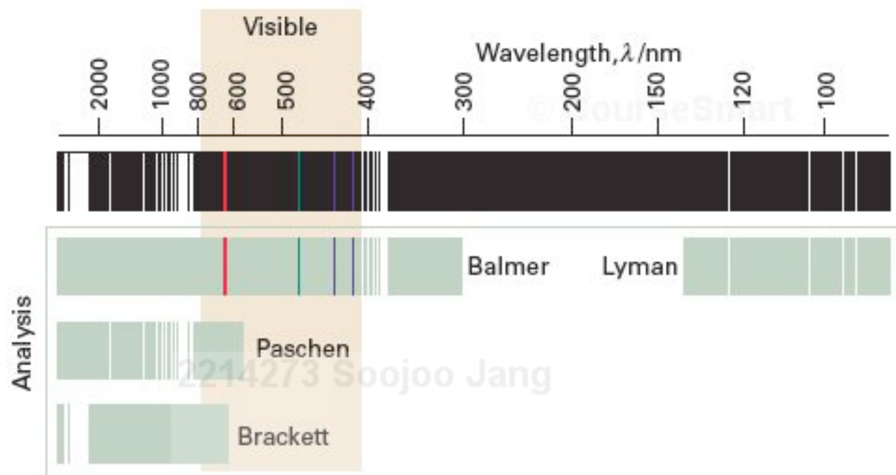
$$\tilde{\nu}_{n_2\to n_1} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

9.1 THE STRU

Lyman Series: n_1=1

Balmer Series: n_1=2

Paschen Series: n_1=3



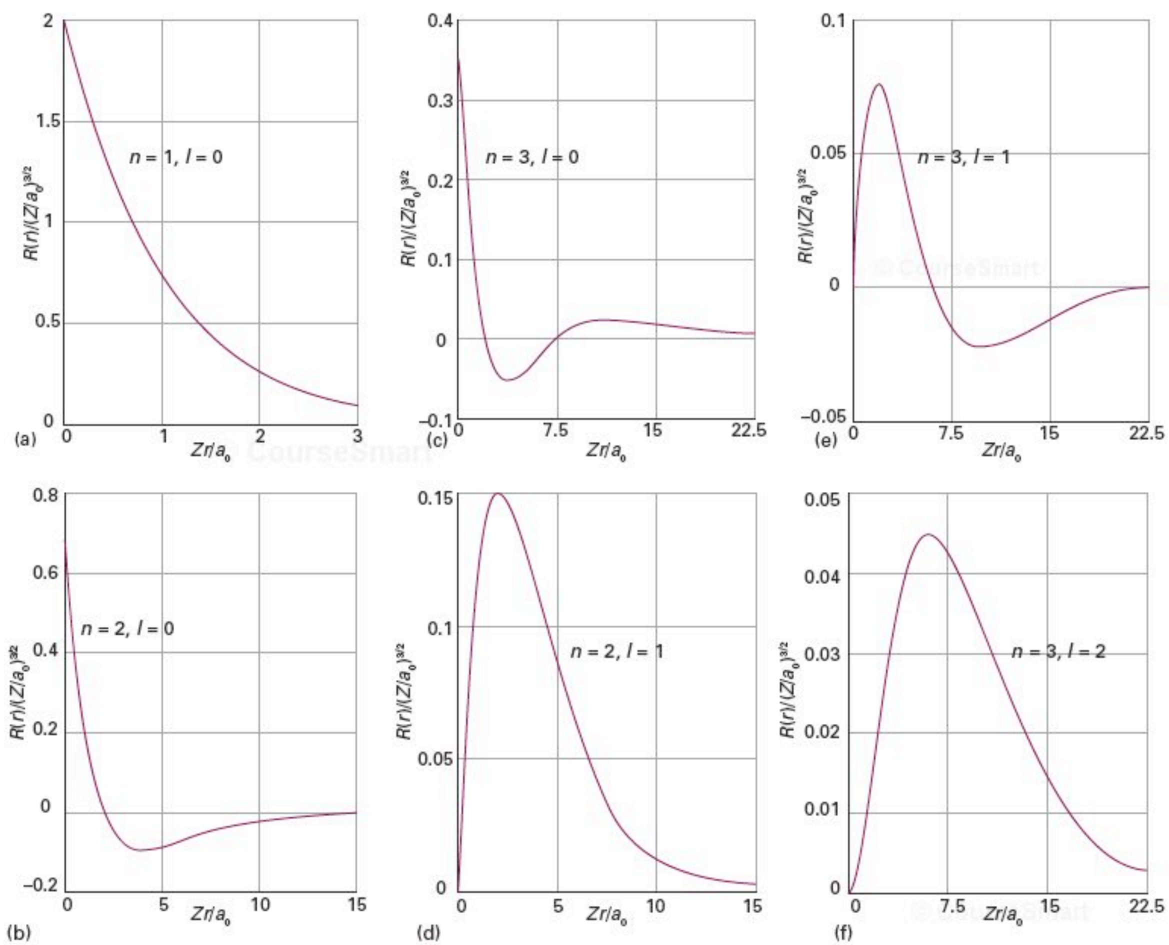
$$R_{n,l}(r) = N_{n,l}\rho^l L_{n+1}^{2l+1}(\rho)e^{-\rho/2}$$

$$\rho = \alpha r$$

Associated Laguerre polynomial

$$\alpha = \frac{2\mu Z e^2}{4\pi\epsilon_0\hbar^2} = \frac{2Z}{a}$$

$$a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$



$R_{n,l}(r)$ has $n - l - 1$ nodes.

Angular distribution function

$|Y_{lm}(\theta,\phi)|^2 d\theta \sin\theta d\phi$: Probabiltiy to find the electron in the angular volume of

$$(\theta, \theta+\delta\theta)\ \&\ (\phi, \phi+\delta\phi)$$

$Y_{lm}(\theta,\phi)$ has l nodal planes.

The angular momentum operator of an electron is denoted as

$$\hat{l} = \hat{l}_x \mathbf{e}_x + \hat{l}_y \mathbf{e}_y + \hat{l}_z \mathbf{e}_z$$

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$$

$$\hat{l}^2 Y_{lm}(\theta,\phi) = \boxed{\hbar^2 l(l+1)} Y_{lm}(\theta,\phi)$$

$$\hat{l}_z Y_{lm}(\theta,\phi) = \boxed{\hbar m} Y_{lm}(\theta,\phi)$$

Spin - cannot be visualized but has almost the same property as the orbital angular momentum except that it can have half-integer quantum numbers.

Eigenvalues of $\hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2$ and $\hat{s}_z$

are $\hbar^2 s(s+1)$ and $\hbar m_s$, $m_s = -s, \ldots, s$ with interval of 1

Spin quantum number "s" is a unique property of a particle.

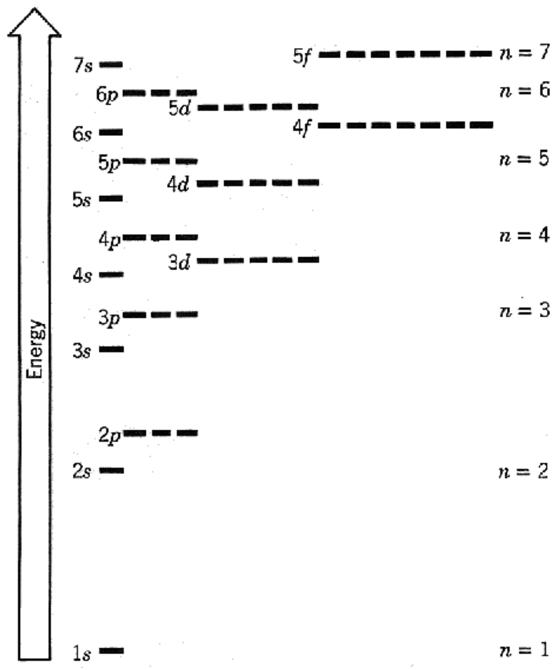
Fermions have half integer value of "s". Two fermions cannot occupy the same quantum state.

Electron, Proton, Neutron: s=1/2

Bosons have full integer value of "s". There is no limitation in the number of bosons that can occupy the same state.

Photon, Deuteron: s=1

Many electron atom - orbitals with the same principal quantum “n” are no longer degenerate.



For a given principal quantum number, the energy is higher for larger angular momentum quantum number.

Why?

Configuration: the manner of filling electrons in the orbitals available. There are numerous configurations possible, but there is only one ground state configuration!

n : principal quantum number (shell)

l, m, s : angular momentum, magnetic momentum (z-component of l), and spin quantum numbers of a single electron

Orbital: specified by *n* and *l*

Configuration - Assignment of electrons to orbitals

L, M, S : quantum numbers for sum over all the electrons

For l_1 and l_2

$$l = |l_1 - l_2|, \ldots, l_1 + l_2$$

Term Symbol: $^{2S+1}\square_{J}$

L =	
0	S
1	P
2	D
3	F
4	G

J: Quantum number for sum of *L* and *S*

Possible combinations of angular momenta and term symbols for two equivalent *p* electrons.

L	S	J	Term Symbols
2	0	2	$^1D_2$
1	1	2,1,0	$^3P_2,\ ^3P_1,\ ^3P_0$
0	0	0	$^1S_0$

Hund's rules - determine the energy levels for the same configuration (generally correct, but not absolutely right)

(i) Among all the terms derived from the same configuration, those with the highest spin multiplicity are the lowest in energy.

(ii) Of the terms with the same multiplicity, the lowest is that with the highest value of L.

Lande's interval rule - determines the energy levels among terms with the same multiplicity and L. Works well mostly for ground state terms.

For less than half-filled orbitals, smaller J has lower energy.
For more than half-filled orbitals, larger J has lower energy.

Hydrogen atom

Ground state ($^2S_{1/2}$) : $n = 1, l = 0, s = 1/2$

Excited states ($^2P_{3/2},\ ^2P_{1/2},\ ^2S_{1/2}$): $n = 2, l = 1, s = 1/2$

Helium atom

Ground state configuration: $1s^2$

Ground state term: $1\ ^1S_0$

Excited state configurations: $1s^1np^1, 1s^1nd^1, \ldots$

Excited state terms:

$n\ ^1S_0,\ ^1P_1,\ ^1D_1$ Singlets

$n\ ^3S_1,\ ^3P,\ ^3D$ Triplets

Selection rules - determine what transition is possible when photon is absorbed or emitted.

$$\Delta S = 0$$

$$\Delta L = \begin{cases} \pm 1, 0 & \text{if } L' \neq 0 \\ 1 & \text{if } L' = 0 \end{cases}$$

$$\Delta J = 0, \pm 1 \text{ (no } 0 \leftrightarrow 0 \text{ transition)}$$

Laporte's Rule $\sum_i l_i :$ even $\leftrightarrow$ odd

This is due to the fact that absorption of photon, which has spin 1, corresponds to odd inversion symmetry and that the sum of l_i dtermines the inversion symmetry of the eigenstate.

Examples of Atomic Spectra

1. Alkali metal atoms (Li,Na, K, Rb, Cs) - (Closed shell)ns^1

$$S : s \rightarrow p$$
$$P : p \rightarrow s$$
$$D : d \rightarrow p$$
$$F : f \rightarrow d$$

Emission has at least three series in the visible region.

Δn : unrestricted

$\Delta l = \pm 1$ ($\Delta l = 0$ is forbidden because of Laporte's rule)

$\Delta J = 0, \pm 1$ except $J = 0 \not\leftrightarrow J = 0$

The principal series in the sodium atom (Na)

$$n\ ^2P_{1/2} \rightarrow 3\ ^2S_{1/2}$$
$$n\ ^2P_{3/2} \rightarrow 3\ ^2S_{1/2}$$

$n \geq 3$

n=3: Sodium D lines: 589.592 nm, 588.995 nm