Brief Summary of Chapter 1

微观粒子波动性--运动粒子在空间出现的几率分布呈现波的特征--几率波！

量子力学的统计学本质

量子力学体系的状态函数--波函数 $\Psi(r,t)$

简单体系：*i*维势箱

1) $\hat{H}\Psi = E\Psi$

2) 边界条件

$$\psi = \prod_{i=1-3}\sqrt{\frac{2}{l_i}}\sin\frac{n_i\pi x_i}{l_i} \quad E = \frac{h^2}{8m}\sum_{i=1-3}\frac{n_i^2}{l_i^2} \quad (n_i = 1,2,3,\ldots)$$

A. 能量量子化

B. 测不准原理：$\Delta x\Delta p$ or $\Delta E\Delta t \geq \hbar$

1. 几率密度分布函数 $|\Psi|^2$

2. 正交归一性：$\int\Psi_i^*\Psi_j d\tau = \delta_{ij}$

3. 本征函数/方程：$\hat{A}\Psi = a\Psi$

4. Schrödinger方程：$i\hbar\partial\Psi/\partial t = \hat{H}\Psi$

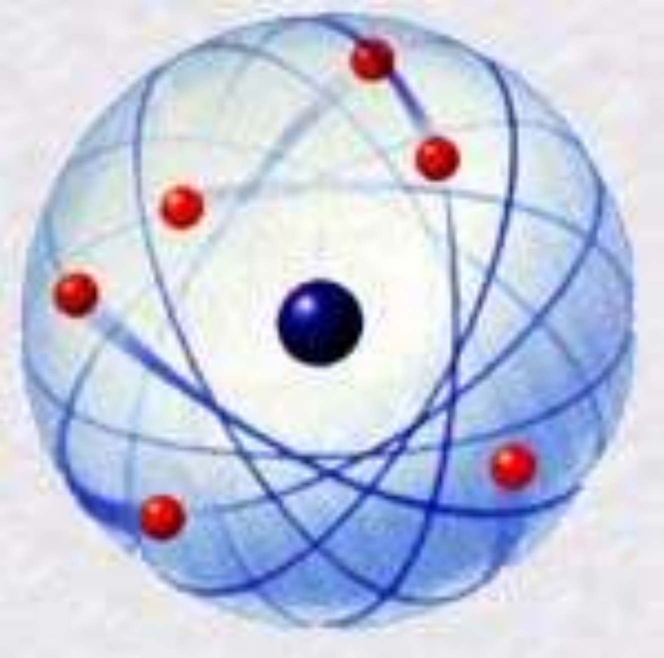
(定态) $\hat{H}\Psi(r) = E\Psi(r)$

5. 态叠加原理: $\Psi = \Sigma c_i\psi_i$, $\hat{A}\psi_i = A_i\psi_i$

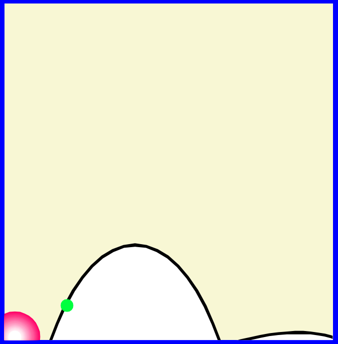
求平均值: $\langle A\rangle = \int\Psi^*\hat{A}\Psi d\tau / \int\Psi^*\Psi d\tau$

$$= \Sigma c_i^2 A_i / \Sigma c_i^2$$

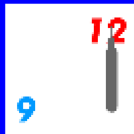
Chapter 2 Atomic structure



Atom



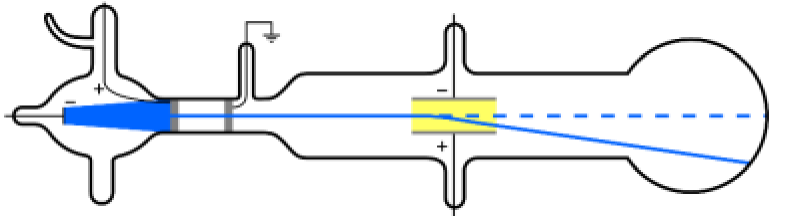
- The basic building block of all matters.
- The smallest particle of an element that has the same properties as the element.
- Composed of a central nucleus and an “electron cloud ” .
- Electron cloud： not really a cloud of electrons, but an informal description of the probability wave of electrons in constant motion!



Evolution of Atomic Models

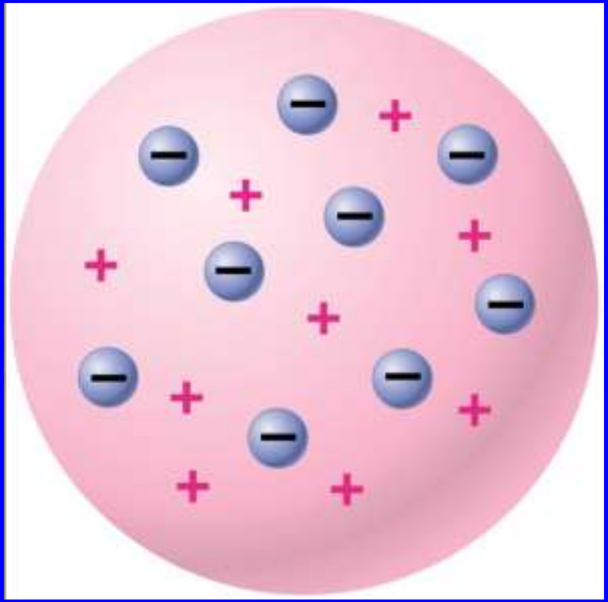
- **1803**, "***Atomic Theory***" by John Dalton.

- **1904**, "***Plum pudding***" model proposed by J.J. Thomson after his discovery of **electron** (1897) in cathode rays.



Crookes tube

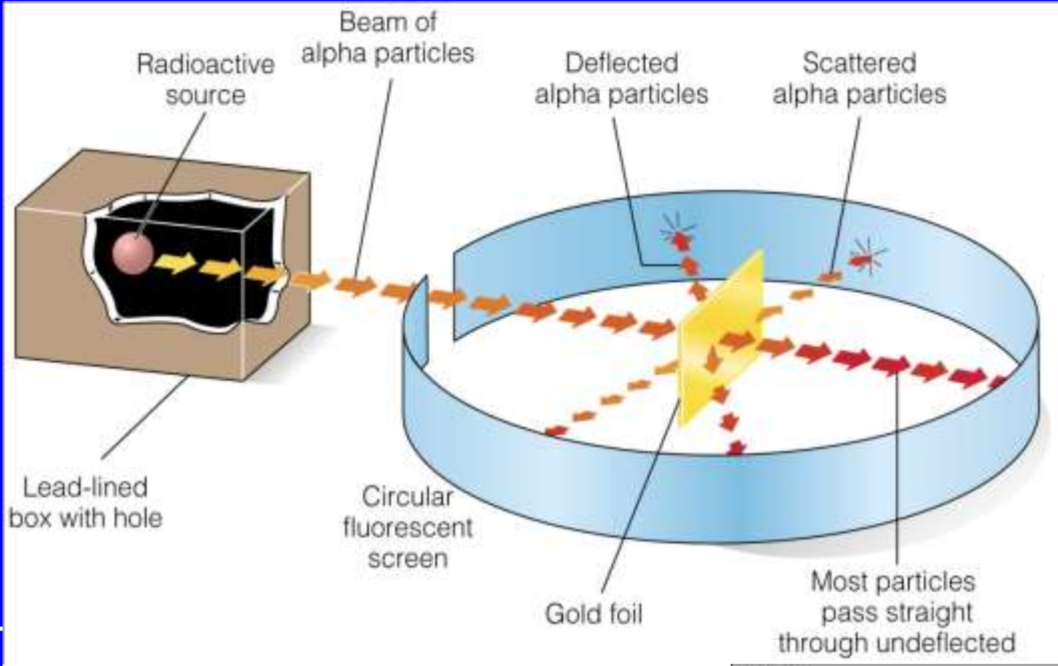
i.e., negatively charged electrons embedded in a uniformly distributed positive charge.



History of Atomic Models

- ***1911**, disproval of **Thomson's** model!*

Geiger and *Marsden* with ***E. Rutherford*** performed a scattering experiment with alpha particles (He^{2+}) shot on a thin gold foil.



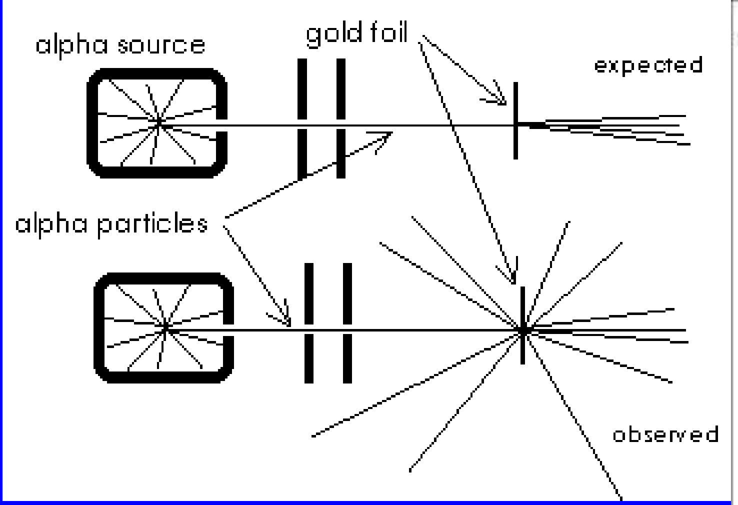
Deflection angle Θ≥ 90°

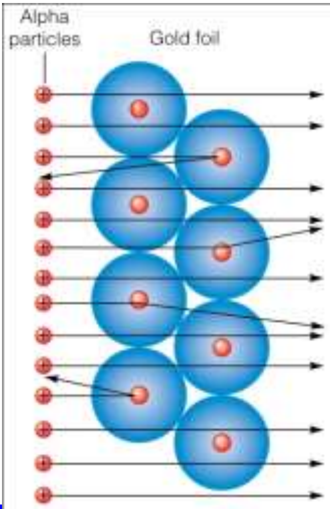
10^{-3500}

(predicted by Thomson model)

10^{-4}

(observed by Rutherford et al.)

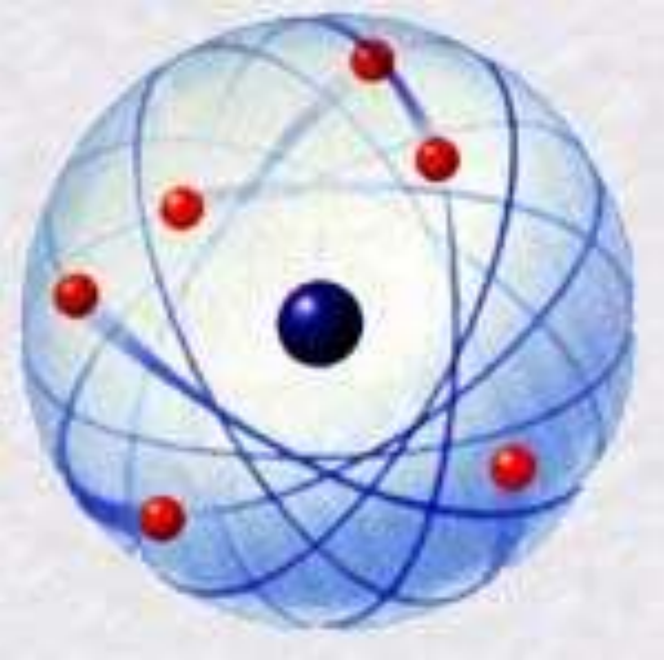




History of Atomic Models

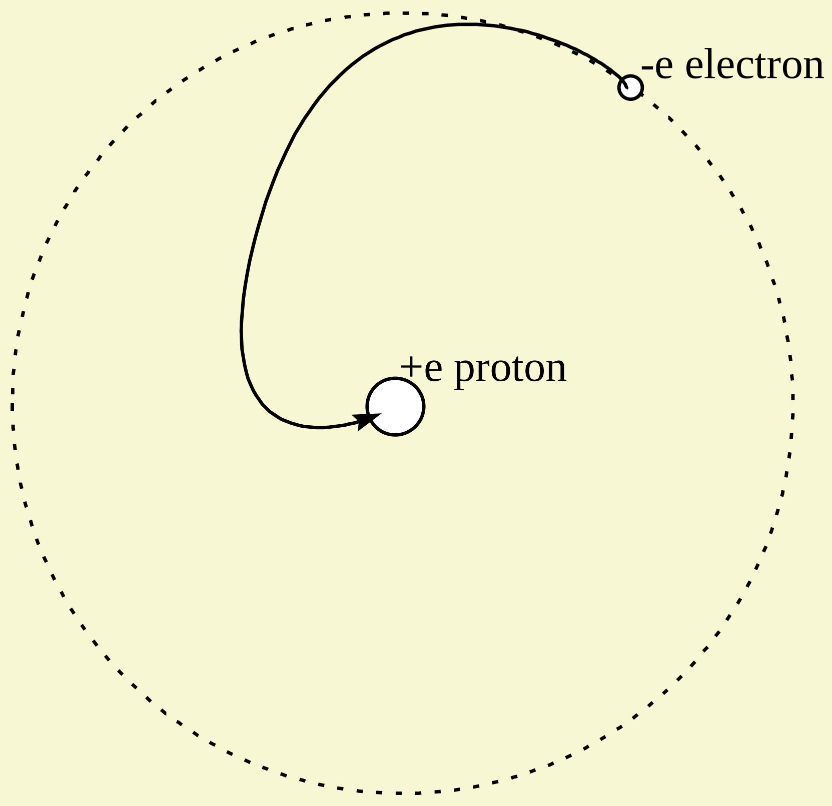
- **1912**: ***Rutherford*** proposed the ***"Planetary Model "*** of the atom, i.e., positively charged core surrounded by electrons.

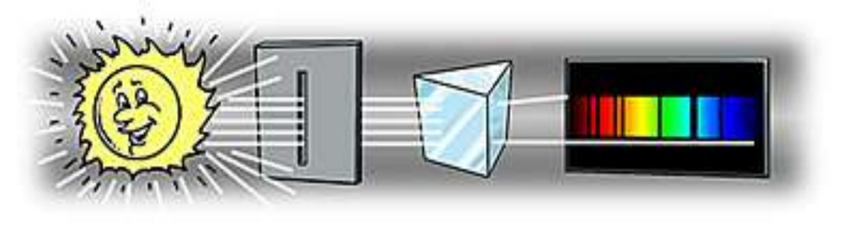
  (1908 Nobel prize
  chemistry of radioactive substances)



Rutherford estimated the diameter of nucleus to be only about 10^{-15} m. The diameter of an atom, however, was known to be 10^{-10} m, about 100 000 times larger. Thus most of an atom is empty space.

The planetary model failed in explaining why collapses of electrons into nucleus do not occur!



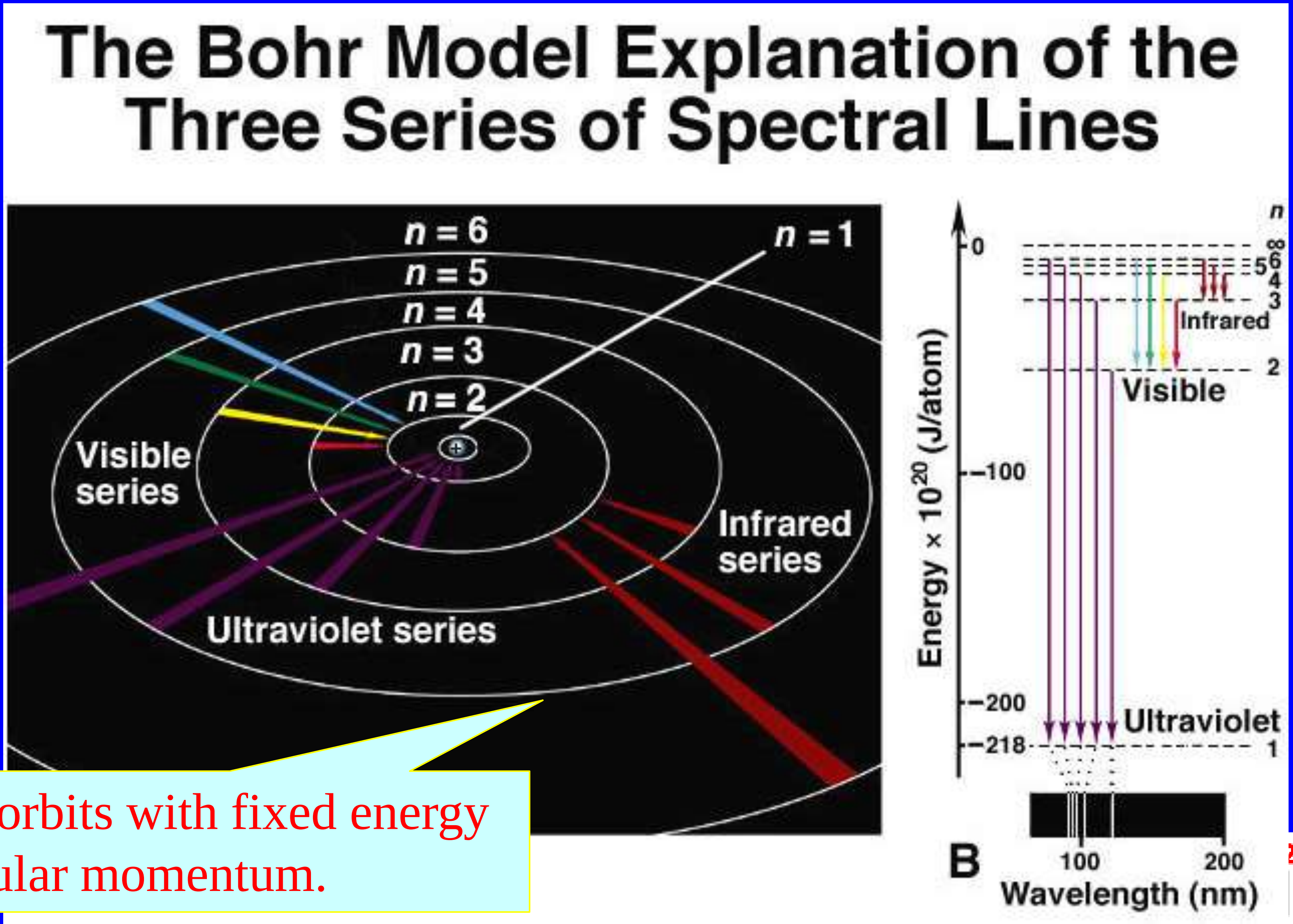


1) According to Maxwell theory of electromagnetism, as the electron orbits around the nucleus, it accelerates and hence radiates energy.

2) The typical time for the electron to collapses into the nucleus would be about 10^{-8} s.

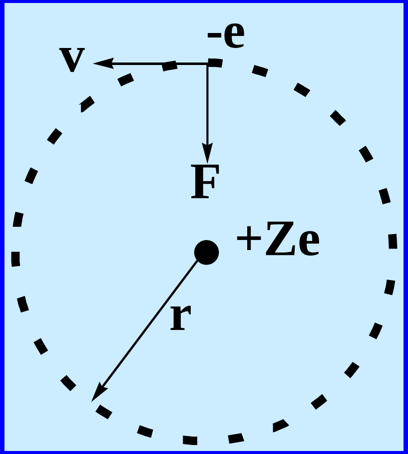
3) The spectrum of radiation would be continuous.

- **1913**: ***Niels Bohr*** proposed his ***Bohr model*** of the atom with incorporation of the idea of "***quanta***" (by *Plank & Einstein*).



circular orbits with fixed energy and angular momentum.

Bohr atom



Merits:

i) Explains why atoms are stable
ii) Predicts energy is quantized
iii) Explains H atom spectra

Demerits:

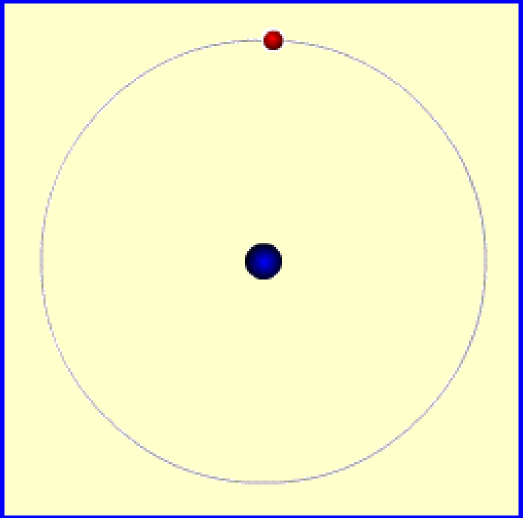
iv) Fails to predict fine spectral structure of H
v) Fails for many-electron atoms

e^- is classical particle
e^- in ‘orbit’ at fixed r corresponding to a quantum number.

Bohr atom

e^- is a classical particle

e^- in 'orbit' at fixed **r**



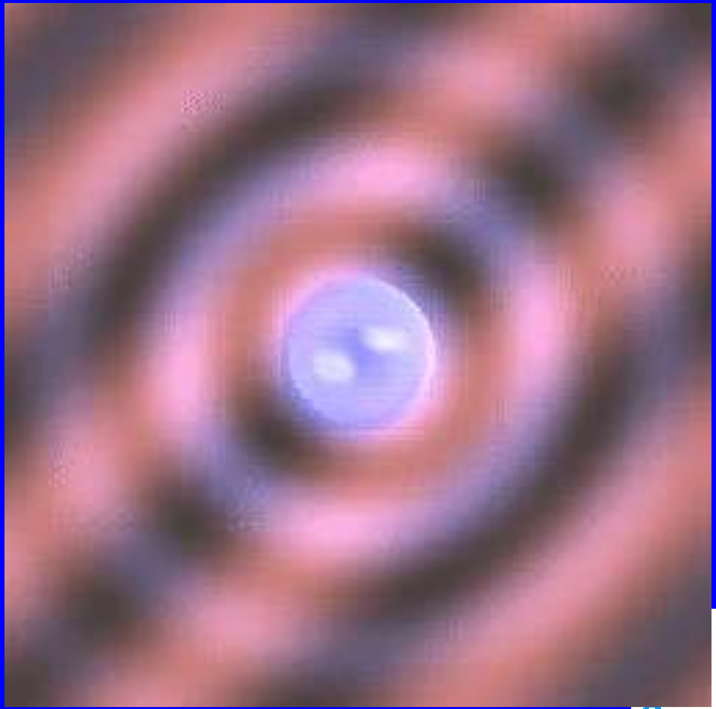
Schrödinger atom (1926)

1) Electron confined in an atom should also behave like a wave.

Schrödinger equation!

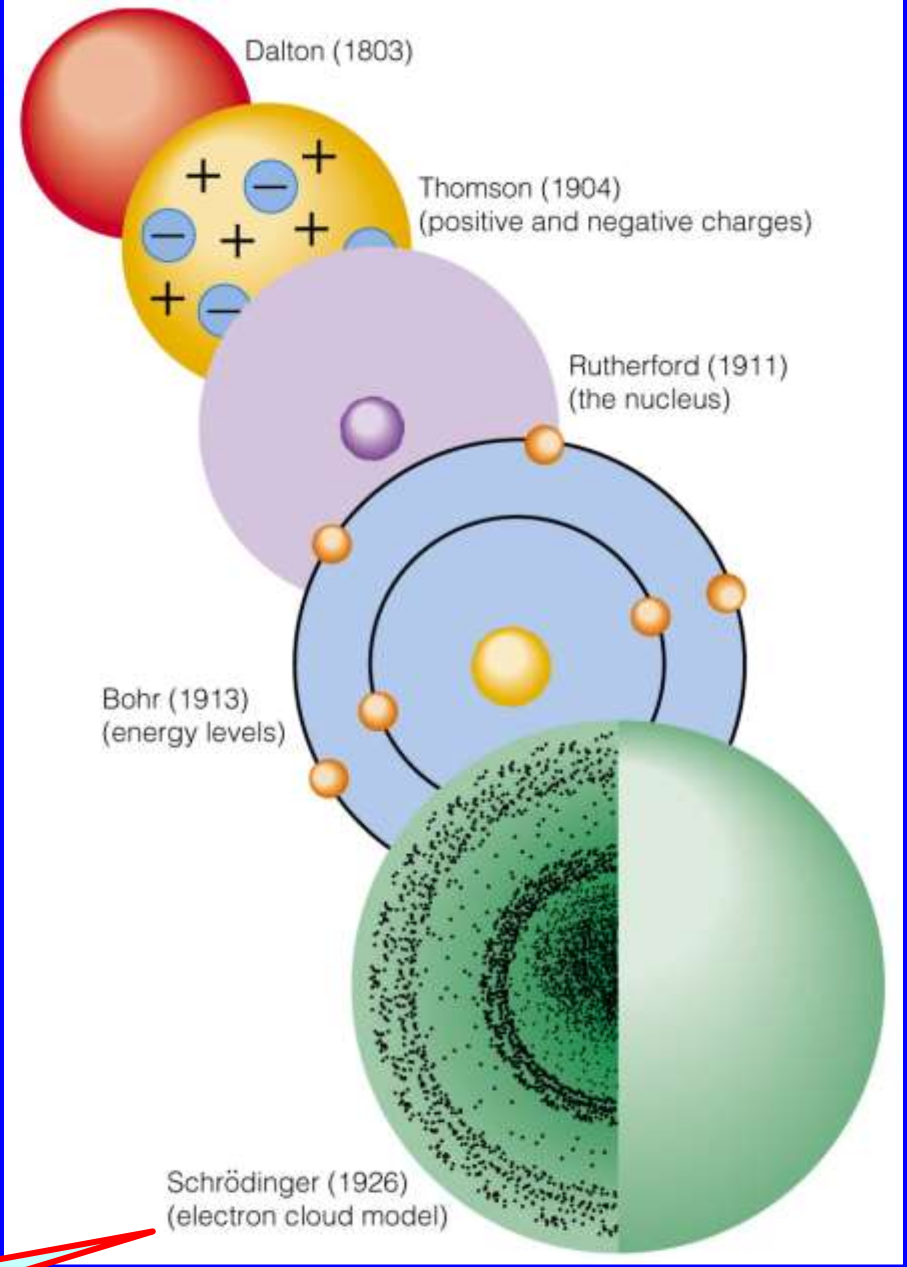
2) No fixed orbits but electron density distribution

3) For 3-D, we need three quantum numbers n, *l*, m_l



History of Atomic Models

- Understanding atomic structure is the first step to understand the Structures of Matters.
- The so-called electron density is actually the probability density of electron wave!



Quantum mechanics

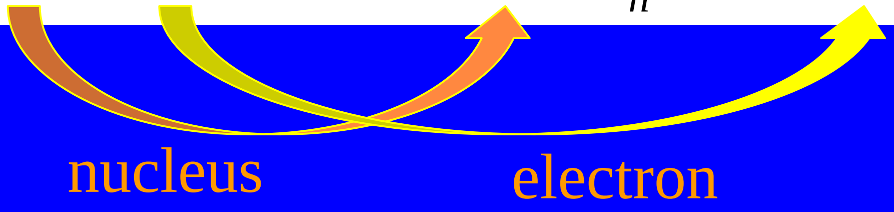
2.1 The Schrödinger equation and its solution for one-electron atoms

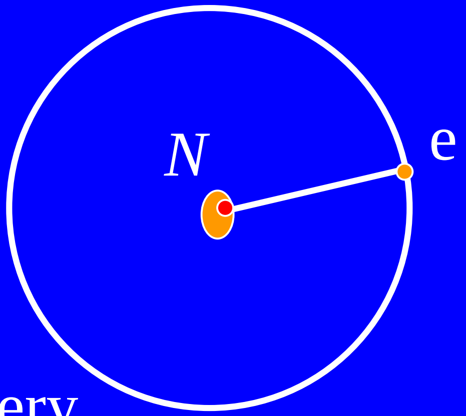
2.1.1 The Schrödinger equation

H atom, He^{+} and Li^{2+}

- The Hamiltonian of a one-electron atom/cation,

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{n-e} = -\frac{h^2}{8\pi^2 m_n}\nabla_n^2 - \frac{h^2}{8\pi^2 m_e}\nabla_e^2 + \hat{V}_{n-e}$$





- The Hamiltonian for a many-electron atom?
- For a many-electron atom, the kinetic-energy operator should sum up the contribution from every electron. The potential energy function should include all those from **n-e** and **e-e** interactions.

Note that the nucleus is much heavier than the electron and the electron moves much quickly around the atomic nucleus! The Hamiltonian can be simplified as

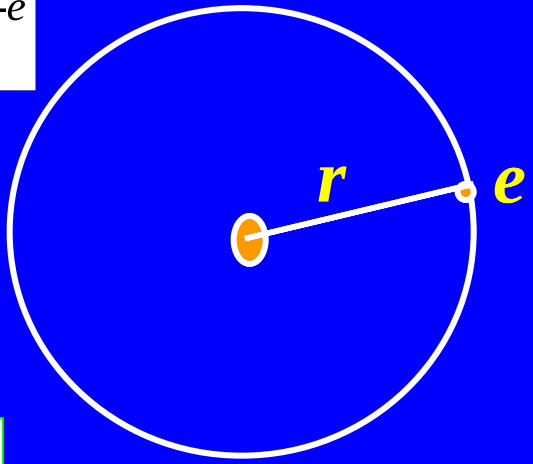
$$\hat{H} = \hat{T}_e + \hat{V}_{n-e} = -\frac{h^2}{8\pi^2 m_e}\nabla_e^2 + \hat{V}_{n-e}$$

One-electron Hamiltonian

$$\hat{H} = -\frac{h^2}{8\pi^2 m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \hat{V}_{n\text{-}e}$$

$$\hat{V}_{n-e} = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

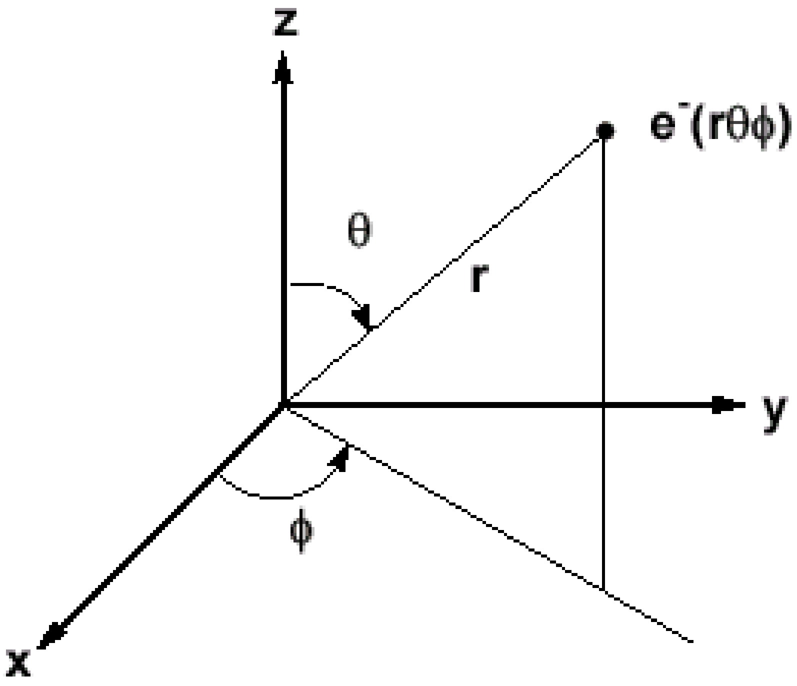
$$r = \sqrt{x^2 + y^2 + z^2}$$



The Schrödinger equation $\hat{H}\psi = E\psi$

Separation of variables (x,y,z) hindered by r ?!

Spherical polar coordinates



x = rsinθcosφ

y = rsinθsinφ

z = rcosθ

$$0 < r < +\infty$$

$$0 \le \theta \le \pi$$

$$0 \le \phi \le 2\pi$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\cos\theta = \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$tg\phi = y / x$$

r : distance from origin (nucleus).

θ : angle drop from the z-axis.

φ : angle from the x-axis (on the x-y plane)

(x,y,z) → (r,θ,φ); $\Psi(x,y,z) = \Psi(r, \theta, \phi)$

Is it possible to make $\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$ *?*

Using spherical polar coordinates, we have

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$V_{n-e} = -\frac{Ze^2}{(4\pi\varepsilon_0)r}$$

$$\hat{H} = -\frac{h^2}{8\pi^2 m_e}\nabla^2 + \hat{V}_{n\text{-}e}$$

The Schrödinger equation $\boxed{\hat{H}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)}$ becomes

$$\left\{-\frac{h^2}{8\pi^2 m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] - \frac{Ze^2}{4\pi\varepsilon_0 r}\right\}\psi = E\psi$$

⇓ divided by $-h^2/(8\pi^2 m_e)$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 m_e}{h^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi = 0$$

Thus it is reasonable to suppose $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$.

2.1.2 The solution --- *separation of variables*

Substitute $\Psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi)$ into the equation

$$\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial\psi}{\partial r})+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\psi}{\partial\theta})+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{8\pi^2 m_e}{h^2}(E+\frac{Ze^2}{4\pi\varepsilon_0 r})\psi=0$$

and multiply with $r^2/[R(r)\Theta(\theta)\Phi(\phi)]$

$$\frac{1}{R(r)}\frac{\partial}{\partial r}(r^2\frac{\partial R(r)}{\partial r})+\frac{1}{\Theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta})$$

$$+\frac{1}{\Phi(\phi)\sin^2\theta}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}+\frac{8\pi^2 m_e}{h^2}(E+\frac{ze^2}{4\pi\varepsilon_0 r})r^2=0$$

$$\frac{1}{R(r)}\frac{\partial}{\partial r}(r^2\frac{\partial R(r)}{\partial r})+\frac{8\pi^2 m_e}{h^2}(E+\frac{ze^2}{4\pi\varepsilon_0 r})r^2$$

$$=-[\frac{1}{\Theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta})+\frac{1}{\Phi(\phi)\sin^2\theta}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}]$$

Now both sides are variable-independent!

$$\text{let}\quad \frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{8\pi^2 m_e}{h^2}\left(E+\frac{ze^2}{4\pi\varepsilon_0 r}\right)r^2=\beta$$

- ▶ Radial part
- ▶ ***R*** eq.

Yet unsolvable!

$$\frac{1}{\Theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\frac{1}{\Phi(\phi)\sin^2\theta}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-\beta$$

- ▶ Angular part

Now multiply with ***sin²θ*** and …

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\beta\sin^2\theta=-\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}$$

Let

$$=m^2$$

$$\left\{\begin{array}{l}\dfrac{\sin\theta}{\Theta(\theta)}\dfrac{\partial}{\partial\theta}\left(\sin\theta\dfrac{\partial\Theta(\theta)}{\partial\theta}\right)+\beta\sin^2\theta=m^2\\[2ex]\dfrac{1}{\Phi(\phi)}\dfrac{\partial^2\Phi(\phi)}{\partial\phi^2}=-m^2\end{array}\right.$$

- ▶ ***Θ*** eq.

Unsolvable yet!

solvable now!

- ▶ ***Φ*** eq.

a. $\Phi(\phi)$ equation

$$\frac{d^2\Phi(\phi)}{d\phi^2} + m^2\Phi(\phi) = 0$$

Its solution in complex form:

→ $\Phi = Ae^{\pm i|m|\phi}$;   Let $m = \pm|m|$, $\Phi = Ae^{im\phi}$

Now normalize Φ:

$$\int_0^{2\pi} \Phi^*\Phi \; d\Phi = \int_0^{2\pi} A^2 e^{-im\phi} e^{im\phi} d\phi = 2\pi A^2 = 1$$

$$\Rightarrow A = (\sqrt{2\pi})^{-1}$$

$$\Phi = \sqrt{1/2\pi}\, e^{im\phi} = \sqrt{1/2\pi}\,(\cos m\phi + i \sin m\phi)$$

m?

$$\because \Phi(\phi) = \Phi(\phi + 2\pi)$$

（**Boundary condition!**）

$$e^{im\phi} = e^{im(\phi+2\pi)} = e^{im\phi} \cdot e^{im2\pi}$$

$$\therefore e^{im2\pi} = 1$$

The values of ***m*** must be $m = 0, \pm 1, \pm 2, \cdots\cdots$

m **(*m*$_l$): magnetic quantum number**

Complex function $$\Phi_m = Ae^{im\phi} \quad (m = 0, \pm 1, \pm 2, \cdots)$$

In case ***m≠0*****,** $$\Phi_{\pm m} = Ae^{\pm im\phi} = A(\cos m\phi \pm i\,\sin m\phi)$$

How to transform these complex functions into real ones for practical use?

Use the superposition principle.

$$\text{Let} \quad \varphi_1 = \Phi_m + \Phi_{-m} = 2A\cos m\phi = B\cos m\phi$$

$$\varphi_2 = \Phi_m - \Phi_{-m} = 2iA\sin m\phi = B'\sin m\phi$$

Now normalize φ_1 and φ_2:

$$\int_0^{2\pi} \varphi_1^* \varphi_1 d\phi = \int_0^{2\pi} (B\cos m\phi)^2 d\phi$$

$$= B^2\pi = 1 \quad \Rightarrow \qquad B = \sqrt{1/\pi}$$

$$\Longrightarrow$$

$$\boxed{\begin{aligned} \varphi_1 &= \sqrt{1/\pi}\cos m\phi \\ \varphi_2 &= \sqrt{1/\pi}\sin m\phi \end{aligned}}$$

The solutions of $\Phi(\phi)$ equation

m	complex form	real form
0	$\Phi_0 = \frac{1}{\sqrt{2\pi}}$	$\Phi_0 = \frac{1}{\sqrt{2\pi}}$
1	$\Phi_1 = \frac{1}{\sqrt{2\pi}} e^{i\phi}$	$\Phi_{\pm 1}^{\cos} = \frac{1}{\sqrt{\pi}} \cos\phi$
-1	$\Phi_{-1} = \frac{1}{\sqrt{2\pi}} e^{-i\phi}$	$\Phi_{\pm 1}^{\sin} = \frac{1}{\sqrt{\pi}} \sin\phi$
2	$\Phi_2 = \frac{1}{\sqrt{2\pi}} e^{i2\phi}$	$\Phi_{\pm 2}^{\cos} = \frac{1}{\sqrt{\pi}} \cos 2\phi$
-2	$\Phi_{-2} = \frac{1}{\sqrt{2\pi}} e^{-i2\phi}$	$\Phi_{\pm 2}^{\sin} = \frac{1}{\sqrt{\pi}} \sin 2\phi$

b. Θ(θ) equation

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

The process to solve this equation is too complicated. However, the solution always has the real form, $\Theta(\theta)=NP_l^{|m|}(\cos\theta)$

$$N=\left[\frac{(2l+1)}{2}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2},\quad P_l^{|m|}(z)=\frac{(1-z^2)^{\frac{|m|}{2}}}{2^l l!}\frac{d^{l+|m|}}{dz^{l+|m|}}(z^2-1)^l$$

Demanding $\beta = l(l+1)$ with l =0,1,2,3,… to make $\Theta(\theta)$ a well-behaved function.

l : angular momentum quantum number (角动量量子数)

necessary condition: $l \geq |m|$ **(m= 0, ±1， …)**

hence, l = 0, 1, 2, 3,…(s,p,d,f,g,h…)

m =0, (-1,0,1), (-2,-1,0,1,2), ……

Examples of Θ(θ):

l	m	$\Theta(\theta)$
0	**0**	$\sqrt{\frac{1}{2}}$
1	**0**	$\frac{\sqrt{6}}{2}\cos\theta$
	±1	$\frac{\sqrt{3}}{2}\sin\theta$

Examples of Θ(θ):

l	m	$\Theta(\theta)$
2	**0**	$\frac{\sqrt{10}}{4}(3\cos^2\theta-1)$
	±1	$\sqrt{\frac{15}{2}}\sin\theta\cos\theta$
	±2	$\sqrt{\frac{15}{4}}\sin^2\theta$

c. Solution of *R* equation

$$\frac{1}{R(r)}\frac{\partial}{dr}\left(r^2\frac{dR(r)}{\partial r}\right)+\frac{8\pi^2 m_e}{h^2}\left(E+\frac{ze^2}{4\pi\varepsilon_0 r}\right)r^2=\beta$$

Solution

$$R(r)=N\cdot e^{-\rho/2}L_{n+l}^{2l+1}(\rho)$$

(real!)

$$L_{n+l}^{2l+1}(\rho)=\sum_{k=0}^{n-l-1}(-1)^{k+1}\frac{[(n+l)!]^2\rho^k}{(n-l-1-k)!(2l+1+k)!k!}$$

$$\rho=2\alpha r,\quad \alpha=\frac{Z}{na_0}\ \&\ a_0=\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}=0.529\ \text{Å}$$

a_0 ~ *Bohr radius*, and also the atomic unit (au) of length.

necessary condition: ***$n \geq l+1$*** ***(l = 0, 1, 2, ……)***

hence, ***n = 1, 2, 3,……***

n: Principal quantum number

Examples of R(r):

n=1, *l*=0

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$$

$$\rho = \frac{2Z}{na_0} r$$

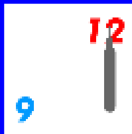
n=2, *l*=0

$$R_{20} = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)e^{-\rho/2}$$

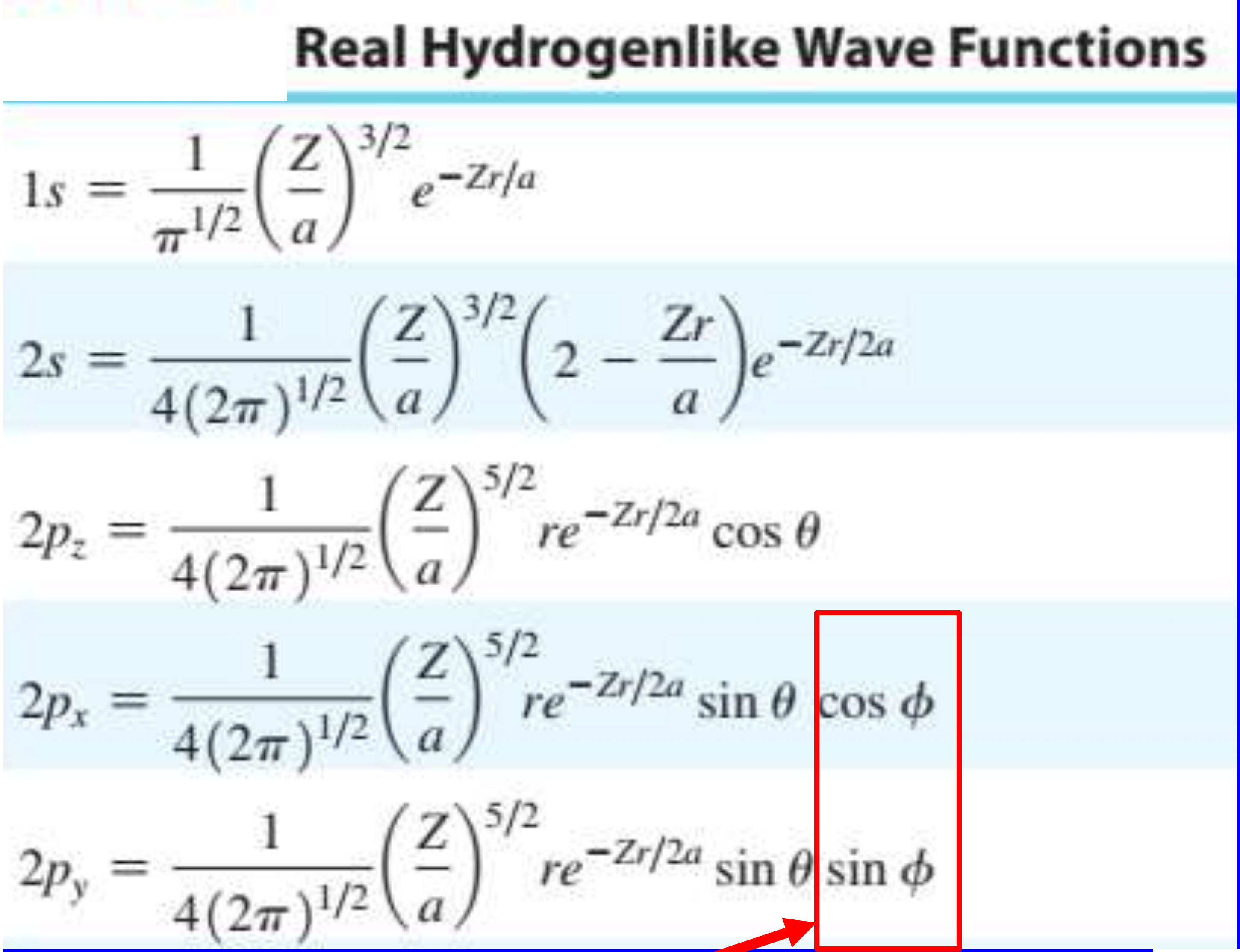
Finally, the ***Rydberg equation*** is obtained to define the energy,

$$E = -\left(\frac{h^2}{8\pi^2 m_e a_0^2}\right)\frac{Z^2}{n^2} = -R\cdot\frac{Z^2}{n^2},\ R = \frac{h^2}{8\pi^2 m_e a_0^2} = 13.6eV$$

R is called *Rydberg constant* with the value of ***13.6 eV***.



$\Psi_{n.l,m}(r,\ \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$



Real Hydrogenlike Wave Functions

n=1,l=0,m=0	$1s = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$
n=2,l=0,m=0	$2s = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(2 - \frac{Zr}{a}\right)e^{-Zr/2a}$
n=2,l=1,m=0	$2p_z = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\cos\theta$
n=2,l=1,m=±1	$2p_x = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\ \boxed{\cos\phi}$
	$2p_y = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\ \boxed{\sin\phi}$

Transformed from the complex form of $\Phi(\phi)$!

Summary

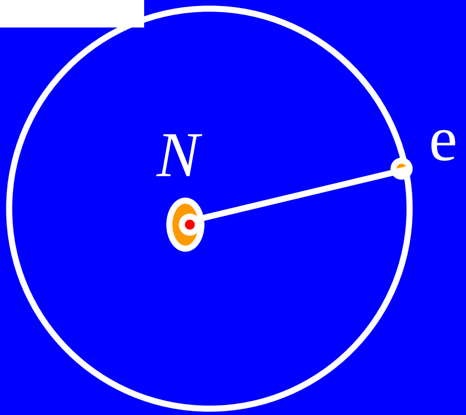
2.1 The Schrödinger equation and its solution for one-electron atoms

2.1.1 The Schrödinger equation

The Hamiltonian Operator of one-electron atoms

H atom, He$^+$ and Li^{2+}

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{n-e} = -\frac{h^2}{8\pi^2 m_n}\nabla_n^2 - \frac{h^2}{8\pi^2 m_e}\nabla_e^2 + \hat{V}_{n-e}$$



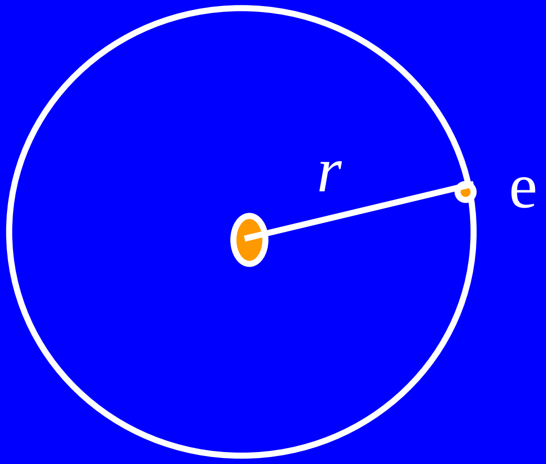
Consider that the electron approximately surrounds the atomic nucleus, the Hamilton operator can be simplified as

$$\hat{H} = \hat{T}_e + \hat{V}_{n-e} = -\frac{h^2}{8\pi^2 m_e}\nabla_e^2 + \hat{V}_{n-e}$$

$$\hat{\mathrm{H}} = -\frac{h^2}{8\pi^2 \mathrm{m_e}}\left(\frac{\partial^2}{\partial \mathrm{x}^2} + \frac{\partial^2}{\partial \mathrm{y}^2} + \frac{\partial^2}{\partial \mathrm{z}^2}\right) + \hat{\mathrm{V}}_{\text{n-e}}$$

$$\hat{V}_{n-e} = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$r = \sqrt{x^2 + y^2 + z^2}$$



The Schrödinger equation $\hat{H}\psi = E\psi$

Separation of variables ?

$$\hat{H} = \hat{T}_e + \hat{V}_{n-e} = -\frac{\hbar^2}{2m_e}\hat{\nabla}_e^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

Spherical polar coordinates

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 m_e}{h^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi = 0$$

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

Separation of variables!

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m_l^2 \longrightarrow \Phi_{m_l}(\phi) = \sqrt{\frac{1}{2\pi}}e^{im_l\phi} \quad (m_l = 0, \pm1, \pm2 \ldots)$$

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right) + \beta\sin^2\theta = m^2 \longrightarrow \Theta_{l,m_l}(\theta), \quad \beta = l(l+1)$$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + r^2\frac{8\pi^2 m_e}{h^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right) = \beta \longrightarrow R_{n,l}(r)$$

Quantum numbers---- n, l, m_l

- For H and H-like ions, their one-electron wavefunction (atomic orbital) can be expressed as,

$$\psi_{n,l,m_l}(r,\theta,\phi)=R_{n,l}(r)\cdot\Theta_{l,m_l}(\theta)\cdot\Phi_{m_l}(\phi)$$

These are the **eigenfunctions** of Hamiltonian, following the **eigenequation**,

$$\hat{H}\psi_{n,l,m_l}(r,\theta,\phi)=E_n\psi_{n,l,m_l}(r,\theta,\phi)$$

with the eigenvalue depending solely on the principal quantum number ***n***, i.e.,

$$E_n=-\frac{Z^2h^2}{8\pi^2m_en^2a_0^2}=-(\frac{h^2}{8\pi^2m_ea_0^2})\frac{Z^2}{n^2}=-R\frac{Z^2}{n^2}$$

R= 13.6 eV --- Rydberg constant

2.2 The physical meaning of quantum numbers

(n, l, m_l)

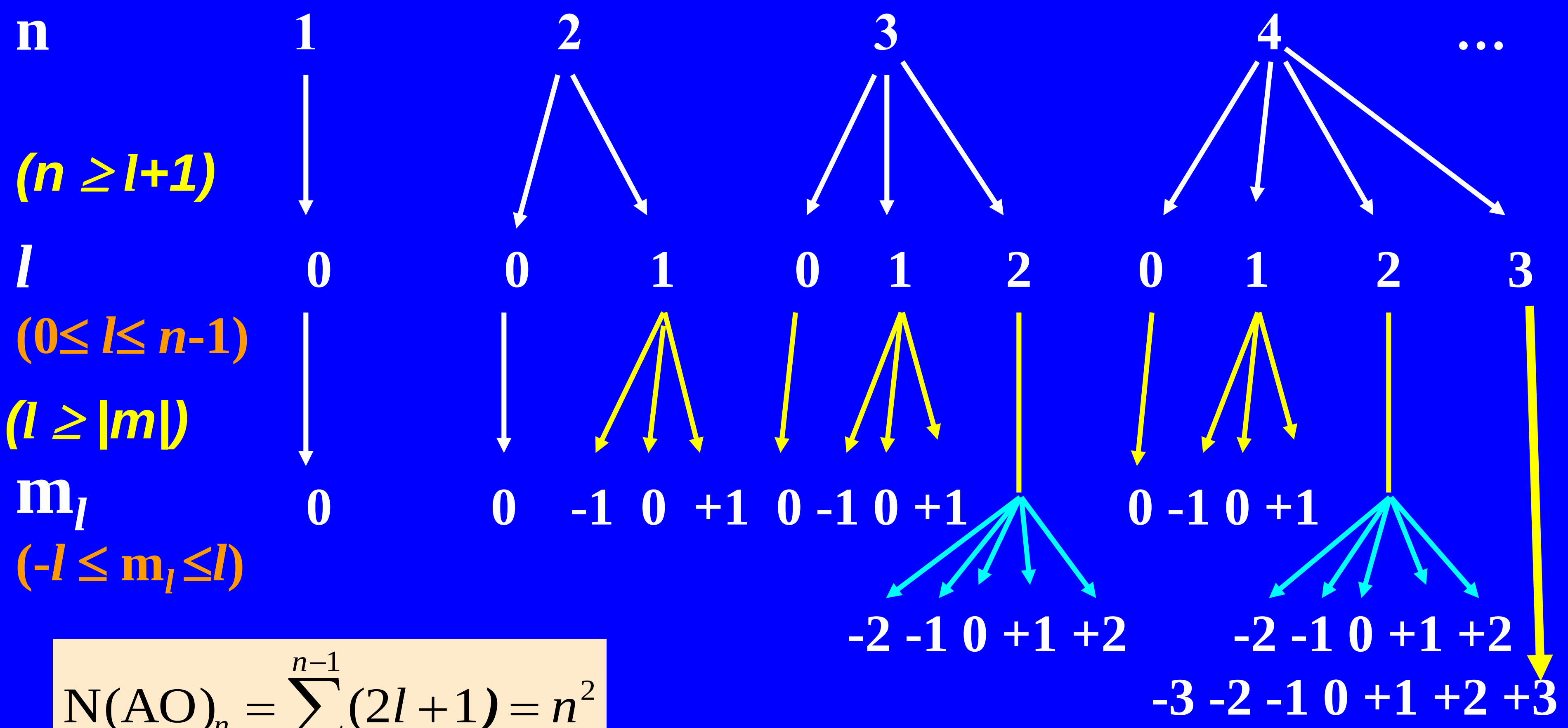
Principal
Quantum Number

Angular Momentum
Quantum Number

Magnetic
Quantum Number

2.2.1 The allowed values of quantum numbers

Quantum Numbers



n 1 2 3 4 …

($n \geq l+1$)

l 0 | 0 1 | 0 1 2 | 0 1 2 3

($0 \leq l \leq n-1$)

($l \geq |m|$)

m_l 0 | 0 | -1 0 +1 | 0 | -1 0 +1 | -2 -1 0 +1 +2 | 0 | -1 0 +1 | -2 -1 0 +1 +2 | -3 -2 -1 0 +1 +2 +3

($-l \leq m_l \leq l$)

$$\mathrm{N(AO)}_n = \sum_{l=0}^{n-1}(2l+1) = n^2$$

- The number of atomic orbitals of a given ***l*** subshell is ***2l+1***.
- The total number of atomic orbitals for a given value of ***n*** is ***n^2***.

2.2.2 The principal quantum number, *n*

- Positive integer values of $n = 1, 2, 3$, etc.
- Also called the "energy" quantum number, indicating the approximate distance from the nucleus.
- Denotes the electron energy shells around the atom, and is derived directly from the Schrödinger equation.
- Higher "n" → higher orbital energy.

$$E_n = -R\frac{Z^2}{n^2} \quad \text{(H - like atom/ions)}$$

- For H-like atom/ion, the orbitals with the same n, but differing in l and m_l, are degenerate (equal in energy!). Accordingly, the degeneracy of an energy level is n^2 (spin-free) or $2n^2$ (including spin).

Example: Energy states of a H atom.

n = *principal*

$$E_n = -R\frac{Z^2}{n^2}$$

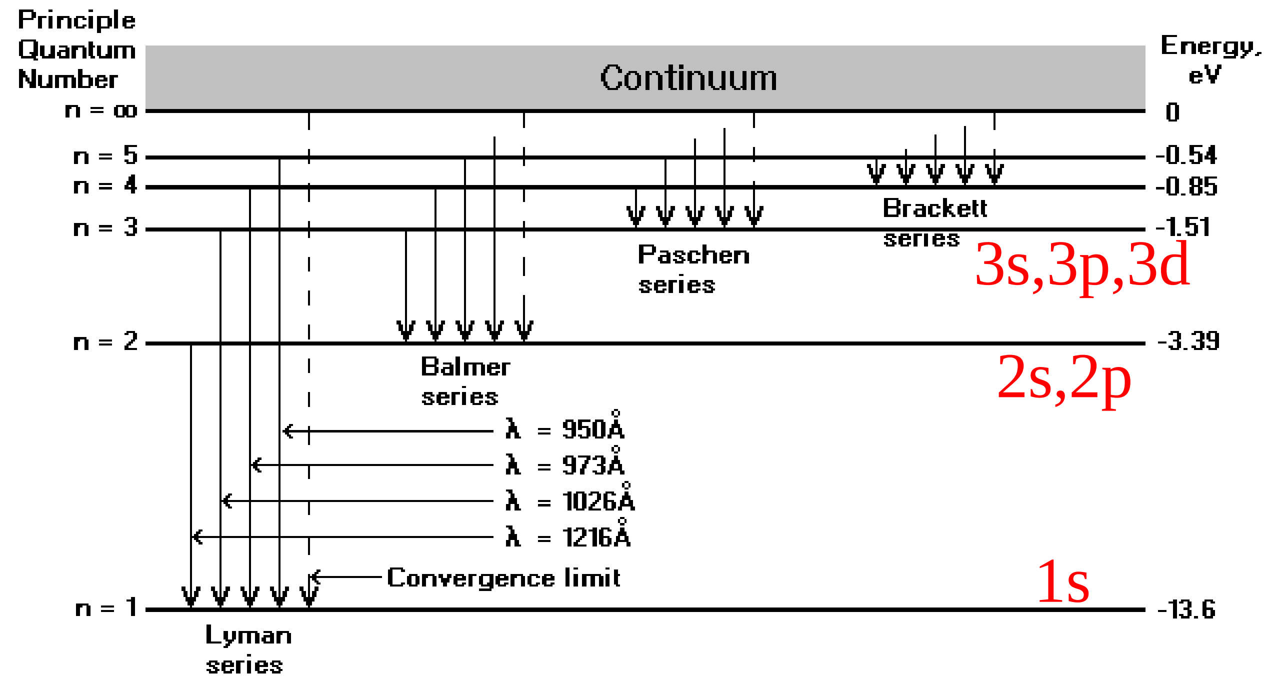
n = 1, 2, 3 …∞

R = 13.6 eV

n = 1 : ground state

n = 2 : first excited states

n = 3 : second excited states



$$E_n = -13.6\left(\frac{1}{n^2}\right)$$

E_1 = -13.6 eV

E_2 = -3.40 eV

E_3 = -1.51 eV

E_4 = -0.85 eV

E_5 = -0.54 eV

•

•

E_∞ = 0 eV

Example: Energy states of a Li$^+$ ion.

For this two-electron cation, electron-electron interaction should be taken into account. However, we may estimate the energy levels of its atomic orbitals by using the formula derived for one-electron atom/cation, i.e.,

$$E_n = -R\frac{Z^2}{n^2}$$

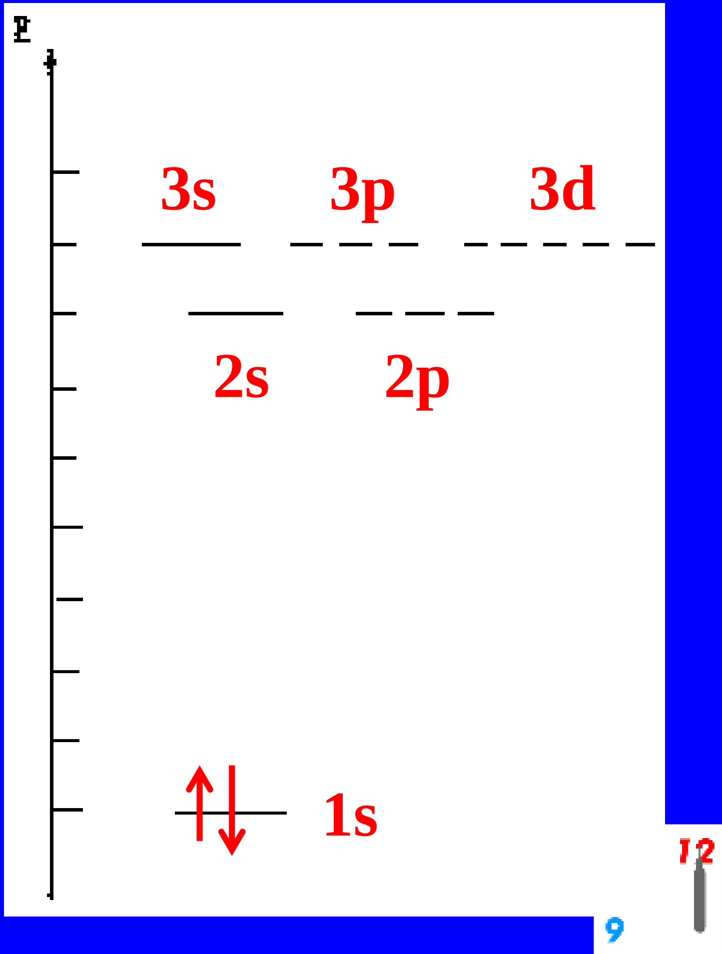
R = 13.6 eV

$$\mathbf{E_{1s} = -\ 9R}$$

$$\mathbf{E_{2s,sp} = -\ (9/4)R}$$

$$\mathbf{E_{3s} = -\ R}$$

- If the ***e-e*** interaction is taken into account, the sublevels with the same ***n*** value should differ in energy. Why?



2.2.3 the *azimuthal* quantum number, *l*

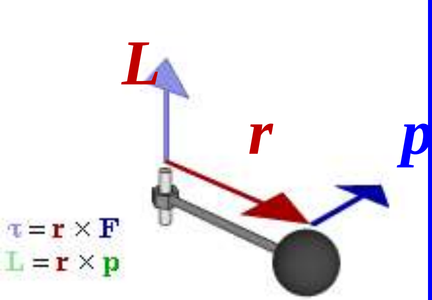
a. Classical Mechanics of **one-particle angular momentum**.

The vector ***r*** from the origin to the instantaneous position of a particle is given by

$$r = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$$

The angular momentum *L* is perpendicular to the plane defined by the particle's position vector *r* and its velocity *v* or momentum *p*.

The particle's angular momentum ***L*** with respect to the coordinate origin is defined as

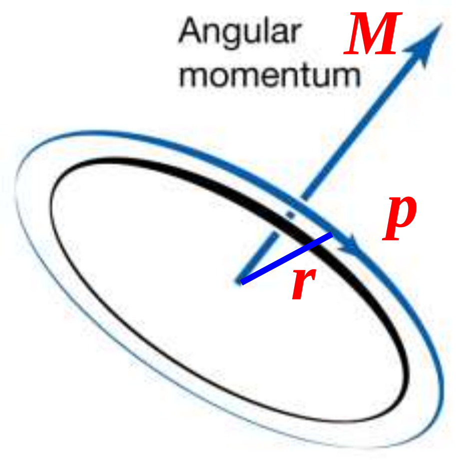


$$L = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$L_x = yp_z - zp_y$$
$$L_y = zp_x - xp_z$$
$$L_z = xp_y - yp_x$$

$$L^2 = |L|^2 = L \cdot L = L_x^2 + L_y^2 + L_z^2$$

b. One-particle ***orbital-angular-momentum*** in Quantum Mechanics.



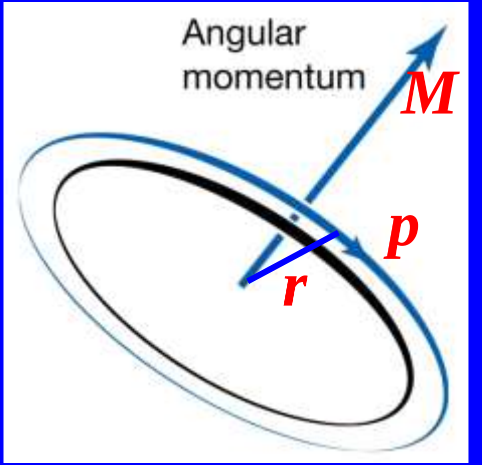
The motion of an electron within an atomic orbital (through-space) results in ***orbital angular momentum M*** (as the analog of the classical mechanical quantity ***angular momentum L***), the operator of which fulfills

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

Its components

$$\left\{\begin{aligned} \hat{M}_x &= y\hat{p}_z - z\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ \hat{M}_y &= z\hat{p}_x - x\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ M_z &= x\hat{p}_y - y\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{aligned}\right.$$

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



In spherical polar coordinates

$$\hat{M}_x = i\hbar(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi})$$

$$\hat{M}_y = -i\hbar(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi})$$

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

$$\Rightarrow \hat{M}^2 = -\hbar^2[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}]$$

These operators are simply related to the azimuthal variables!

$$\hat{M}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Similarity

$$\frac{1}{\Theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\frac{1}{\Phi(\phi)\sin^2\theta}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-\beta$$

Angular eq.

$\boldsymbol{\beta = l(l+1)}$

$$\hat{M}^2\,\Theta(\theta)\Phi(\phi) = -\hbar^2\left[\frac{\Phi(\phi)}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\frac{\Theta(\theta)}{\sin^2\theta}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}\right]$$

$$=\left\{-\hbar^2\boxed{\left[\frac{1}{\Theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\frac{1}{\Phi(\phi)\sin^2\theta}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}\right]}\right\}\Theta\Phi$$

$$=\hbar^2\beta\Theta(\theta)\Phi(\phi)$$

$$\because \Psi = R(r)\Theta(\theta)\Phi(\phi)$$

$$\therefore \hat{M}^2\Psi = \hbar^2\beta\Psi = \lambda^2\Psi$$

eigenequations

$$\lambda^2 = l(l+1)\hbar^2\ ,\ \lambda = \sqrt{l(l+1)}\hbar$$

$$\therefore |M| = \lambda = \sqrt{l(l+1)}\hbar$$

magnitude

$$\cancel{\hat{M}\Psi_{n,l,m} = \sqrt{l(l+1)}\hbar\Psi_{n,l,m}}$$

The one-electron wavefunctions (AO's) of H-like atom/ion are eigenfunctions of $\hat{M}^2$!

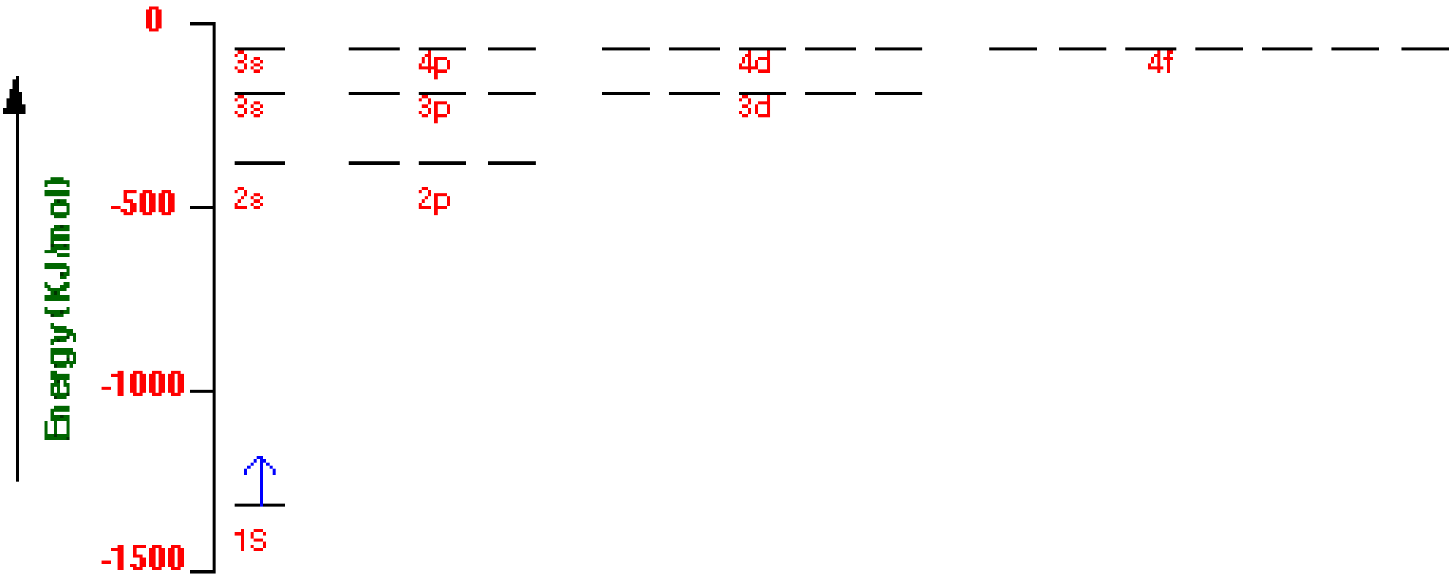
l denotes the orbital angular momentum.

- Indicates the shape of the orbitals around the nucleus.
- Denotes the different sublevels within the same main level "*n*".

Spatial quantization of electron motion.

ℓ = 0, 1, 2 …n –1 **degeneracy = 2 ℓ + 1**

ℓ	**0**	**1**	**2**	**3**	**4, 5, 6 …**
type	**s**	**p**	**d**	**f**	**g, h, i …**
degeneracy	**1**	**3**	**5**	**7**	**9, 11, 13 …**



（Electromagnetic induction） When there exists an angular momentum of electron motion, there is a magnetic (dipole) moment.

Such a magnetic moment is defined as

$$\boldsymbol{\mu} = \frac{Q}{2m_e}\mathbf{M} = -\frac{e}{2m_e}\mathbf{M}$$

with its magnitude being

$$|\mu| = \frac{e}{2m_e}|M| = \frac{e\hbar}{2m_e}\cdot\sqrt{l(l+1)} = \beta_e\sqrt{l(l+1)}$$

$$\beta_e = \frac{e\hbar}{2m_e} = 9.274\times10^{-24}\,J\cdot T^{-1}$$

Bohr magneton (μ_B)

$$|\mu|_s = 0,\ |\mu|_p = \sqrt{2}\beta_e,\ |\mu|_d = \sqrt{6}\beta_e,\ |\mu|_f = 2\sqrt{3}\beta_e$$

- When ***l*** increases, the magnetic moment increases, and the influence of external magnetic field on the electron motion is enhanced.

- **Zeeman effect**: splitting of atomic spectral lines (of the same ***n***) caused by an external magnetic field.

2.2.4 **Magnetic Quantum Number, m_l**

$$\Phi_{m_l} = Ae^{im_l\phi}$$

i) Define the ***z***-component (***M$_z$***) of the orbital angular momentum.

ii) Determine the component (***μ_z***) of the magnetic moment ***μ*** in the direction of an external magnetic field.

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

$$\hat{M}_z\Phi_{m_l} = -i\hbar\frac{\partial}{\partial\phi}(Ae^{im_l\phi}) = m_l\hbar(Ae^{im_l\phi}) = m_l\hbar\Phi_{m_l}$$

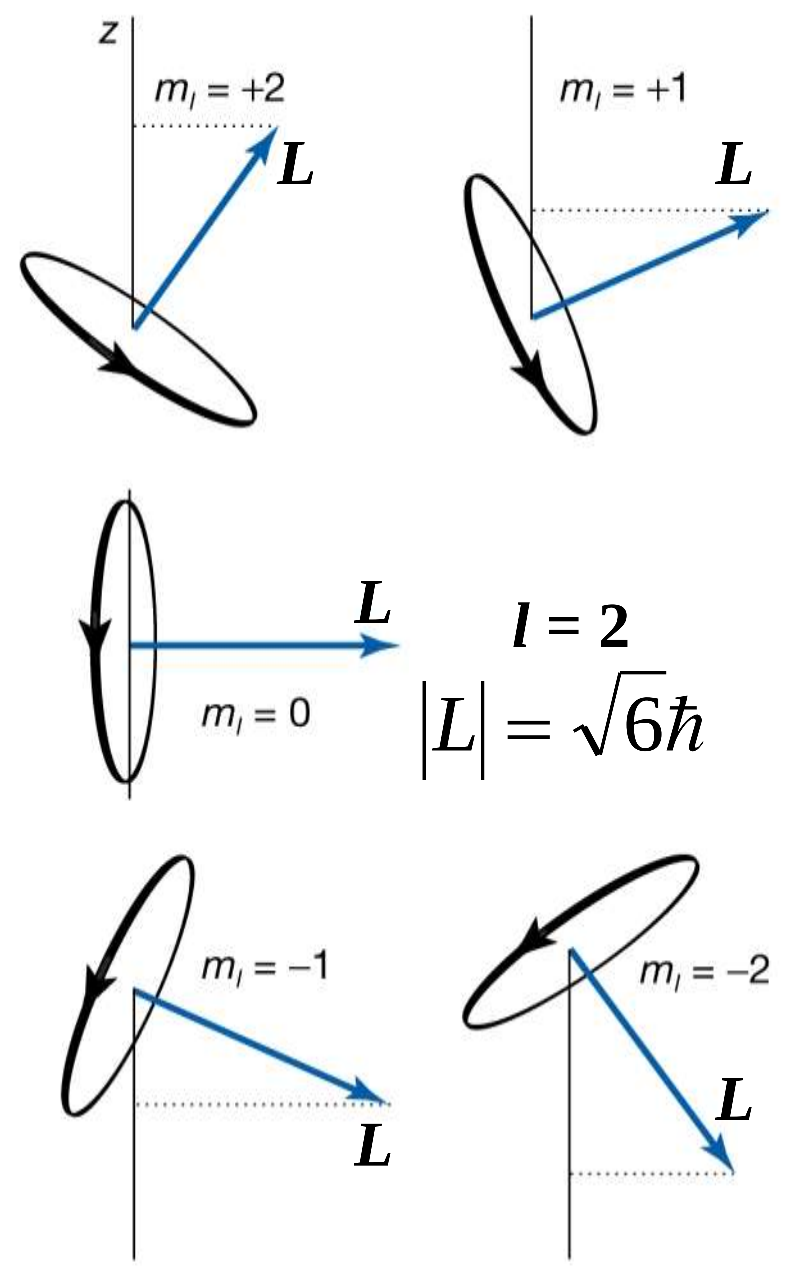
$$\hat{M}_z\Psi_{n,l,m_l} = \hat{M}_z(R\Theta\Phi) = R\Theta(\hat{M}_z\Phi) = m_l\hbar R\Theta\Phi = m_l\hbar\Psi_{n,l,m_l}$$

$$\therefore \hat{M}_z\Psi_{n,l,m_l} = m_l\hbar\Psi_{n,l,m_l}$$

$$\Rightarrow M_z = m_l\hbar \ \ (\text{a vector !})$$

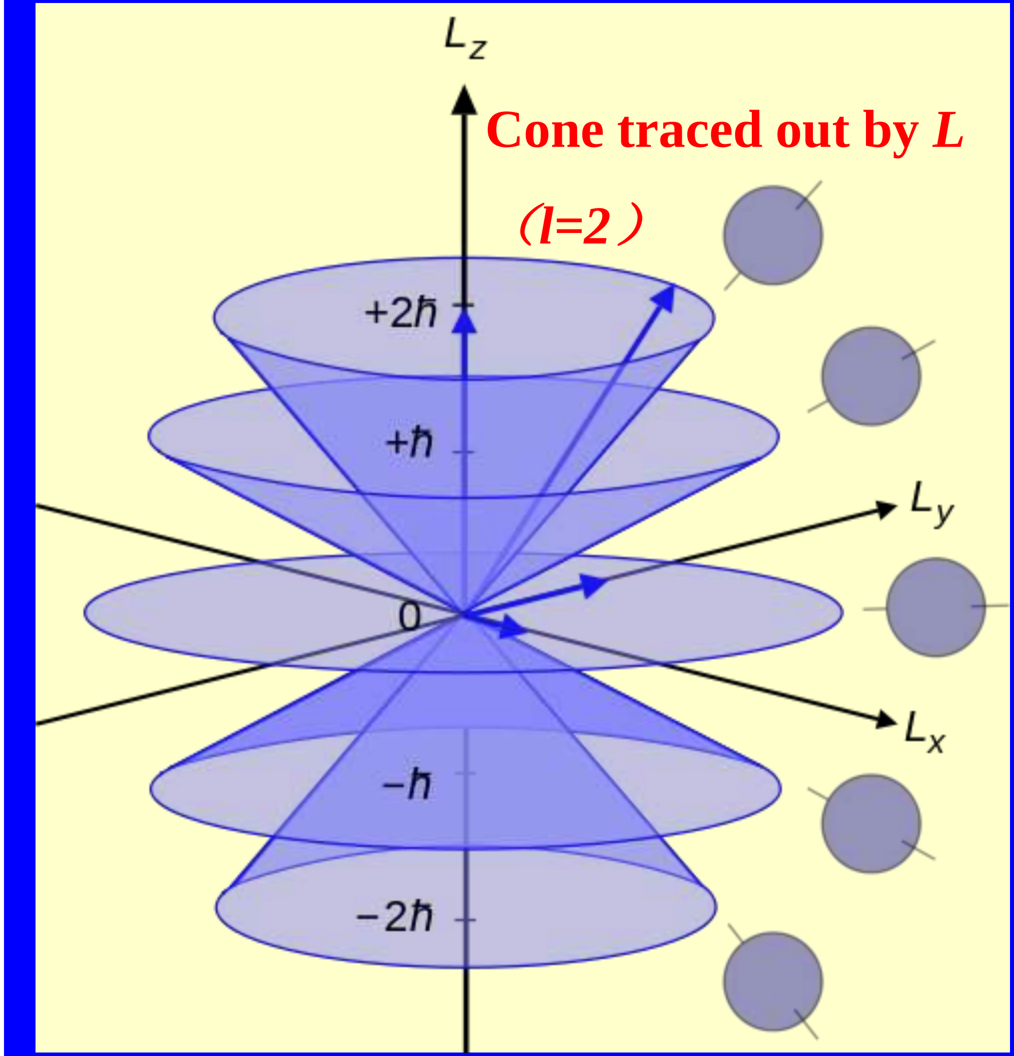
→ *Both Ψ* and Φ are eigenfunctions of ***$\hat{M}_z$!***

$$\mu_z = -\frac{e}{2m_e}M_z = \frac{-e\hbar m_l}{2m_e} = -m_l\beta_e \quad (\because \beta_e = \frac{e\hbar}{2m_e})$$



$l = 2$

$$|L| = \sqrt{6}\hbar$$



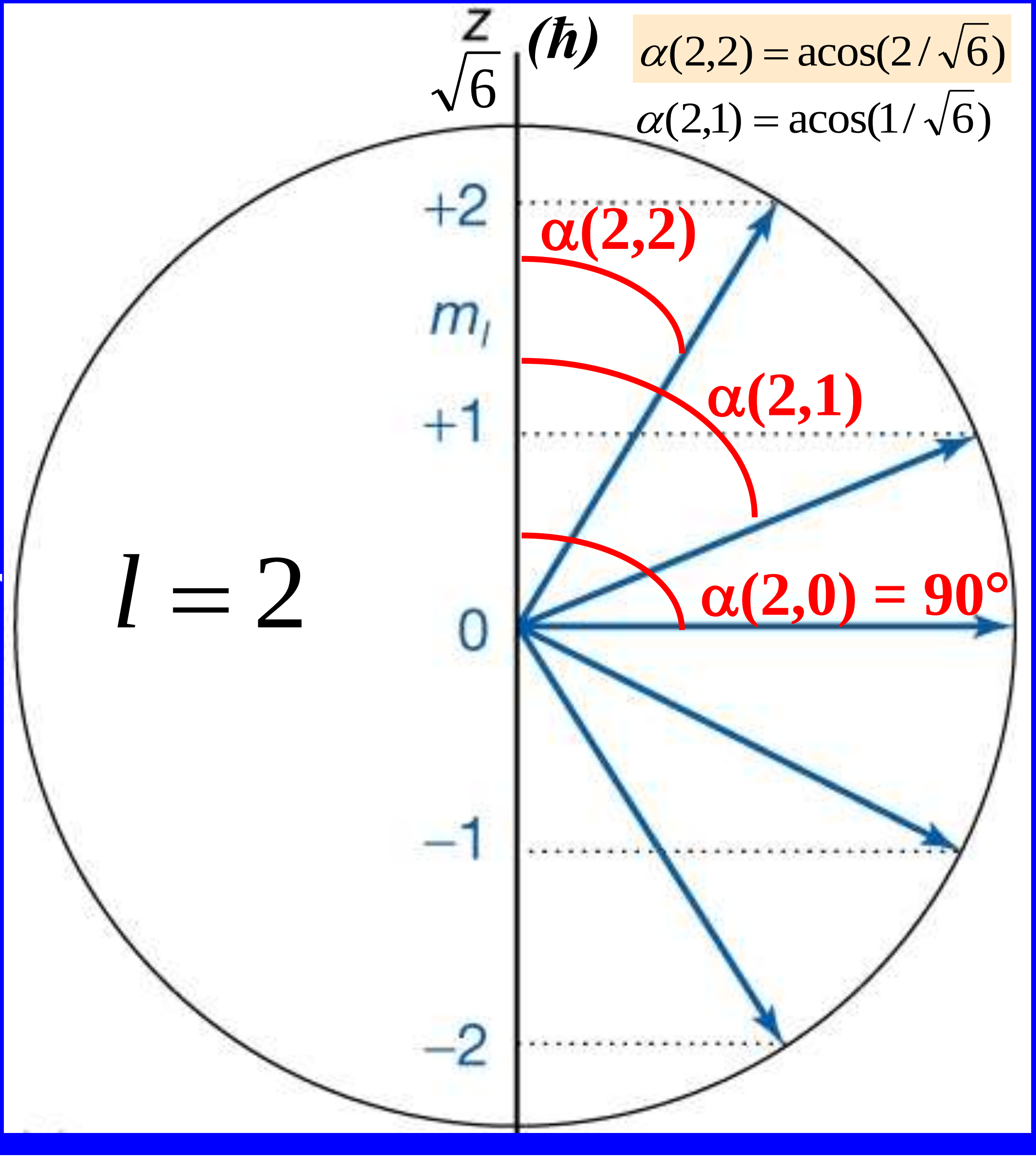
Cone traced out by *L*

（*l*=2）

Space quantization!!

Space quantization of orbital angular momentum.

Here the orbital quantum number is ***l*=2** and there are accordingly ***2l+1=5*** possible values of the magnetic quantum number ***m_l***, with each value corresponding to a different orientation of orbital angular momentum ***L*** relative to the ***z*** axis.



$$\alpha(2,2) = \operatorname{acos}(2/\sqrt{6})$$

$$\alpha(2,1) = \operatorname{acos}(1/\sqrt{6})$$

$$|L| = \sqrt{l(l+1)}\hbar$$

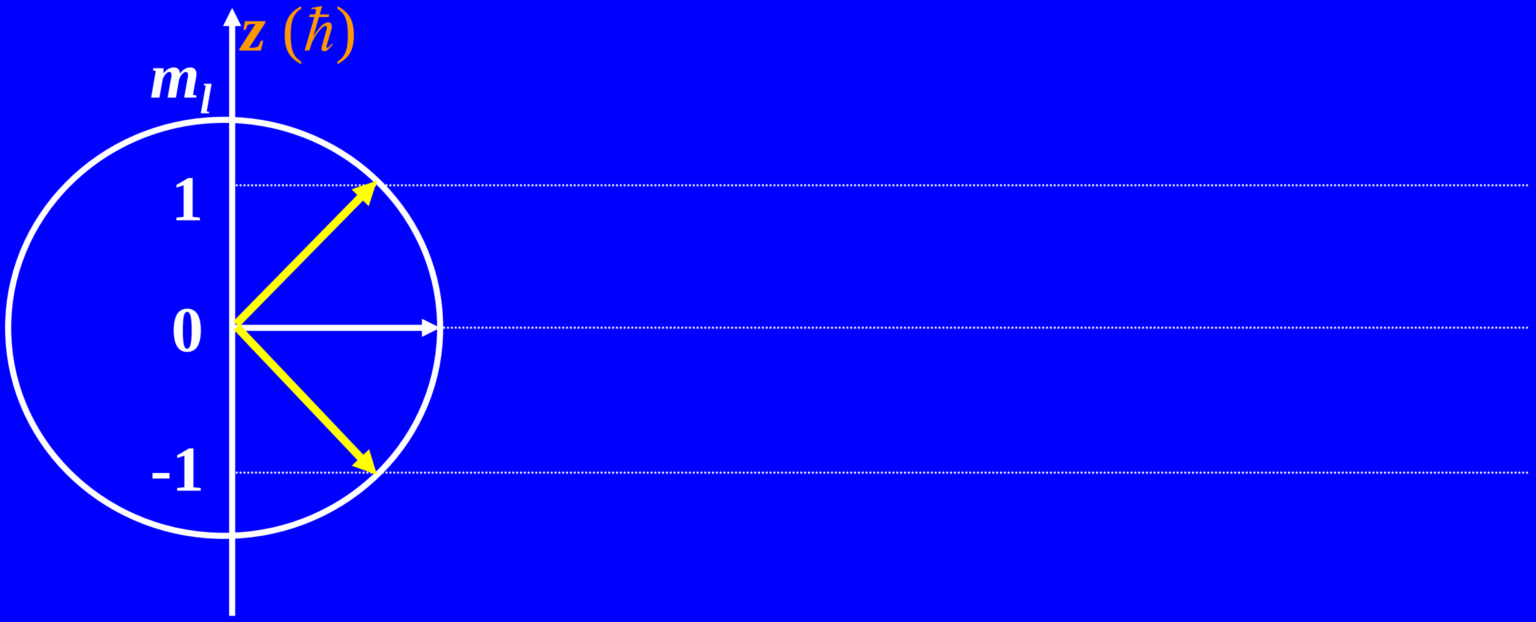
$$L_z = m_l\hbar$$

$$\alpha(l,m_l) = \operatorname{acos}(L_z/|L|) = \operatorname{acos}\left(\frac{m_l}{\sqrt{l(l+1)}}\right)$$

Example: Please derive the angle between the orbital angular momentum of the AO p_{+1} and the z-axis.

$$\because \alpha(l,m_l) = \mathrm{acos}(L_z/|L|) = \mathrm{acos}\left(\frac{m_l}{\sqrt{l(l+1)}}\right)$$

$$\therefore \alpha(1,1) = \mathrm{acos}\left(\frac{1}{\sqrt{2}}\right) = \pi/4$$



Magnetic Quantum Number , m_l

- Denotes the direction or orientation of an atomic orbital.

$m_l = 0, \pm 1, \pm 2 \ldots \pm l$

Number of orbitals in a subshell

$= 2l + 1$

ℓ	m_l	Atomic orbital	
		complex	real
0	0	s	s
1	0	p_0	p_z
	+1	p_{+1}	p_x & p_y
	-1	p_{-1}	
2	0	d_0	$d_{2z^2-x^2-y^2} = d_{z^2}$
	+1	d_{+1}	d_{xz} & d_{yz}
	-1	d_{-1}	
	+2	d_{+2}	$d_{x^2-y^2}$ & d_{xy}
	-2	d_{-2}	

Key points: For H-like atom/ions, the wavefunctions to describe their atomic orbitals (AO′s) that are derived from their Schrödinger equations can be characterized using three quantum numbers, i.e., ***n, l, m***, and symbolized as ψ_{nlm}.

$$\psi_{nlm} = R_{n,l}(r)\cdot Y_{l,m}(\theta,\phi) \text{ with } Y_{l,m}(\theta,\phi) = \Theta_{l,m}(\theta)\cdot\Phi_m(\phi)$$

They are eigenfunctions of those Hermitian operators $\hat{H}$, $\hat{L}^2$ ($\hat{M}^2$) and $\hat{L}_z$ ($\hat{M}_z$), by the following eigenequations,

$$\hat{H}\psi_{nlm} = E_n\psi_{nlm} \quad E_n = -RZ^2/n^2$$

$$\hat{L}^2\psi_{nlm} = l(l+1)\hbar^2\psi_{nlm} \quad \&$$

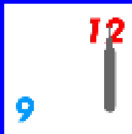
$$\hat{L}^2 Y_{l,m} = l(l+1)\hbar^2 Y_{l,m} \text{ with } L^2 = l(l+1)\hbar^2 \Rightarrow |L| = \sqrt{l(l+1)}\hbar$$

Magnitude of orbital angular momentum

$$\hat{L}_z\psi_{nlm} = m\hbar\,\psi_{nlm} \quad \& \hat{L}_z Y_{l,m} = m\hbar Y_{l,m}$$

$$\& \hat{L}_z\Phi_m = m\hbar\Phi_m \quad \text{with } L_z = m\hbar$$

Note: Angular momentum ***L*** is a vector!



2.3 The wavefunction and electron cloud

2.3.1 The wave-functions of hydrogen-like ions

$$\psi_{nlm} = R_{n,l}(r) \cdot \Theta_{l,m}(\theta) \cdot \Phi_m(\phi)$$

$$\psi_{1s} = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-\frac{Zr}{a_0}}$$

$$\psi_{2s} = \frac{1}{4}\sqrt{\frac{Z^3}{2\pi a_0^3}}\left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}$$

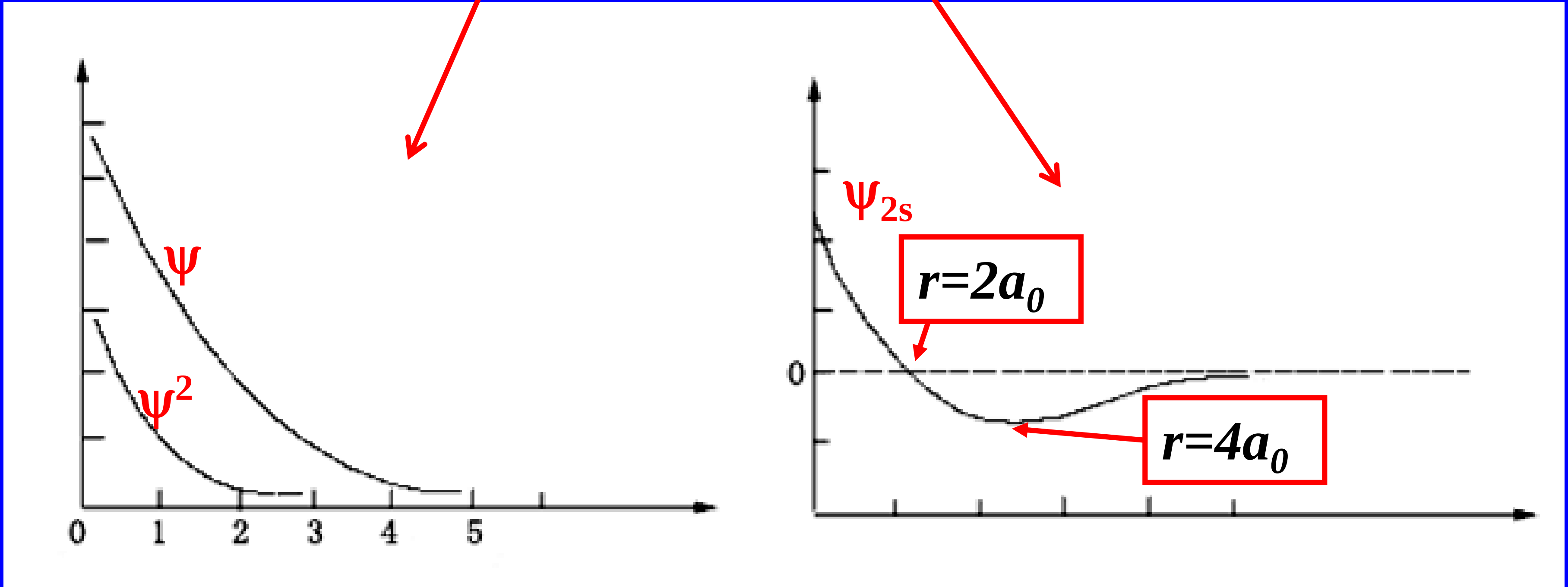
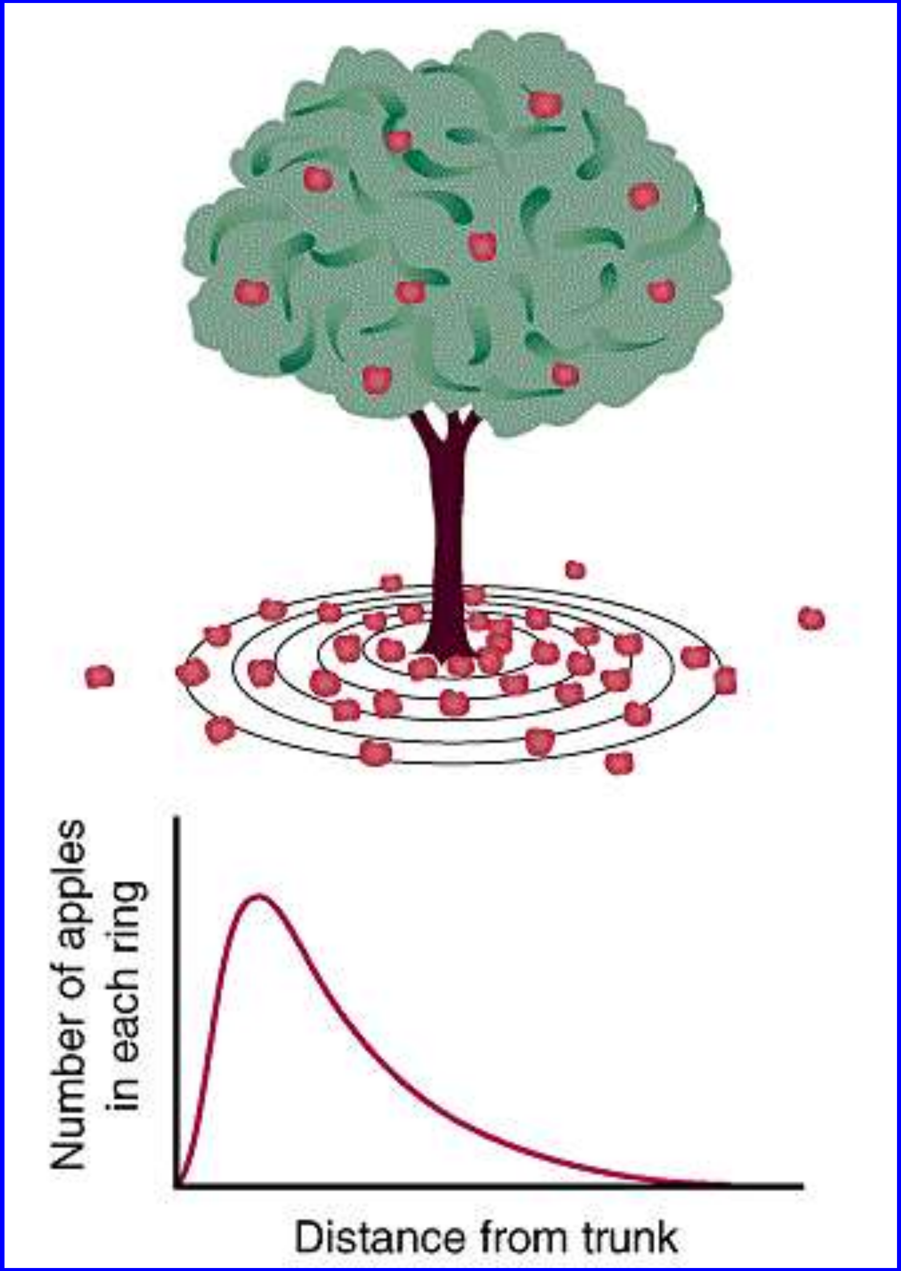


Fig. (left) The **ψ-r** and **ψ^2-r** diagrams of the ***1s*** state of the hydrogen atom; (right) The ***ψ-r*** of the ***2s*** state .

A Radial Probability Distribution of Apples



2.3.2 The radial distribution function

- Probability distribution function $|\psi|^2$ with

$$\psi = R_{n,l}(r)\cdot\Theta_{l,m}(\theta)\cdot\Phi_m(\phi) = R_{n,l}(r)\cdot Y_{l,m}(\theta,\phi)$$

$$\text{Define } Y_{l,m}(\theta,\phi) = \Theta_{l,m}(\theta)\Phi_m(\phi)$$

Normalized spherical harmonics

- The probability of finding electron in the region of space ***r → r+dr***, ***$\theta \rightarrow \theta+d\theta$***, ***$\phi \rightarrow \phi+d\phi$*:**

$$d\tau = r^2 \sin\theta dr d\theta d\phi$$

$$|\psi|^2 d\tau = [R_{n,l}(r)]^2 |Y_{l,m}(\theta,\phi)|^2 r^2 \sin\theta dr d\theta d\phi$$

- The probability of electron in a thin spherical shell ***r→r+dr***:

$$dr\int_0^{2\pi}\int_0^{\pi}|\psi|^2 r^2 \sin\theta d\theta d\phi$$

$$= R_{n,l}^2(r) r^2 dr \int_0^{2\pi}\int_0^{\pi}|Y_{l,m}(\theta,\phi)|^2 \sin\theta d\theta d\phi = r^2 R_{n,l}^2(r) dr$$

Normalized spherical harmonics

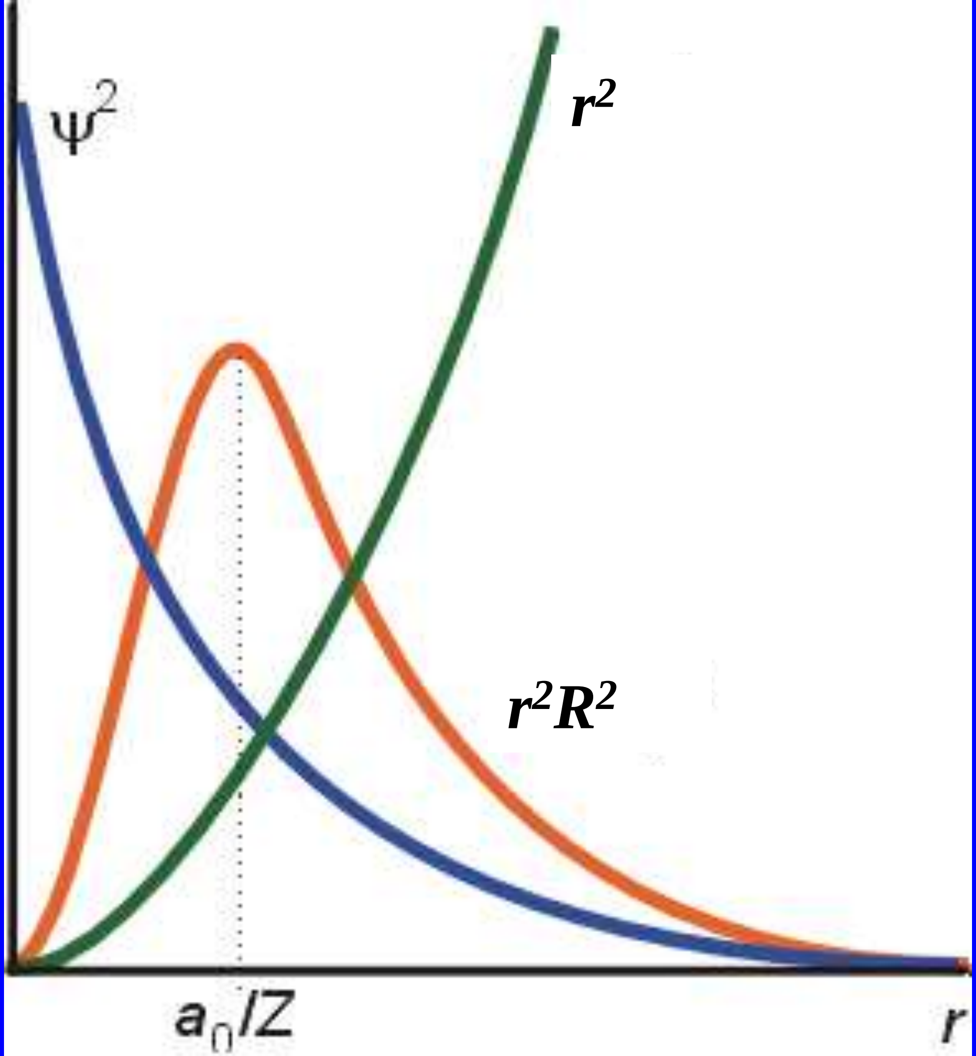
$$D(r) = r^2 R_{n,l}^2(r)$$

← **Radial distribution function**

Ψ = AO wave function

$|\Psi|^2$ = probability density

r^2R^2 = radial probability function



Calculating the most probable radius

$$\frac{dD(r)}{dr} = 0$$

Expectation value of r

$$\langle r \rangle = \int \psi^* r \psi dV$$

$$= \int_0^\infty \int_0^\pi \int_0^{2\pi} rR_{n,l}^2 \left| Y_{l,m} \right|^2 r^2 dr \sin\theta d\theta d\phi = \int_0^\infty R_{n,l}^2 r^3 dr$$

Example: please derive the radial probability distribution function of the H 1s orbital and the radium of its maximum.

$$\psi_{1s} = \sqrt{\frac{1}{\pi a_0^3}} e^{\frac{-r}{a_0}}$$

Its radial probability distribution function is

$$D(r)_{1s} = \int_0^{2\pi}\int_0^{\pi} \left|\psi_{1s}\right|^2 r^2 \sin\theta d\theta d\phi = 4\pi r^2 \left|\psi_{1s}\right|^2 = \frac{4r^2}{a_0^3} e^{\frac{-2r}{a_0}}$$

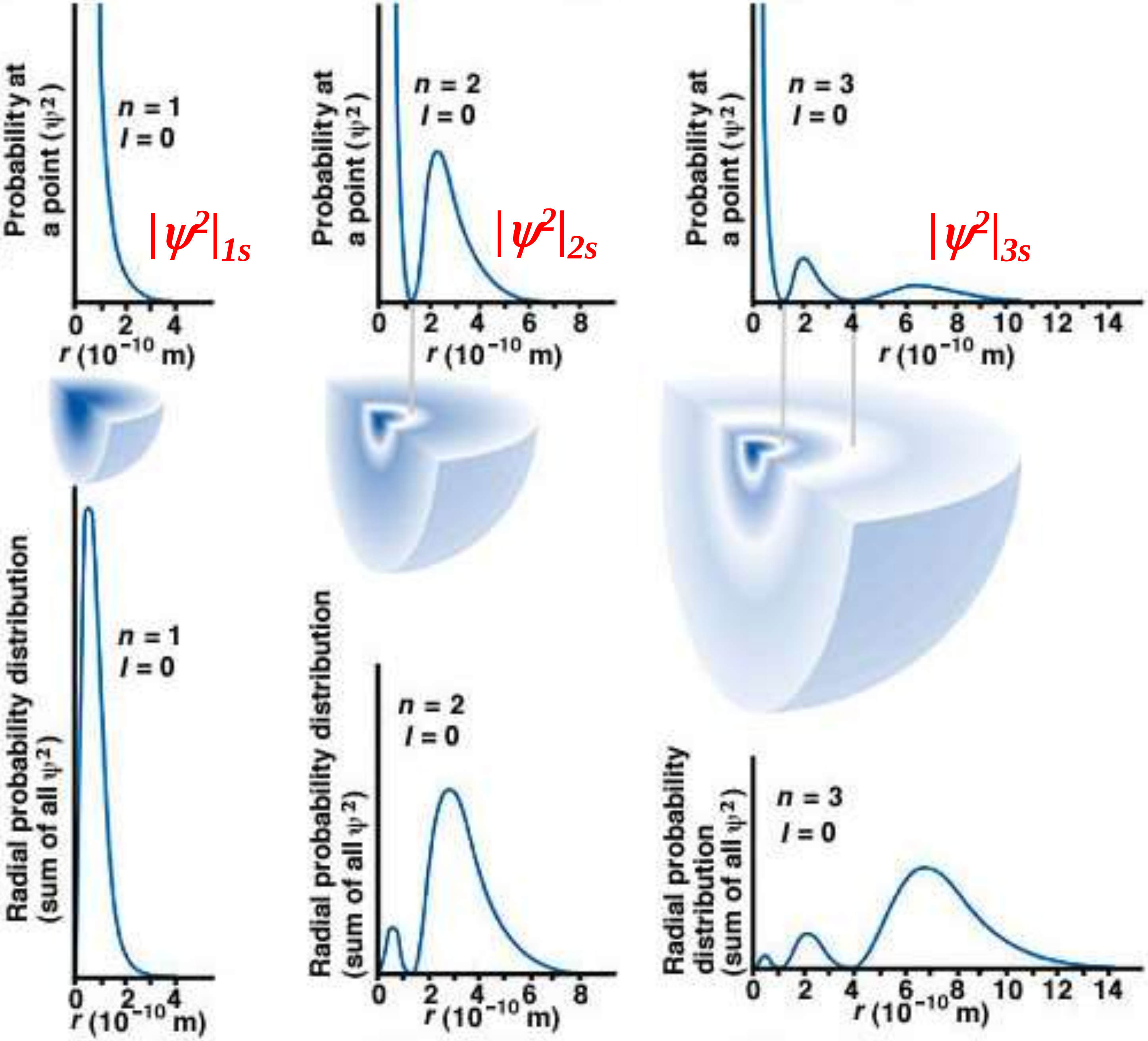
To derive the radium of its maximum, we have

$$\frac{dD(r)_{1s}}{dr} = 0 \Rightarrow \frac{8r}{a_0^3} e^{\frac{-2r}{a_0}} (1 - \frac{r}{a_0}) = 0$$

$$\because r \neq 0, \therefore 1 - \frac{r}{a_0} = 0$$

$$\Rightarrow r = a_0$$

The 1*s*, 2*s*, 3*s* Orbitals



$|\psi^2|_{1s}$

$|\psi^2|_{2s}$

$|\psi^2|_{3s}$

D(r)

The point/surface with $\rho_e = 0$ is called a *node/nodal surface*.

- **D(r) has (*n-l*) maxima and (*n-l-1*) nodal surfaces.**
- **Orbital penetration**: Penetration describes the proximity to which an electron can approach to the nucleus. In a multi-electron system, electron penetration is defined by an electron's relative electron density (probability density) near the nucleus.

  i) Within the same shell value (***n***), the penetrating power of an electron follows this trend in subshells(***l***):

  ***s>p>d>f*.**

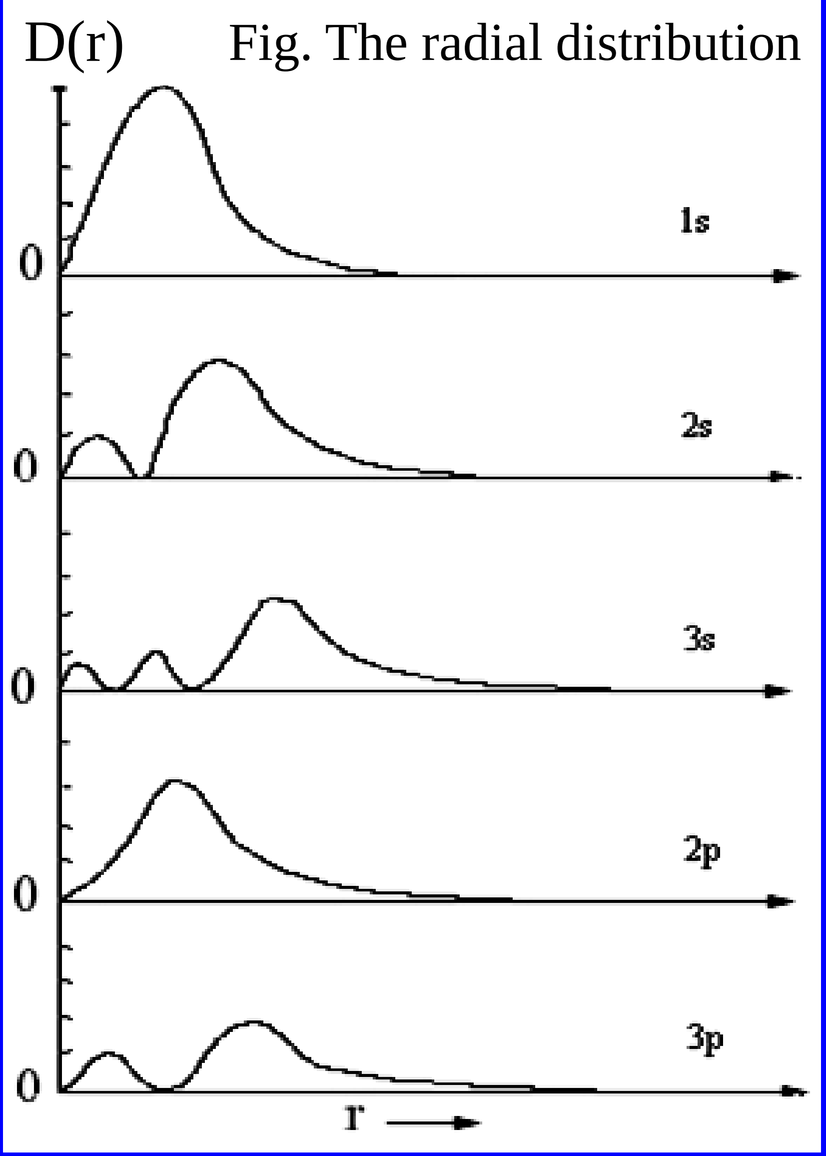


Fig. The radial distribution

ii) Penetrating power of an electron follows this trend: ***1s>2s>2p>3s>3p>4s>3d>4p>5s>4d>5p>6s>4f***.

2.3.3 The angular function ($Y_{lm}(\theta, \phi)$)

$$\Psi(r,\theta,\phi) = R\Theta\Phi = RY(\theta,\phi)$$

- Angular part

$$Y_{lm}(\theta,\phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$$

It indicates the angular distribution of an atomic orbital and is the eigenfunction of ***M*²** and ***M*$_z$** operators.

$$\hat{M}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

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

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

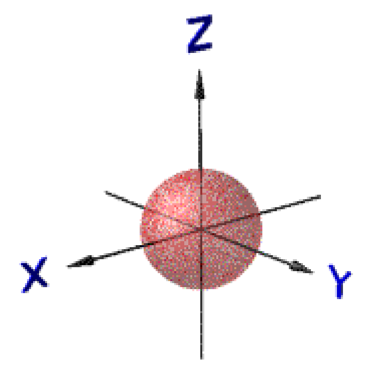
Angular function ($Y_{lm}(\theta,\phi)$)

s-orbital (l=0, 2l+1=1)

Y_{00}

$$Y_{00} = 1/\sqrt{4\pi}$$

Y of s-orbital



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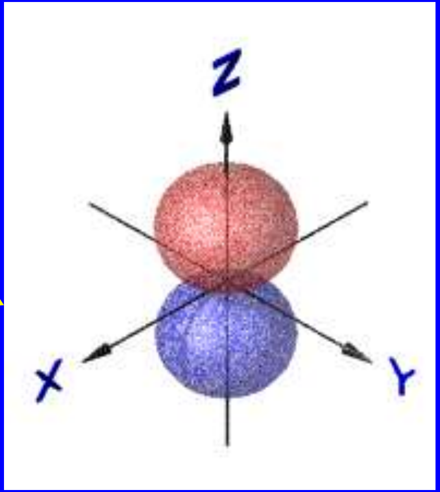
p-orbital (l=1, 2l+1=3)

Y_{10}

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\,\boldsymbol{\cos}\,\theta$$

$$Y(\,p_z\,) = \sqrt{\frac{3}{4\pi}}\,\boldsymbol{\cos}\,\theta$$

Real form



$Y_{1\pm1}$

Complex form

$$Y_{11} = \frac{\sqrt{3}}{2}\boldsymbol{\sin}\theta\cdot\frac{1}{\sqrt{2\pi}}e^{i\phi}$$

$$Y_{1\text{-}1} = \frac{\sqrt{3}}{2}\boldsymbol{\sin}\theta\cdot\frac{1}{\sqrt{2\pi}}e^{-i\phi}$$

$$\frac{1}{\sqrt{2}}(Y_{11} + Y_{1\text{-}1}) = \frac{\sqrt{3}}{4\sqrt{\pi}}\boldsymbol{\sin}\theta(e^{i\phi} + e^{-i\phi})$$

$$-i\frac{1}{\sqrt{2}}(Y_{11} - Y_{1\text{-}1}) = -i\frac{\sqrt{3}}{4\sqrt{\pi}}\boldsymbol{\sin}\theta(e^{i\phi} - e^{-i\phi})$$

Real form

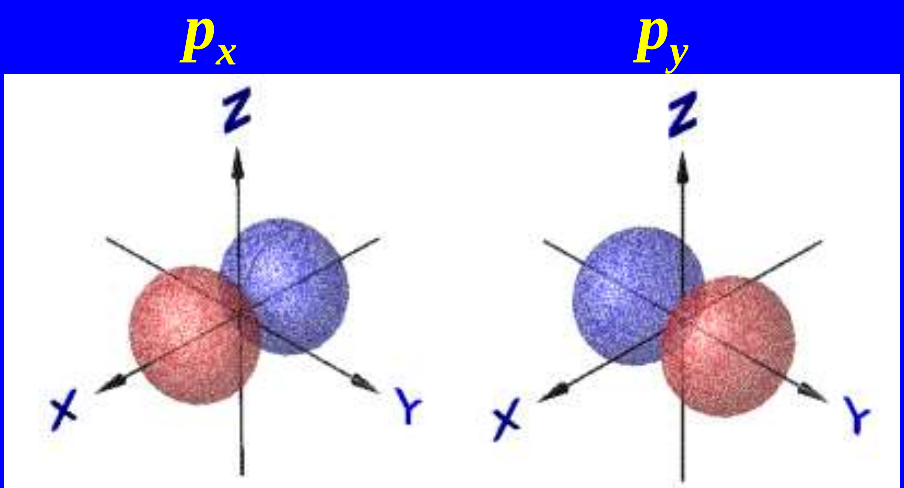
$$Y(\,p_x\,) = \sqrt{\frac{3}{4\pi}}\,\boldsymbol{\sin}\,\theta\,\boldsymbol{\cos}\,\phi$$

$$Y(\,p_y\,) = \sqrt{\frac{3}{4\pi}}\,\boldsymbol{\sin}\,\theta\,\boldsymbol{\sin}\,\phi$$

p-orbital

$$Y(p_x) = \sqrt{\frac{3}{4\pi}}\,\sin\theta\cos\phi$$

$$Y(p_y) = \sqrt{\frac{3}{4\pi}}\,\sin\theta\sin\phi$$



Question： Are these two angular functions the eigenfunctions of operators $\hat{M}_x$ and $\hat{M}_y$, respectively?

---

d-orbital (l=2, 2l+1=5)

Eigenfunctions of M^2 and M$_z$.

Y_{20} $Y_{2\pm1}$ $Y_{2\pm2}$

$$Y(d_{z^2}) = \frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$$

$$Y(d_{xz}) = \frac{1}{4}\sqrt{\frac{15}{\pi}}\,\sin 2\theta\cos\phi$$

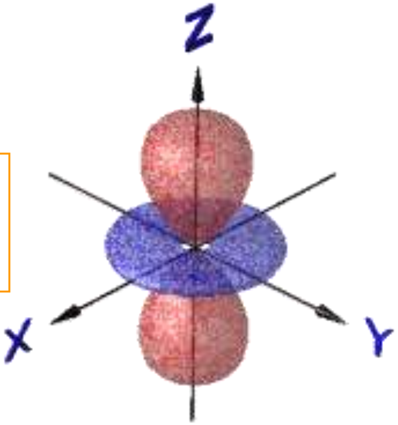
$$Y(d_{x^2-y^2}) = \frac{1}{4}\sqrt{\frac{15}{\pi}}\,\sin^2\theta\cos 2\phi$$

$$Y(d_{yz}) = \frac{1}{4}\sqrt{\frac{15}{\pi}}\,\sin 2\theta\sin\phi$$

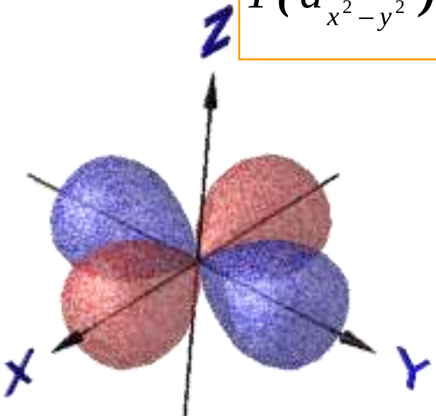
$$Y(d_{xy}) = \frac{1}{4}\sqrt{\frac{15}{\pi}}\,\sin^2\theta\sin 2\phi$$

Note: These are not eigenfunctions of M^2 and M$_z$.

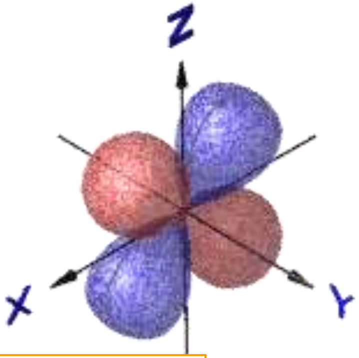
d-Orbital



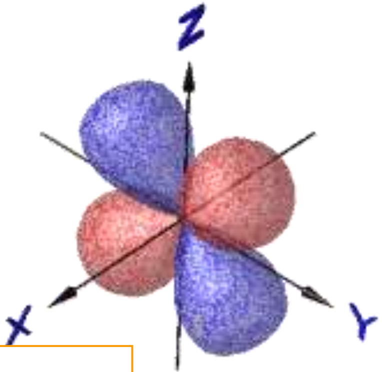
$$Y(d_{z^2}) = \frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$$



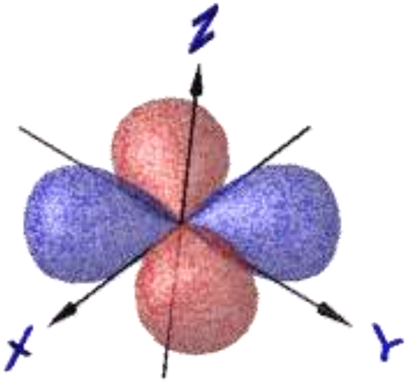
$$Y(d_{x^2-y^2}) = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos 2\phi$$



$$Y(d_{xz}) = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin 2\theta\cos\phi$$



$$Y(d_{yz}) = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin 2\theta\sin\phi$$



$$Y(d_{xy}) = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\sin 2\phi$$

Angular functions

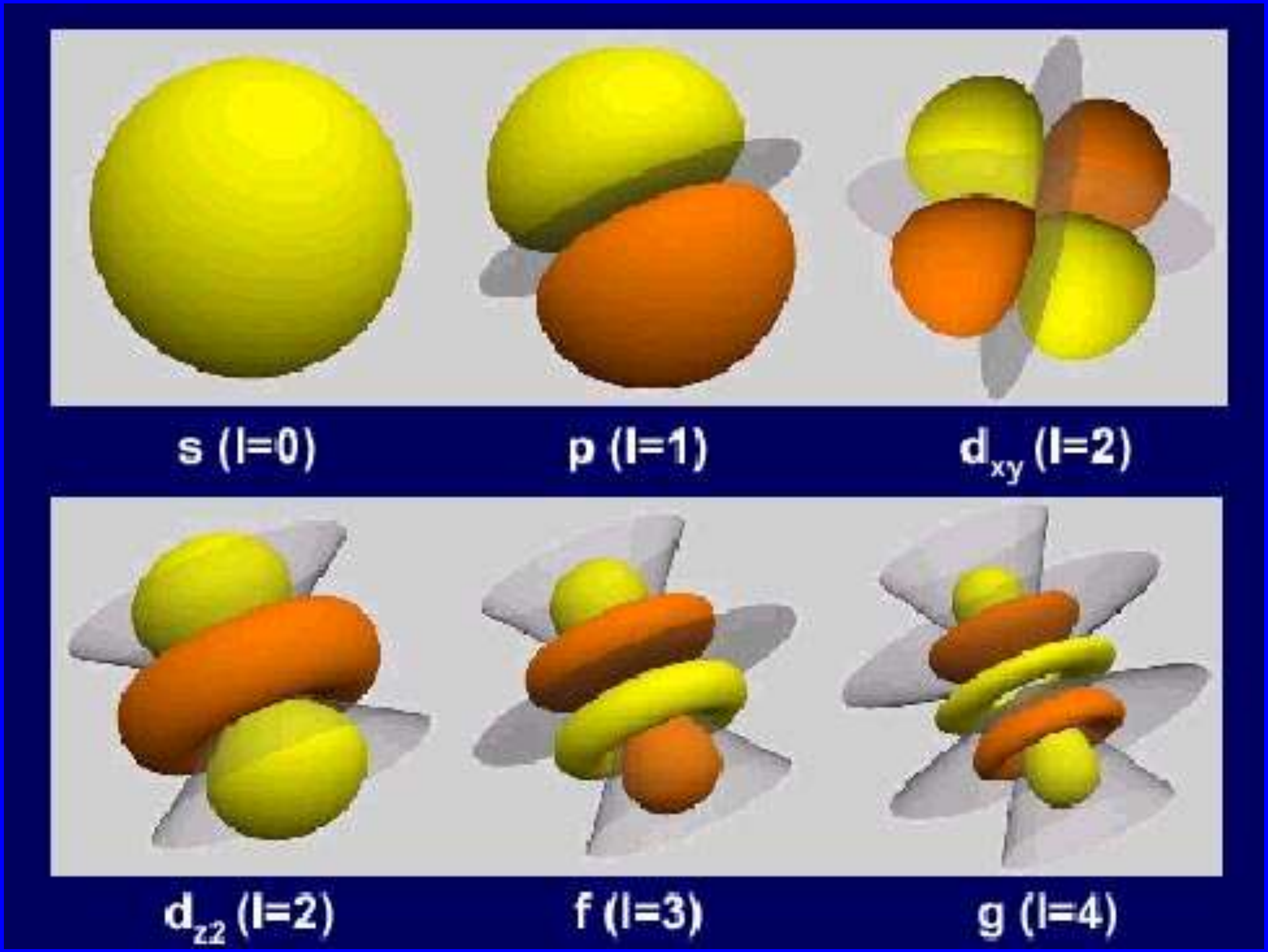
Complex form vs. Real form

When $m \neq 0$, the angular functions Y_{lm} adopt complex forms, linear combination of which with the same $|m|$ gives rise to the real forms of angular functions.

ℓ	m_ℓ	Orbital (Real)
0	0	s
1	0	p_z
	±1	p_x
	±1	p_y
2	0	$d_{2z^2-x^2-y^2} = d_{z^2}$
	±1	d_{xz}
	±1	d_{yz}
	±2	$d_{x^2-y^2}$
	±2	d_{xy}

Nodes:

- **For a given orbital, the number of angular nodes is l.**



- **Accordingly, the total number of nodes equals to $n-1$, including l angular nodes and $n-l-1$ radial nodes.**

Energy of electron in H-like atom/ion(s):

Average potential energy & kinetic energy:

$$\hat{V} = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\langle V\rangle = \int \psi^*_{nlm}\hat{V}\psi_{nlm}d\tau = \iiint \hat{V}\left|\psi_{nlm}\right|^2 r^2\, \mathbf{sin}\theta drd\theta d\phi$$

$$= -\frac{2RZ^2}{n^2}$$

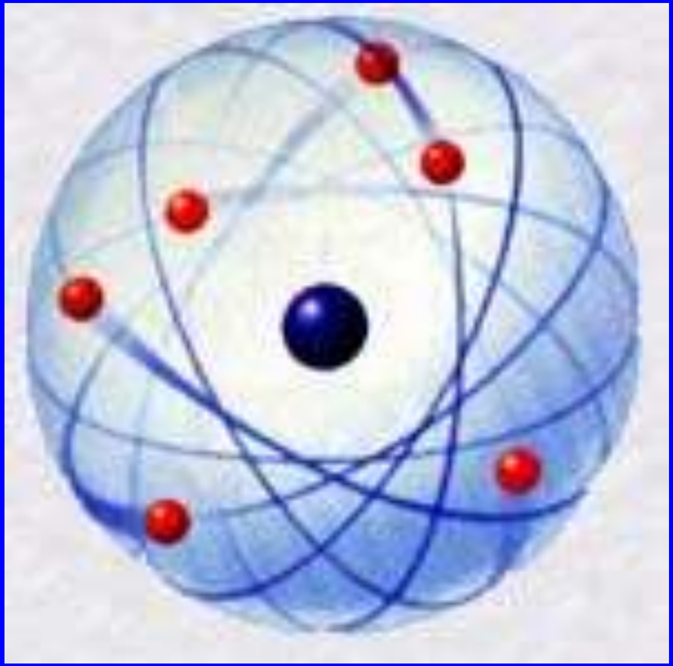
$$\because E_{nlm} = \langle V\rangle_{nlm} + \langle T\rangle_{nlm}$$

$$\& \; E_{nlm} = -\frac{RZ^2}{n^2}$$

$$\Rightarrow < T >_{nlm} = E_{nlm} - < V >_{nlm} = \frac{RZ^2}{n^2}$$

Average kinetic energy

2.4 The structure of many-electron atoms (multi-electron atoms)



2.4.1 Schrödinger equation for many-electron atoms

For hydrogen-like atom/ions :

$$\hat{H}\Psi = E\Psi, \quad \hat{H} = -\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \quad (in\ atomic\ units)$$

$m_e = 1$ a.u.

$e = 1$ a.u.

$a_0 = 1$ a.u.

$\hbar = \frac{h}{2\pi} = 1$ a.u.

$4\pi\varepsilon_0 = 1$ a.u.

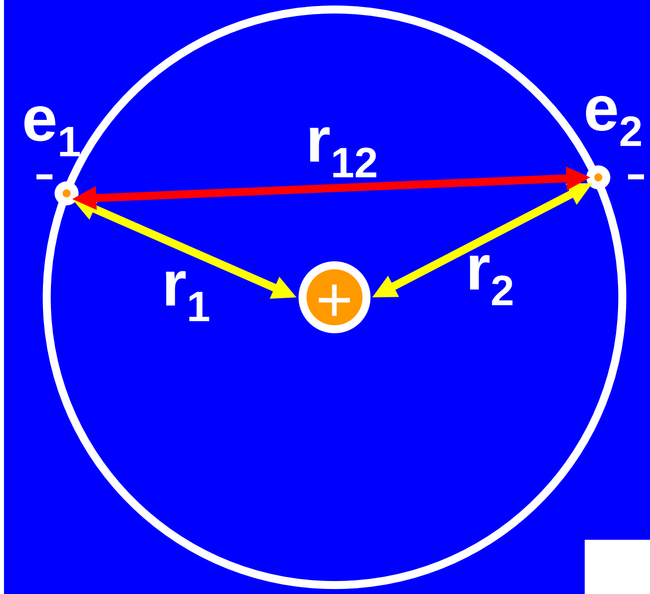
For He atom (2-electron)

$$\hat{H} = -\frac{1}{2}(\nabla_1^{\,2} + \nabla_2^{\,2}) - (\frac{Z}{r_1} + \frac{Z}{r_2}) + \frac{1}{r_{12}}$$

$$r_{12} = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$$

$$\nabla^2 = \frac{\partial^2}{\partial x_1^{\,2}} + \frac{\partial^2}{\partial y_1^{\,2}} + \frac{\partial^2}{\partial z_1^{\,2}} + \frac{\partial^2}{\partial x_2^{\,2}} + \frac{\partial^2}{\partial y_2^{\,2}} + \frac{\partial^2}{\partial z_2^{\,2}}$$

$$\hat{V} = -(\frac{Z}{r_1} + \frac{Z}{r_2}) + \frac{1}{r_{12}}$$



For many – electron atoms:

$$\hat{H} = -\frac{1}{2}\sum_{i}\nabla_i^{\,2} - \sum_{i}\frac{Z}{r_i} + \sum_{i}\sum_{j>i}\frac{1}{r_{ij}}$$

Separation of variables becomes impractical due to the complicated term of e-e interactions.

If ***e-e*** interactions were neglected, the ***1/r**$_{ij}$* terms became omitted.

$$\hat{H} = \sum_{i}\left(-\frac{1}{2}\nabla_i^{\,2} - \frac{Z}{r_i}\right) = \sum_{i}\hat{h}_i$$

$$\hat{h}_i = -\frac{1}{2}\nabla_i^{\,2} - \frac{Z}{r_i}$$

The electrons are thus independent! Thus Let

$$\Psi(1,2,3,\ldots,N) = \psi_1\cdot\psi_2\cdot\psi_3\cdots\psi_N = \prod_{i=1}^{N}\psi_i$$

Wavefunction of *i*th e.

$$\Rightarrow \hat{H}\Psi = [\sum_{i}\hat{h}_i]\prod_{i=1}\psi_i = \Psi\sum_{i}[(\hat{h}_i\psi_i)/\psi_i] = [\sum_{i}\varepsilon_i]\Psi = E\Psi$$

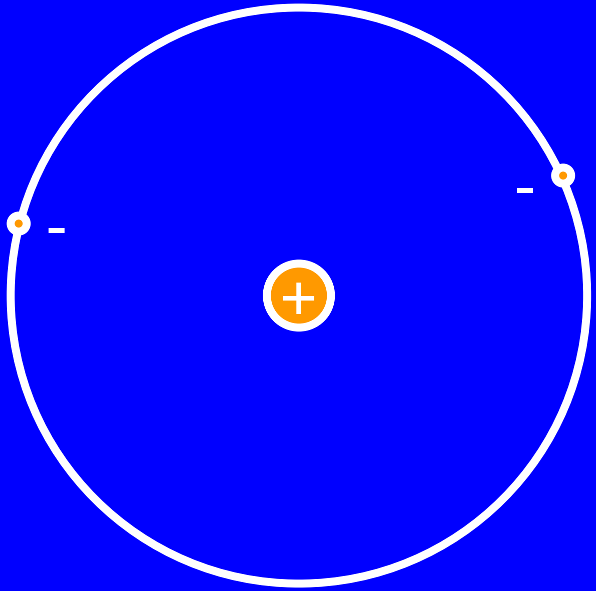
$$\text{with}\quad \underline{\hat{h}_i\psi_i = \varepsilon_i\psi_i}\quad \&\quad E = \sum_{i}\varepsilon_i$$

Single-particle eigenequation

i.e., Bohr’s atomic model !

Many-electron atoms

e.g., He, Z = 2



Orbital energy derived from Bohr's model

$$E_n = -\mathcal{R}\left(\frac{Z^2}{n^2}\right)$$

$$E_1 = -\mathcal{R}\left(\frac{2^2}{1^2}\right)$$

Predict: E_1 = -54.4 eV

Actual: E_1 = -24.6 eV

- **When it comes to a many-electron atom, something is wrong with the simple Bohr Model!**
- **The *e*-*e* interactions are too large to be negligible!**

How to realistically solve the many-electron problem?

Central field approximation (中心力场近似)

Also known **as independent electron approximation**: Suppose that in a ***n***-electron atom, each electron move in an average (central) field ***V(i)*** exerted by the nucleus and the other electrons.

$$\hat{H}(1,2,3,..,n)=\sum_{i=1}^{n}\left(-\frac{1}{2}\nabla_i^2\right)+\sum_{i=1}^{n}\left[-\frac{Z}{r_i}+\sum_{j\neq i}^{n}\frac{1}{r_{ij}}\right]$$

The coordinates of ***i***th e.

Now Let $-\frac{Z}{r_i}+\sum_{j\neq i}^{n}\frac{1}{r_{ij}}\approx V_i(i)$ i.e., central field exerted on ***i***th e.

$$\Rightarrow \hat{H}(1,2,...,n)\Psi(1,2,...,n)=\sum_{i=1}^{n}\hat{h}_i\Psi(1,2,...,n)=E\Psi(1,2,...,n)$$

Single-particle equations!

with $\hat{h}_i=-\frac{1}{2}\nabla_i^2+V_i(i)$ $\{\hat{h}_i\varphi_i(i)=\varepsilon_i\varphi_i(i)\}$

with $\Psi(1,2,3\cdots n)=\varphi_1(1)\varphi_2(2)\cdots\varphi_n(n)$ & $E=\sum_i\varepsilon_i$

Central field approximation (中心力场近似)

$$V_i(1,2,3,\ldots.N) = -\frac{Z}{r_i} + \sum_{j\neq i}^{n}\frac{1}{r_{ij}} \approx V_i(i) \Rightarrow \hat{H}(1,2,\ldots,n) = \sum_{i=1}^{n}\hat{h}_i$$

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 + V_i(i) \xrightarrow{\hat{H}\Psi = E\Psi} \{\hat{h}_i\varphi_i(i) = \varepsilon_i\varphi_i(i)\}$$

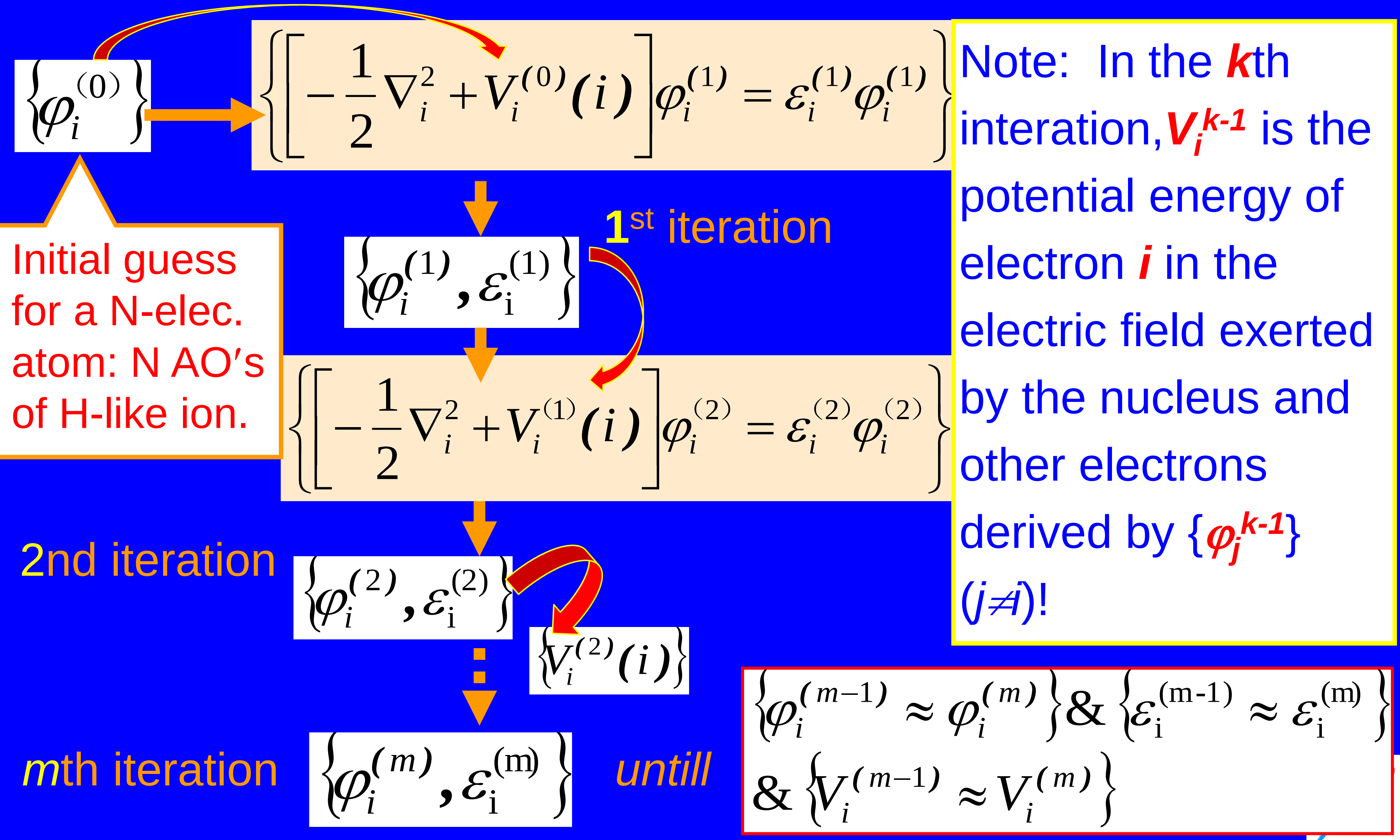
$$\text{with } \Psi(1,2,3\cdots n) = \varphi_1(1)\varphi_2(2)\cdots\varphi_n(n) \quad \& \ E = \sum_i \varepsilon_i$$

- Note that ***$V_i(i)$ is not spherical*** in most cases. Only the ***$V_i(i)$*** exerted by a closed-shell configuration is spherical.
- Suppose ***$V_i(i)$*** is spherically symmetric around the nucleus. Then ***$\varphi_i(i)$*** can adopt the form $\varphi_i(i) = R_i(i)Y_{l_i,m_i}(\theta_i,\phi_i)$
- Accordingly, the equation can be solved by means of the **Hartree-Fock self-consistent field** (**HF-SCF**) method.

Self-consistent Field method

$$\left\{\hat{h}_i\varphi_i = \varepsilon_i\varphi_i\right\}$$

First proposed by Hartree in 1928, then improved by Fock.



$$\left\{\varphi_i^{(0)}\right\}$$

Initial guess for a N-elec. atom: N AO′s of H-like ion.

$$\left\{\left[-\frac{1}{2}\nabla_i^2 + V_i^{(0)}(i)\right]\varphi_i^{(1)} = \varepsilon_i^{(1)}\varphi_i^{(1)}\right\}$$

1st iteration

$$\left\{\varphi_i^{(1)}, \varepsilon_i^{(1)}\right\}$$

$$\left\{\left[-\frac{1}{2}\nabla_i^2 + V_i^{(1)}(i)\right]\varphi_i^{(2)} = \varepsilon_i^{(2)}\varphi_i^{(2)}\right\}$$

2nd iteration

$$\left\{\varphi_i^{(2)}, \varepsilon_i^{(2)}\right\}$$

$$\left\{V_i^{(2)}(i)\right\}$$

*m*th iteration

$$\left\{\varphi_i^{(m)}, \varepsilon_i^{(m)}\right\}$$

untill

$$\left\{\varphi_i^{(m-1)} \approx \varphi_i^{(m)}\right\} \& \left\{\varepsilon_i^{(m-1)} \approx \varepsilon_i^{(m)}\right\} \& \left\{V_i^{(m-1)} \approx V_i^{(m)}\right\}$$

Note: In the ***k***th interation, V_i^{k-1} is the potential energy of electron ***i*** in the electric field exerted by the nucleus and other electrons derived by $\{\varphi_j^{k-1}\}$ ($j \neq i$)!

Example: initial guess for Li atom ($1s^2 2s^1$)

Note that the AO's of H-like atom/ions are in the forms,

$$\varphi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{\boxed{Z}}{a_0}\right)^{3/2} \exp\left(-\frac{\boxed{Z}}{a_0} r\right) \qquad \varphi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{\boxed{Z}}{a_0}\right)^{3/2} \left(2 - \frac{\boxed{Z}}{a_0} r\right) \exp\left(-\frac{\boxed{Z}}{2a_0} r\right.$$

Now supposed the valence AO's of Li atom have similar forms

$$\varphi_{1s}^0 = \frac{1}{\sqrt{\pi}} \left(\frac{\boxed{b_1}}{a_0}\right)^{3/2} \exp\left(-\frac{\boxed{b_1}}{a_0} r\right) \qquad \varphi_{2s}^0 = \frac{1}{4\sqrt{2\pi}} \left(\frac{\boxed{b_2}}{a_0}\right)^{3/2} \left(2 - \frac{\boxed{b_2}}{a_0} r\right) \exp\left(-\frac{\boxed{b_2}}{2a_0} r\right.$$

in which the coefficients $\boldsymbol{b_1}$, $\boldsymbol{b_2}$ etc evolve upon the proceeding of the **HF-SCF** procedure.

The converged values for the coefficients $\boldsymbol{b_1}$, $\boldsymbol{b_2}$ etc are definitely smaller than the Z value of Li atom.

Why? Plz figure out the physical meaning of these coefficient!

Practical method before the computer-era:

Slater's approximate method for central field

$$\hat{V}_i = -\frac{Z}{r_i} + \frac{\boxed{\sigma_i}}{r_i} = -\frac{Z-\sigma_i}{r_i}$$

The presence of other electrons around a nucleus "***screens***" an electron from the full charge of the nucleus.

$$Z^* = Z - \sigma$$

σ: Screen constant

Z*: Effective nuclear charge

→ **Modified Rydberg equation:**

$$E_i == -R \cdot \left(\frac{Z*}{n*}\right)^2$$

$$= -R \cdot \left(\frac{Z-\sigma_i}{n*}\right)^2$$

n:* Effective principal quantum number

n* = n   **(when n ≤ 3)**

n* = 3.7 (when n = 4)

n* = 4.0 (when n = 5)

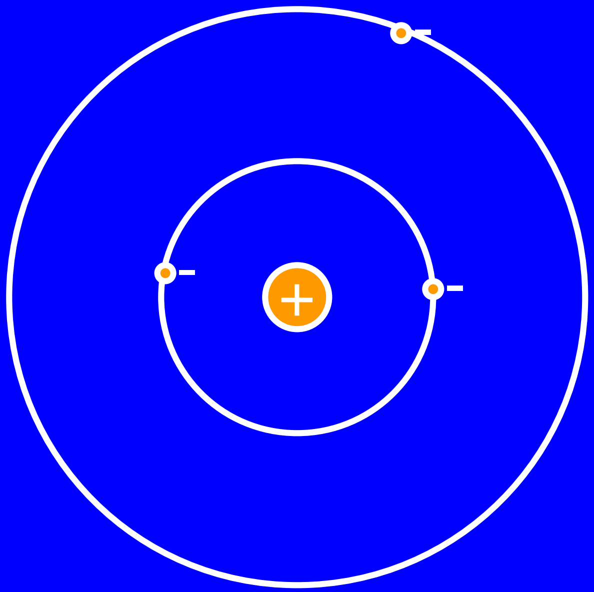
Lithium , $Z = 3$

Bohr's atomic model:

$$E_n = -R\left(\frac{Z}{n}\right)^2 \Rightarrow E_{2s} = -13.6\left(\frac{3}{2}\right)^2$$

Predicted: $E_{2s} = -30.6$ eV

Actual: $E_{2s} = -5.4$ eV



Empirical determination of Z* and σ:

$$\because E_n = -R(Z^*/n)^2$$

$$\Rightarrow Z^* = n\sqrt{(-E_n / R)}$$

$$\Rightarrow \sigma = Z - Z^*$$

For 2s of Li

$$Z^*_{2s} = n\sqrt{(-E_{2s} / R)}$$

$$= 2\sqrt{5.4 / 13.6} = 1.26$$

$\sigma = Z - Z^* = 1.74$

A. Screen (shielding) constant

Slater’s rules for the prediction of σ for an electron:

1. First group electronic configuration as follows:

   (1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p) etc.

2. An electron is not shielded by electrons in the right shells (in higher subshells and shells).

3. For ns or np electrons:

   a) each other electron in the same group contributes 0.35 (but 0.30 for 1s)

   b) each electron in an n-1 group(s) contributes 0.85

   c) each electron in an n-2 or lower group contributes 1.00.

4. For nd or nf electrons:

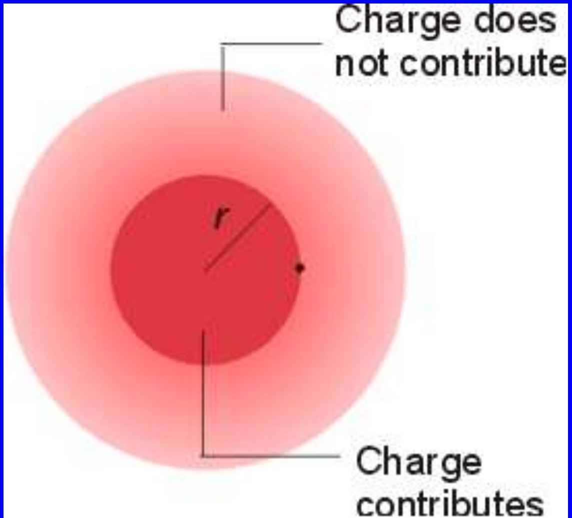
   a) each other electron in the same group contributes 0.35.

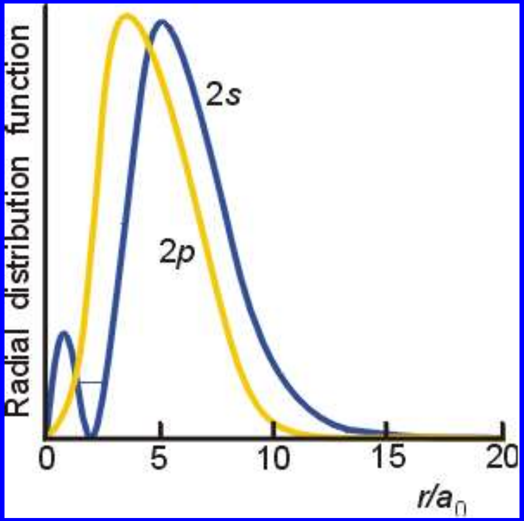
   b) each electron in a lower group contributes 1.00.

The basis of Slater's rules for σ

s and ***p*** orbitals have better "penetration" to the nucleus than ***d*** (or ***f***) orbitals for any given value of ***n*** .

i.e. there is a greater probability of ***s*** and ***p*** electrons being near the nucleus.





This means:

1. ***n*s** and ***n*p** orbitals completely shield ***n*d** orbitals.

2. ***(n-1)s/p*** orbitals don't completely shield ***n*s** and **np** orbitals.

$\boxed{Z^* = Z - \sigma}$

Example : O, Z = 8

Electron configuration: $1s^2\,2s^2\,2p^4$

a) $(1s^2)\ (2s^2\,2p^4)$

b) For a 2s/2p electron: $\sigma = (2 * 0.85) + (5 * 0.35) = 3.45$

1s **2s,2p**

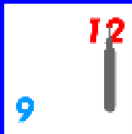
→ $Z^* = Z - \sigma = 8 - 3.45 = 4.55$

for six electrons in 2s/2p orbitals.

i.e., any of the ***2s/2p*** electrons is actually held by about ***57%*** of the force that one would expect for a **+8** nucleus.

c) For a 1s electron:

$\sigma = 1 * 0.3; \quad Z^*(1s) = 8 - 0.3 = 7.7$!



$$\boxed{Z^* = Z - \sigma}$$

Example: Ni, *Z* = 28

Electron configuration: $\mathbf{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2}$

Then $\mathbf{(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6)\ (3d^8)\ (4s^2)}$

For a 3d electron:

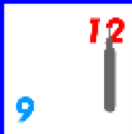
$$\sigma = \underbrace{(18 * 1.00)}_{1s,2s,2p,3s,3p} + \underbrace{(7 * 0.35)}_{3d} = 20.45$$

$Z^* = Z - \sigma$ $\quad$ $Z^*(3d) = 28 – 20.45 = 7.55$

For a 4s electron:

$$\sigma = \underbrace{(10 * 1.00)}_{1s,2s,2p} + \underbrace{(16 * 0.85)}_{3s,3p,3d} + \underbrace{(1 * 0.35)}_{4s} = 23.95$$

$Z^* = Z - \sigma$ $\quad$ $Z^*(4s) = 28 – 23.95 = 4.05$



B. Approximation of the atomic orbital energy

$$E_n = -R\cdot\left(\frac{Z-\sigma_i}{n^*}\right)^2$$

Example: Mg, $1s^2 2s^2 2p^6 3s^2$

1s

$$E_{1s} = -R\frac{(12-\sigma)^2}{1^2} = -136.89R = -R\frac{(12-0.3)^2}{1^2} = -136.89R$$

1s **2s/2p**

$$E_{2s,2p} = -R\frac{(12-0.85\times 2-0.35\times 7)^2}{2^2} = -R\frac{7.85^2}{4} = -15.40R$$

1s **2s/2p** **3s**

$$E_{3s} = -R\frac{(12-1.00\times 2-0.85\times 8-0.35)^2}{3^2} = -0.9025R$$

2.4.2 The ionization energy (IE) and the electron affinity (EA)

I. Ionization energy:

The minimum energy required to remove an electron from one of the atomic orbitals (in the gas phase) to the vaccum.

$$A(g) \rightarrow A^{+}(g) + e$$

$$I_1 = E(A^{+}) - E(A)$$

The first ionization energy

$$I_2 = E(A^{2+}) - E(A^{+})$$

The second ionization energy

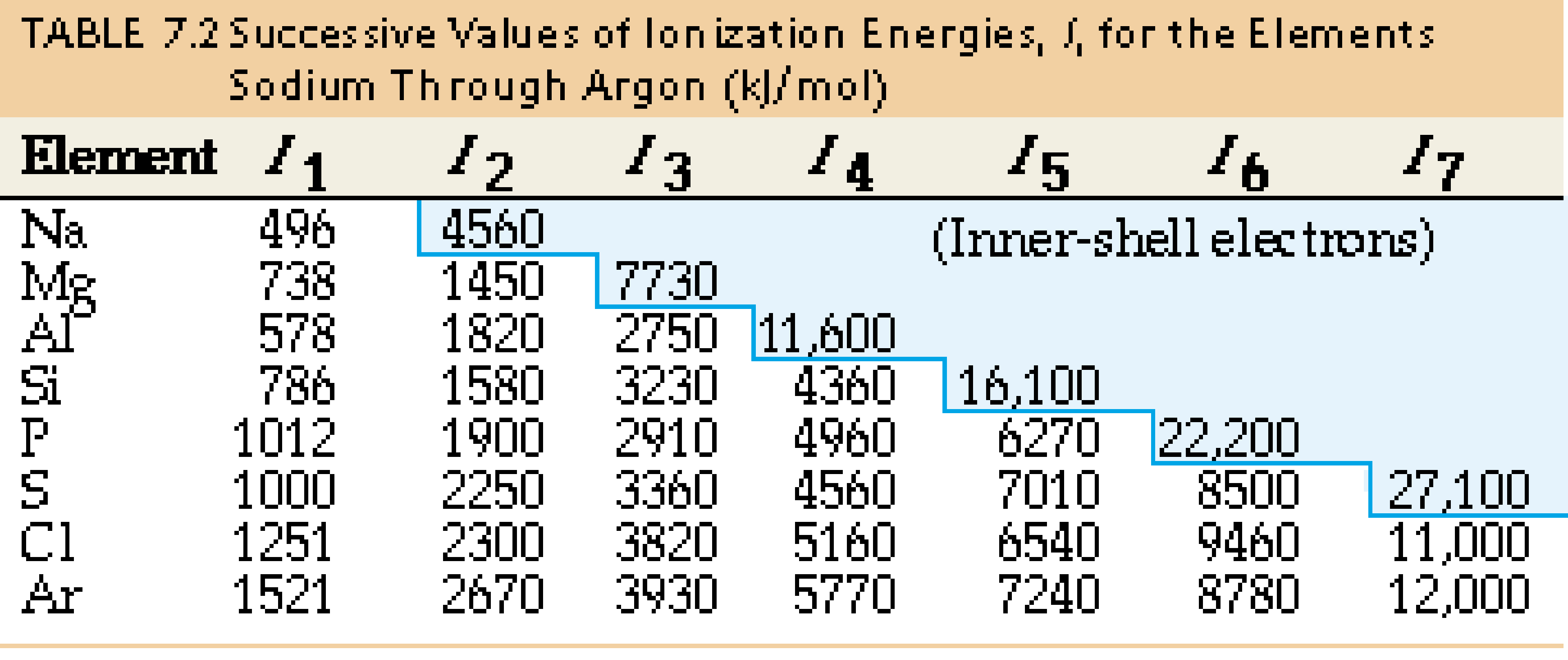
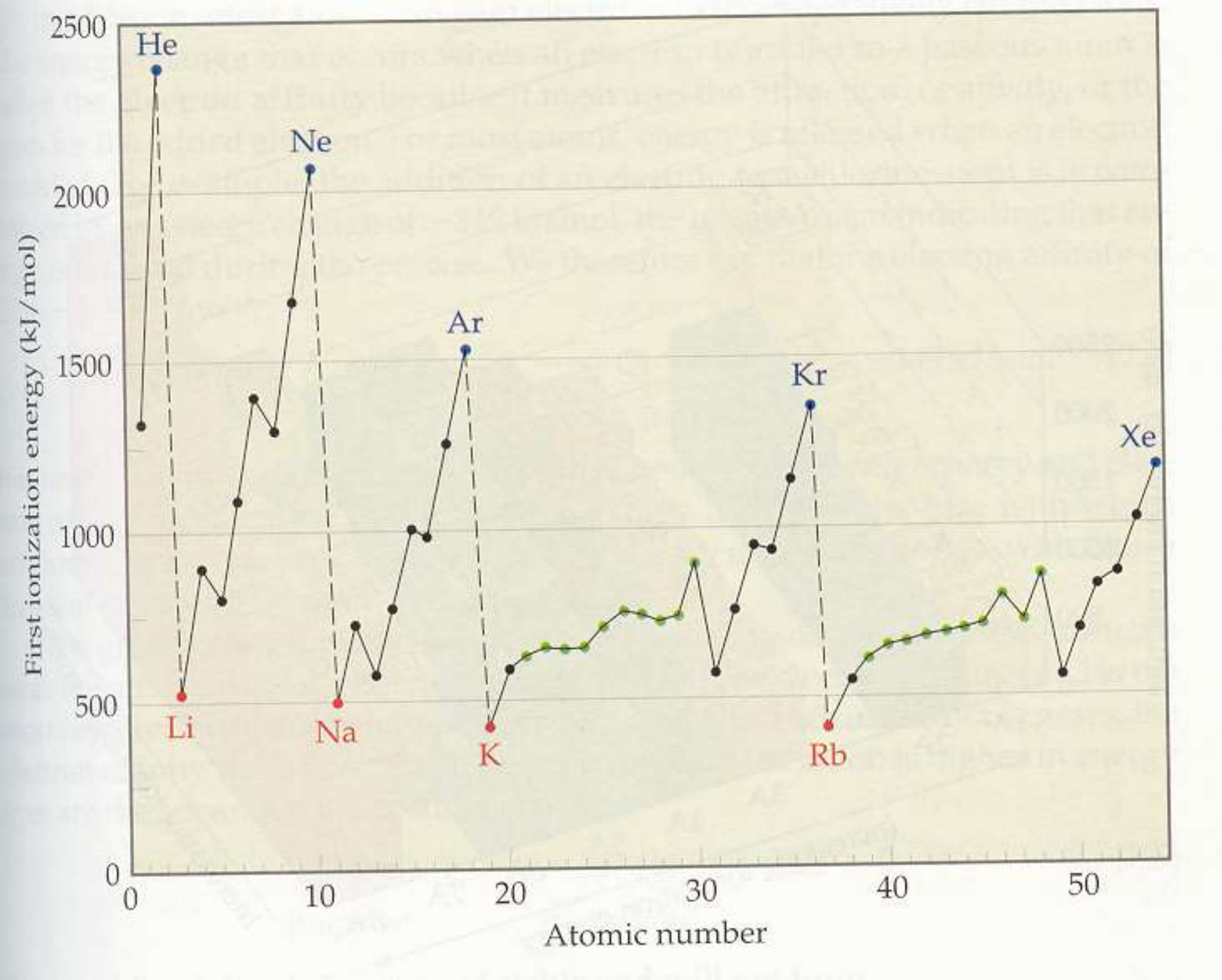


TABLE 7.2 Successive Values of Ionization Energies, I, for the Elements Sodium Through Argon (kJ/mol)

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	496	4560					
Mg	738	1450	7730				
Al	578	1820	2750	11,600			
Si	786	1580	3230	4360	16,100		
P	1012	1900	2910	4960	6270	22,200	
S	1000	2250	3360	4560	7010	8500	27,100
Cl	1251	2300	3820	5160	6540	9460	11,000
Ar	1521	2670	3930	5770	7240	8780	12,000

(Inner-shell electrons)

Periodic Trends in Ionization Potentials



II. Estimation of ionization energy

$$E_n = -R\cdot\left(\frac{Z-\sigma_i}{n^*}\right)^2$$

Example: **$C \rightarrow C^+$, $1s^2 2s^2 2p^2 \rightarrow 1s^2 2s^2 2p^1$**

$I_1 = \Delta E = E(C^+) - E(C)$ i.e., depletion of a 2p electron.

- Both C^+ and C have the same value of σ_{1s}, i.e. $\boldsymbol{E_{1s(C+)} = E_{1s(C)}}$
- For their 2s/2p electrons, we have

$$\begin{aligned} &for \qquad C^+ \\ &Z-\sigma = 6-(2\times 0.35+2\times 0.85) = 3.60 \end{aligned}$$

$$\begin{aligned} &for \qquad C \\ &Z-\sigma = 3.25 \end{aligned}$$

$$I_1 = 2\times E_{1s(C^+)} + 3\times E_{2s2p(C^+)} - 2\times E_{1s(C)} - 4\times E_{2s2p(C)}$$

$$= -[3\times(\frac{3.6}{2})^2 - 4\times(\frac{3.25}{2})^2]\cdot R = 11.44\,eV$$

$$I_{\exp t.} = 11.22\ eV$$

Estimation of ionization energy

Example: Fe → Fe^+, depletion of a 1s electron.

a) Fe^+ for lacking of a *K*-shell electron, $Z = 26$

Electron configuration: **$1s^1\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$**

$(1s^1)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6)\ (3d^6)\ (4s^2)$

$$E_n = -R \cdot \left(\frac{Z^*}{n^*}\right)^2$$

$$Z^* = Z - \sigma$$

1s: 26 – **0***0.30 = 26.00

2s,2p: 26 – 7*0.35 – 1*0.85 = 22.70

3s,3p: 26 – 7*0.35 – 8*0.85 – 1*1.0 = 15.75

3d: 26 – 5*0.35 – 17*1.0 = 7.25

4s: 26 – 1*0.35 – **14***0.85 – 9*1.0 = 4.75

J. C. Slater, Phys. Rev. 36(1930)57

Example: Fe, Z = 26

Electron configuration: **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$**

$(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6)\ (3d^6)\ (4s^2)$

$$\boxed{Z^* = Z - \sigma}$$

1s: 26 – 0.30 = 25.70

2s,2p: 26 – 7*0.35 – 2*0.85 = 21.85

3s,3p: 26 – 7*0.35 – 8*0.85 – 2*1.0 = 14.75

3d: 26 – 5*0.35 – 18*1.0 = 6.25

4s: 26 – 1*0.35 – 14*0.85 – 10*1.0 = 3.75

J. C. Slater, Phys. Rev. 36(1930)57

Estimation of ionization energy

Example: Fe → Fe$^+$, depletion of a 1s electron.

$$E_i = -\mathrm{R}\cdot\left(\frac{Z^*}{n^*}\right)^2$$

	Fe (Z*)	**Fe$^+$(Z*)**
$(1s)^{2-1}$	**25.70**	**26.00**
$(2s,2p)^8$	**21.85**	**22.70**
$(3s,3p)^8$	**14.75**	**15.75**
$(3d)^6$	**6.25**	**7.25**
$(4s)^2$	**3.75**	**4.75**

$$E(\mathrm{Fe})=-2(25.70/1)^2-8(21.85/2)^2 -8(14.75/3)^2-6(6.25/3)^2 -2(3.75/3.7)^2=-2497.3$$

$$E(\mathrm{Fe}^+)=-1(26.00/1)^2-8(22.70/2)^2 -8(15.75/3)^2-6(7.25/3)^2 -2(4.75/3.7)^2=-1965.4$$

J. C. Slater, Phys. Rev. 36(1930)57

$$I_{1K} = \Delta E = E(\mathrm{Fe}^+) - E(\mathrm{Fe})$$

$$= -1965.4 + 2497.3 = 531.9\ (524.0\ \text{expt.})$$

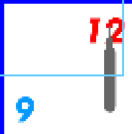
III. Electron Affinity

- The electron affinity (EA) is the energy change that occurs when an electron is added to a gaseous atom.

$$\mathbf{B(g) + e^{-} \rightarrow B^{-}(g) \; + A}$$

1. EA of an atom can be empirically predicted using the Slater's rules.
2. In practice, EA of an atom can be measured by measuring the first ionization potential of its monoanion in gas phase!

- Electron affinity usually increases as the radii of atoms decrease.
- Electron affinity decreases from the top to the bottom of the periodic table.



IV. The Electronegativity

- Electronegativity was proposed by Pauling to evaluate the relative capability of atoms to attract bonding electrons.

It can be concluded that:

1. The electronegativities of metals are small while those of non-metal are large.
2. Generally, the electronegativity increases from left to right across the periodic table, but decreases from top to bottom within a group.
3. Elements with great difference in electronegativities tend to form ionic bonds.

2.4.3 The building-up principle and the electronic configurations

I. The building-up principle (for ground states of atoms)

Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$

a. **Pauli exclusion principle.**

Every orbital may contain up to two electrons of opposite spins.

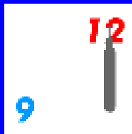
b. **The principle of minimum energy. (*Aufbau* principle)**

Whilst being compatible with the Pauli principle, electrons occupy the orbital with the lowest energy first.

Problem:

For a many-electron atom, its energy levels are not faithfully aligned in the order of principal quantum numbers, e.g., for transition-metal atoms!

Fe: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

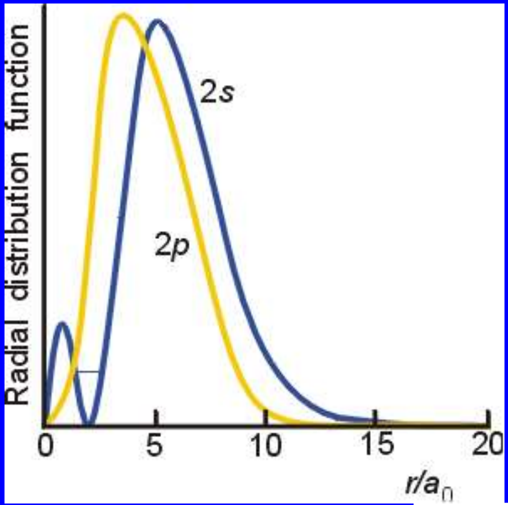


For multi-electron atoms:

Due to electron-electron repulsions, atomic orbitals with the same ***n*** but different ***l*** are no longer degenerate in energy. For this case, both the penetration effects and the average radii of AOs are decisive.

1) Average radii of AO: In general, the AO with higher *n* value has a larger average radii, thus is higher in energy due to smaller electron-nucleus interactions.

2) Penetration effects: the radial distribution of a AO (***n,l***) has ***n-l*** maxima. Thus for AOs with the same ***n***, the one with a lower ***l*** has more local maxima near the nucleus and thus has a higher probability for electron to appear near the nucleus. i.e., being lower in energy (less screened by inner-shell electrons!)



For multi-electron atoms:

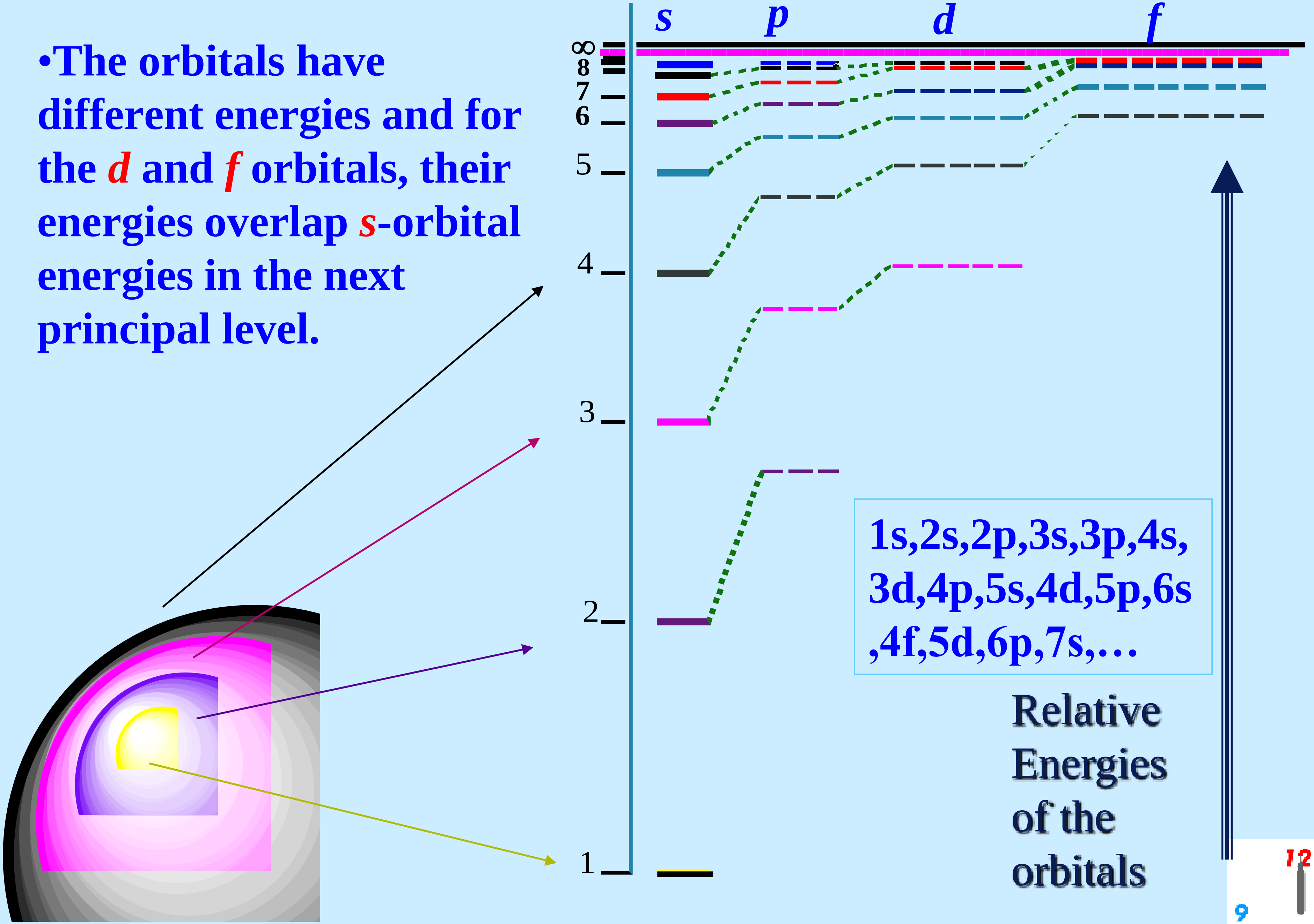
The energy level can be estimated by $n+0.7l$. *(proposed by G.X. Xu .)*

1s	**2s**	**2p**	**3s**	**3p**	**3d**	**4s**	**4p**	**4d**	**4f**
1.0	**2.0**	**2.7**	**3.0**	**3.7**	**4.4**	**4.0**	**4.7**	**5.4**	**6.1**
5s	**5p**	**5d**	**5f**	**6s**	**6p**	**6d**	**6f**		
5.0	**5.7**	**6.4**	**7.1**	**6.0**	**6.7**	**7.4**	**8.1**		

Therefore, the sequence of the atomic orbitals is: ***1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 5p, 6s, 4f, 5d, 6p***, …

Relative Energies for Shells and Orbitals

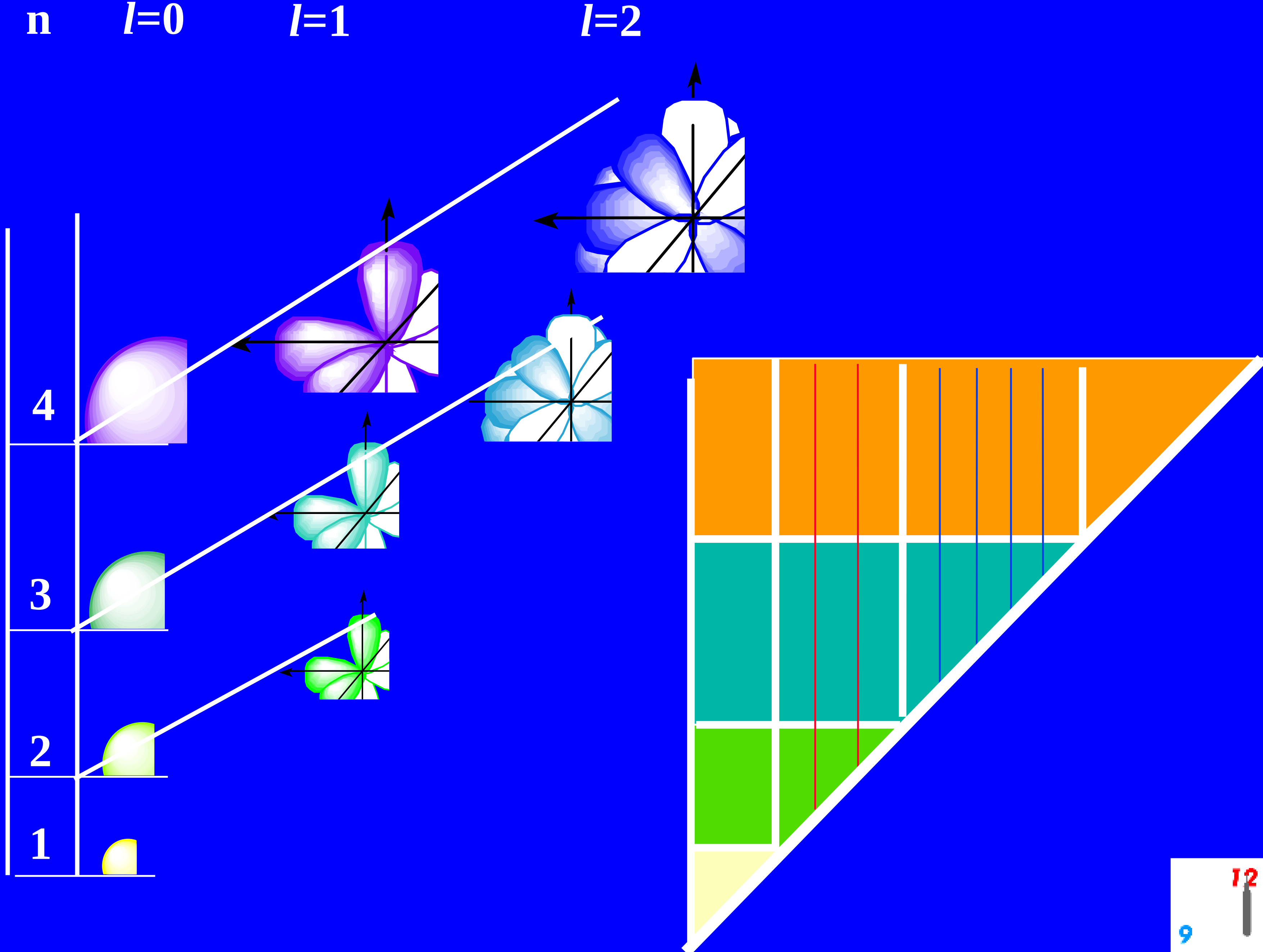
- **The orbitals have different energies and for the *d* and *f* orbitals, their energies overlap *s*-orbital energies in the next principal level.**



1s,2s,2p,3s,3p,4s, 3d,4p,5s,4d,5p,6s ,4f,5d,6p,7s,…

Relative Energies of the orbitals

The principle of minimum energy.



n *l*=0 *l*=1 *l*=2

4

3

2

1

I. The building up principle (for ground state)

a. **Pauli exclusion principle.**

Every orbital may contain up to two electrons of opposite spins.

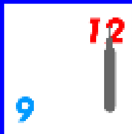
b. **The principle of minimum energy (*Aufbau* principle)**

Whilst being compatible with the Pauli principle, electrons occupy the orbital with the lowest energy first.

c. **Hund’s rule.**

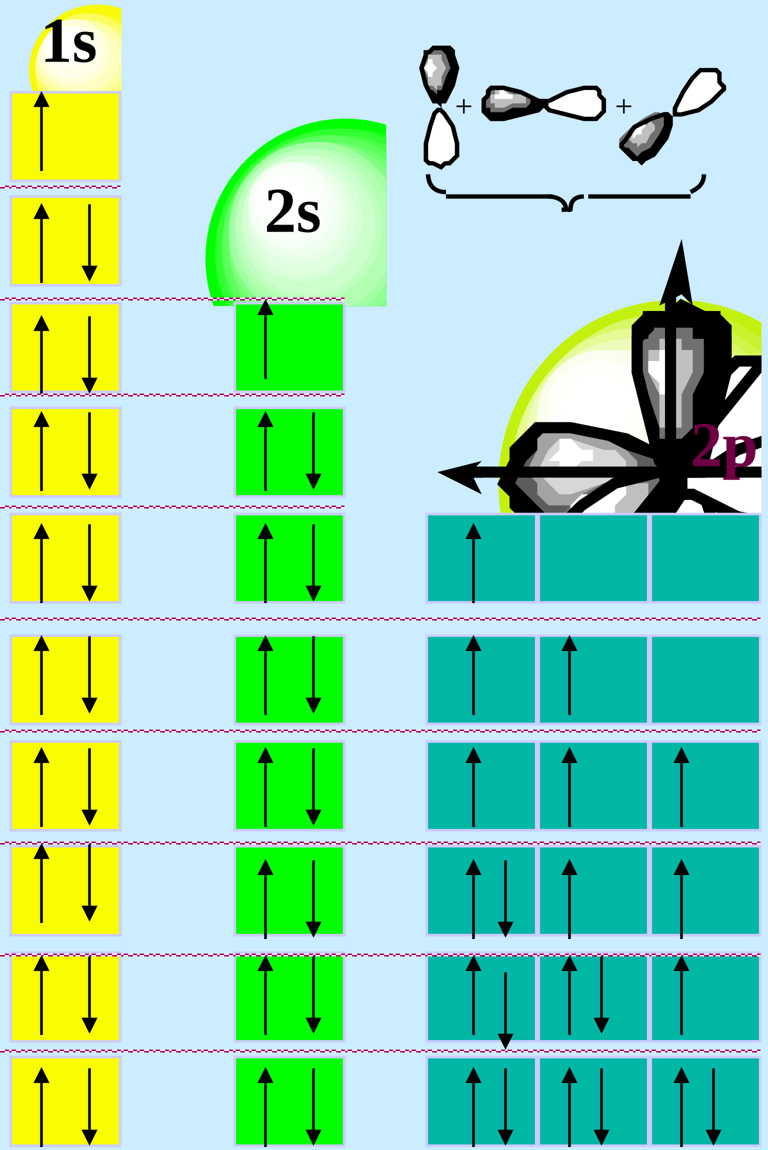
In degenerate energy states, electrons tend to occupy as many degenerate orbitals as possible. (The number of unpaired electrons is a maximum.)

Note: The electronic configuration for the ground state of a molecule also follows these rules!

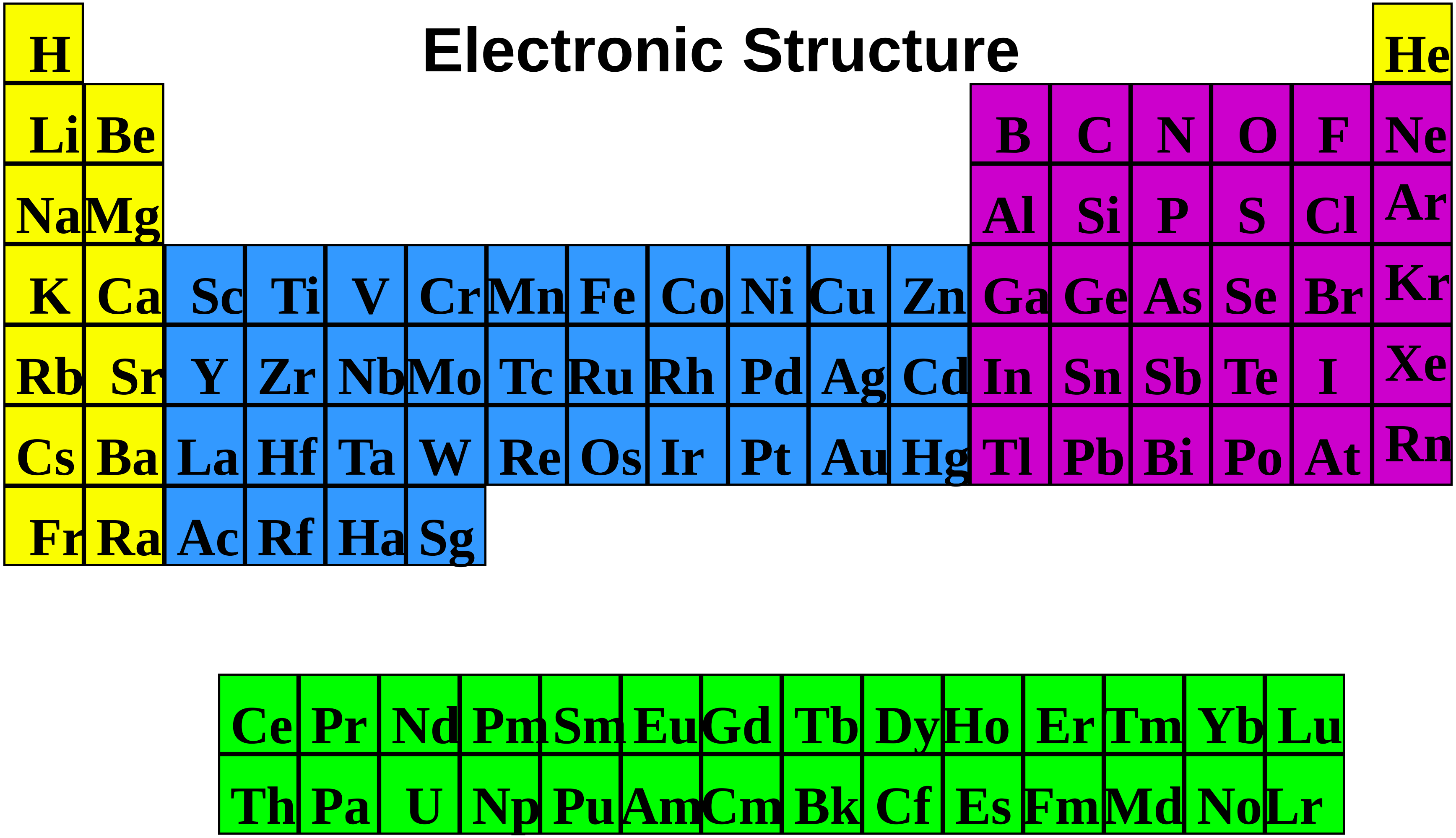


II. The ground-state electronic configurations of atoms

- H = $1s^1$
- He = $1s^2$
- Li = $1s^2 2s^1$
- Be = $1s^2 2s^2$
- B = $1s^2 2s^2 2p^1$
- C = $1s^2 2s^2 2p^2$
- N = $1s^2 2s^2 2p^3$
- O = $1s^2 2s^2 2p^4$
- F = $1s^2 2s^2 2p^5$
- Ne = $1s^2 2s^2 2p^6$



The Periodic Table of the Elements
Electronic Structure



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Ha	Sg												

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

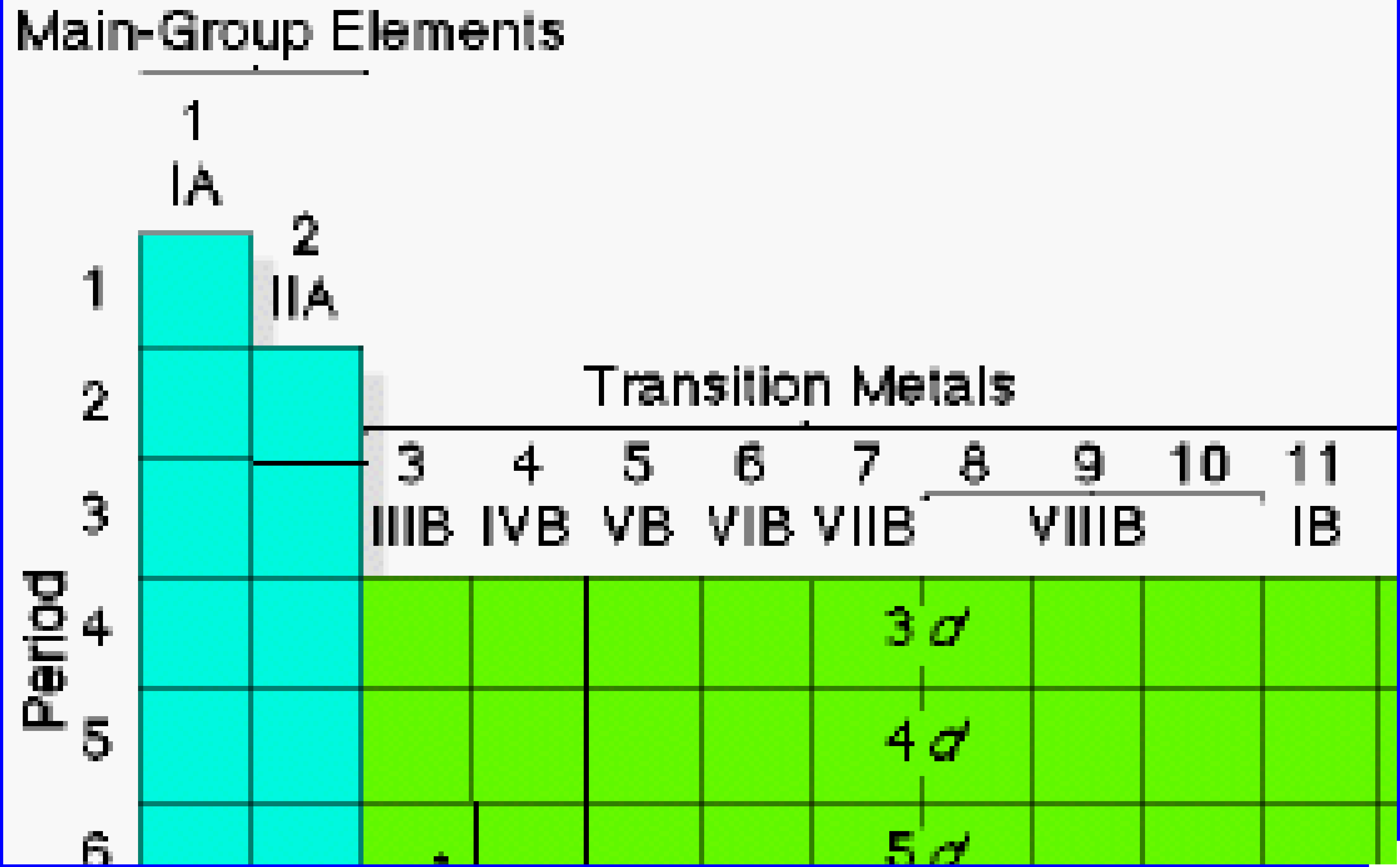
🟨 “ s” Orbitals

🟪 “ p” Orbitals

🟦 “ d” Orbitals

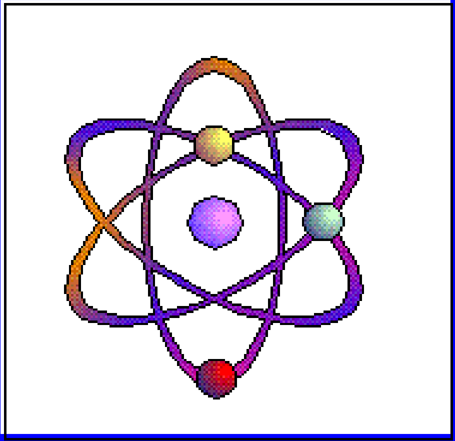
🟩 “ f ” Orbitals

Electron Configuration using the Periodic Table



2.5 Atomic spectra and spectral term

The wavefunction to describe the motion of a electron in an AO of a many-electron atom (derived from the ***central-field approx***.):



orbital part

Spin part:

α or β

$$\varphi = [R_n(r)\cdot Y_{\ell,m}(\theta,\phi)]\cdot\sigma(s)$$

$$n = 1, 2, 3, \ldots$$

$$l = 0, 1, \ldots, (n\text{-}1)$$

$$m_l = 0, \pm 1, \ \ldots, \pm l$$

$$m_s = \pm 1/2$$

n	**(principal quantum number)**
l	**(orbital quantum number)**
***m*(*m*$_l$)**	**(magnetic quantum number)**
***m*$_s$**	**(spin magnetic quantum number)**

For electron & proton, spin quantum number ***s*** ≡ ½

(i.e., defining the magnitude of spin angular momentum)!

Seemingly similar to that for the one-electron H-like atom/ion.

Difference:

- For a 1-electron atom/ion, AO′s of the same shell (***n***) are degenerate.

For a many-electron atom, the e-e interactions result in:

i) The electronic orbitals within a given shell (***n***) are divided into energy-sublevels differing in ***l***. (***ns<np< nd*** …)

ii) The electrostatic potential exerted on each electron is not spherical, and, consequently, the angular momentum of any individual electron is not as conserved as that of the electron within a 1-e atom/ion. In other words, the individual orbital-angular-momentum operators $\hat{L}_i$ of the electrons do not commute with the atomic Hamiltonian, but their sum does.

$$\hat{H}\Psi(1,2,...N) = E\Psi(1,2,...,N)$$

$$[\hat{H},\hat{L}_i] \neq 0; \qquad [\hat{H},\hat{L}_i^2] \neq 0$$

- The electronic wave function of an atom in a given quantum state satisfies

Atomic Hamiltonian

$$\hat{H}\Psi(1,2,...N)=E\Psi(1,2,...,N)$$

L: total electronic orbital angular momentum

$$\hat{L}^2(1,2,...,N)\Psi=L(L+1)\hbar^2\Psi$$

L*$_z$**: z-component of ***L

$$\hat{L}_z(1,2,...,N)\Psi=M_L\hbar\Psi$$

Total orbital-angular-momentum quantum number *L*

$$\hat{L}^2(1,2,...,N)=\sum_i\hat{L}^2(i) \qquad \hat{L}_z(1,2,...,N)=\sum_i\hat{L}_z(i)$$

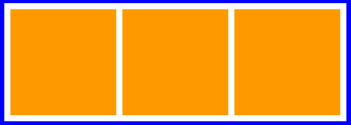
$$[\hat{H},\hat{L}^2(1,2,...,N)]=0\ \&\ [\hat{H},\hat{L}_z(1,2,...,N)]=0$$

- Therefore, we can characterize an atomic state by the quantum numbers *L* and M_L (as well as the spin quantum numbers *S* and *Ms*) .

→ Spectral term!

Example: C $1s^2 2s^2 2p^2$

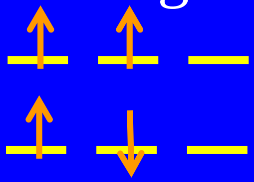
np^2



$(l=1)$

m_l 1 0 - 1

- A total of 15 (i.e., C_6^2) microstates differing in the orbitals and spin states of the two electrons, e.g.,



- These microstates differing subtly in e-e electron interactions are not in the same energy. More importantly, the wave functions to describe each of these microstates may not be the eigenfunction of atomic Hamiltonian. How to discern them?

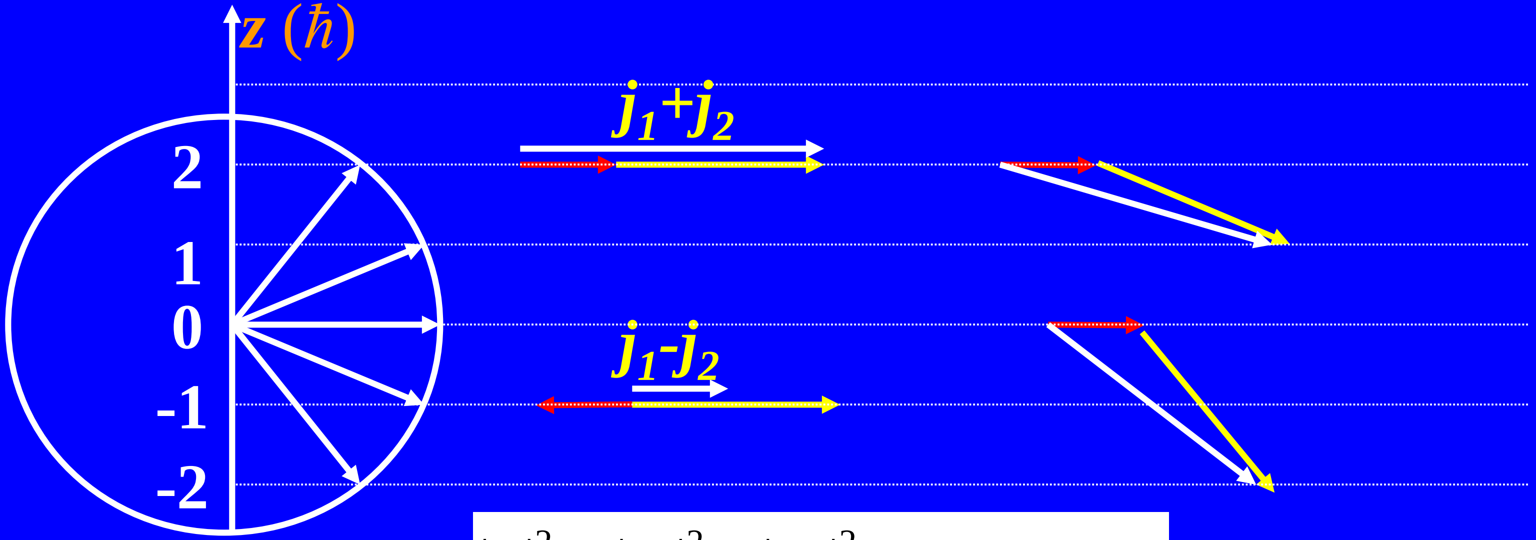
- Spectral term!

2.5.1 Total Electronic Orbital and Spin Angular Momenta

a. Addition of two angular momenta:

The addition of two angular momenta characterized by quantum number j_1 and j_2 results in a total angular momentum whose quantum number J has the possible values:

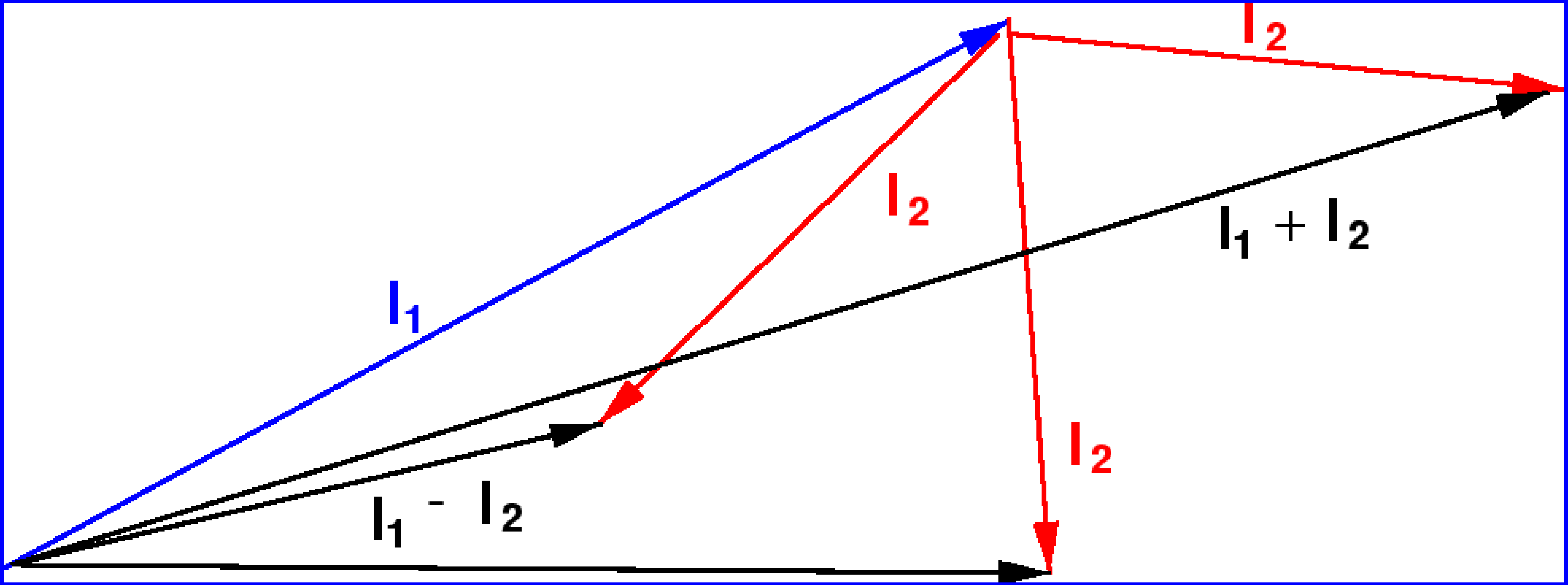
$$J = j_1+j_2,\ j_1+j_2-1,\ \ldots,\ |j_1-j_2|; \quad \text{or} \quad |j_1-j_2| \le J \le j_1+j_2$$



$$\vec{L} \vec{=} \vec{L}_1 + \vec{L}_2$$

$$|L|^2 = |L_1|^2 + |L_2|^2 + 2L_1 \bullet L_2$$
$$= |L_1|^2 + |L_2|^2 + 2|L_1||L_2| \boldsymbol{\cos} \theta_{12}$$

$$|L|^2 = L(L+1)\hbar^2$$

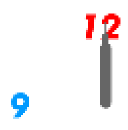


***Example*:** Find the possible values of the total-angular-momentum quantum number resulting from the addition of two angular momenta with quantum number $j_1 = 2$ and $j_2 = 3$.

Solution: $J_{max} = j_1 + j_2 = 2+3 = 5$

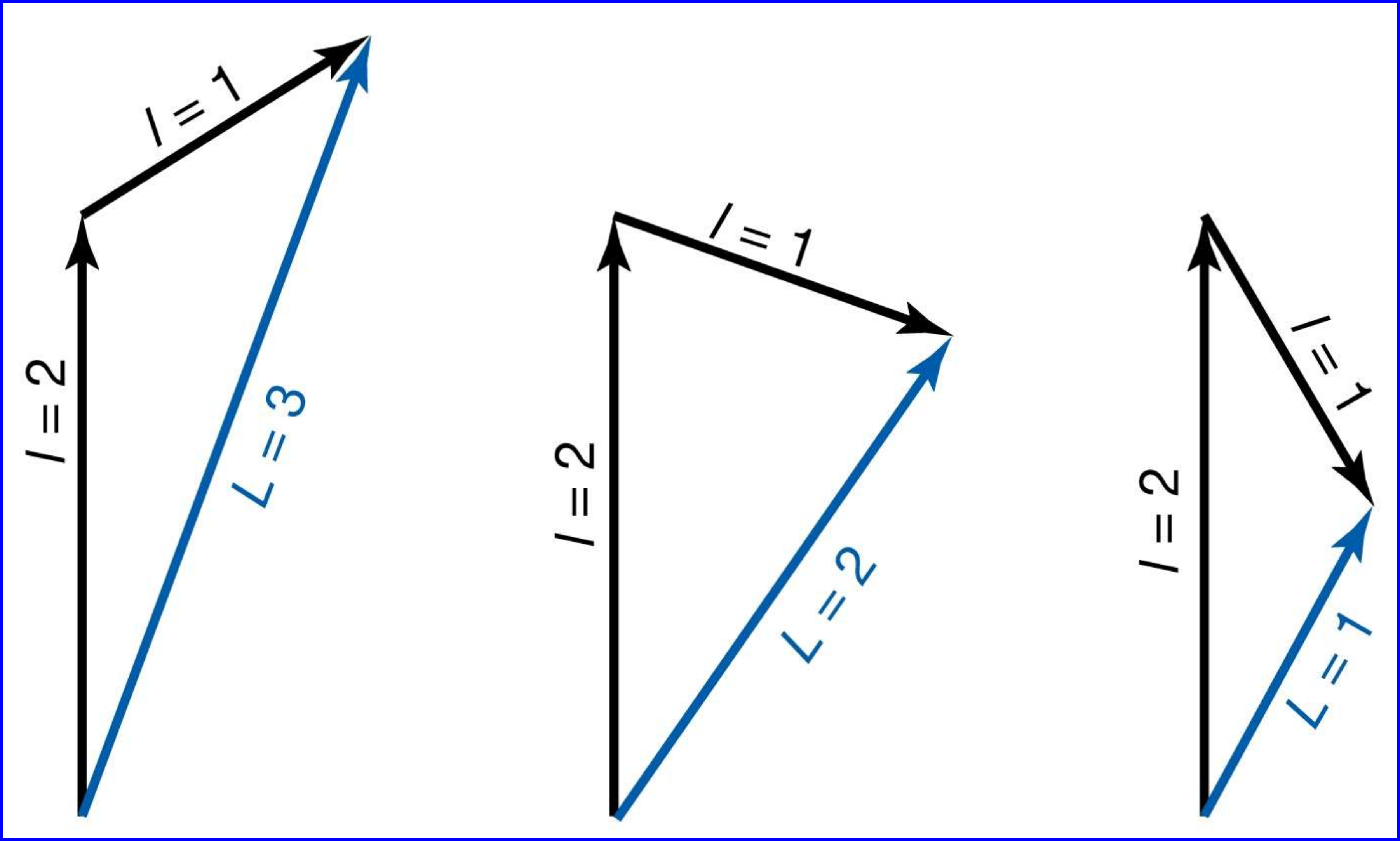
$J_{min} = |j_1 - j_2| = |2-3| = 1$

→ *The possible J values are:* 5, 4, 3, 2, 1



d^1p^1

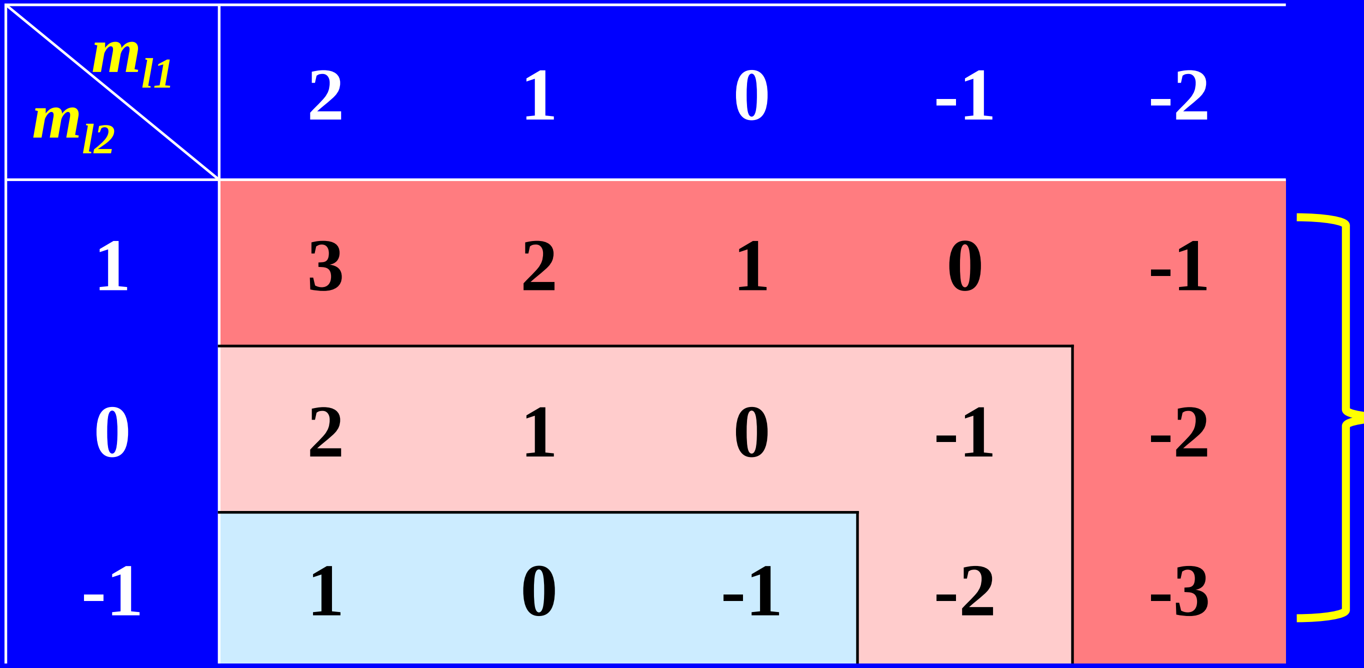
Angular momenta are vectors!



(Note: for an electron in a given AO, its orbital angular momentum is jointly defined by *l* (magnitude) and *m_l* (direction)!)

e.g., d^1p^1

$l_1=2$ **(with 5 possible directions differing in m_l.)**



$l_2 = 1$

m_{l2} \ m_{l1}	**2**	**1**	**0**	**-1**	**-2**
1	**3**	**2**	**1**	**0**	**-1**
0	**2**	**1**	**0**	**-1**	**-2**
-1	**1**	**0**	**-1**	**-2**	**-3**

$$M_L = \sum_i m_l(i)$$

L=1 ***L=2*** ***L=3***

$$|L|^2 = L(L+1)\hbar^2$$

$$|\vec{L}| = \sqrt{2}\hbar \qquad |\vec{L}| = \sqrt{6}\hbar \qquad |\vec{L}| = \sqrt{12}\hbar$$

⇒ 15 possible total angular momenta differing in ***L*** (magnitude) and ***M_L*** (direction): ***L = 3, 2, 1*** (For each ***L***, ***M_L*** ranges from ***–L*** to ***L***.)

M_L: L, L-1, …, -L+1, -L

B. The total electronic orbital angular momentum

The total electronic orbital angular momentum of an ***n***-electron atom is defined as the vector sum of the angular momenta of the individual electrons:

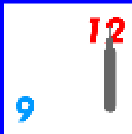
$$\vec{L} = \sum_i \vec{m}_l(i)$$

The orbital angular momentum of ***i***th e defined by two quantum numbers ***l*** (magnitude) and $\boldsymbol{m_l}$ (direction).

The total-electronic-orbital-angular-momentum quantum number **L** of an atom is indicated by a code letter:

L	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Letter	**S**	**P**	**D**	**F**	**G**	**H**	**I**	**K**

For a given **L** value, the quantum number M_L ($M_L\hbar$---the z component of the total electronic orbital angular momentum) takes on **2L+1** values ranging from **–L** to **L**.



- ***For single particle (single electron)***

Eigenequations

Orbital symbol

$$\hat{M}^2\psi_{nlm} = l(l+1)\hbar^2\psi_{nlm}$$

$$\hat{M}_z\psi_{nlm} = m_l\hbar\psi_{nlm}$$

l	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Letter	***s***	***p***	***d***	***f***	***g***	***h***	***i***	***k***

- ***For two or more electrons***

Ψ

All-electron wavefunction of atom in a given energy state.

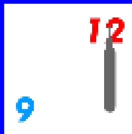
$$\hat{L}^2\Psi = L(L+1)\hbar^2\Psi$$

$$\hat{L}_z\Psi = M_L\hbar\Psi$$

Term symbol

L	**0**	**1**	**2**	**3**	**4**	**5**		**7**
Letter	***S***	***P***	***D***	***F***	***G***	***H***	**……**	

M_L = -*L*, -*L*+1, …, *L*　　　　(2*L* + 1)



Note: For any fully occupied sublevel (e.g, ns^2, np^6 , nd^{10} etc), the total electronic orbital angular momentum is,

$$\sum_i \vec{m}_l(i) = 0$$

Example: Find the possible values of the quantum number ***L*** for states of carbon atom that arise from the electron configuration ***$1s^2 2s^2 2p^1 3d^1$*.**

Solution: Simply consider ***$2p^1 3d^1$*.**

s *l=0* *p^1* *l=1* *d^1* *l=2*

↓ *Addition of angular momenta rule*

The total-orbital-angular-momentum quantum number ranges from **1+ 2 = 3** to **|1-2| = 1**

↓

***L* = 3, 2, 1**

C. The total electronic spin angular momentum

a. ***Electron spin***: Uhlenbeck and Goudsmit proposed in 1925 that the electron has an intrinsic ***"spin" angular momentum*** in addition to its orbital angular momentum, like the Earth revolving about both the Sun and its own axis.

However, electron "spin" is not a classical effect, and the picture of an electron rotating about an axis has no physical reality.

b. **The total electronic spin angular momentum** ***S*** of an N-electron atom is defined as the vector sum of the spins of the individual electrons:

$$\vec{S} = \sum_i \vec{m}_s(i)$$

Total spin quantum number S.

$$\hat{S}^2\Psi = S(S+1)\hbar^2\Psi$$

$$\hat{S}_z\Psi = M_S\hbar\Psi$$

For a fixed ***S*** value, the quantum number M_S takes on **2S+1** values ranging from **–*S*** to ***S*** (to reflect the different directions of the total spin angular momentum)

Example: Find the possible values of the quantum number ***S*** for states of carbon atom that arise from the electron configuration ***$1s^2 2s^2 2p^1 3d^1$.***

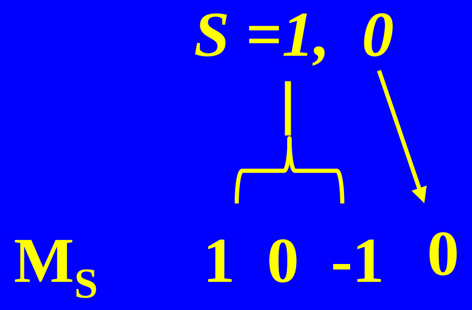
Solution:

1s electrons: $M_s = +\frac{1}{2} - \frac{1}{2} = 0$ Pauli exclusion principle

2s electrons: $M_s = +\frac{1}{2} - \frac{1}{2} = 0$ Pauli exclusion principle

2p electron: $s_1 = \frac{1}{2}$ ($m_s = 1/2$ or $-1/2$) 3d electron: $s_2 = \frac{1}{2}$

Addition of two angular momenta rule ↓ ***$S = s_1 + s_2, \ldots, |s_1 - s_2|$***



$S = 1, 0$

M_S 1 0 -1 0

D. ***The total angular momentum***

$$\vec{J} = \vec{L} + \vec{S}$$

Total angular momentum quantum number

$$J = (L + S),\ (L + S) - 1, \ldots /L - S/$$

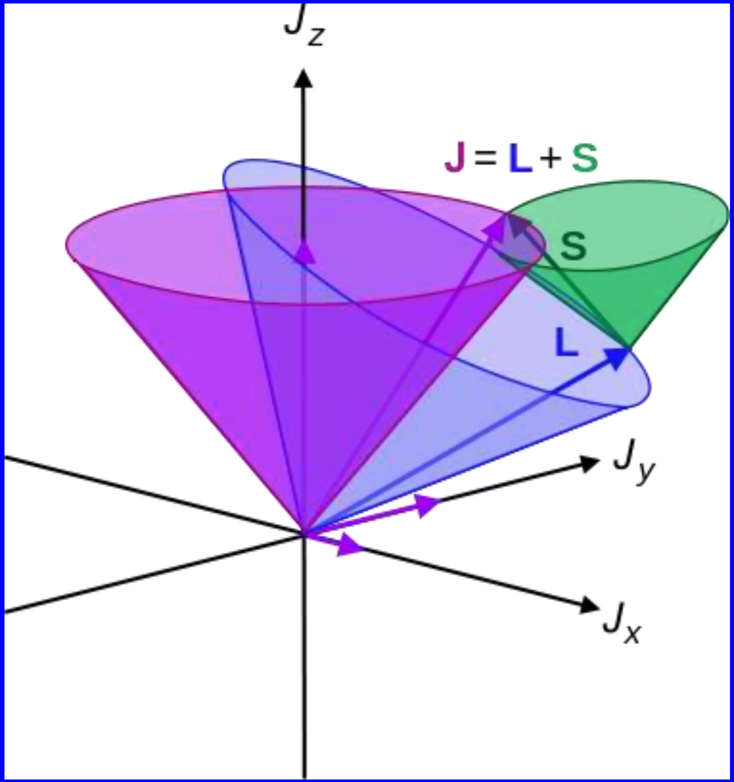
Spin – orbit coupling

For a given J, there are (2J+1) values of M_J ranging from J to –J.

$$J \geq M_J \geq -J$$

e.g., J = 3/2,

M_J = 3/2, 1/2, -1/2, -3/2



2.5.2 Atomic term and term symbol

A set of equal-energy atomic states that arise from the same electronic configuration and that have the same ***L*** value and the same ***S*** value constitute an ***atomic term***.

Term symbol: ^{2S+1}L

*Each term consists of **(2L+1)(2S+1)** microstates. (In case spin-orbit interaction can be neglected!)*

- The quantity **2S + 1** is called the ***electron-spin multiplicity***, reflecting that a given total spin angular momentum quantum number S has **2S+1** possible M_S values (different directions of total spin angular momentum.

2.5.3 Derivation of Atomic Term

a. Configurations of completely filled subshells (ns^2, np^6, nd^{10} etc.):

$$M_S=\sum_i m_s(i)=0 \Rightarrow S=0; \quad M_L=\sum_i m_l(i)=0 \Rightarrow L=0$$

→ only **^1S**

s^2 ↑↓ ← **One microstate** → p^6 ↑↓ ↑↓ ↑↓

d^{10} ↑↓ ↑↓ ↑↓ ↑↓ ↑↓

m_{s1} = 1/2 , m_{s2} = -1/2 , $M_S = 0$

m_{l1} = 0 , m_{l2} = 0, $M_L = 0$

---

b. Nonequivalent electrons in open subshells.

$(2p)^1(3p)^1$ Total number of microstates = (3x2) x (3x2) = 36.

We need not worry about any restrictions imposed by the Exclusion Principle!

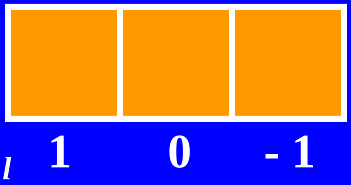
$l_1=1$, $l_2=1$ → L = 2, 1, 0

s_1 = ½, s_2 = ½ → S = 1, 0

→ **^3D, ^1D, ^3P, ^1P, ^3S, ^1S**

terms

c. Equivalent electrons. E.g., np^2



The number of microstates: $C_6^2 = 15 \neq C_6^1 \times C_6^1$

Equivalent electrons (x) having common n and l values should avoid to have the same four quantum numbers (i.e., differing in m_l or m_s)! -- Pauli exclusion principle

The number of allowed microstates: $C_{2(2l+1)}^{x}$

l_1=1, l_2=1 → L = 2, 1, 0

m_{s1} = ½, m_{s2} = ½ → S = 1, 0

$\not\longrightarrow$ **^3D, ^1D, ^3P, ^1P, ^3S, ^1S**

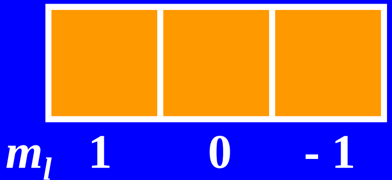
terms

Instead, np^2 $\longrightarrow$ **^1D, ^3P, ^1S**

Only three terms, why?

A simple deduction for two equivalent electrons: L + S = even!

c. Equivalent electrons. E.g., np^2

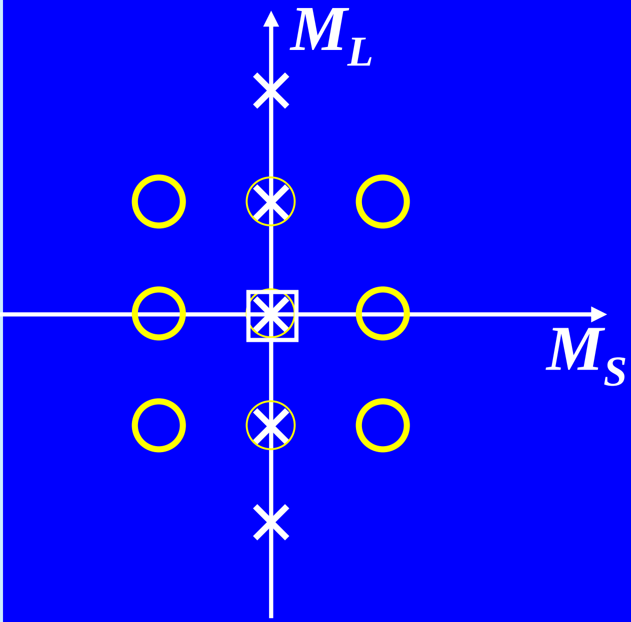


Enumeration method!

The number of microstates: $C^2_6 = 15$

* $(M_L)_{max}=2$ accompanied by $M_s = 0$ → $L = 2$, $S = 0$; (5)
* $(M_s)_{max} = 1$ accompanied by $M_L = 1$, and $= 0$ & -1 → $S=1$, $L=1$; (9)
* $M_L = 0$, $M_s = 0$, → $L=0, S=0$; (1)

No	m_l			$M_L = \sum_i m_l(i)$	$M_S = \sum_i m_s(i)$	Term
	1	0	-1			
1	↓↑			2	0	^1D
2	↑	↑		1	1	^3P
3	↑	↓		1	0	^1D ^3P
4	↓	↑		1	0	
5	↓	↓		1	-1	^3P
6		↑↓		0	0	^1D ^3P ^1S
7	↑		↓	0	0	
8	↓		↑	0	0	
9	↑		↑	0	1	^3P
10	↓		↓	0	-1	^3P
11		↑	↓	-1	0	^1D ^3P
12		↓	↑	-1	0	
13		↑	↑	-1	1	^3P
14		↓	↓	-1	-1	^3P
15			↓↑	-2	0	^1D



^1D, ^3P, ^1S

5 + 9 + 1 -> 15

As mentioned above, the microstate with both electrons in the AO ($l=1, m_l=0$) contributes to three different energy-states (i.e. spectral terms ^1D, ^3P, ^1S). How to understand this?

e_1: $l=1$, $m_l=0$; e_2: $l=1$, $m_l=0$ → $M_S = 0$ **(may belong to S = 1 or 0)**

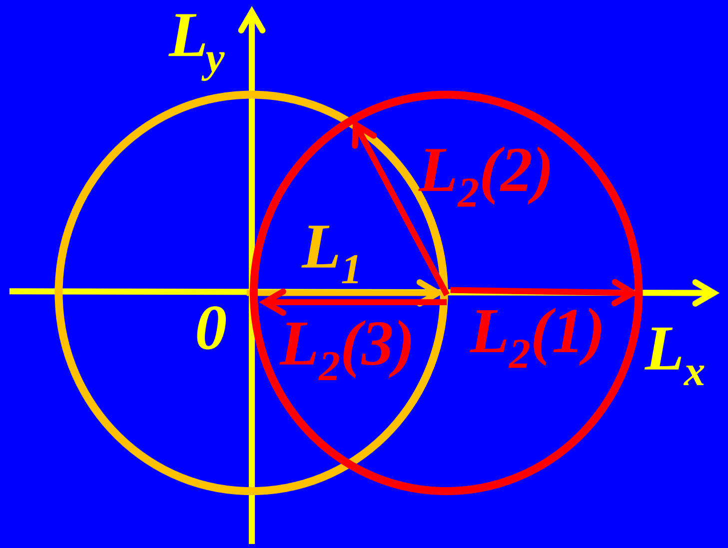
→ $M_L = 0$, but L can be 2, 1, or 0.

Case 1: $L=2$, $M_L=0$

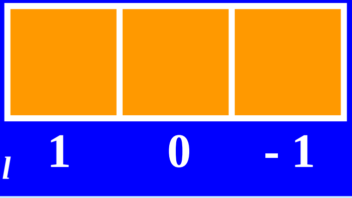
Case 2: $L=1$, $M_L=0$

Case 3: $L=0$, $M_L=0$

- This microstate contains ***three*** different patterns of e-e interactions and is not an eigenfunction of atomic Hamiltonian!
- Two other microstates contain similar patterns of e-e interactions.
- Linear combinations of all three microstates can be the eigenfunctions of atomic Hamiltonian.



Alternative process to determine the spectral terms of np^2



The number of microstates: $N_{ms} = C^2_6 = 15$

$l_1=1, \quad l_2=1 \rightarrow L = 2, 1, 0$

$m_{s1} = ½, m_{s2} = ½ \rightarrow S = 1, 0$

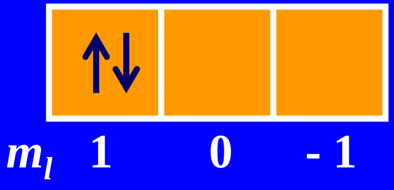
*Pauli exclusion: Equivalent electrons have the same value of **n** and the same value of **l**. Two electrons should avoid to have the same four quantum numbers!*

$^3D, ^1D, ^3P, ^1P, ^3S, ^1S$

However, combination of the computed *L* and *S* values is no longer arbitarily due to Pauli exclusion!

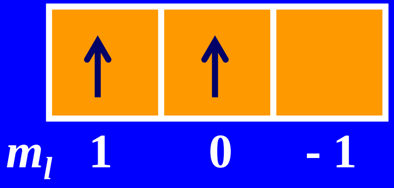
1) $L = 2 \rightarrow (M_L)_{max} = 2 = 1(m_{l1}) + 1(m_{l2})$

$\rightarrow (M_S)_{max} = 0 \rightarrow S = 0 \rightarrow {}^1D \quad N_1 = 5$



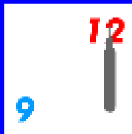
2) $S =1 \rightarrow (M_S)_{max} = 1 \rightarrow (M_L)_{max} = 1(m_{l1}) + 0(m_{l2})$

$\rightarrow L = 1 \rightarrow {}^3P \quad N_2 = 9$

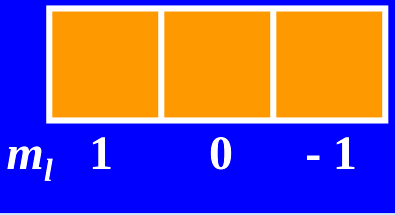


3) $N_3 = N_{ms} – N_1 –N_2 = 1 \rightarrow {}^1S$

Not strict!



Example: np^3



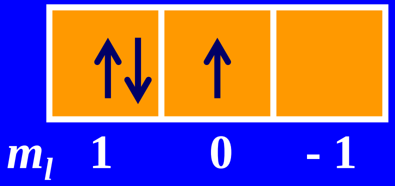
The number of microstates: $N_{ms} = C^3_6 = 20$

$l_1=1, l_2=1, l_3=1$ → L = 2, 1, 0

$m_{s1} = m_{s2} = m_{s3} = ½$ → S = 3/2, 1/2

*Pauli exclusion: Equivalent electrons have the same value of **n** and the same value of **l**. The electrons should avoid to have the same four quantum numbers!*

No need to consider the details of all possible 20 microstates!

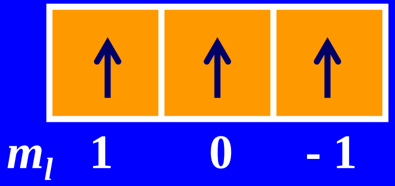


1) L=2 → $(M_L)_{max} = 2 = 1(m_{l1}) + 1(m_{l2}) + 0\ (m_{l3})$

→ S = 1/2 → ^2D $N_{ms1} = 10$

2) S = 3/2 → $(M_S)_{max}=3/2$ → $(M_L)_{max} = 1(m_{l1}) + 0(m_{l2}) -1(m_{l3})$

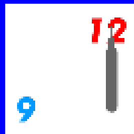
→ L = 0 → ^4S $N_{ms2} = 4$



3) $N_{ms3} = N_{ms} – N_{ms1} –N_{ms2} = 6$ & L = 1

→ S = 1/2 → ^2P

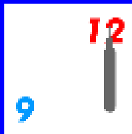
Not strict!



- The terms arising from a subshell containing ***N*** electrons are the same as the terms for a subshell that is ***N*** electrons short of being full.

				Terms
Term :	p^0	===	p^6	^1S
	p^1	===	p^5	^2P
	p^2	===	p^4	$^1D, ^3P, ^1S$
	p^3			$^2D, ^4S, ^2P$

- For ***m*** electrons within a ***(n,l)*** subshell, the total number of allowed microstates is $C_{2(2l+1)}^{m}$.
- So far, we have introduced ***two different ways*** to describe the microstates pertaining to a electronic configuration of a many-electron atom!



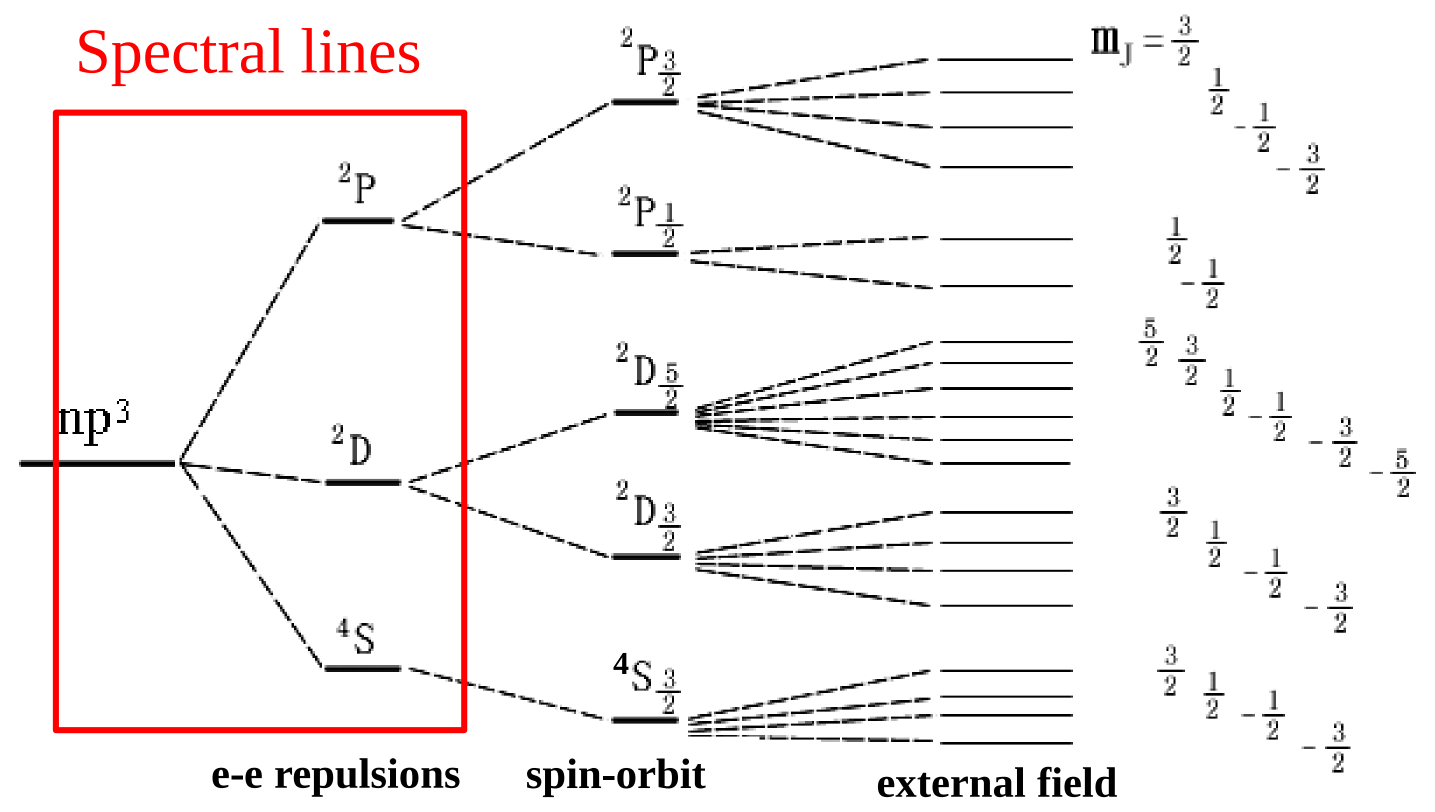
D. Energy level of spectral terms (microstates).

Hund's Rule: (works very well for ground-state configuration!)

1. For terms arising from the same electron configuration, the term with the largest value of ***S*** lies lowest!

np^2 : ^3P < ^1D < ^1S

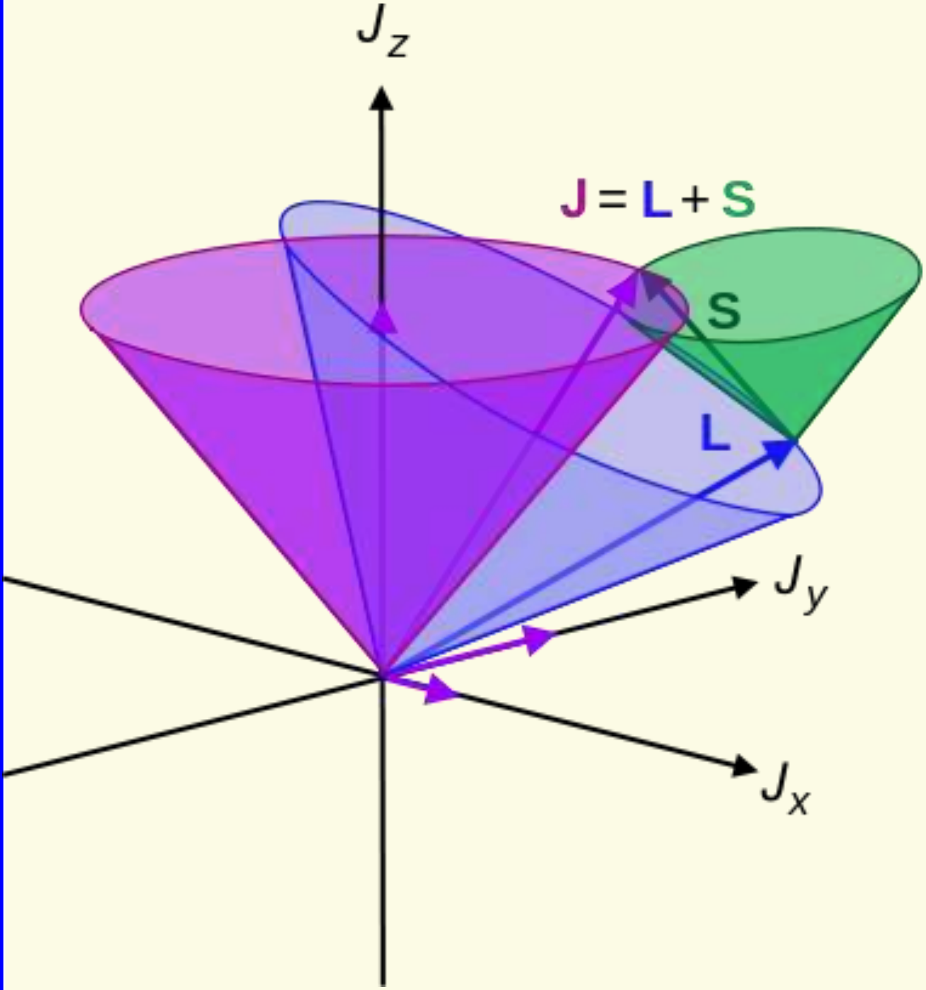
2. For the same ***S***, the term with the largest ***L*** lies lowest.



***np*^{3}:**

^4S < ^2D < ^2P

E. Spin-orbit Interaction & Total angular momentum



Spin-orbital angular momentum coupling

$$\vec{J} = \vec{L} + \vec{S}$$

The total angular momentum

$J = (L + S),\ (L + S) - 1, \ldots |L - S|$

Spin – orbit coupling

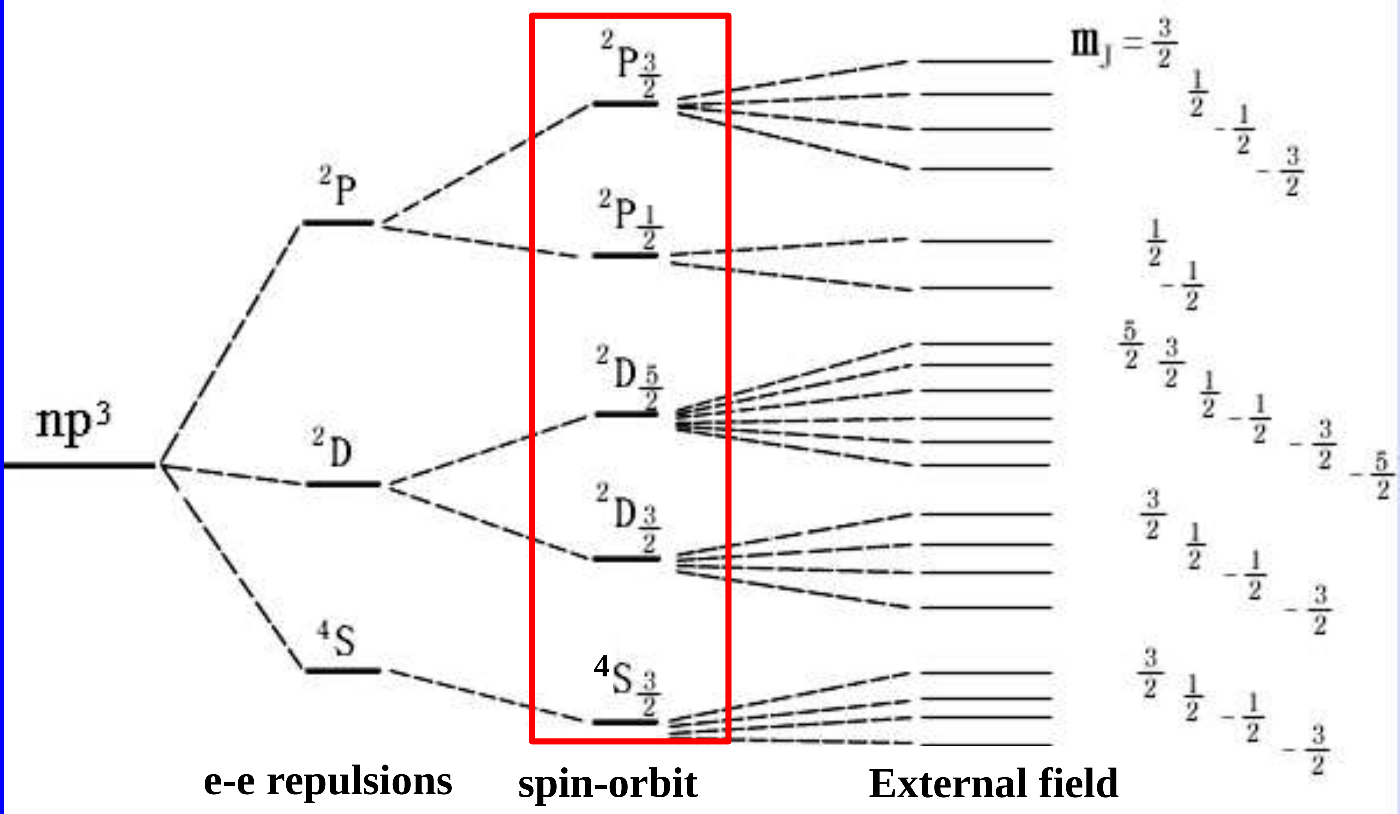
Term symbol:

$^{2S+1}L_J$

E. Spin-Orbit interaction.

The spin-orbit interaction splits an atomic term into levels, giving rise to the observed fine structure in atomic spectra.

$$^{2S+1}L \rightarrow {}^{2S+1}L_J \quad (J = L+S, L+S-1, \ldots, |L-S|)$$



np^3 : ^4S, ^2D, ^2P

$^4S \rightarrow {}^4S_{3/2}$

$^2D \rightarrow {}^2D_{5/2}$, $^2D_{3/2}$

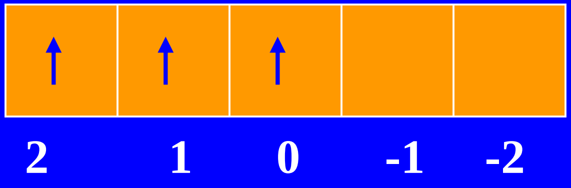
$^2P \rightarrow {}^2P_{3/2}$, $^2P_{1/2}$

F. Ground state of the terms (ground-state term)

Hund’s Second Rule:

3. For the same ***L*** and ***S*** values, when the number of electrons is half-filled or less, the term with the smallest ***J*** lies lowest; whereas when the number of electrons is more than half-filled, the term with the largest ***J*** lies lowest.

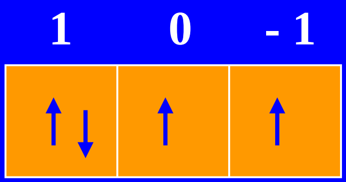
nd^3



M_S(max) =3/2 with M_L(max) = 3

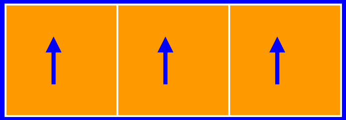
L=3, S=3/2, J_{min}=3/2 → $^4F_{3/2}$

np^4



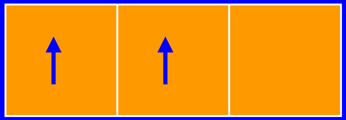
L=1, S=1, J_{max}= 2 → $^3P_2$

np^3



L=0, S=3/2, J_{min}=3/2 → $^4S_{3/2}$

np^2



L=1, S=1, J_{min}=0 → $^3P_0$

By following Pauli exclusion and Hund’s Rules, a practical way to derive the ground-state term for a given electronic configuration can be drawn:

1. Equivalent vs. nonequivalent electrons; for equivalent ones, please follow steps 2-4 derived from Hund’s rule.

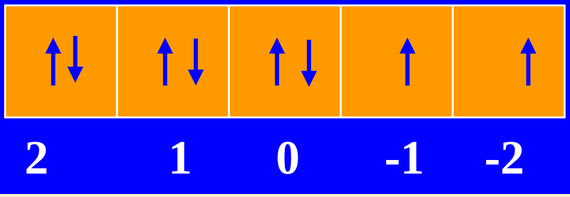
2. Find $(M_S)_{max}$, which gives the ground-state S value.

3. For thus-defined S, find $(M_L)_{max}$, as the ground-state L value.

4. find $J_{min} = |L - S|$ in case $n_e \le 2l+1$,

or $J_{max} = L+S$ in case $n_e \ge 2l+1$, for the ground-state J value.

nd^8



$(M_S)_{max} = 1 \rightarrow S = 1 \rightarrow$

$(M_L)_{max} = 3 \rightarrow L=3, S=1 \rightarrow {}^3F$

$(3\times2+1)(1\times2+1)= 21$ microstates!

As $n_e=8 \ge 5 \rightarrow J_{max} = 4 \rightarrow {}^3F_4$

$(4\times2+1)= 9$ microstates!

Likewise, the ground term is ${}^3F_2$ for nd^2.

Example: Why does Cu _Kα_ radiation (X-ray) consist of Kα_1 and Kα_2 radiations?

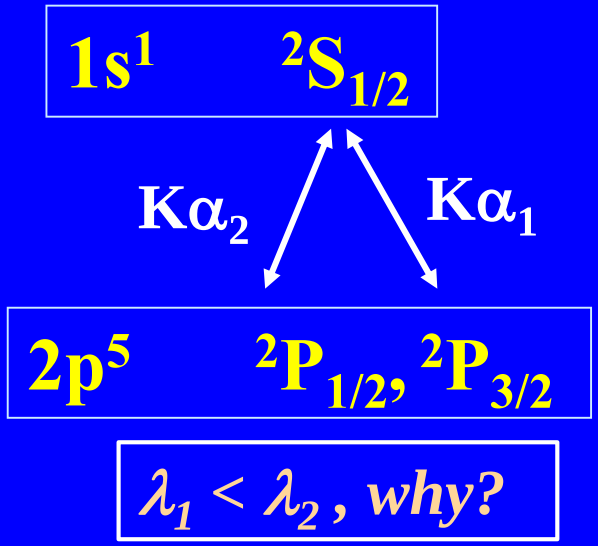
Ground state of **Cu**: $1s^2\,2s^2\,2p^6 3s^2$…..

Depletion of a K-shell electron!

Excited state of **Cu**$^+$: $1s^{\mathbf{1}}\,2s^2\,2p^6 3s^2$…..

X-ray Kα radiation

$1s^2\,2s^2\,2p^{\mathbf{5}} 3s^2$…..



$1s^1$ $\quad {}^2S_{1/2}$

Kα_2

Kα_1

$2p^5$ $\quad {}^2P_{1/2},\ {}^2P_{3/2}$

$\lambda_1 < \lambda_2$, why?

Question: Why is the atomic transition from 2p →1s allowed?

Selection rule for atomic transition: $\Delta l = \pm 1$, $\Delta j = 0, \pm 1$; $\Delta m_j = 0, \pm 1$,

Atomic spectra

Electronic configurations

↓ Interelectronic repulsions

Terms — Spectral lines

↓ Spin-orbital interaction

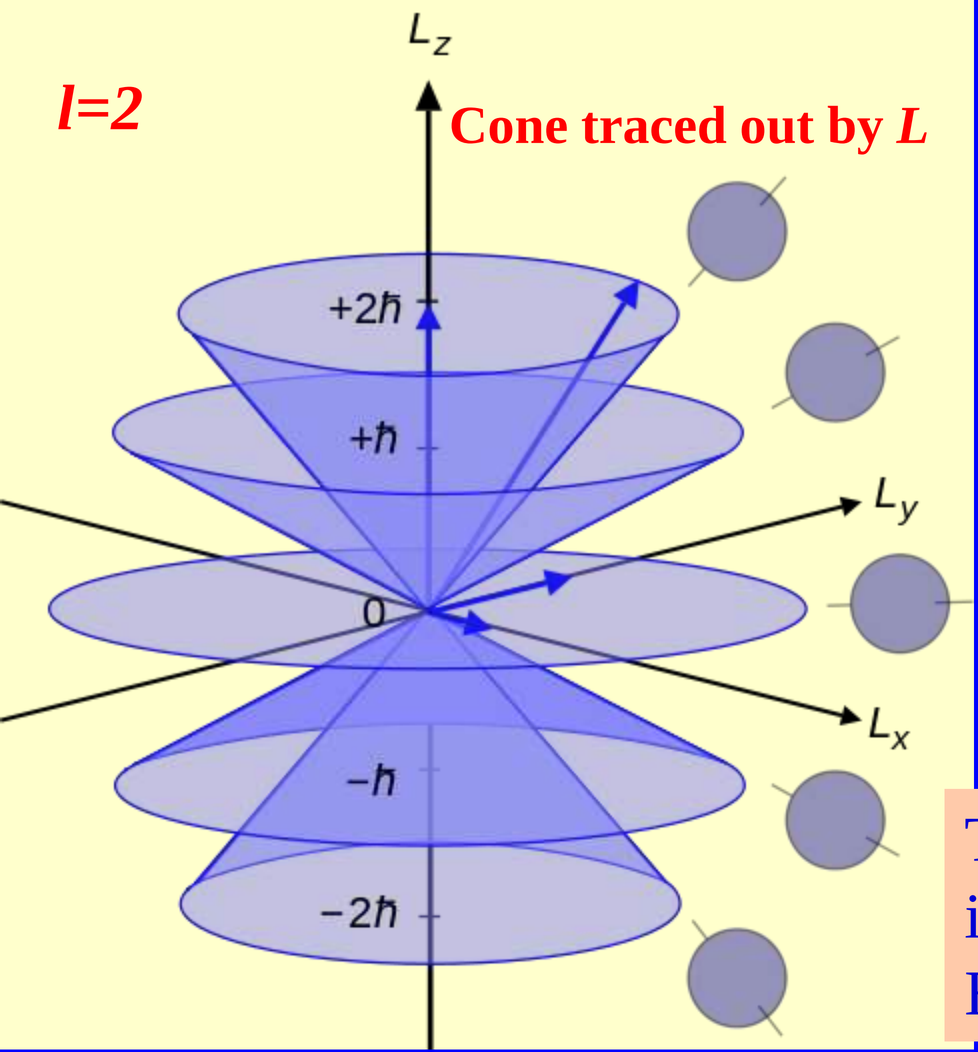
Levels — Fine spectral lines

↓ external field

States — Ultra-fine spectral splittings in external field – Zeeman effects

2.5 Atomic spectra and spectral term

Note that the orbital angular momenta of an electron in a given AO are distributed in a cone shape!



***l*=2**

Cone traced out by *L*

Suppose a microstate with

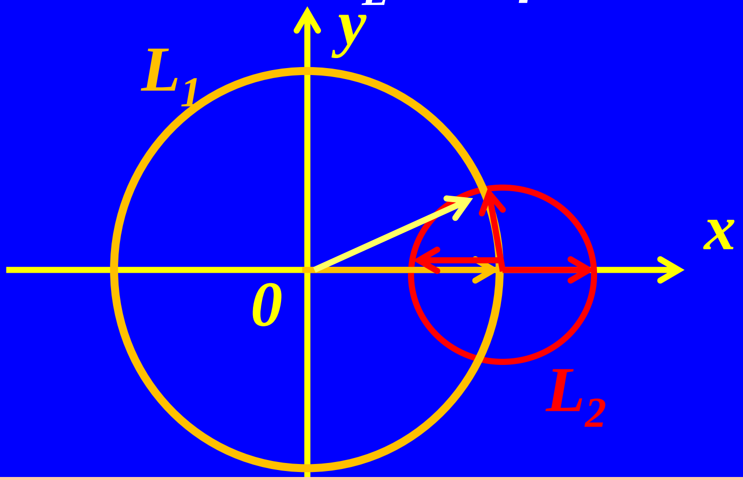
e_1: l=2, m_l=0 ***e_2: l=1, m_l=0***

$$M_L = \sum_i m_l(i) = 0$$

Case 1: M_L =0 of L = 3

Case 2: M_L =0 of L= 2

Case 3: M_L =0 of L= 1



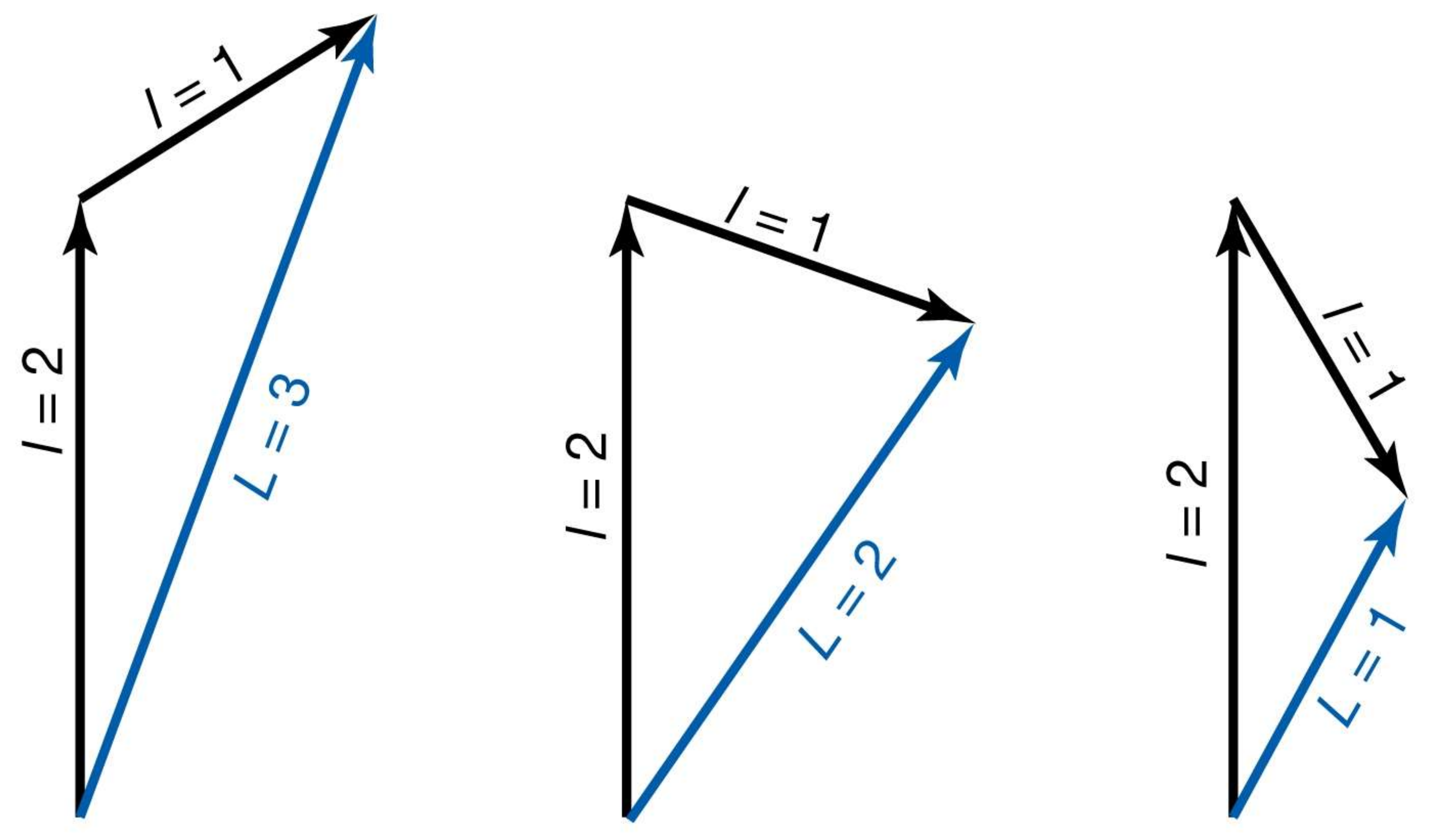
The wavefunction of this microstate is not an eigen-function of atomic Hamiltonian!!

2.5.1 Total Electronic Orbital and Spin Angular Momenta

a. Addition of two angular momenta:

The addition of two angular momenta characterized by quantum number j_1 and j_2 results in a total angular momentum whose quantum number J has the possible values:

$$J = j_1 + j_2,\ j_1 + j_2 - 1,\ \ldots,\ |j_1 - j_2|$$



d^1p^1

Angular momenta are vectors!

B. The total electronic orbital angular momentum

The total electronic orbital angular momentum of an n-electron atom is defined as the vector sum of the angular momenta of the individual electron:

$$\vec{L} = \sum_i \vec{m}_l(i)$$

The total-electronic-orbital-angular-momentum quantum number ***L*** of an atom is indicated by a code letter:

L	***0***	***1***	***2***	***3***	***4***	***5***	***6***	***7***
Letter	***S***	***P***	***D***	***F***	***G***	***H***	***I***	***K***

For a fixed L value, the quantum number M_L ($M_L\hbar$--- the z component of the total electronic orbital angular momentum) takes on $2L+1$ values ranging from $-L$ to L.

Orbital symbol

$$\hat{M}^2\psi_i = l(l+1)\hbar^2\psi_i$$

$$\hat{M}_z\psi_i = m_l\hbar\psi_i$$

l	0	1	2	3	4	5	6	7
Letter	s	p	d	f	g	h	i	k

Term symbol

$$\hat{L}^2\Psi = L(L+1)\hbar^2\Psi$$

$$\hat{L}_z\Psi = M_L\hbar\Psi$$

L	0	1	2	3	4	5	6	7
Letter	S	P	D	F	G	H	I	K

M_L = -L, -L+1, …, L

(2L + 1)

C. The total electronic spin angular momentum

The total electronic spin angular momentum **S** of an n-electron atom is defined as the vector sum of the spins of the individual electron:

$$\vec{S} = \sum_i \vec{m}_s(i)$$

For a fixed S value, the quantum number M_S takes on 2S+1 values ranging from –S to S.

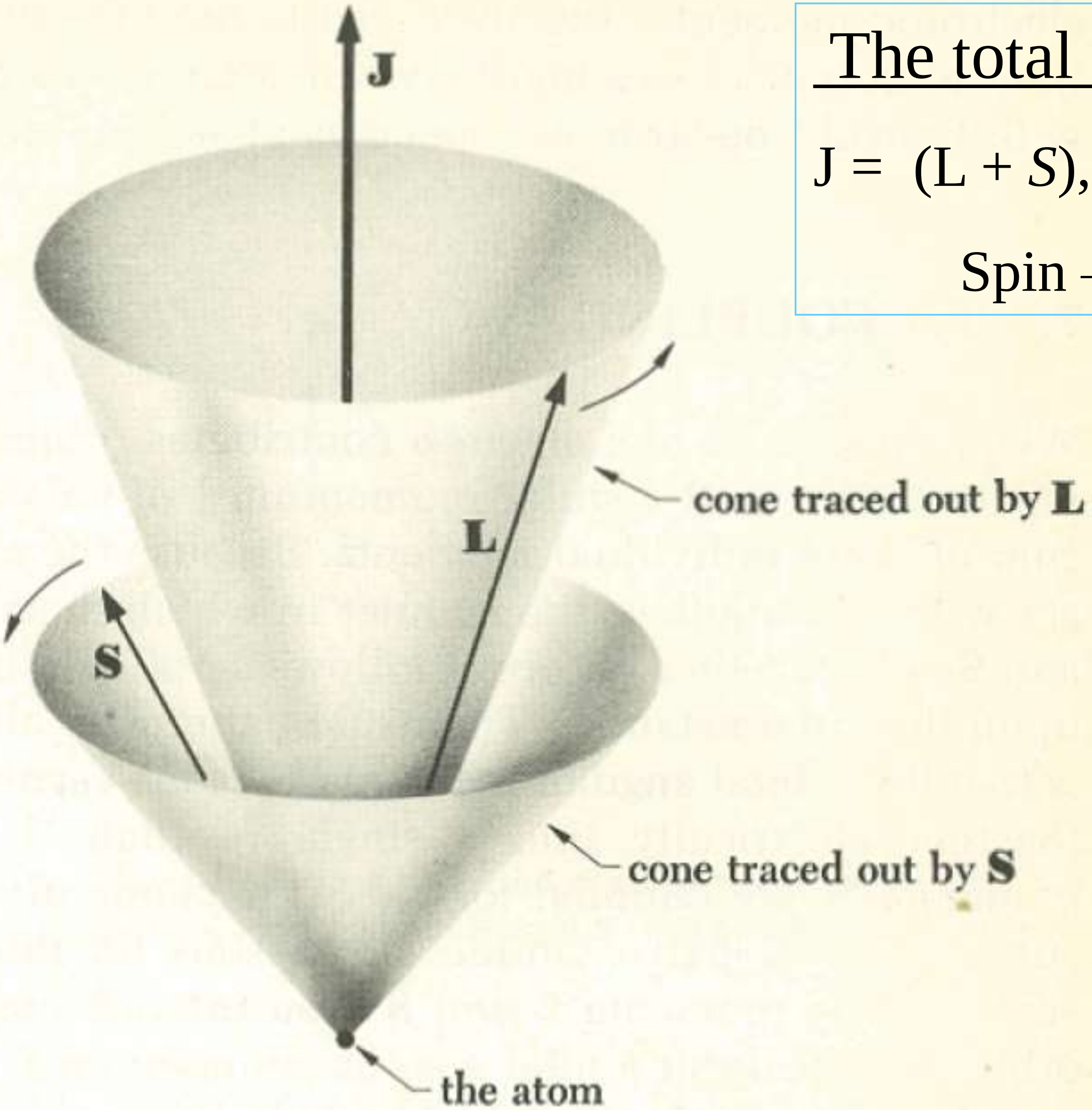
D. The total angular momentum

$$\vec{J} = \vec{L} + \vec{S}$$

$J = (L + S),\ (L + S) - 1, \ldots /L - S/$

Spin – orbit coupling

2.5.2 **Atomic term** and **term symbol**



The total angular momentum

$J = (L + S), (L + S) - 1, \ldots |L - S|$

Spin – orbit coupling

$$\vec{J} = \vec{L} + \vec{S}$$

Term symbol:

$^{2S+1}L_J$

2.5.3 Derivation of Atomic term

a. Configurations of Completely filled subshells

$M_S=\Sigma_i m_s(i)=0$ → $S=0$

$M_L=\Sigma_i m_l(i)=0$ → $L=0$

Only one term: ^1S

b. Nonequivalent electrons.

$(2p)^1(3p)^1$

Here we need not worry about any restrictions imposed by the exclusion principle.

$l_1=1$, $l_2=1$ $L=2, 1, 0$

$m_{s1}=½$ $m_{s2}=½$ $S=1, 0$

→

^3D, ^1D, ^3P, ^1P, ^3S, ^1S

terms

c. Equivalent electrons

$1s^2 2s^2 2p^2$ (two electrons in the same subshell)

$l_1=1$, $l_2=1$ L= 2, 1, 0

$s_1 = ½$, $s_2 = ½$ S=1, 0

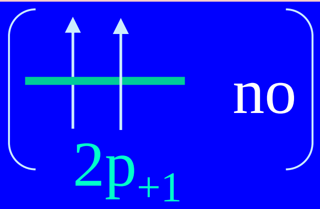
Only when L+S is even, the Pauli exclusion principle is fulfilled

^1D, ^3P, ^1S

5 9 1 → 15

^3D (x)

$M_L=2$, $M_s=1$ (x)



$p^2 \longleftrightarrow p^4$

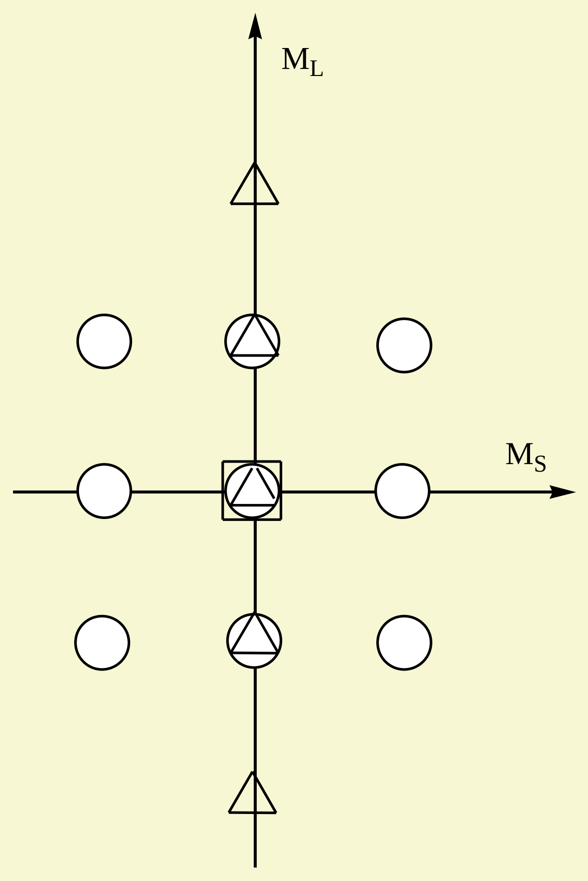
No	m_l			$M_L = \sum_i m_l(i)$	$M_S = \sum_i m_s(i)$
	1	0	-1		
1	↓↑			2	0
2	↑	↑		1	1
3	↑	↓		1	0
4	↓	↑		1	0
5	↓	↓		1	-1
6		↑↓		0	0
7	↑		↓	0	0
8	↓		↑	0	0
9	↑		↑	0	1
10	↓		↓	0	-1
11		↑	↓	-1	0
12		↓	↑	-1	0
13		↑	↑	-1	1
14		↓	↓	-1	-1
15			↓↑	-2	0

c. Equivalent electrons

$1s^2 2s^2 2p^2$ (two electrons in the same subshell)

^1D, ^3P, ^1S

5 9 1 → 15



M_L 2, 1, 0, -1, -2
M_S 0

L=2
S=0

^1D

M_L 1, 0, -1
M_S 1, 0, -1

L=1
S=1

^3P

M_L 0
M_S 0

L=0
S=0

^1S

- The term arising from a subshell containing N electrons are the same as the terms for a subshell that is N electrons short of being full.

Term : p^0 === p^6

p^1 === p^5

p^2 === p^4

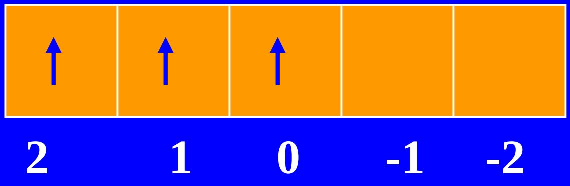
D. Energy level of microstates: (terms).

Hund's Rule:

1. For terms arising from the same electron configuration the term with the largest value of S lies lowest.

2. For the same S, the term with the largest L lies lowest.

nd^3



^4F

E. Spin-Orbit interaction.

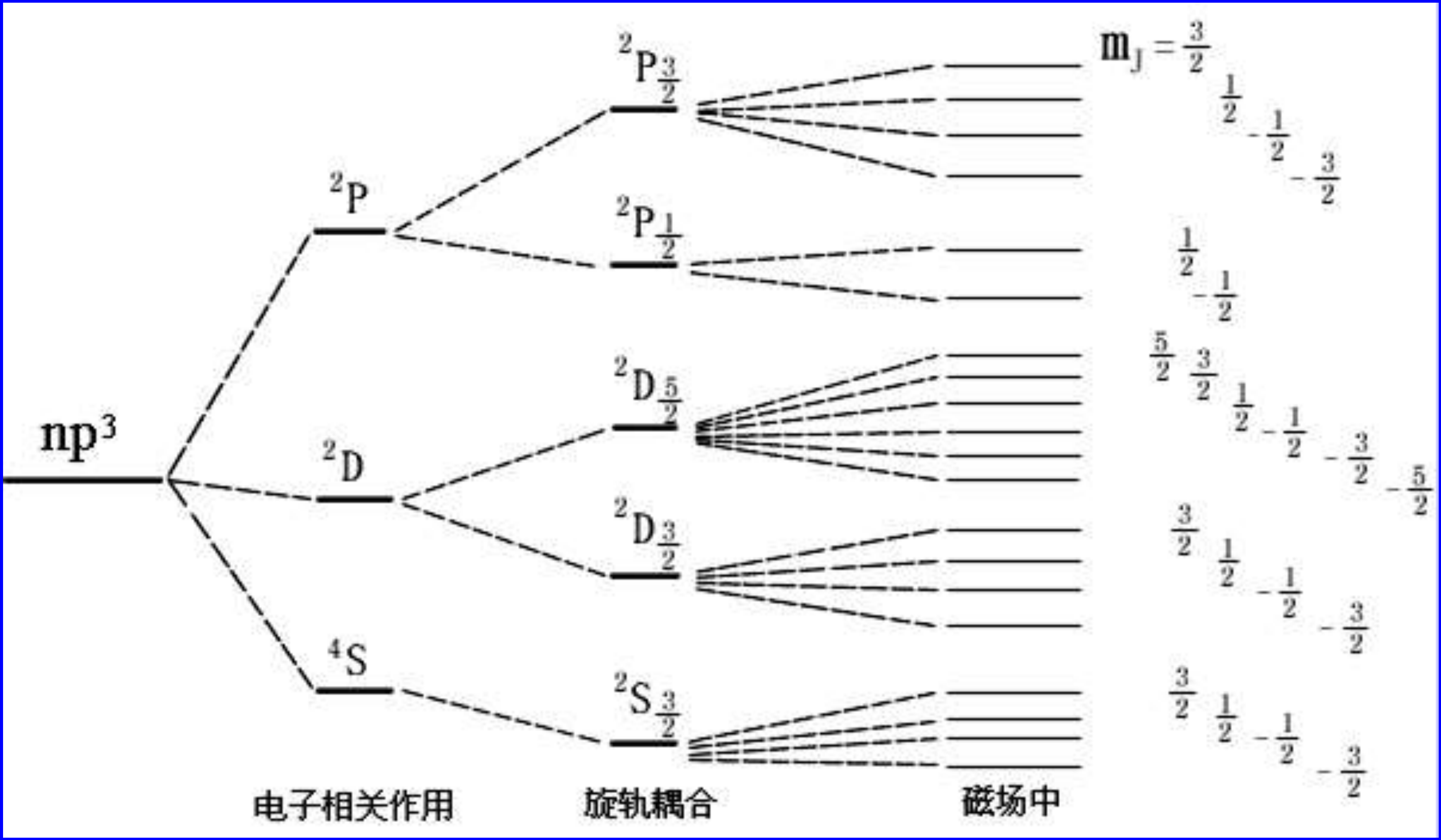
The spin-orbit interaction gives the observed fine structure in atomic spetra.

$^{2S+1}L \rightarrow {}^{2S+1}L_J$ $\quad J = L+S, L+S-1, \ldots, |L-S|$

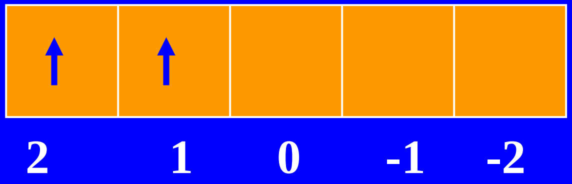
$^4S \rightarrow {}^4S_{3/2},\quad {}^2D \rightarrow {}^2D_{5/2}, {}^2D_{3/2}$

np^3 --- ^4S , ^2D, ^2P

20 microstates in total.



nd^2



L=3, S=1 → $^3F_2$

N(microstate) = $C_{10}^{\ 2}$ = 45

1) Ms(overall max) = 1 → S =1, (Ms = 1, 0, -1) & ML(Max) =3,
→ L =3 → ^3F , N(microstate) = (2L+1)(2S+1) = 28

2) M_L(overallmax) = 4 → L = 4, Ms (max) = 0, → S= 0

→ ^1G , N(microstate) = (2L+1)(2S+1) = 9

Nobel Prizes in Chemistry (1980-present) Awarded to Theoretical and Computational Chemists

- 2013:

Martin Karplus, **Michael Levitt** and **Arieh Warshel**

"for the development of multiscale models for complex chemical systems"

- 1998:

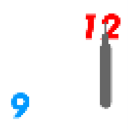
Walter Kohn "for his development of the density-functional theory"

John A. Pople "for his development of computational methods in quantum chemistry"

- 1981:

Kenichi Fukui and **Roald Hoffmann**

"for their theories, developed independently, concerning the course of chemical reactions"



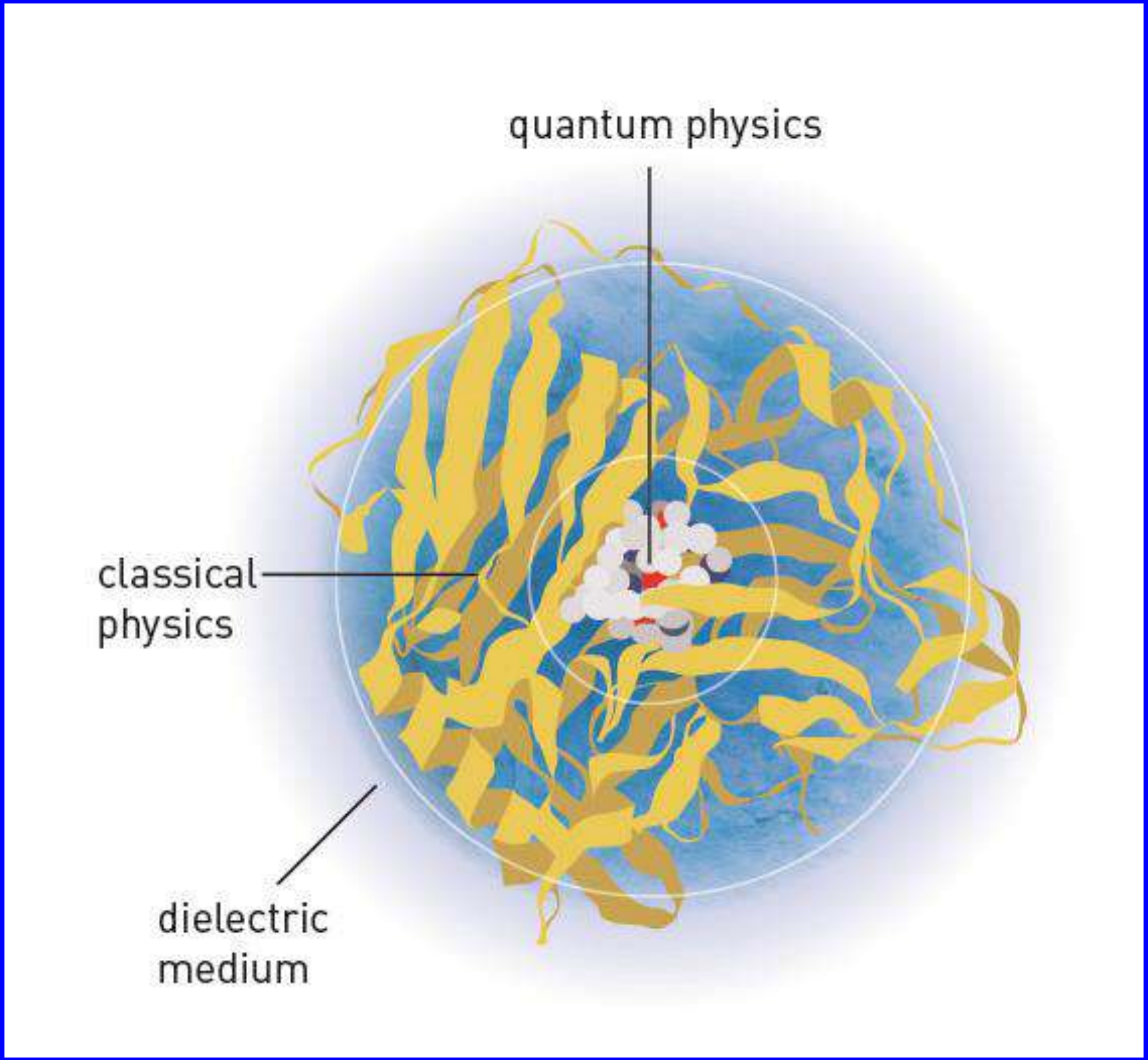
Example: Find the possible values of the total-angular-momentum quantum number resulting from the addition of two angular momenta with quantum number $j_1 = 2$ and $j_2 = 3/2$.

Solution: $J_{max} = j_1 + j_2 = 2+3/2 = 7/2$

$J_{min} = |j_1 - j_2| = |2-3/2| = 1/2$

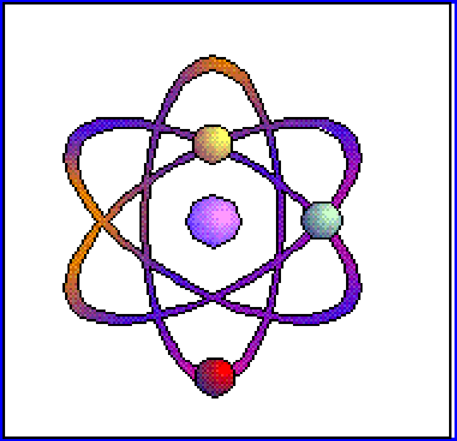
→ *The possible J values are:* ***7/2, 5/2, 3/2, 1/2***

Multiscales modelling of Multi-copper-oxidase embedded in water



* Nobel Prizes in Physics for Quantum mechanics: M. Planck (1918), N. Bohr (1922), Prince de Broglie (1929), W. Heisenberg (1932), E. Schrödinger (1933)

Effects of e-e interactions in an atom:



1) For the same ***n***, different ***l*** → different ***E***(AO)
2) Different occupation patterns for a given number of electrons within the same subshell differ in energy.

	Single electron **No e-e interaction**	**Many-e atom** **e-e interactions**
Energy	***n (shell)***	***Electronic configurations***
Angular momentum **orbital**	$\vec{M}$ ***or l, m_l***	$\vec{L} = \sum_i \vec{m}_l(i)$ ***or L***
Spin	$\vec{m}_s$ ***or m_s***	$\vec{S} = \sum_i \vec{m}_s(i)$ ***or S***

The energy of the interaction between a magnetic dipole μ and an external magnetic field $\boldsymbol{B}$ is

$$E_B = -\boldsymbol{\mu} \bullet \mathbf{B} = \frac{e}{2m_e} \mathbf{M} \bullet \mathbf{B}$$

angular momentum

Magnetic induction or magnetic flux density

We take the z axis along the direction of the applied field: $\boldsymbol{B} = B\boldsymbol{k}$, where $\boldsymbol{k}$ is a unit vector in the z direction. We have

$$E_B = \frac{e}{2m_e} B(\underline{M_x \mathbf{i} + M_y \mathbf{j} + M_z \mathbf{k}}) \bullet \mathbf{k} = \frac{e}{2m_e} BM_z = \frac{\beta_e}{\hbar} BM_z$$

angular momentum

z-component of angular momentum

We now replace $\boldsymbol{M_z}$ by the operator $\boldsymbol{M_z}$ to give the additional term in the Hamiltonian operator:

$$\hat{\mathrm{H}}_B = \beta_e B \hbar^{-1} \hat{M}_z$$

The Schrodinger equation for the H-like atom in a magnetic field is

$$(\hat{H}_0 + \hat{H}_B)\psi = E\psi$$

$$\psi_{n,l,m} = R_{n,l}(r)\Theta_{l,m}(\theta)\Phi_{m}(\phi) = R(r)Y_l^m(\theta,\phi)$$

$$(\hat{H}_0 + \hat{H}_B)R(r)Y_l^m(\theta,\phi) = \hat{H}_0 R(r)Y_l^m + \hbar^{-1}\beta_e B\hat{M}_z R(r)Y_l^m$$

Field-free Hamiltonian

$$= \left(-\frac{Z^2R}{n^2} + \beta_e Bm\right)R(r)Y_l^m$$

- There is an additional term in the energy.
- The external magnetic field removes the ***m*** degeneracy of AO’s in the same ***l*** subshell.
- For such obvious reasons, ***m*** is often called the ***magnetic quantum number***.