Chapter 2 Atomic structure

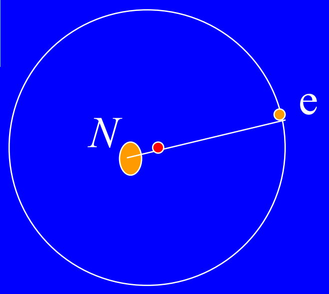
2.1 The Schrödinger equation and its solution for one-electron atoms

2.1.1 The Schrödinger equation

The Hamiltonian Operator of one-electron atoms

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

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



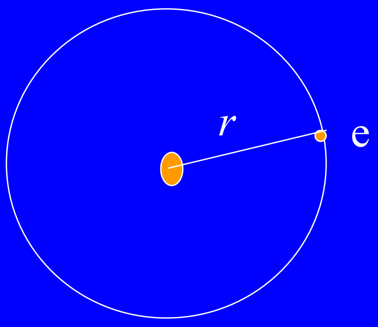
Consider that the electron approximately surrounds the atomic nucleus, the Hamilton operator can be simplified as

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

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

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

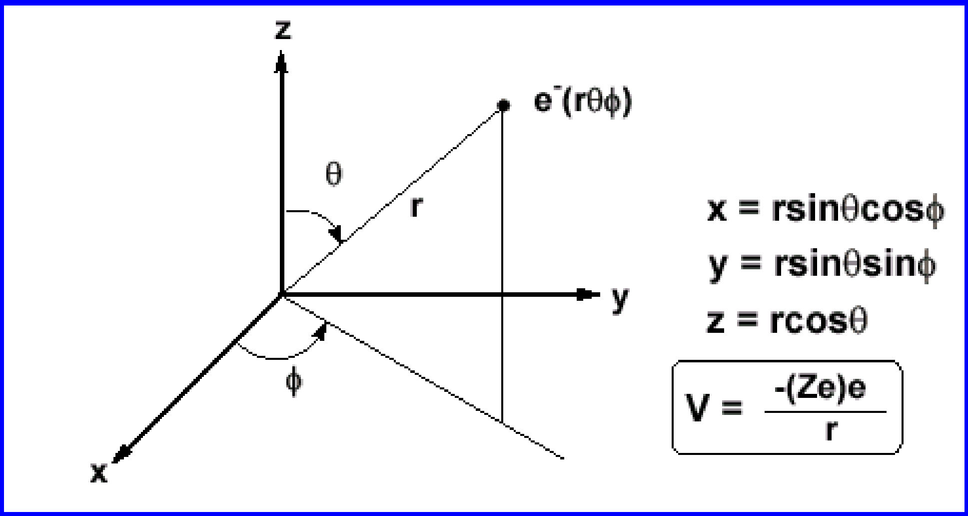
$$r = \sqrt{x^2 + y^2 + z^2}$$



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

Separation of variables ?

Spherical polar coordinates



x = rsinθcosϕ

y = rsinθsinϕ

z = rcosθ

$$V = \frac{-(Ze)e}{r}$$

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

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

$$tg\phi = y / x$$

r ➔ distance from origin.

θ ➔ angle drop from the z-axis.

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

(x,y,z) ➔ (r,θ,ϕ)

Ψ(x,y,z) → Ψ(r, θ, ϕ)

Ψ(r, θ, ϕ) =R(r)Θ(θ)Φ(ϕ)

Spherical polar coordinates

$$\frac{\partial}{\partial x}=(\frac{\partial r}{\partial x})\frac{\partial}{\partial r}+(\frac{\partial\theta}{\partial x})\frac{\partial}{\partial\theta}+(\frac{\partial\phi}{\partial x})\frac{\partial}{\partial p}$$

$$=\sin\theta\cos\phi\frac{\partial}{\partial r}+\frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta}-\frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial y}=\sin\theta\sin\phi\frac{\partial}{\partial r}+\frac{\cos\theta\sin\phi}{r}\cdot\frac{\partial}{\partial\theta}+\frac{\cos\phi}{r\sin\theta}\cdot\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial z}=\cos\theta\frac{\partial}{\partial r}-\frac{\sin\theta}{r}\cdot\frac{\partial}{\partial\theta}$$

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

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

The Schrödinger equation

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

2.1.2 The solution --- separation of variables

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

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

and multiply with $\frac{r^2}{R(r)\Theta(\theta)\Phi(\phi)}$

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

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

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

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

▶ Radial part, R eq.

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

▶ Angular part

$$multiplied\qquad \sin^2\theta$$

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

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

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

▶Θ eq.

$$\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-m^2$$

▶Φ eq.

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a. Φ(ϕ) equation

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

Its complex form:

$\Phi = Ae^{\pm i|m|\phi}$, let m= ±|m|, $\Phi = Ae^{im\phi}$

Normalization

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

$$A=\sqrt{\frac{1}{2\pi}}$$

$$\Phi_m=\sqrt{\frac{1}{2\pi}}e^{im\phi}=\frac{1}{\sqrt{2\pi}}\cos m\phi+\frac{i}{\sqrt{2\pi}}\sin m\phi$$

$$\Phi_m(\phi)=\Phi_m(\phi+2\pi)$$

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

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

$$\cos 2m\pi+i\sin 2m\pi=1$$

The values of m must be

$$m=0,\pm1,\pm2,\cdots\cdots$$

m : magnetic quantum number

complex function

$$\Phi_m = Ae^{im\varphi} \qquad (m = 0, \pm 1, \pm 2, \cdots\cdots)$$

Usually, real functions are used, which are deduced from the complex function according to the assumption of the linear combination of these states .

$$\Phi_m = Ae^{im\varphi} = A\cos m\varphi + iA\sin m\varphi$$

$$\Phi_{-m} = Ae^{-im\varphi} = A\cos m\varphi - iA\sin m\varphi$$

$$\Phi_1 = \Phi_m + \Phi_{-m} = 2A\cos m\varphi = B\cos m\varphi$$

$$\Phi_2 = \Phi_m - \Phi_{-m} = 2iA\sin m\varphi = B'\sin m\varphi$$

$$\Phi_1 = \sqrt{\frac{1}{\pi}}\cos m\varphi$$

$$\Phi_2 = \sqrt{\frac{1}{\pi}}\sin m\varphi$$

normalization condition

$$\int_0^{2\pi} \Phi_1^* \Phi_1 d\Phi = \int_0^{2\pi} (B\cos m\varphi)^2 d\Phi = B^2\pi = 1$$

$$B = \sqrt{\frac{1}{\pi}}$$

Table The solution of Φ(ϕ) equation

m	complex form	real form
0	$\Phi_0 = \frac{1}{\sqrt{2\pi}}$	$\Phi_0 = \frac{1}{\sqrt{2\pi}}$
1	$\Phi_1 = \frac{1}{\sqrt{2\pi}}e^{i\varphi}$	$\Phi_{\pm1}^{\cos} = \frac{1}{\sqrt{\pi}}\cos\varphi$
-1	$\Phi_{-1} = \frac{1}{\sqrt{2\pi}}e^{-i\varphi}$	$\Phi_{\pm1}^{\sin} = \frac{1}{\sqrt{\pi}}\sin\varphi$
2	$\Phi_2 = \frac{1}{\sqrt{2\pi}}e^{i2\varphi}$	$\Phi_{\pm2}^{\cos} = \frac{1}{\sqrt{\pi}}\cos 2\varphi$
-2	$\Phi_{-2} = \frac{1}{\sqrt{2\pi}}e^{-i2\varphi}$	$\Phi_{\pm2}^{\sin} = \frac{1}{\sqrt{\pi}}\sin 2\varphi$

b. Θ(θ) equation

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

When $\beta=l(l+1)$, l =0,1,2,3,…… Θ(θ) is a well behaved function,

l : angular momentum quantum number

necessary condition: $l \geq |m|$

hence, $l = 0, 1, 2, 3, \ldots (s,p,d,f,g,h\ldots)$

$m=0,(-1,0,1),(-2,-1,0,1,2)\ldots\ldots$

Examples of Θ(θ):

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

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

Solution

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

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

$$a_0=\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}=0.529\ \overset{\mathrm{o}}{\mathrm{A}}$$

a_0 is called Bohr radius

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

necessary condition: n ≥ l+1

hence, *n = 1, 2, 3,……*

l = 0, 1, 2, ……

n: Principal quantum number

$$E=-\frac{Z^2h^2}{8\pi^2mn^2a_0^2}=-(\frac{h^2}{8\pi^2ma_0^2})\cdot\frac{Z^2}{n^2}=-R\frac{Z^2}{n^2}$$

R is called Rydberg constant with the value of 13.6 eV

Example:

n=1, l=0 $$R_{10}=2\left(\frac{Z}{a_0}\right)^{3/2}e^{-\rho/2}$$

n=2, l=0 $$R_{20}=\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)e^{-\rho/2}$$

Some wavefunctions of hydrogen atom and hydrogen-like ions

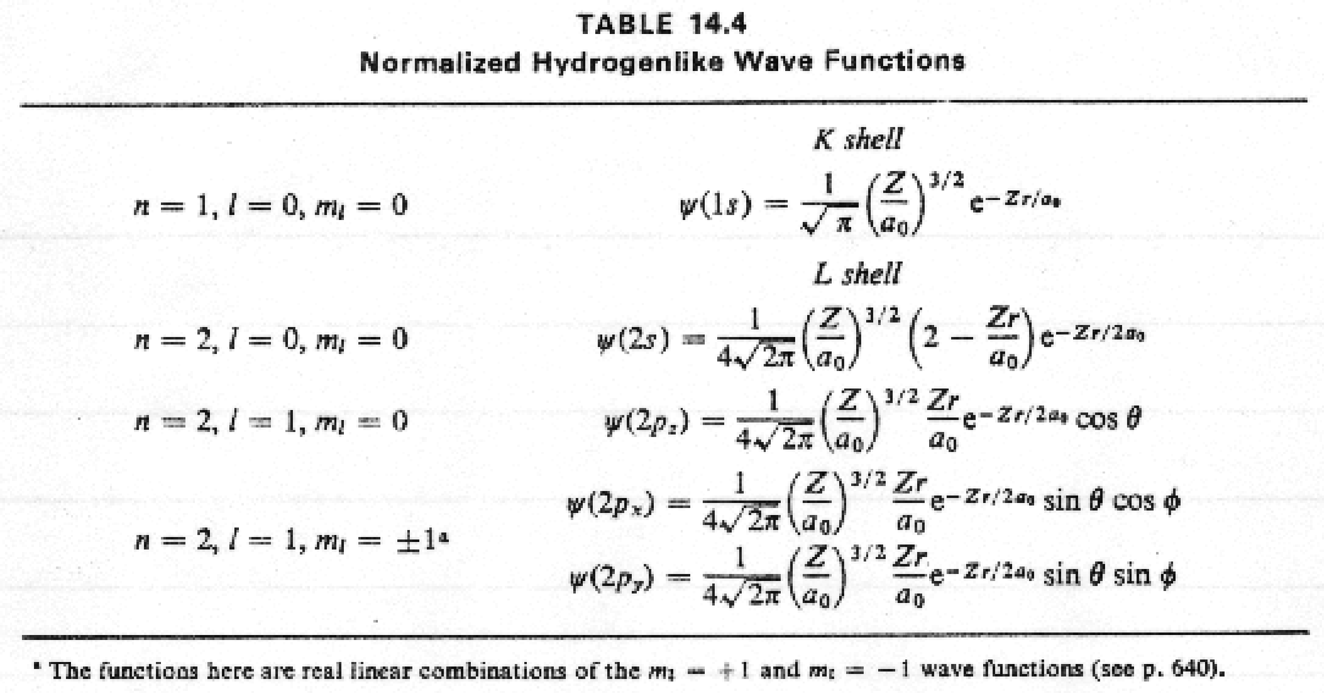


TABLE 14.4

Normalized Hydrogenlike Wave Functions

	K shell
$n = 1, l = 0, m_l = 0$	$\psi(1s) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
	L shell
$n = 2, l = 0, m_l = 0$	$\psi(2s) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
$n = 2, l = 1, m_l = 0$	$\psi(2p_z) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$
$n = 2, l = 1, m_l = \pm 1$[a]	$\psi(2p_x) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta \cos\phi$ $\psi(2p_y) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta \sin\phi$

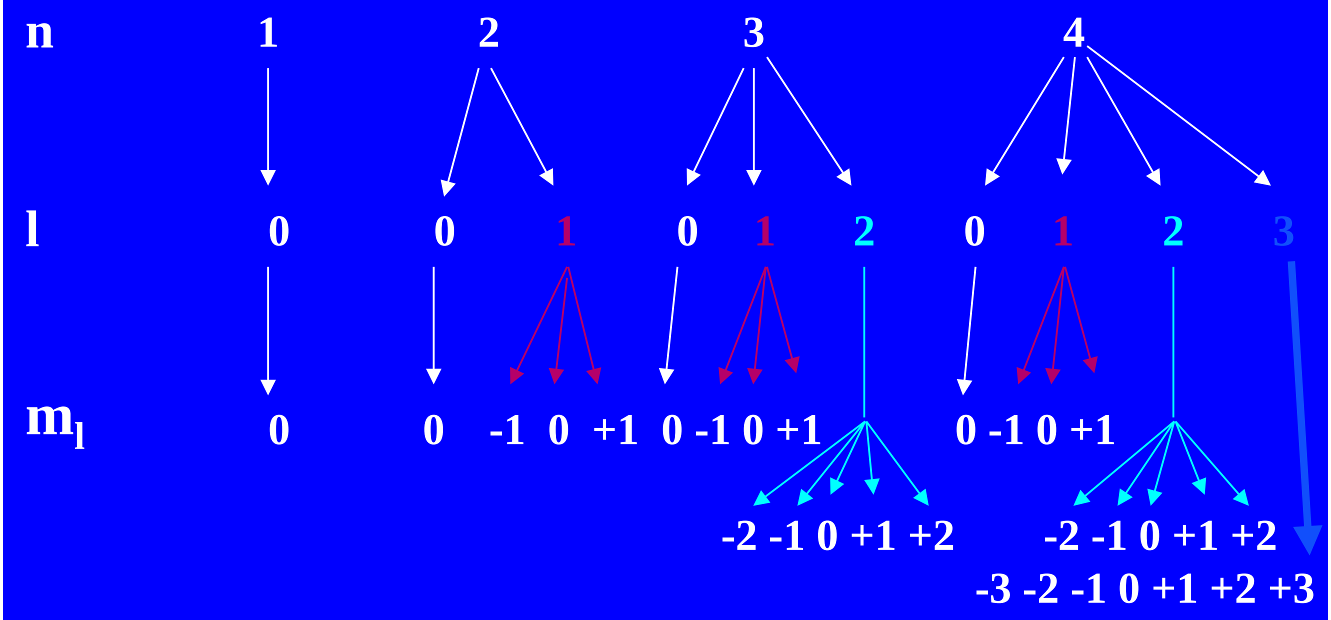
[a] The functions here are real linear combinations of the $m_l = +1$ and $m_l = -1$ wave functions (see p. 640).

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

2.2 The physical significance of quantum number

2.2.1 The allowed values of quantum numbers

Quantum Numbers



n **1** **2** **3** **4**

l **0** **0** **1** **0** **1** **2** **0** **1** **2** **3**

m_l **0** **0** **-1 0 +1** **0 -1 0 +1** **0 -1 0 +1**

-2 -1 0 +1 +2 **-2 -1 0 +1 +2**

-3 -2 -1 0 +1 +2 +3

Problem: What values of the azimuthal (l) and magnetic (m) quantum numbers are allowed for a principal quantum number (n) of 4? How many orbitals are allowed for n=4?

Solution: The l values go from 0 to (n-1), and for n=3 they are:

l = 0,1,2,3. The values for m go from -l to zero to +l

For l = 0, **m_l = 0**

l = 1, **m_l = -1, 0, +1**

l = 2, **m_l = -2, -1, 0, +1, +2**

l = 3, **m_l = -3, -2, -1, 0, +1, +2, +3**

There are 16 m_L values, so there are 16 orbitals for n=4!

- The total number of orbitals for a given value of n is n^2.

2.2.2 The principal quantum number, n

- Also called the “energy “ quantum number, indicates the approximate distance from the nucleus .
- Denotes the electron energy shells around the atom, and is derived directly from the Schrodinger equation.
- The higher the value of “n” , the greater the energy of the orbital.
- Positive integer values of n = 1 , 2 , 3 , etc.

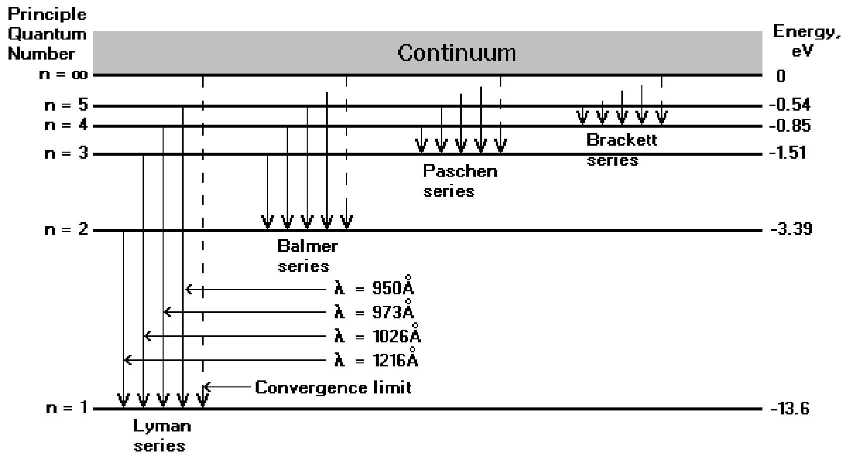
Example: Energy states of a H atom.

n = *principal*

n = 1, 2, 3 …∞
n = 1 : ground state
n = 2 : first excited state
n = 3 : second excited state

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

R = 13.6 eV



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

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

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E_∞ = 0 eV

Example: Energy states of a Li⁺ ion.

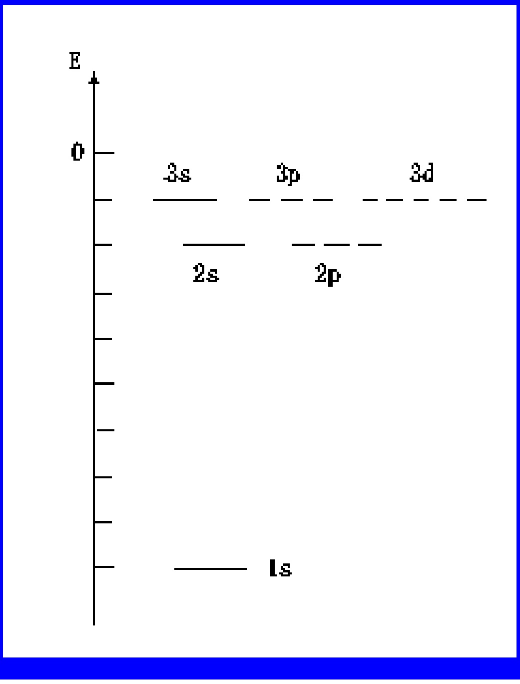
$$E_n = -R\frac{Z^2}{n^2}$$

R = 13.6 eV

E_{1s}= - 9R

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

E_{3s}= - R



2.2.3 the *azimuthal* quantum number, *l*

The operator of angular momentum

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

$$\hat{M}_x = -i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})$$

$$\hat{M}_y = -i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})$$

$$M_z = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$$

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

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

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

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

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

▶ Angular part

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

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

▶ Angular part

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

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

$$\hat{M}^2\Psi = \lambda^2\Psi$$

$$\lambda^2 = l(l+1)\hbar^2$$

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

$$|M| = \sqrt{l(l+1)}\hbar \qquad (l = 0,1,2,3\cdots)$$

- *Denote the orbital angular momentum.*

When there exist an angular momentum, there is also a magnetic moment.

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

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

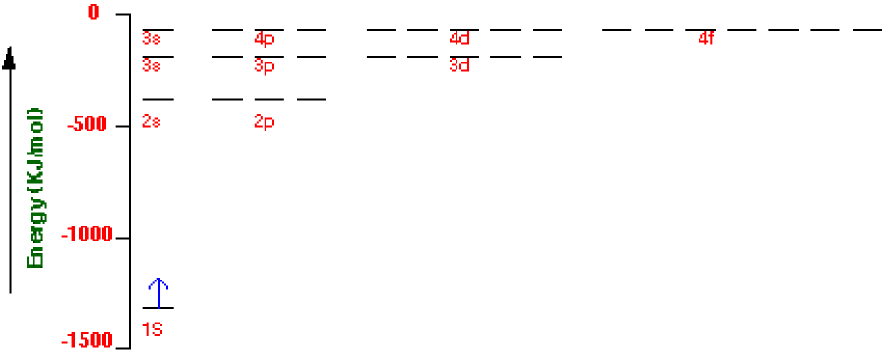
$$\beta_e = \frac{e\hbar}{2m_e} = 9.274\times10^{-24}J\cdot T^{-1} \qquad \textit{Bohr magneton}$$

Denote the orbital angular momentum.

- Indicates the shape of the orbitals around the nucleus.
- Denotes the different energy sublevels within the main level “n”

$l = 0, 1, 2 \ldots n-1$ degeneracy $= 2l + 1$

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



2.2.4 **Magnetic Quantum Number** , *m*

- Determine the z-component of the orbital angular momentum of the atom.
- Determine the component μ_z of the magnetic moment in the direction of the magnetic field.

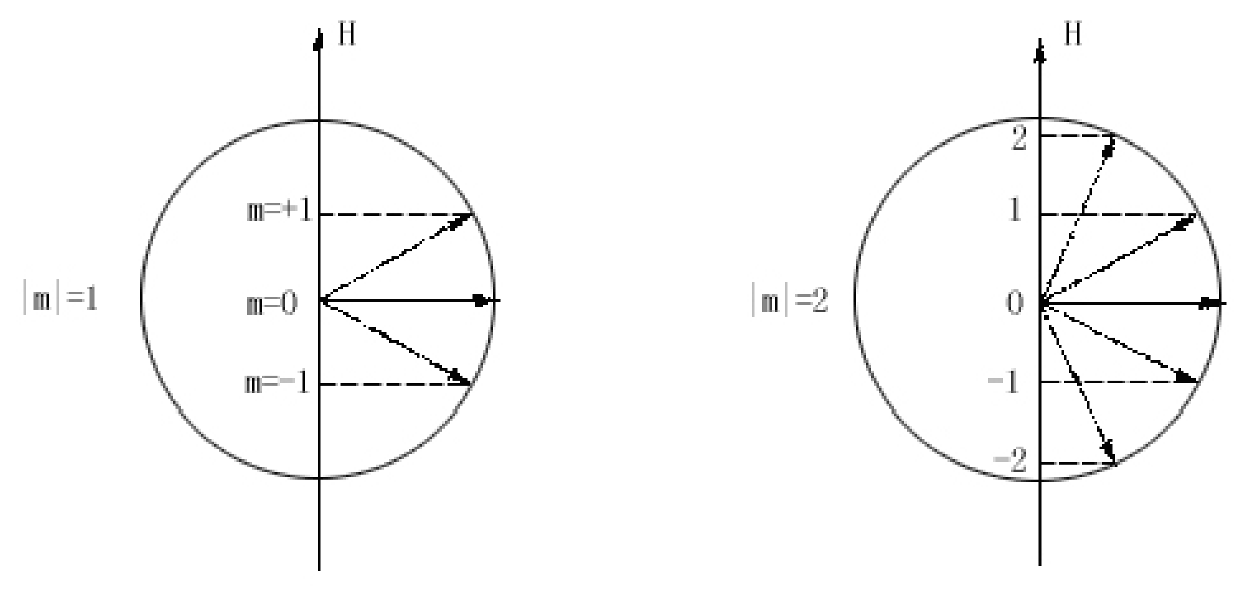
$$\hat{M}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -i\hbar\frac{\partial}{\partial \phi}$$

$$\hat{M}_z\Psi = -i\hbar\frac{\partial}{\partial \phi}\Psi = -i\hbar\frac{\partial}{\partial \phi}R\Theta\Phi = -i\hbar R\Theta\frac{\partial \Phi}{\partial \phi} = -i\hbar R\Theta\frac{\partial}{\partial \phi}Ae^{im\varphi}$$

$$= -i\hbar R\Theta A ime^{im\varphi} = m\hbar R\Theta Ae^{im\varphi} = m\hbar\Psi$$

$$\hat{M}_z\Psi = m\hbar\Psi$$

$$M_z = m\hbar \qquad \mu_z = -m\beta_e$$



2.2.4 **Magnetic Quantum Number ,** *m*

- Denotes the direction or orientation of an orbital

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

number of orbitals in a subshell

$= 2\,l + 1$

l	m_l	orbital
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}

2.3 The wave-function and electron cloud

2.3.1 The wave-functions of hydrogen-like ions

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

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

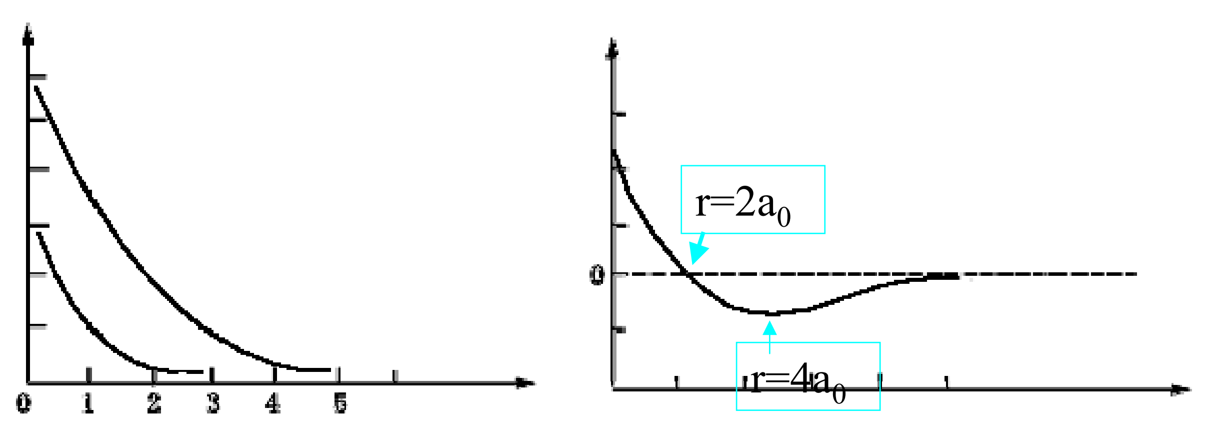
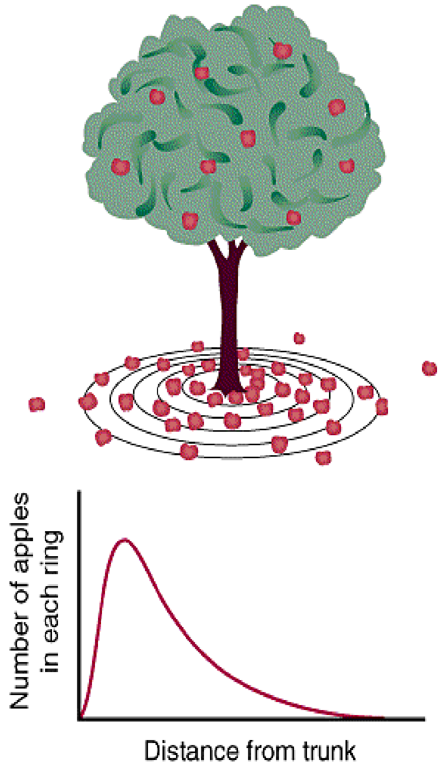


Fig. (left) The ψ-r and ψ^2-r diagram of the 1s state of the hydrogen atom. (right) The ψ-r of the 2s state .

A Radial Probability Distribution of Apples



2.3.2 The radial distribution function

- The probability of finding electron in the region of space $r + dr$, $\theta + d\theta$, $\varphi + d\varphi$

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

$$|\psi|^2 d\tau = [R_{nl}(r)]^2 |Y_l^m(\theta,\varphi)|^2 r^2 \sin\theta dr d\theta d\varphi$$

•What is the probability of electron at $r + dr$,(in a thin spherical shell centered at the origin)?

$$R_{nl}^2(r) r^2 dr \int_0^{2\pi} \int_0^{\pi} |Y_l^m(\theta,\varphi)|^2 \sin\theta d\theta d\varphi = r^2 R_{nl}^2(r) dr$$

Normalized spherical harmonics

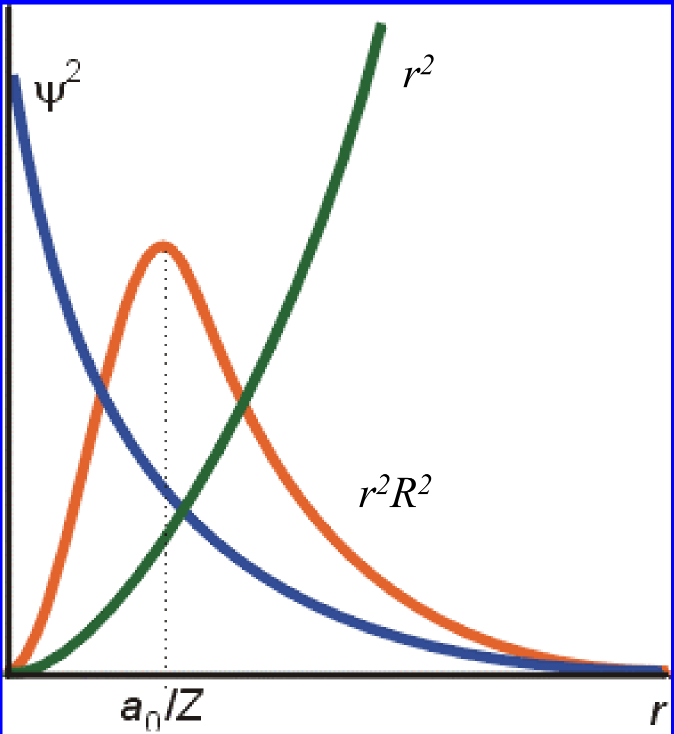
$$D = r^2 R_{nl}^2(r)$$

← Radial distribution function

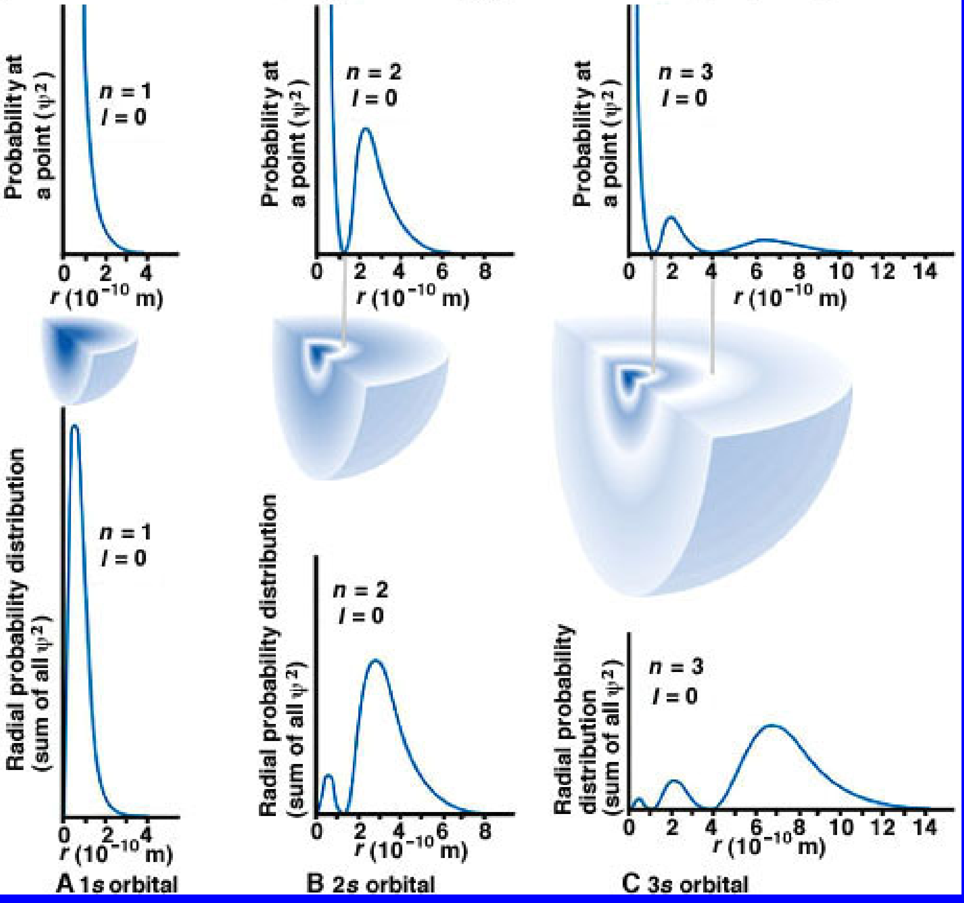
Ψ = wave function

Ψ^2 = probability density

r^2R^2 = radial probability function



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



- A spherical surface with the electron density of zero is called a *node*, or *nodal surface*.

The radial distribution function has (n-*l*) maxima and (n-*l*-1) nodal surfaces

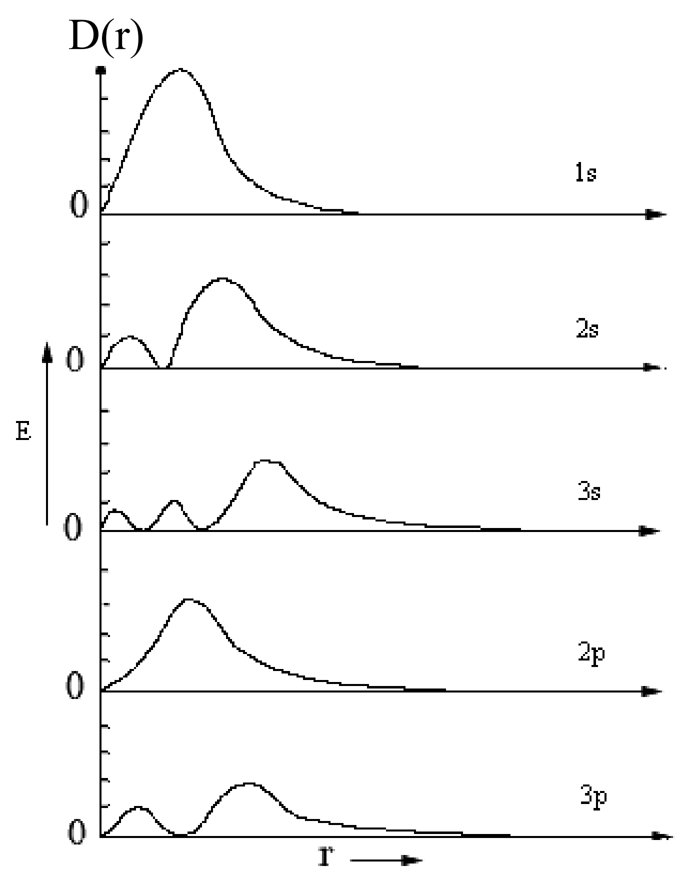


Fig. The radial distribution diagram (D(r)-r)

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

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

▶ Angular part

$$Y_{lm}(\theta,\varphi) = \Theta_l(\theta)\Phi_m(\varphi)$$

Indicates the angular distribution of an atomic orbital.

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

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

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

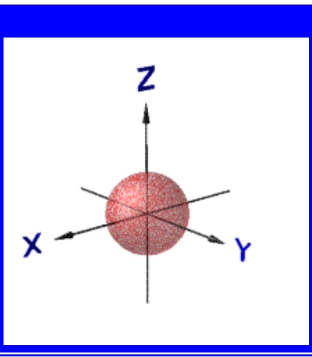
Angular function ($Y_{lm}(\theta,\varphi)$)

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

Y_{00}

$$Y_{0,0}=\frac{1}{\sqrt{4\pi}}$$

$$s=\frac{1}{\sqrt{4\pi}}$$



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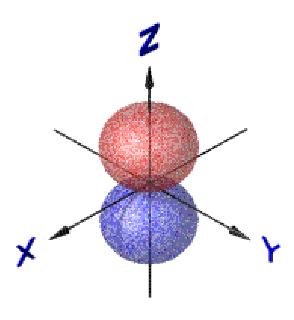
p-Orbital (l=1, 2l+1=3)

Y_{10}

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

$$p_z=\sqrt{\frac{3}{4\pi}}\cos\theta$$



$Y_{1\pm1}$

$$Y_{1,1}=\frac{\sqrt{3}}{2}\sin\theta\cdot\frac{1}{\sqrt{2\pi}}e^{i\varphi}$$

$$Y_{1,-1}=\frac{\sqrt{3}}{2}\sin\theta\cdot\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$$

$$\frac{1}{\sqrt{2}}(Y_{1,1}+Y_{1,-1})=\frac{\sqrt{3}}{4\sqrt{\pi}}\sin\theta(e^{i\varphi}+e^{-i\varphi})$$

$$-i\frac{1}{\sqrt{2}}(Y_{1,1}-Y_{1,-1})=-i\frac{\sqrt{3}}{4\sqrt{\pi}}\sin\theta(e^{i\varphi}-e^{-i\varphi})$$

$$p_x=\sqrt{\frac{3}{4\pi}}\sin\theta\cos\varphi$$

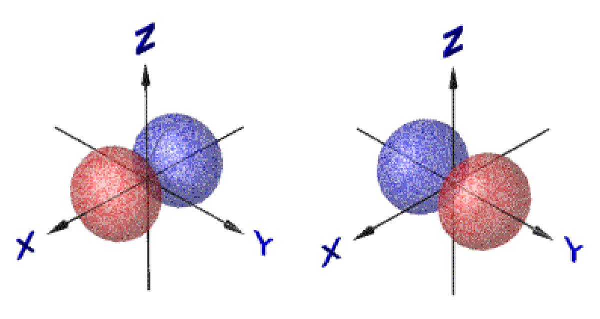
$$p_y=\sqrt{\frac{3}{4\pi}}\sin\theta\sin\varphi$$

---

p-Orbital

$$p_x=\sqrt{\frac{3}{4\pi}}\sin\theta\cos\varphi$$

$$p_y=\sqrt{\frac{3}{4\pi}}\sin\theta\sin\varphi$$



p_x p_y

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

Y_{20}

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

$Y_{2\pm1}$

$$d_{xz}=\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin2\theta\cos\varphi$$

$$d_{yz}=\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin2\theta\sin\varphi$$

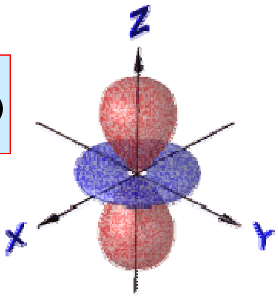
$Y_{2\pm2}$

$$d_{x^2-y^2}=\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos2\varphi$$

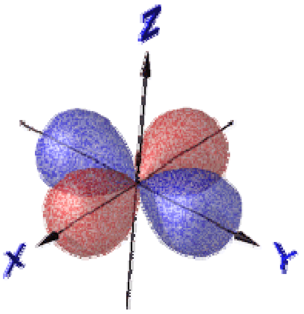
$$d_{xy}=\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\sin2\varphi$$

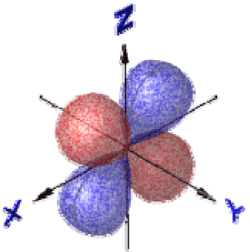
d-Orbital

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

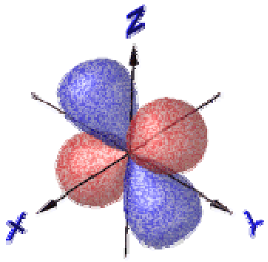


$$d_{x^2-y^2} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos 2\varphi$$



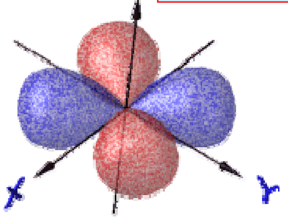


$$d_{xz} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin 2\theta\cos\varphi$$



$$d_{xy} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\sin 2\varphi$$

$$d_{yz} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin 2\theta\sin\varphi$$



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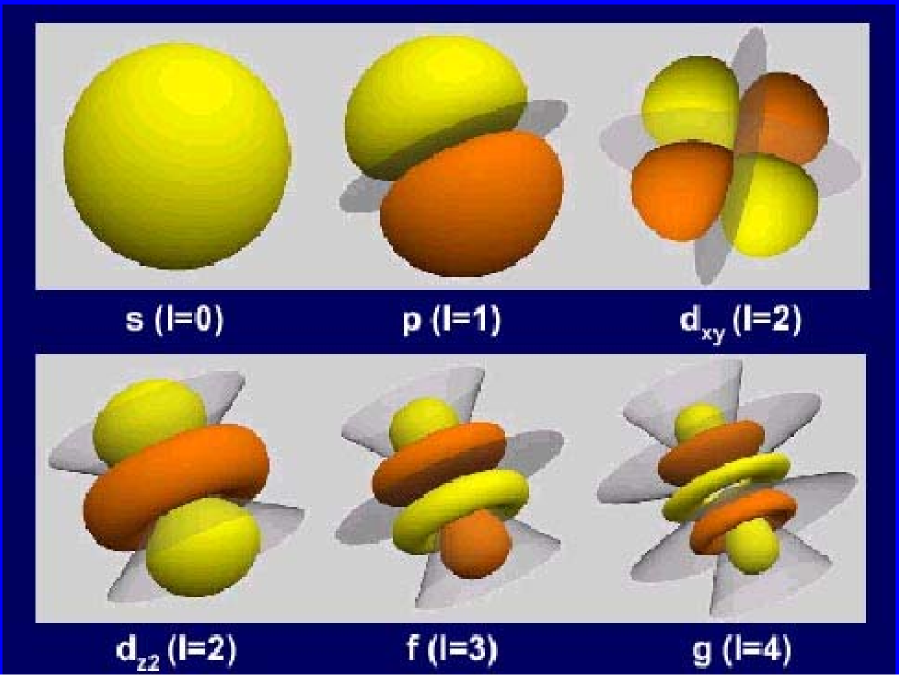
l	m_l	orbital
0	0	s
1	0	p_z
	±1	p_x
	±1	p_y
2	0	$d_{2z^2-x^2-y^2} = d_{z^2}$
	±1	d_{xz}
	±1	d_{yz}
	±2	$d_{x^2-y^2}$
	±2	d_{xy}

Nodes

A node is a surface on which an electron is not found.

For a given orbital, the total number of nodes equals n-1.

The number of angular nodes is *l*.



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

2.4.1 Schroedinger equation of many-electron atoms

For hydrogen - like atoms :

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

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

$$atom \qquad unit \qquad (a.u.)$$

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \qquad (\hat{H} = \hat{T} + \hat{V})$$

$$m_e = 1 \qquad a.u.$$

$$e = 1 \qquad a.u.$$

$$a_0 = 1 \qquad a.u.$$

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

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

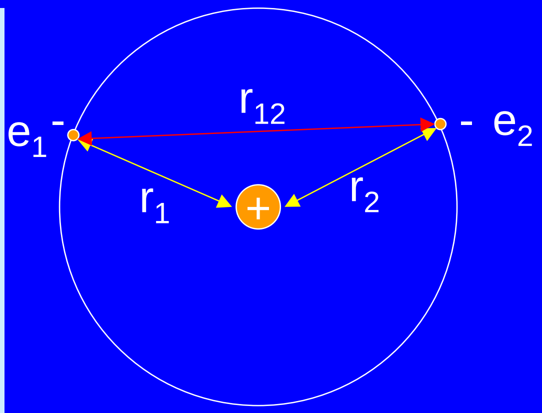
$$for \qquad He \qquad atom$$

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

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

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

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



$$for \qquad many - electron \qquad atoms$$

$$\hat{H} = -\frac{1}{2}\sum_i {\nabla_i}^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_j \frac{1}{r_{ij}}$$

$$if \qquad \frac{1}{r_{ij}} \qquad is \qquad omitted$$

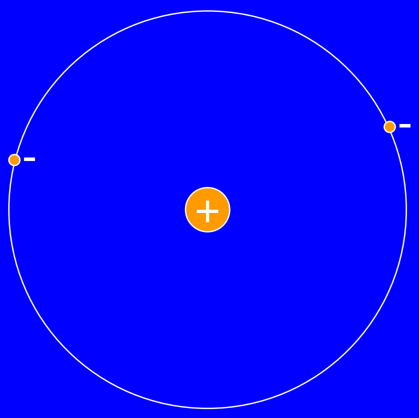
$$\hat{H} = -\frac{1}{2}\sum_i {\nabla_i}^2 - \sum_i \frac{Z}{r_i}$$

$$\Psi = \psi_1 \cdot \psi_2 \cdot \psi_3 \cdots \psi_n = \prod_{i=1} \psi_i$$

$$E = E_1 + E_2 + E_3 + \cdots = \sum_i E_i$$

Many electron atoms

He, Z = 2



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

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

Predict: E_1 = -54.4 eV

Actual: E_1 = -24.6 eV

Something is wrong with the Bohr Model!

Self-consistent-field (SCF) method

Central field method

The electron moves in an average field contributed from the nucleus and the other electrons.

$$\hat{H}(1,2\cdots n) = \sum_i \hat{h}_i = \sum_i [-\frac{1}{2}\nabla_i^2 + V(i)]$$

$$\psi(1,2,3\cdots n) = \varphi_1(1)\varphi_2(2)\cdots\varphi_n(n)$$

$$\hat{h}_i\,\varphi_i = \varepsilon_i\varphi_i$$

$$E = \varepsilon_1 + \varepsilon_2 + \cdots\varepsilon_n$$

Slater approximate method for central field

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

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

$$R_{n,l} = (2\xi)^{n+\frac{1}{2}} r^{n-1} e^{-\xi r}$$

$$\xi = \frac{Z-\sigma_i}{n^*}$$

$$E_i = \left(\frac{Z-\sigma_i}{n^*}\right)^2 \cdot \frac{-e^2}{4\pi\varepsilon_0 a_0}$$

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

$$= -13.6\text{eV}\cdot\left(\frac{Z-\sigma_i}{n^*}\right)^2$$

σ: Screen constant

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

Z*: Effective nuclear charge

n*: Effective principal quantum number

n*=n (when n ≤ 3)

n*=3.7 (when n = 4)

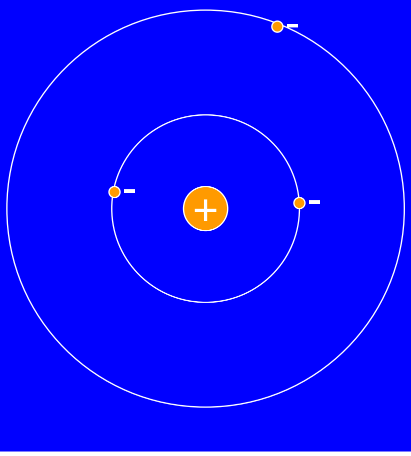
n*=4.0 (when n = 5)

Lithium , *Z* = 3

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

Predicted: E_1 = -30.6 eV

Actual: E_1 = -5.4 eV



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

$$-5.4 = -13.6\left(\frac{Z^{*2}}{2^2}\right)$$

$$Z^* = \sqrt{\frac{5.4\times 2^2}{13.6}}$$

Z^* = 1.26

1.26 = 3 - σ

σ = 1.74

a. Screen (shielding) constant

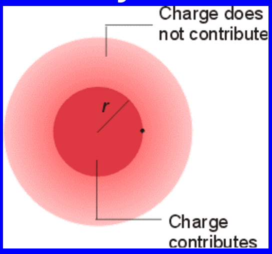
Slater's rules for the prediction of σ for an electron:

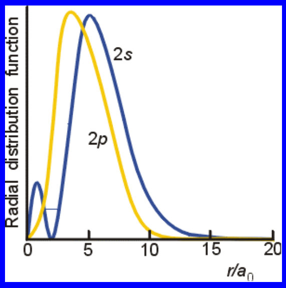
1. Group electron configuration as follows:
   (1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p) etc.
2. Electrons in the right shells (in higher subshells and shells) of an electron do not shield it.
3. For ns or np valence electrons:
   a) each other electron in the same group contributes 0.35 (0.30 for 1s)
   b) each electron in an n-1 group(s) contribute 0.85
   c) each electron in an n-2 or lower group contributes 1.00
4. For nd or nf valence electrons:
   a) each other electron in the same group contributes 0.35
   b) each electron in a lower group (to the left) 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. ns and np orbitals completely shield nd orbitals

2. (n-1) s and p orbitals don't completely shield n s and p 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) $\sigma = \underset{1s}{(2 * 0.85)} + \underset{2s,2p}{(5 * 0.35)} = 3.45$

$Z^* = Z - \sigma$

$Z^* = 8 – 3.45 = 4.55$

This electron is actually held with about 57% of the force that one would expect for a +8 nucleus.

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

Example: Ni, $Z = 28$
Electron configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$

$(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6)\ (3d^8)\ (4s^2)$

For a 3d electron:
$\sigma = \underset{1s,2s,2p,3s,3p}{(18 * 1.00)} + \underset{3d}{(7 * 0.35)} = 20.45$

$Z^* = Z - \sigma \qquad Z^* = 28 – 20.45 = 7.55$

For a 4s electron:
$\sigma = \underset{1s,2s,2p}{(10 * 1.00)} + \underset{3s,3p,3d}{(16 * 0.85)} + \underset{4s}{(1 * 0.35)} = 23.95$

$Z^* = Z - \sigma \qquad Z^* = 28 – 23.95 = 4.05$

B. Approximation of the atomic orbital energy

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

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

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

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

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

2.4.2 The ionization energy and the affinity energy

I. Ionization energy:

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

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

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

The first ionization energy

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

The second ionization energy

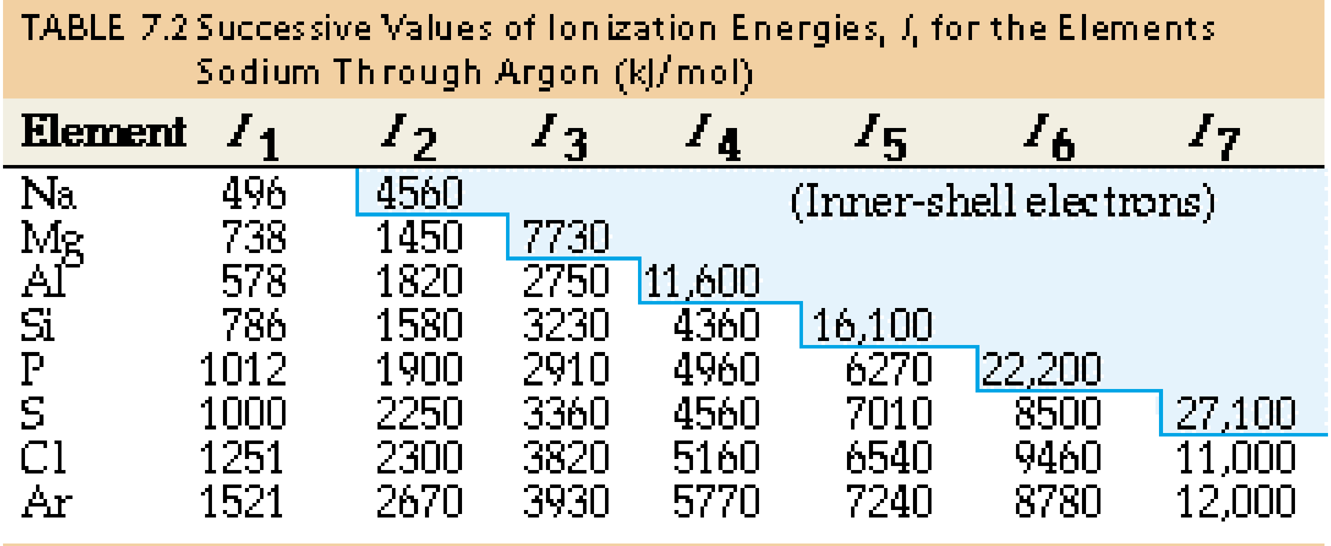
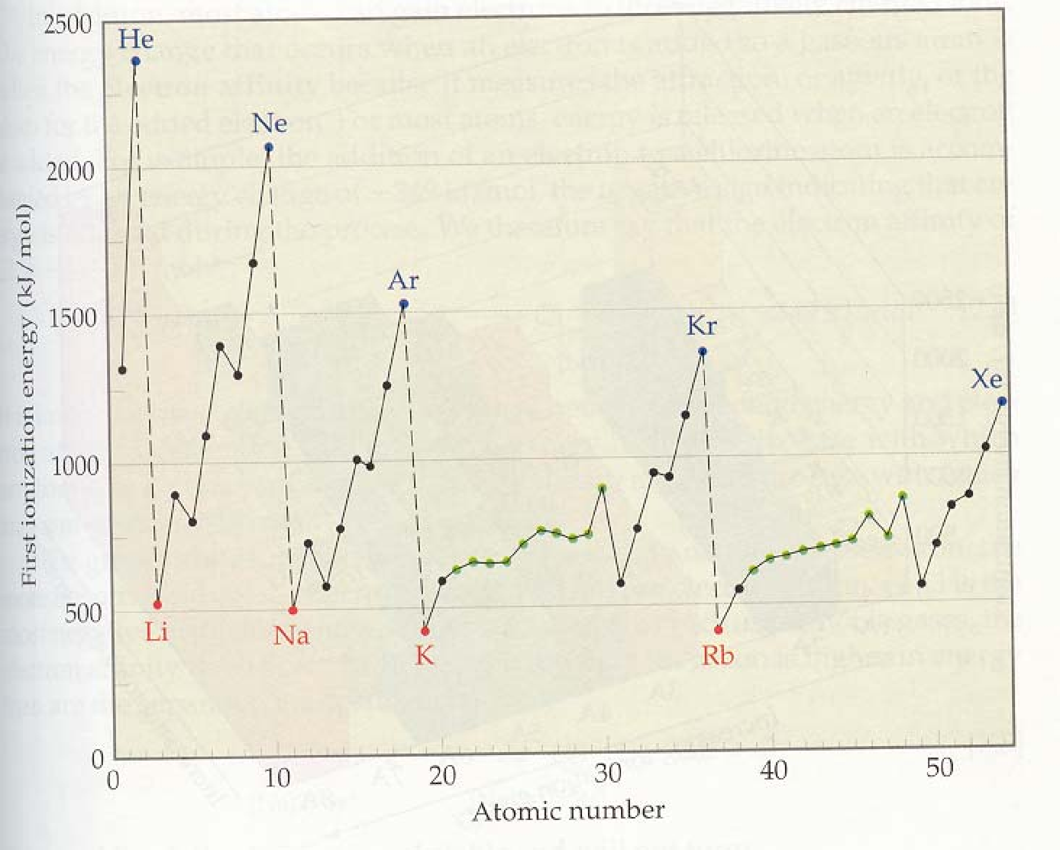


TABLE 7.2 Successive Values of Ionization Energies, I, for the Elements Sodium Through Argon (kJ/mol)

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

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

$I_1 = \Delta E = E(C^+) - E(C)$

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

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

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

$$\begin{aligned} &I_1 = -[3 \times (\frac{3.6}{2})^2 - 4 \times (\frac{3.25}{2})^2] \cdot R = 11.44ev \\ &I_{actual} = 11.22ev \end{aligned}$$

III. Electron Affinity

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

$$B(g) + e^- \rightarrow B^-(g) + A$$

- 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 comparative attraction of the bonding electrons by the atoms.

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 it decrease 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 state)

a. Pauli exclusion principle.

Every orbital may contain only two electrons of opposite spins.

b. The principle of minimum energy.

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

For multi-electron atoms:

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

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

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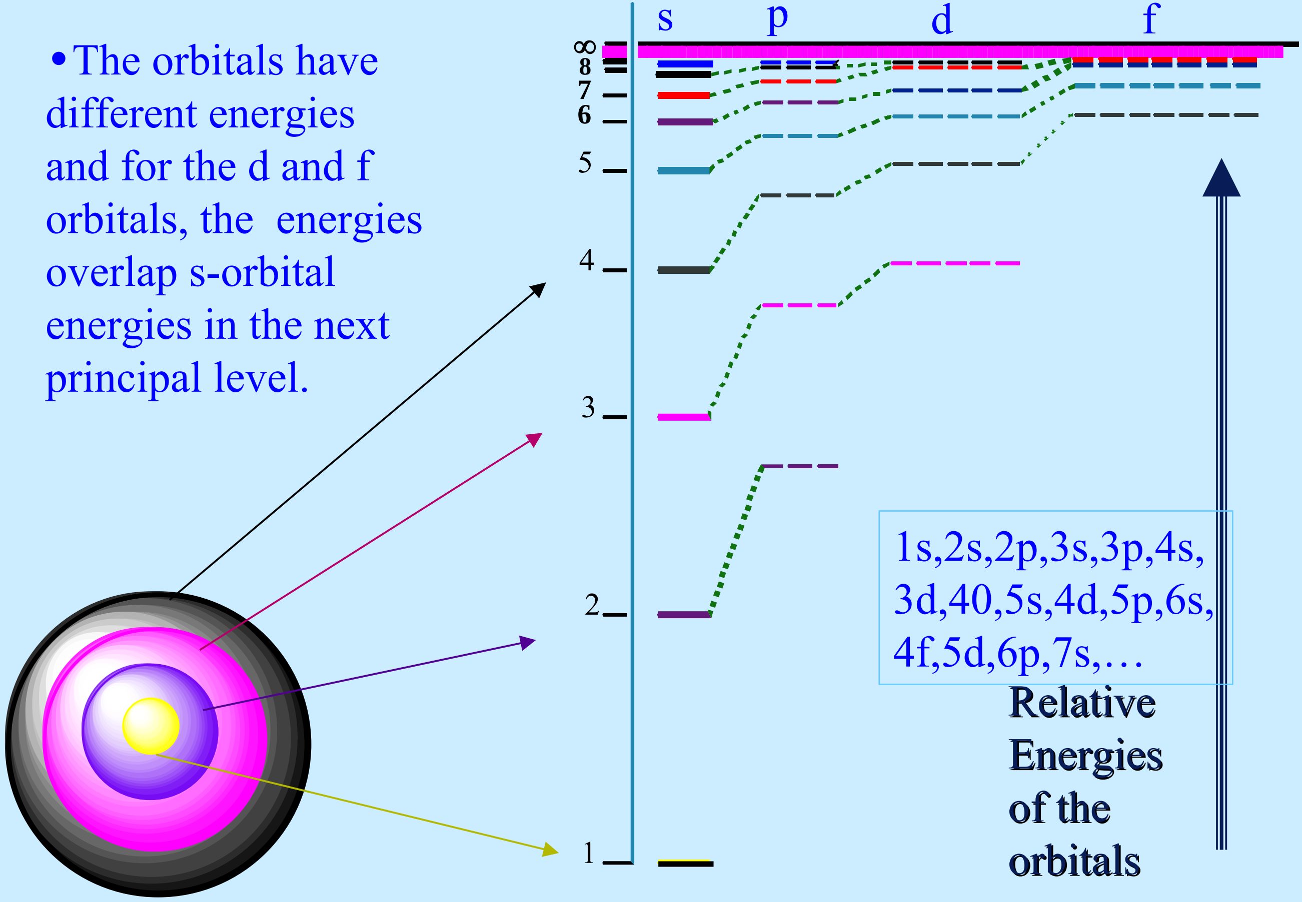
Relative Energies for Shells and Orbitals

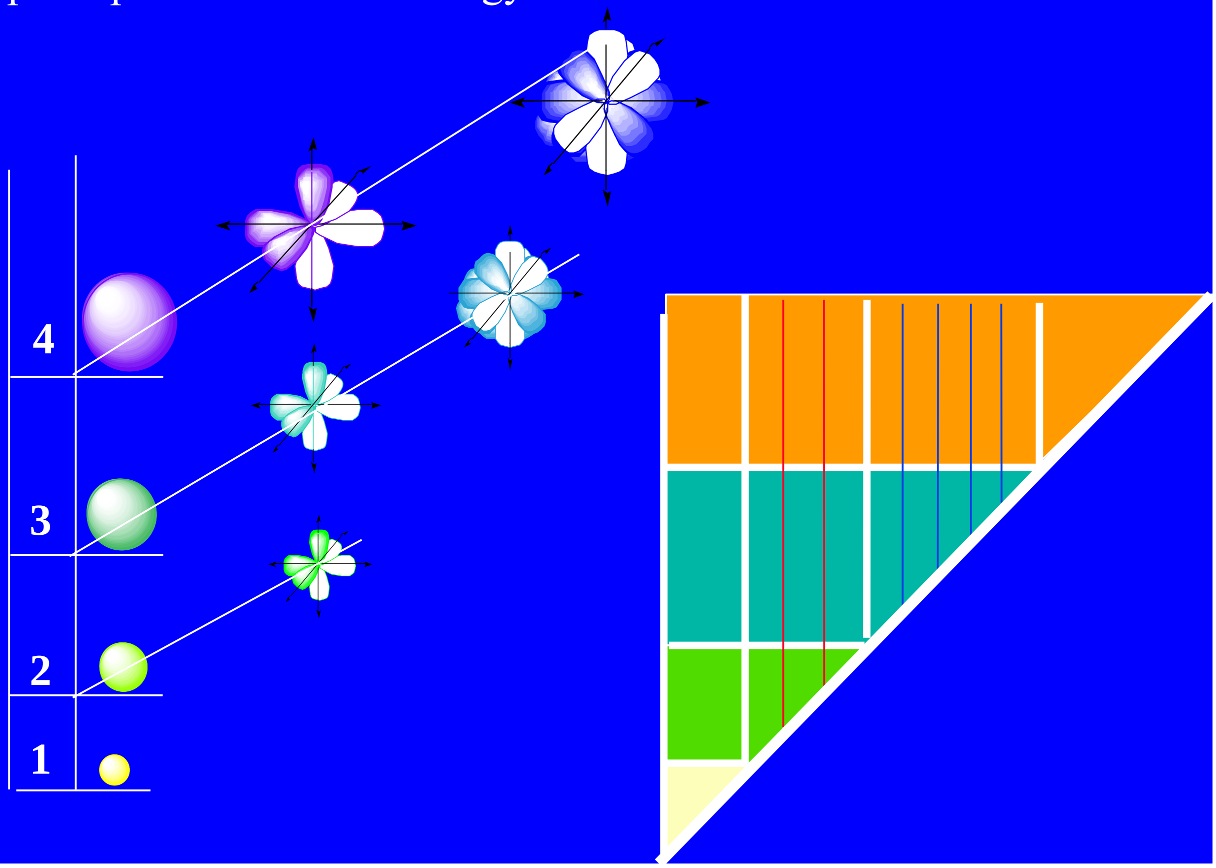
- The orbitals have different energies and for the d and f orbitals, the energies overlap s-orbital energies in the next principal level.



1s,2s,2p,3s,3p,4s,
3d,40,5s,4d,5p,6s,
4f,5d,6p,7s,…

Relative Energies of the orbitals

The principle of minimum energy.



I. The building up principle (for ground state)

- Pauli exclusion principle.

  Every orbital may contain only two electrons of opposite spins.

b. The principle of minimum energy.

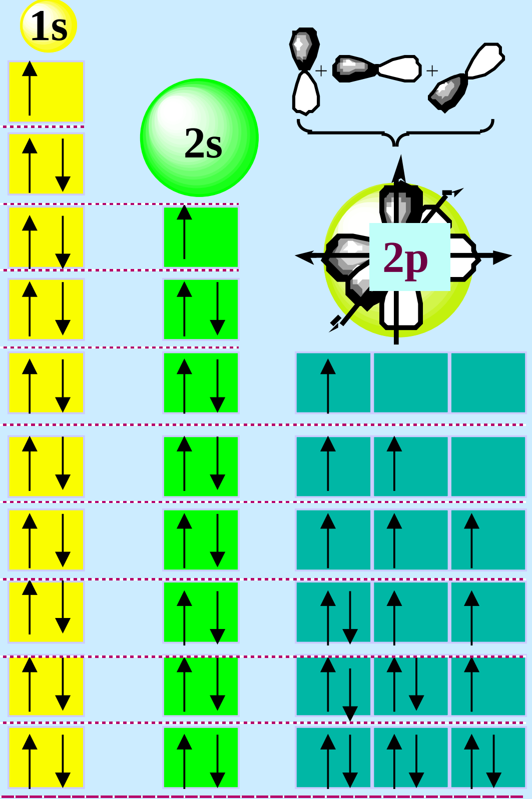
Whilst being compatible with the Pauli principle, electrons occupy the orbital with the lowest energy first.

c. Hund’s rule.

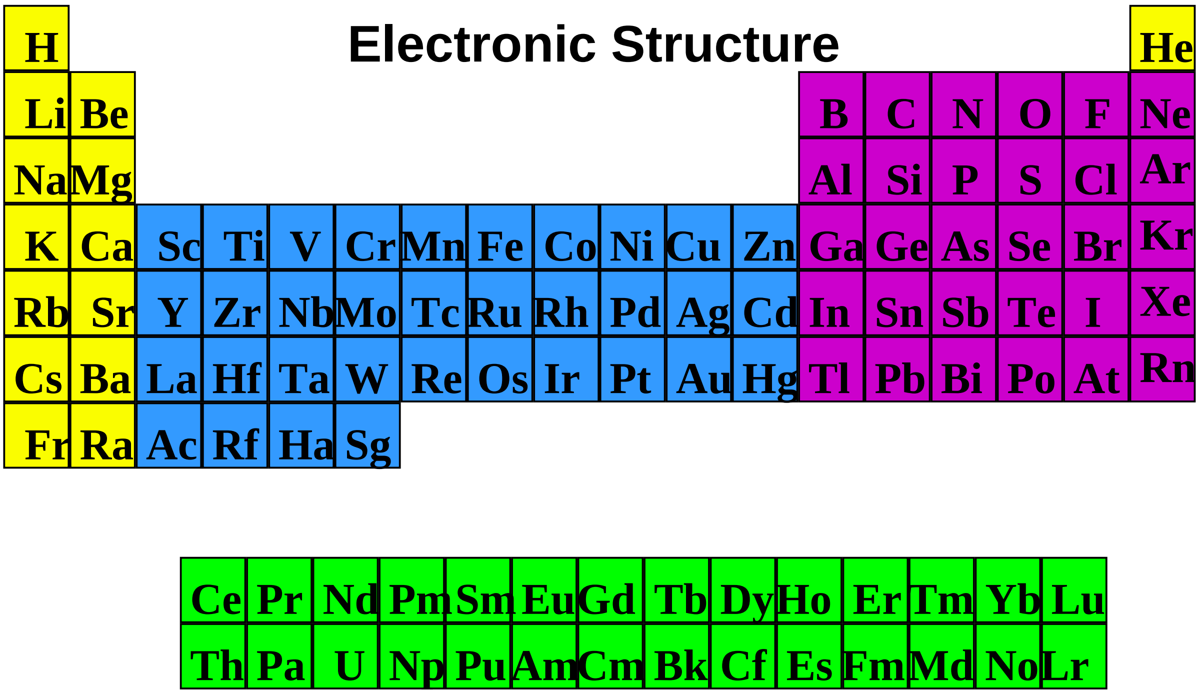
In degenerate energy states, electrons tend to occupy as many degenerate orbitals as possible. (The number of unpaired electrons is a maximum.)

II. The electronic configuration (for ground state)

- 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

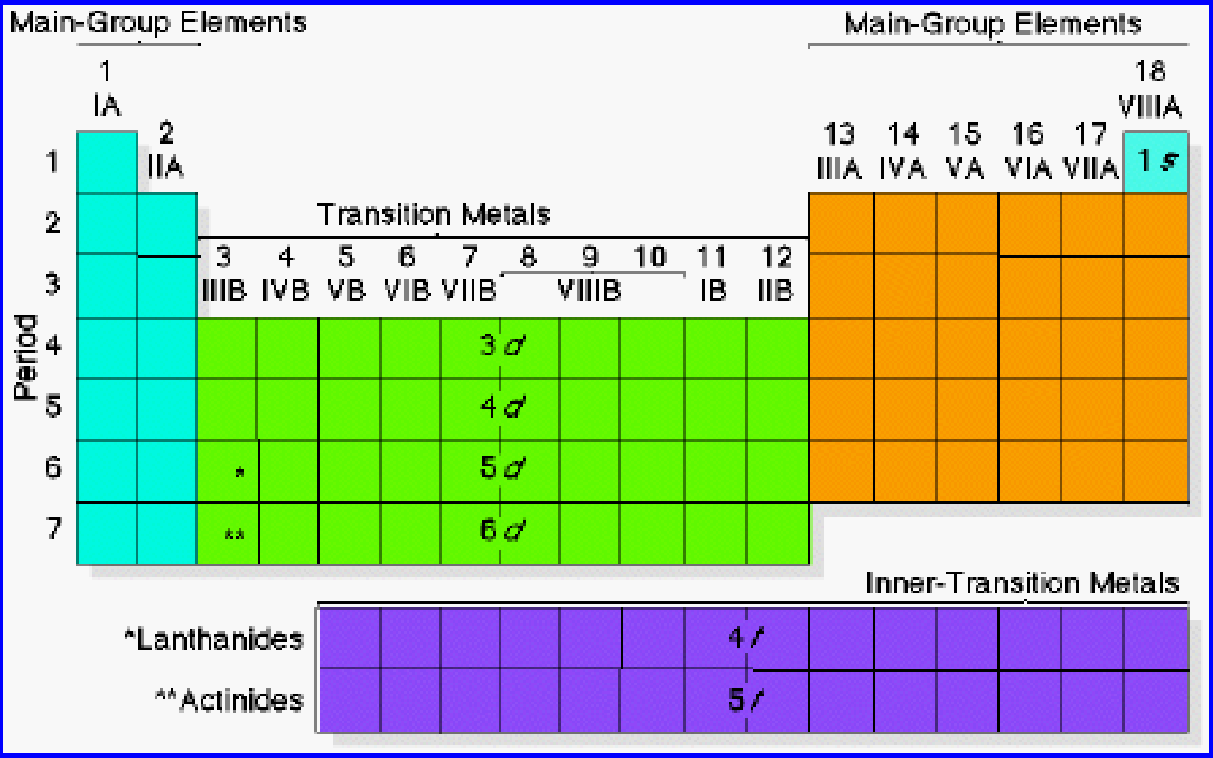
🟨 " s" Orbitals

🟪 " p" Orbitals

🟦 " d" Orbitals

🟩 " f " Orbitals

Electron Configuration using the Periodic Table



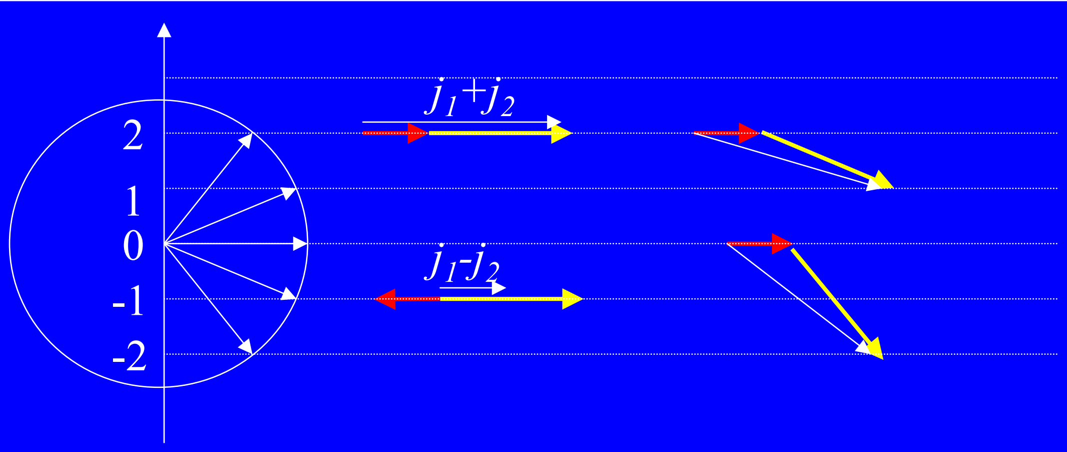
2.5 Atomic spectra and spectral term

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:

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



<u>Example:</u> 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: $j_1+j_2=2+3=5$

$|j_1-j_2|=|2-3|=1$

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

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: $j_1+j_2=2+3/2=7/2$

$|j_1-j_2|=|2-3/2|=1/2$

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

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.

Example: Find the possible values of the quantum number L for states of carbon atom that arise from the electron configuration $1s^2 2s^2 2p3d$.

Solution:

$s \quad l=0 \qquad p \quad l=1 \qquad d \quad l=2$

↓ *Addition of two 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

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.

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

Solution:

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

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

$$\underbrace{\textit{2p electrons: } m_s = \tfrac{1}{2} \qquad \textit{3d electrons: } m_s = \tfrac{1}{2}}_{\downarrow}$$

Addition of two angular momenta rule

$S = 1, 0$

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**

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

Term symbol: ^{2S+1}L

Each term consists of (2L+1)(2S+1) atomic states. (spin-orbit interaction neglected)

^3D : $L=2, S=1$

^2P: $L=1, S=1/2$

2.5.3 Derivation of **Atomic term**

a. Configurations of Completely filled subshells

$M_S=\Sigma_i m_{si}=0$ --→ $S=0$

$M_L=\Sigma_i m_i=0$ --→ $L=0$

Only one term: ^1S

b. Nonequivalent electrons.

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

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.

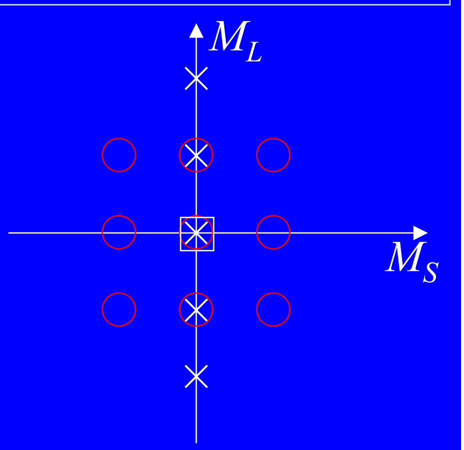
$1s^2 2s^2 2p^2$ -→ np^2 (two electrons in the same subshell)

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.

The number of microstates:

$C^2_6 = 15$

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



^1D, ^3P, ^1S

5 9 1 -> 15

- 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.

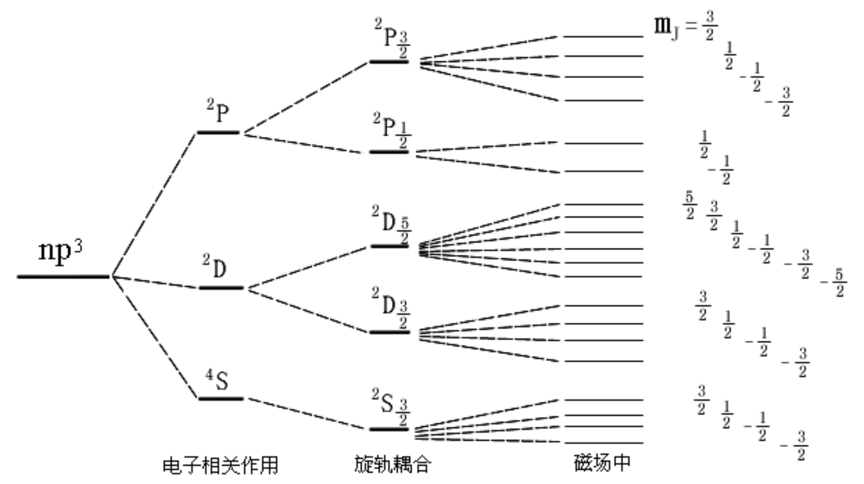
Term : p^0 === p^6
p^1 === p^5
p^2 === p^4

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.

$np^3\ {}^4S,\ {}^2D,\ {}^2P$



p^2 : ${}^3P,\ {}^1D,\ {}^1S$

E. Spin-Orbit interaction.

The spin-orbit interaction splits an atomic term into levels.

The splitting of these levels gives the observed fine structure in atomic spetra.

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

np^3 ${}^2P,\ {}^2D,\ {}^4S$

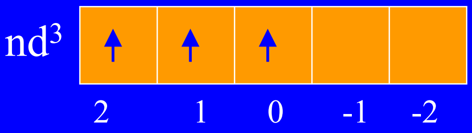
${}^4S \rightarrow {}^4S_{3/2}$

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

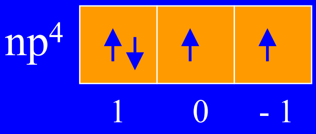
E. Ground state of the terms

Hund's 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.

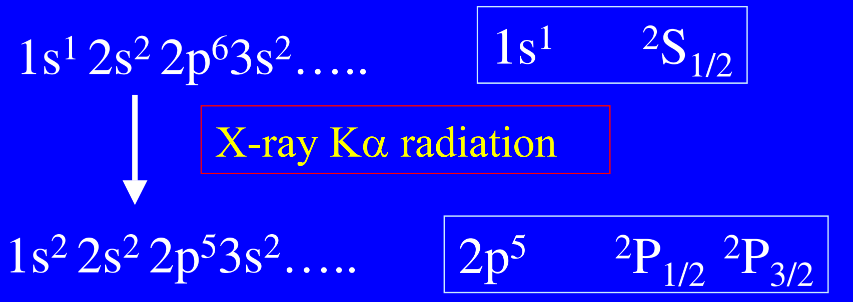


$L=3,\ S=3/2 \ \ -> {}^4F_{3/2}$



$L=1,\ S=1 \ \ -> {}^3P_2$

Example: Why does Cu Kα radiation (X-ray) consist of $K\alpha_1$ and $K\alpha_2$ radiations?



Ground state $1s^2\,2s^2\,2p^6 3s^2$…..

Excited state $1s^1\,2s^2\,2p^6 3s^2$….. $1s^1 \quad {}^2S_{1/2}$

X-ray Kα radiation

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