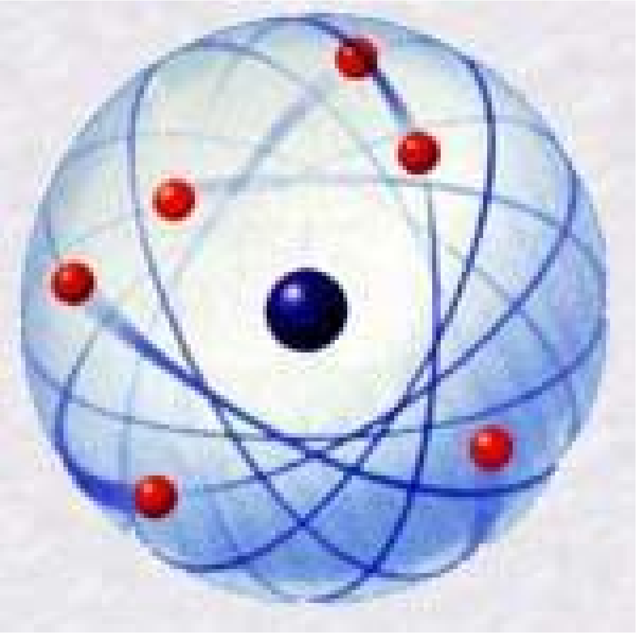
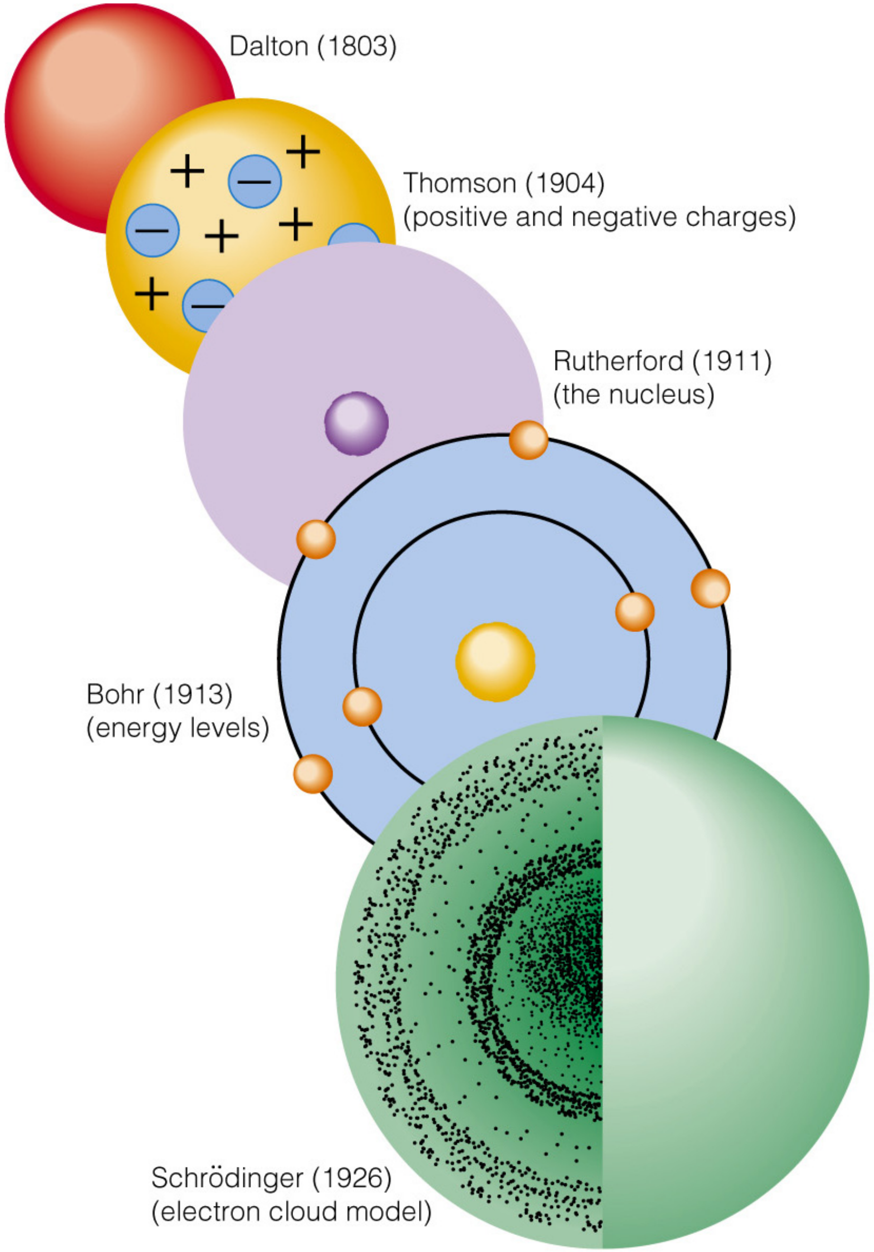
Chapter 2 Atomic Structure



History of Atomic Models

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



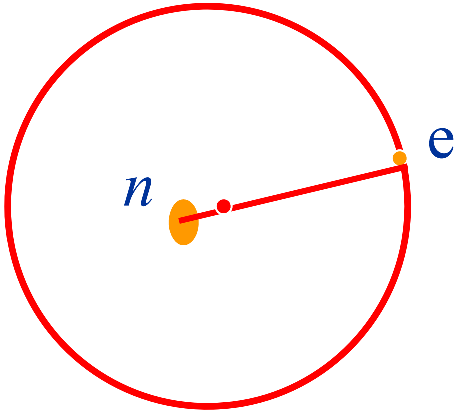
2.1 The Schrödinger equation and its solution for one-electron atoms

2.1.1 The Schrödinger equation

The Hamiltonian Operator of one-electron atoms

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

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



The reduced mass

$$\mu = \frac{M \cdot m_e}{M + m_e} = \frac{1836 m_e}{(1+1836) m_e} \approx 0.999 m_e$$

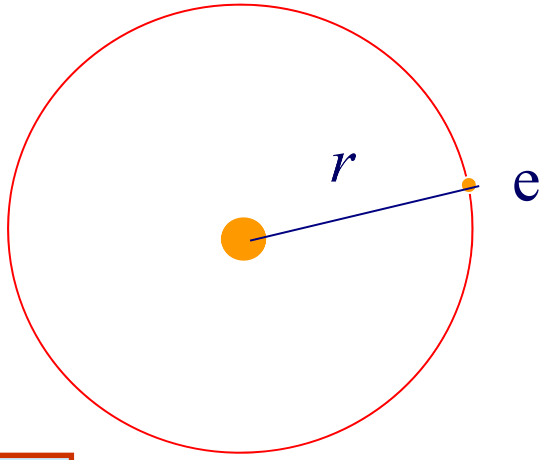
Consider that the electron approximately surrounds the atomic nucleus, the Hamilton operator can be simplified as

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

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

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

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



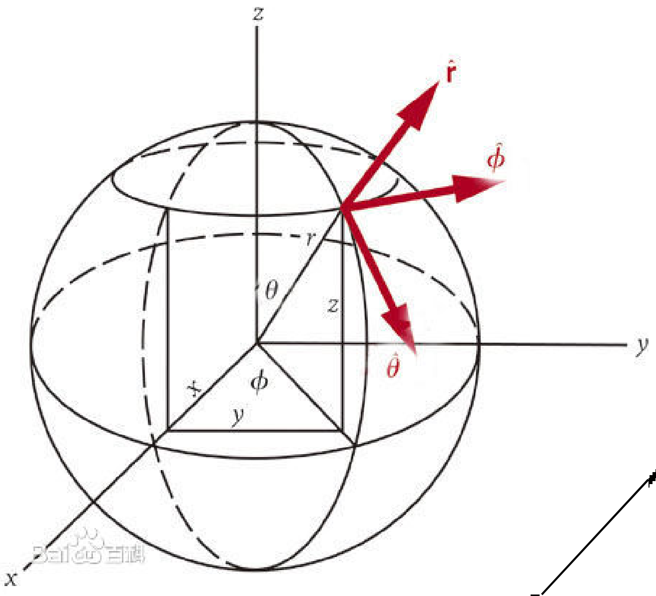
The Schrödinger equation

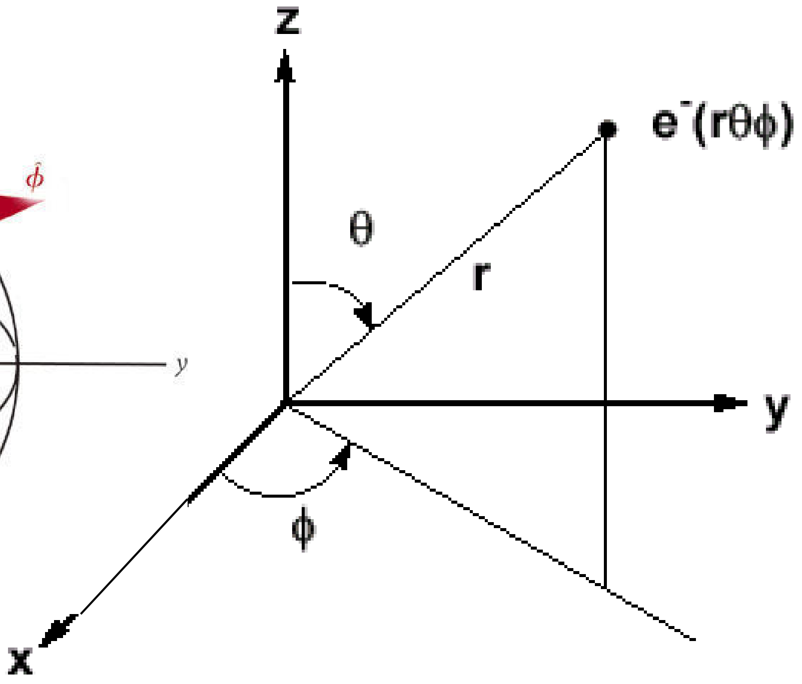
$$\hat{H}\psi = E\psi$$

Separation of variables ?

Spherical polar coordinates

$$d\tau = dx\,dy\,dz$$
$$= r^2 \sin\theta\, dr\, d\theta\, d\phi$$





$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$

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

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

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

$$tg\phi = y/x$$

r ➔ distance from origin.

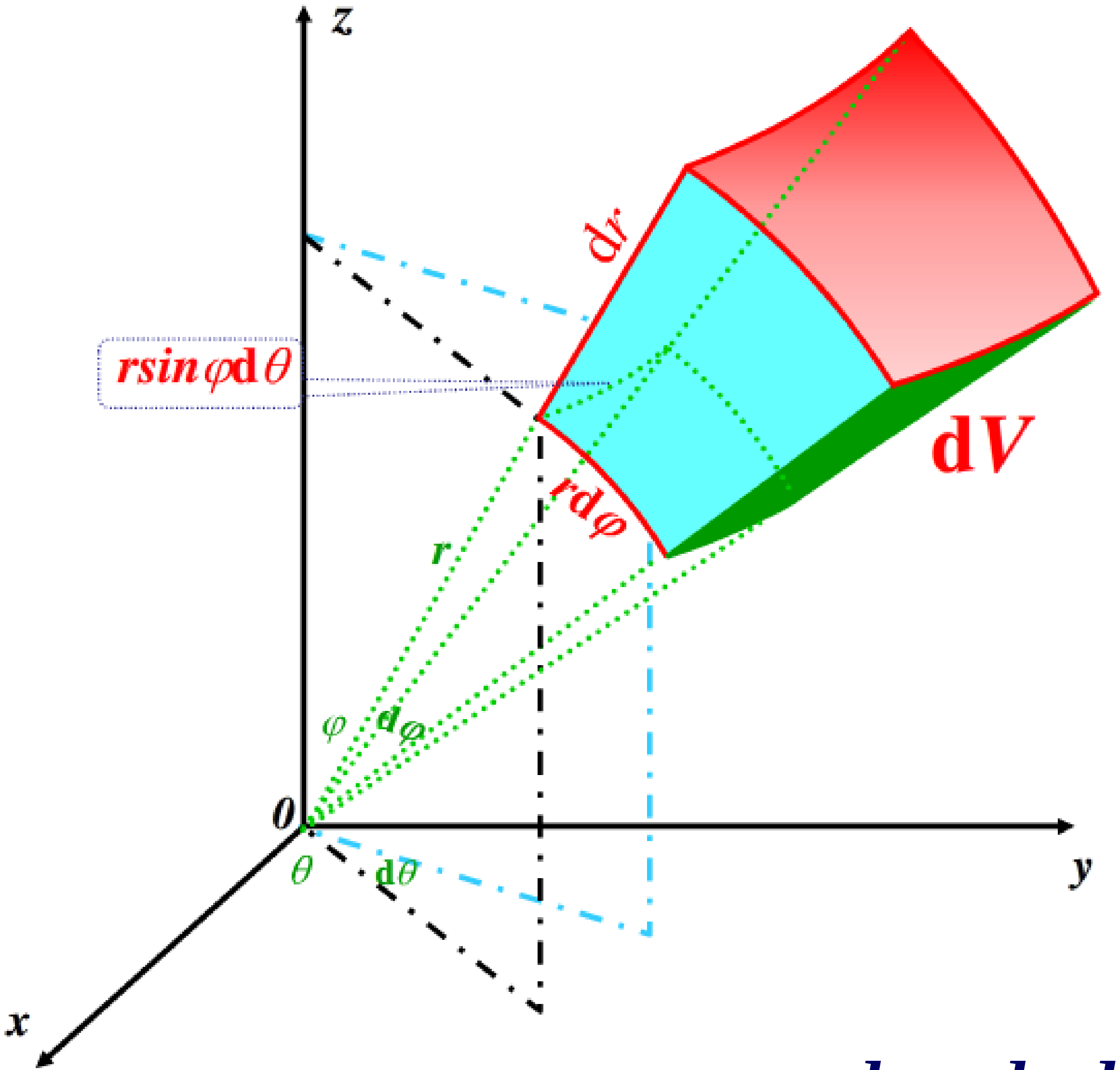
θ ➔ angle drop from the z-axis.

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

$(x,y,z) \rightarrow (r,\theta,\phi)$

$\Psi(x,y,z) \rightarrow \Psi(r, \theta, \phi)$

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



$$\begin{aligned} d\tau &= dx\,dy\,dz \\ &= r^2 \sin\theta\, dr\, d\theta\, d\phi \end{aligned}$$

Partial derivatives

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

$$\boldsymbol{x = r \sin\theta \cos\phi}$$
$$\boldsymbol{y = r \sin\theta \sin\phi}$$
$$\boldsymbol{z = r \cos\theta}$$

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

$$tg\phi = y / x$$

$$\frac{\partial r}{\partial x} = \frac{1}{2}(x^2 + y^2 + z^2)^{-\frac{1}{2}} 2x = \frac{x}{r} = \sin\theta\cos\phi$$

$$-\sin\theta \frac{\partial\theta}{\partial x} = z(-\frac{1}{2})(x^2 + y^2 + z^2)^{-3/2} 2x = -\frac{zx}{r^3}$$

$$\frac{\partial\theta}{\partial x} = \frac{\cos\theta\cos\phi}{r}$$

Spherical polar coordinates

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

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

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

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

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

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

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

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

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

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

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

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

▶Radial part

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

▶Angular part

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

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

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

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

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

a. $\Phi(\phi)$ 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

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

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

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

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

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

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

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

The values of m must be

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

m : magnetic quantum number

complex function

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

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

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

its linear combination

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

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

normalization condition

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

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

real function

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

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

$$\sin 2\alpha = 2\sin\alpha\cos\alpha$$

$$\sin^2\alpha + \cos^2\alpha = 1$$

$$\cos 2\alpha = 2\cos^2\alpha - 1$$

$$\cos(\alpha \pm \beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta$$

$$\sin\alpha + \sin\beta = 2\sin\frac{\alpha+\beta}{2}\cos\frac{\alpha-\beta}{2}$$

$$\sin\alpha - \sin\beta = 2\cos\frac{\alpha+\beta}{2}\sin\frac{\alpha-\beta}{2}$$

$$\cos\alpha + \cos\beta = 2\cos\frac{\alpha+\beta}{2}\cos\frac{\alpha-\beta}{2}$$

$$\cos\alpha - \cos\beta = -2\sin\frac{\alpha+\beta}{2}\sin\frac{\alpha-\beta}{2}$$

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	$\Phi_1 = \frac{1}{\sqrt{2\pi}} e^{i\varphi}$	$\Phi_{\pm 1}^{\cos} = \frac{1}{\sqrt{\pi}} \cos\varphi$
-1	$\Phi_{-1} = \frac{1}{\sqrt{2\pi}} e^{-i\varphi}$	$\Phi_{\pm 1}^{\sin} = \frac{1}{\sqrt{\pi}} \sin\varphi$
2	$\Phi_2 = \frac{1}{\sqrt{2\pi}} e^{i2\varphi}$	$\Phi_{\pm 2}^{\cos} = \frac{1}{\sqrt{\pi}} \cos 2\varphi$
-2	$\Phi_{-2} = \frac{1}{\sqrt{2\pi}} e^{-i2\varphi}$	$\Phi_{\pm 2}^{\sin} = \frac{1}{\sqrt{\pi}} \sin 2\varphi$

b. Θ(θ) equation

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

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

$$\Theta(\theta)=c(1-x^2)^{\frac{|m|}{2}}\frac{d^{l+|m|}}{d_x^{\;l+|m|}}[(x^2+1)^l]$$

$$x=\cos\theta$$

$$c=\frac{1}{2^l l!}\sqrt{\frac{(2l+1)}{2}\frac{(l-|m|)}{(l+|m|)}}$$

$$\text{Necessary condition :}\qquad l\geq|m|$$

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, calculating 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

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

Solution

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

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

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

a_0 is called as Bohr radius

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

necessary condition: $n \geq l+1$

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

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

n: Principal quantum number

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

R is called as 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

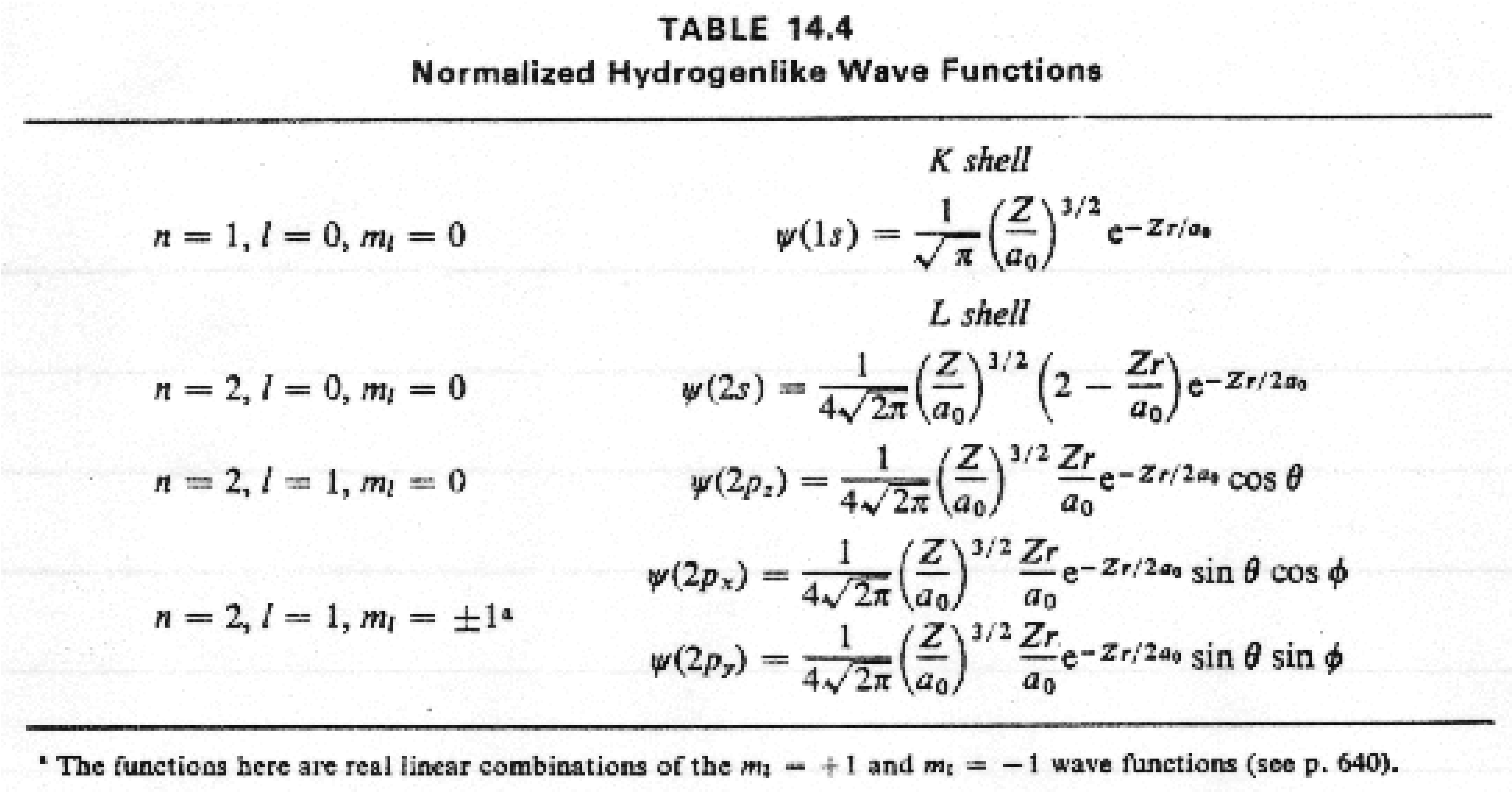


TABLE 14.4

Normalized Hydrogenlike Wave Functions

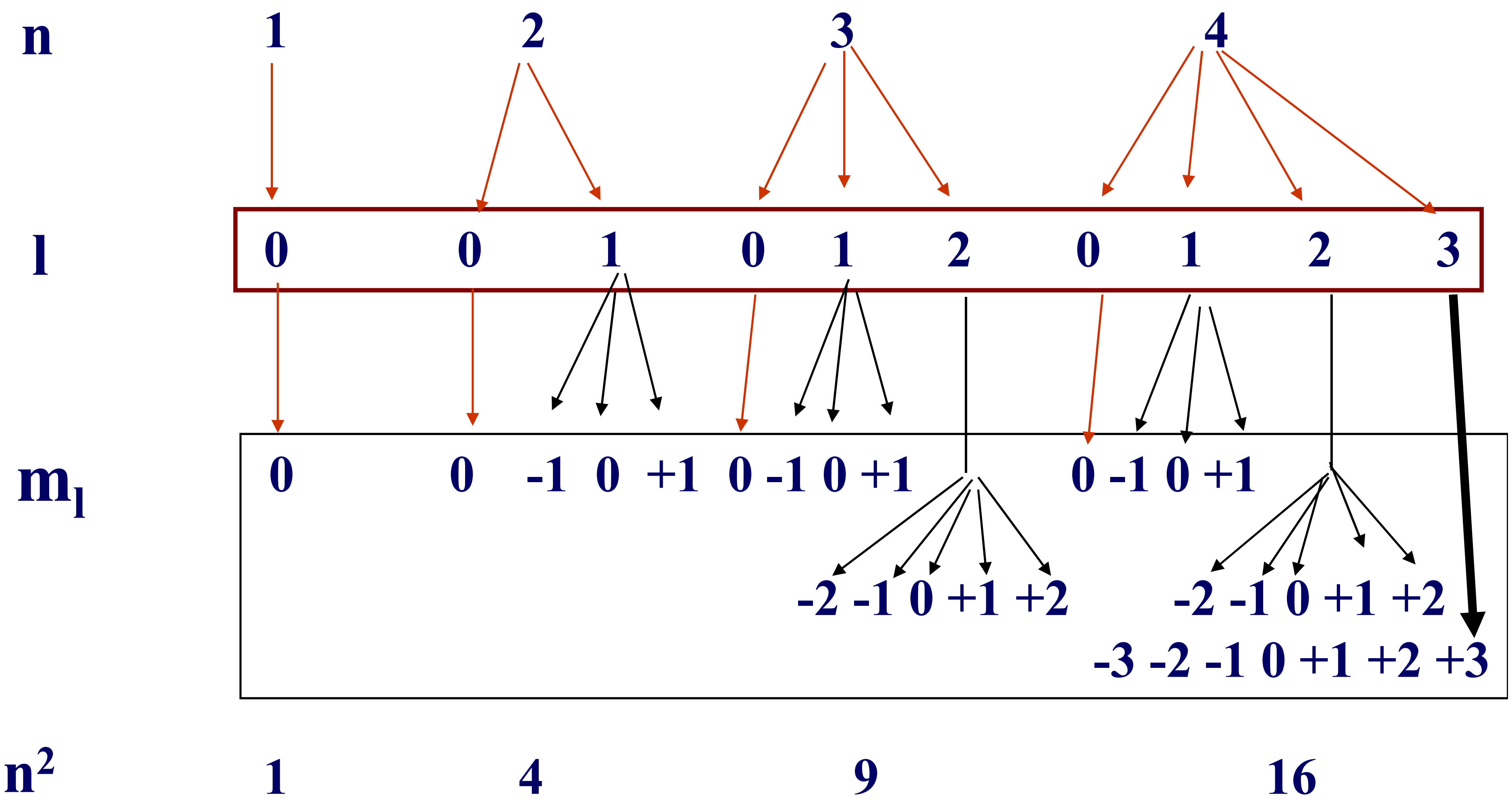
	K shell
$n = 1, l = 0, m_l = 0$	$\psi(1s) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
	L shell
$n = 2, l = 0, m_l = 0$	$\psi(2s) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
$n = 2, l = 1, m_l = 0$	$\psi(2p_z) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}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

2.2 The physical significance of quantum numbers

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

n^2 1 4 9 16

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?

Plan: We determine the allowable quantum numbers by the rules given in the text.

Solution: The l values go from 0 to (n-1), and for n=4 they are:

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

For $l = 0$, $\mathbf{m_l = 0}$

$l = 1$, $\mathbf{m_l = -1, 0, +1}$

$l = 2$, $\mathbf{m_l = -2, -1, 0, +1, +2}$

$l = 3$, $\mathbf{m_l = -3, -2, -1, 0, +1, +2, +3}$

There are 16 $\mathbf{m_L}$ values, so there are 16 orbitals for n=4!

as a check, the total number of orbitals for a given value of n is n^2, so for n = 4 there are 4^2 or 16 orbitals!

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 it 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.

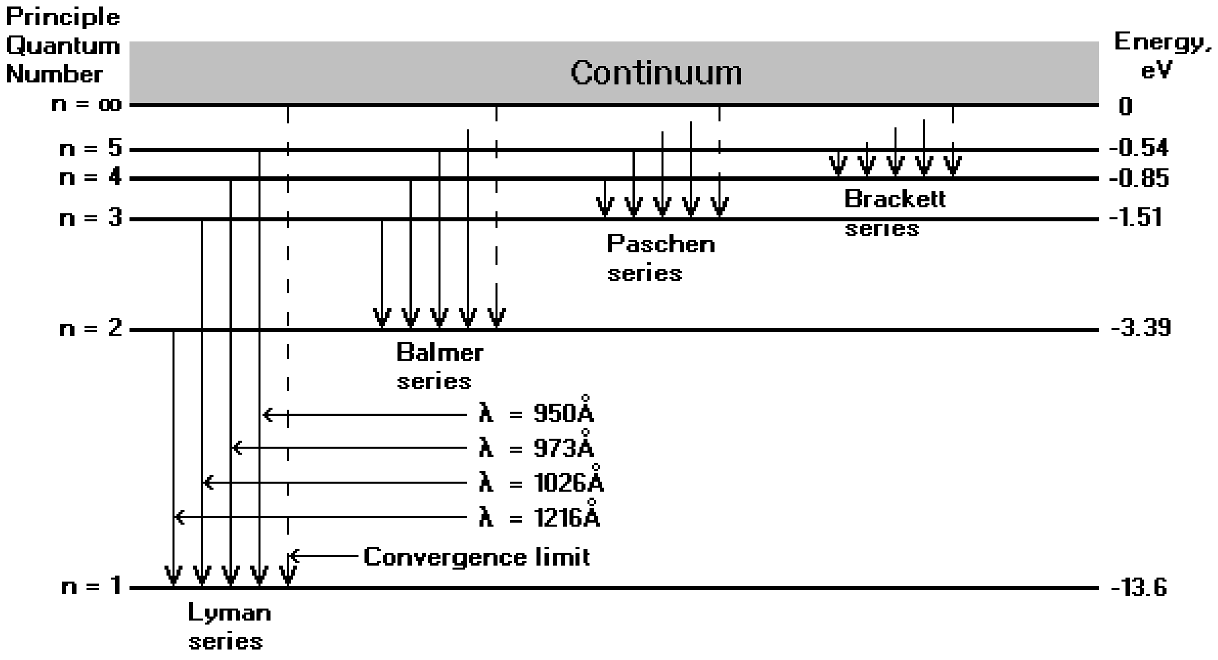
n = *principal*

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

$n = 1$: ground state

$n = 2$: first excited state

$n = 3$: second excited state



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

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^{2+} ion.

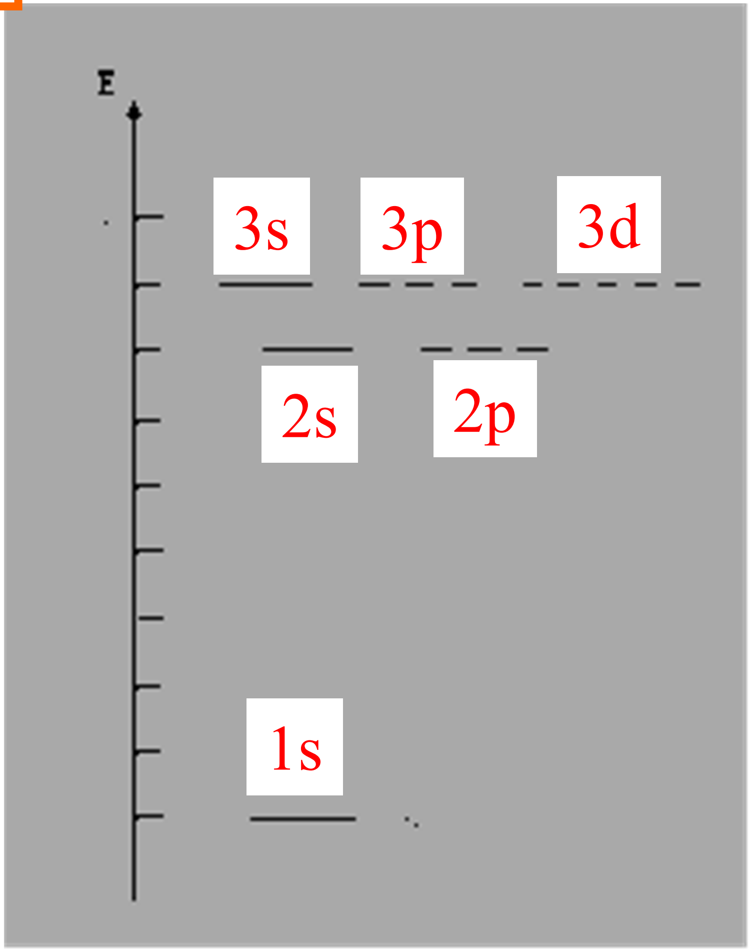
$$E_n = -R\frac{Z^2}{n^2}$$

R = 13.6 eV

E_{1s}= - 9R

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

E_{3s}= - R



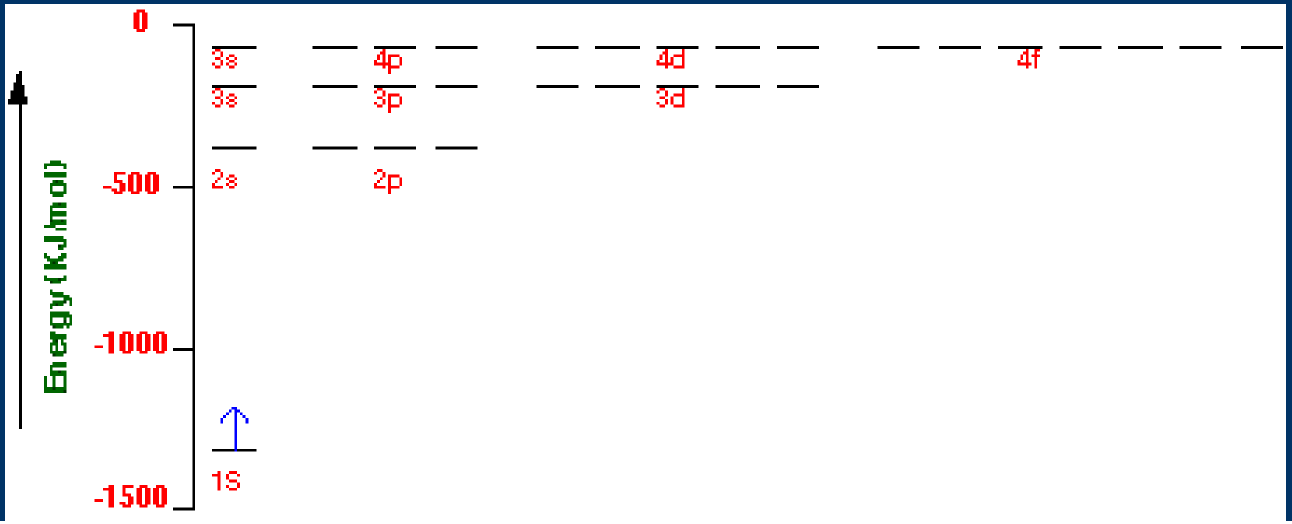
2.2.3 the *azimuthal*, orbital angular momentum, l

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

orbital angular momentum → degeneracy,

$l = 0, 1, 2 \ldots n - l$ 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 …



The operator of angular momentum

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

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

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

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

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

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

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

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

The operator of angular momentum

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

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

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_{l,m}(\theta,\varphi)}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y_{l,m}(\theta,\varphi)}{\partial\varphi^2}=-\beta Y_{l,m}(\theta,\varphi)$$

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_{l,m}(\theta,\varphi)}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y_{l,m}(\theta,\varphi)}{\partial\varphi^2}\right]=\beta\hbar^2 Y_{l,m}(\theta,\varphi)$$

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

$$where \quad Y_{l,m}(\theta,\varphi)=\Theta(\theta)\Phi(\varphi); \quad \beta=l(l+1)$$

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

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

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

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

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

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

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

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

2.2.4 Magnetic Quantum Number , *m*

- Denotes the direction or orientation of an orbital

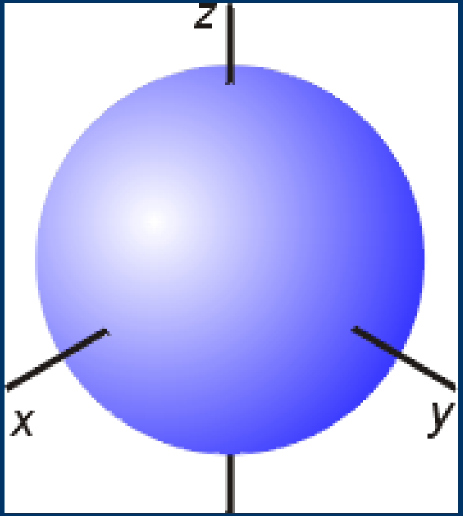
m_l = *magnetic* → type, “orientation in space” → ORBITAL

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

number of orbitals in a subshell

$= 2l + 1$

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}



1s orbital

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.

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

$$\hat{M}_z \Psi = \lambda \Psi$$

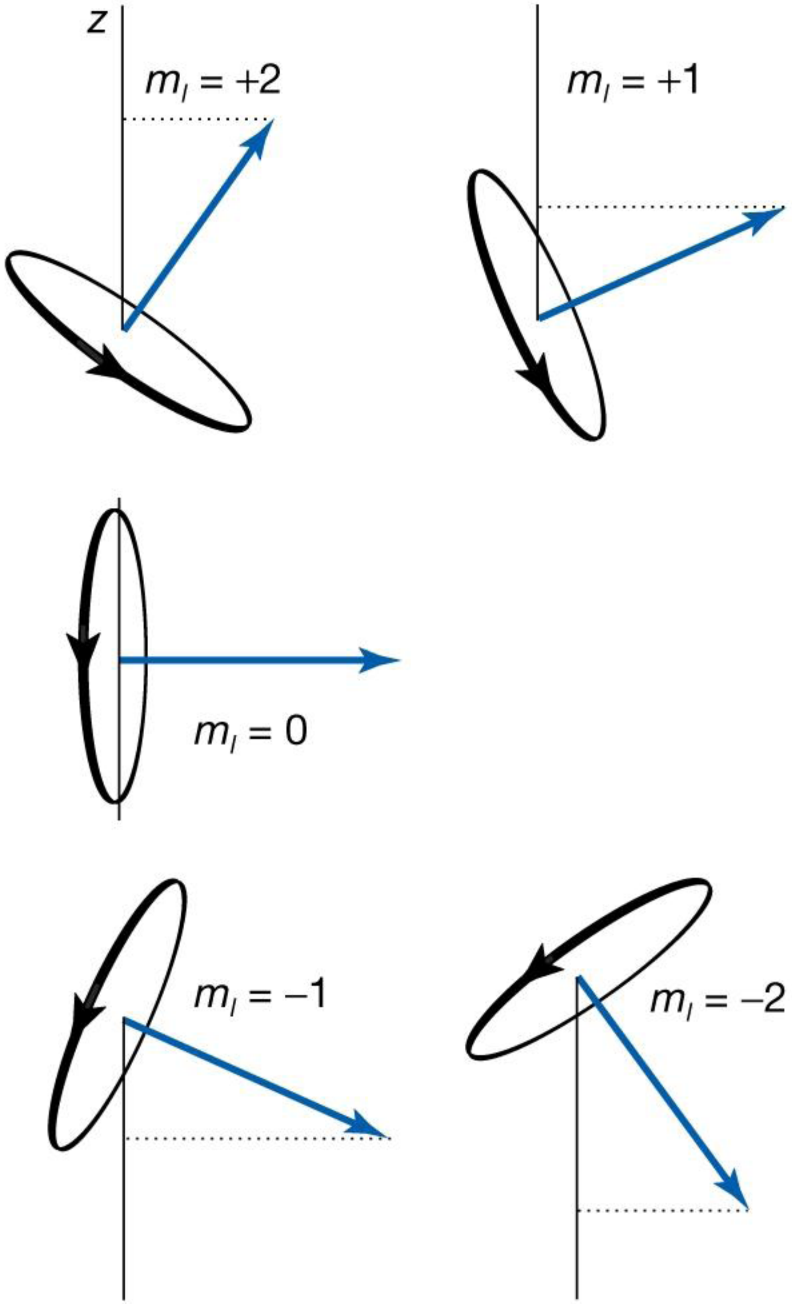
$$\hat{M}_z \Psi = -i\hbar\frac{\partial}{\partial \varphi}\Psi = -i\hbar\frac{\partial}{\partial \varphi}R\Theta\Phi = -i\hbar R\Theta\frac{\partial \Phi}{\partial \varphi} = -i\hbar R\Theta\frac{\partial}{\partial \varphi}Ae^{im\phi}$$

$$= -i\hbar R\Theta Aime^{im\phi} = m\hbar R\Theta Ae^{im\phi} = m\hbar\Psi$$

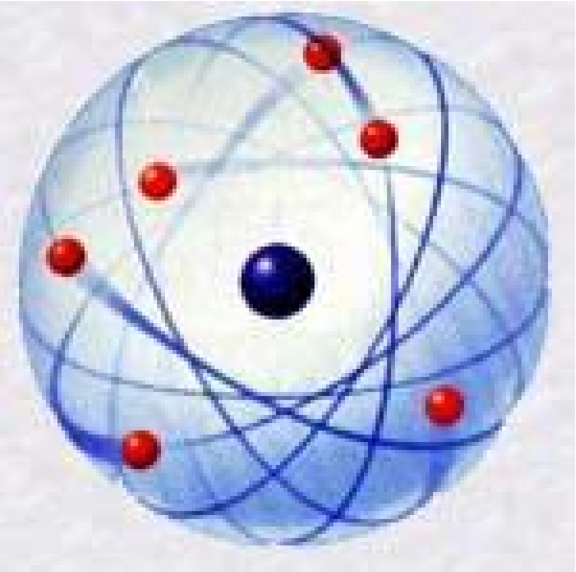
$$\hat{M}_z \Psi = m\hbar\Psi$$

$$\lambda = m\hbar$$

$$M_z = m\hbar \qquad \mu_z = -\frac{e}{2m_e}M_z = \frac{-e\hbar m}{2m_e} = -m\beta_e$$



Space quantization



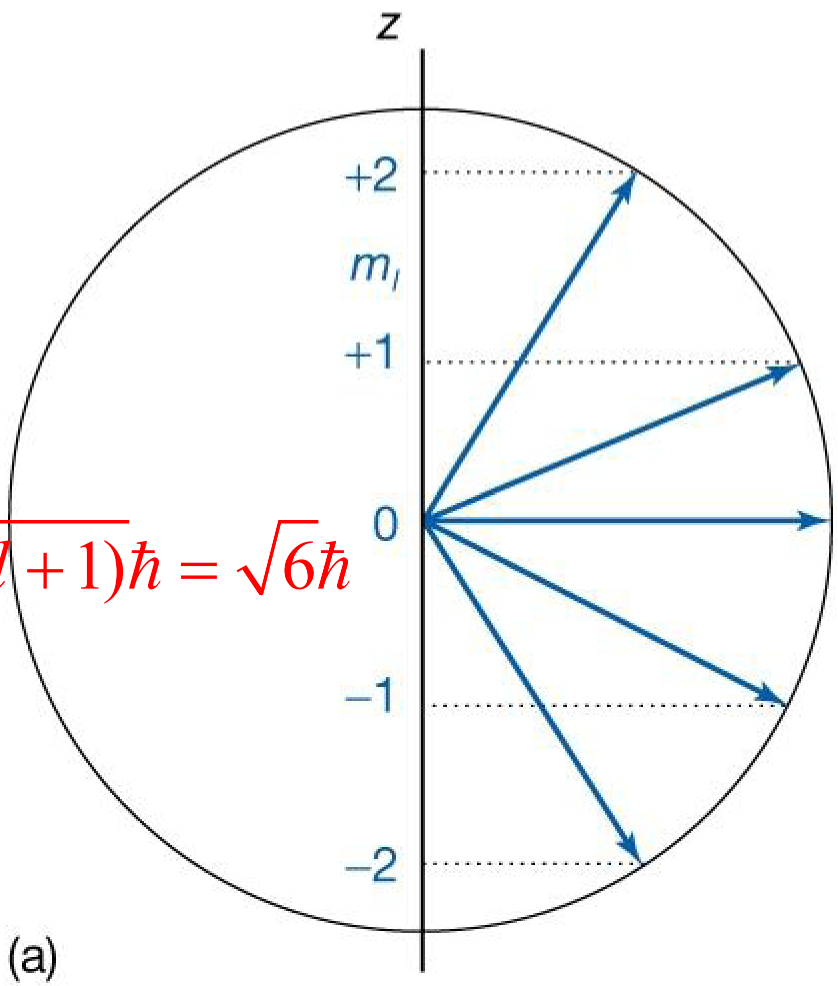
Hence an atomic electron that possesses angular momentum interacts with an external magnetic field *B*.

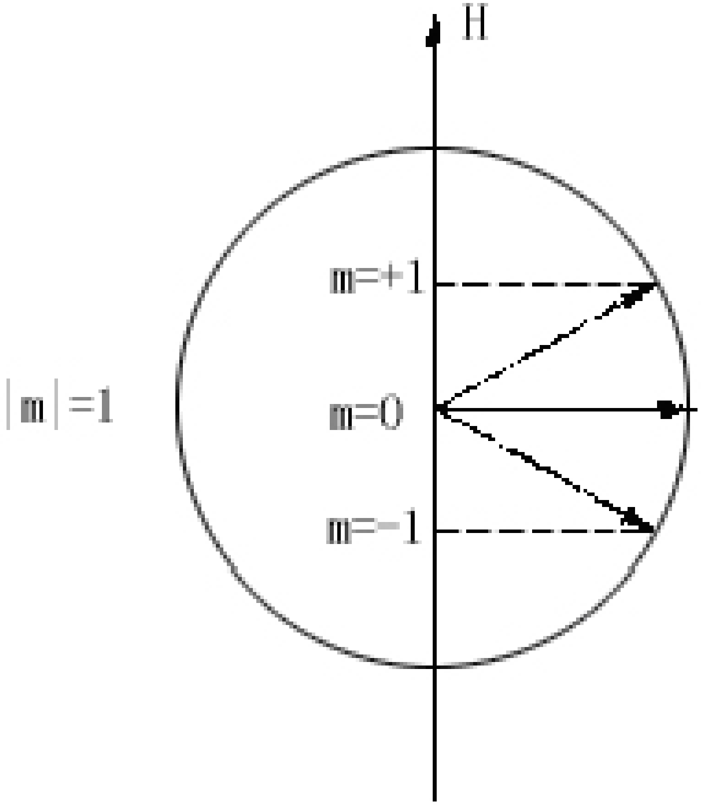
Space quantization of orbital angular momentum. Here the orbital quantum number is *l*=2 and there are accordingly 2*l*+1=5 possible values of the magnetic quantum number *ml*, with each value corresponding to a different orientation relative to the z axis.

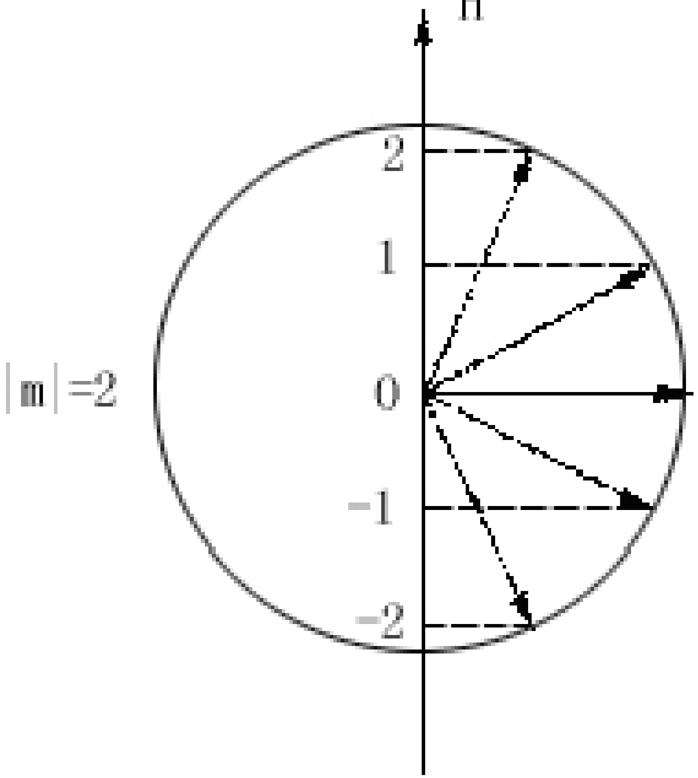
$$L_z = m\hbar$$

$$l = 2$$

$$|L| = \sqrt{l(l+1)}\hbar = \sqrt{6}\hbar$$




H
|m|=1
m=+1
m=0
m=−1


H
|m|=2
2
1
0
−1
−2

2.3 The wave function and electron cloud

2.3.1 The wave-functions of hydrogen-like ions

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

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

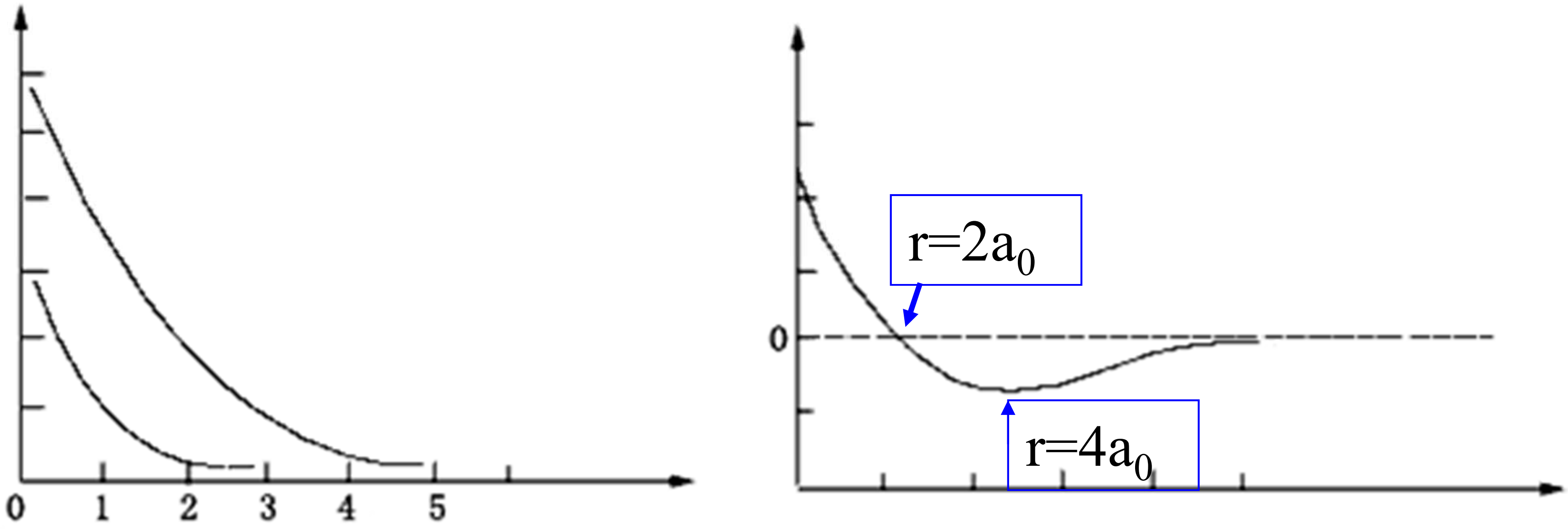
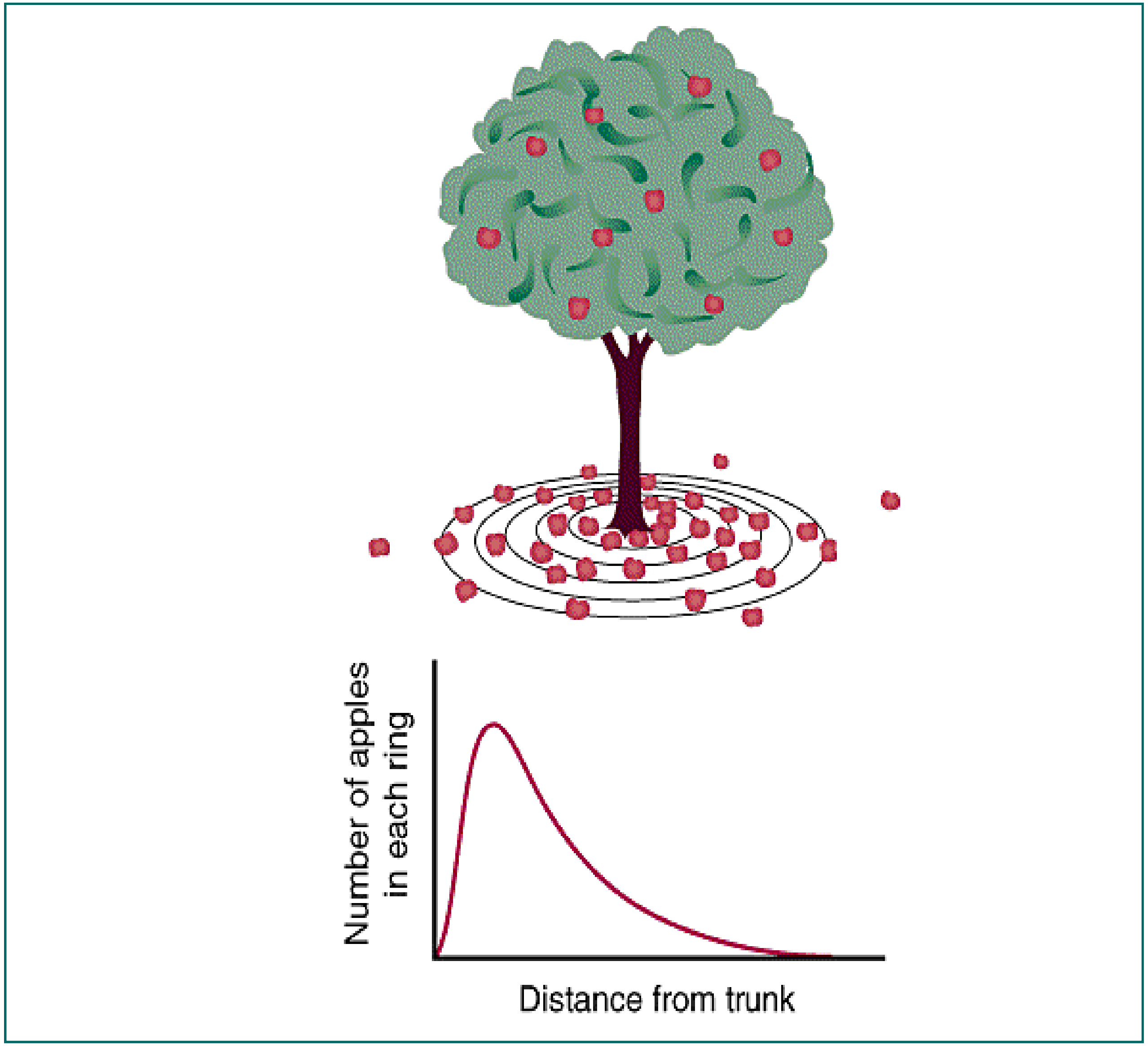


Fig. (left) The ψ-r and ψ^2-r diagram of the 1s state of the hydrogen atom. (right) The ψ-r of the 2s state .

A Radial Probability Distribution of Apples



2.3.2 The radial distribution function

- The probability of finding electron in the region of space

  $r + dr,\ \theta + d\theta,\ \varphi + d\varphi$

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

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

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

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

Normalized spherical harmonics

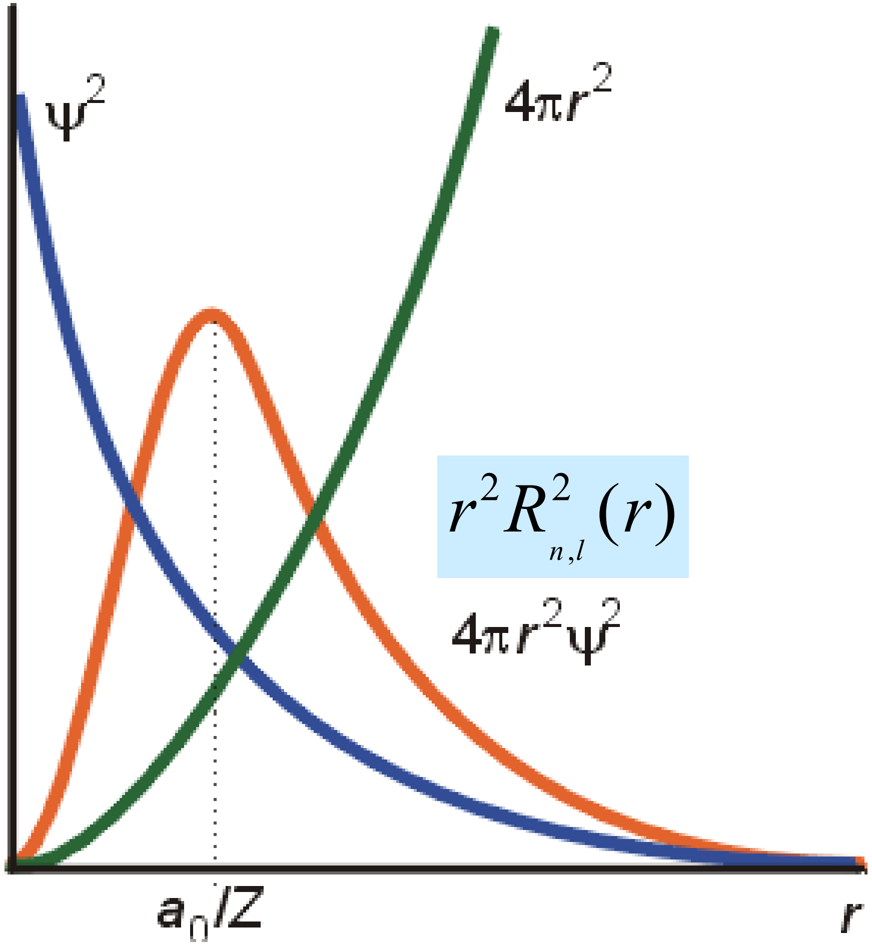
$$D = r^2 R_{nl}^2(r)$$

Radial distribution function

Ψ = wave function

Ψ^2 = probability density

r^2R^2 = radial probability function



Calculating the most probable radius

$$\frac{\partial D(r)}{\partial r} = 0$$

Expectation value of r

$$\langle r \rangle = \int \psi^* r \psi d\tau$$

$$= \int_0^\infty \int_0^\pi \int_0^{2\pi} rR^2_{n,l} \, |Y_{l,m}|^2 \, r^2 dr \sin\theta d\theta d\phi = \int_0^\infty R^2_{n,l} r^3 dr$$

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 radical probability distribution function is

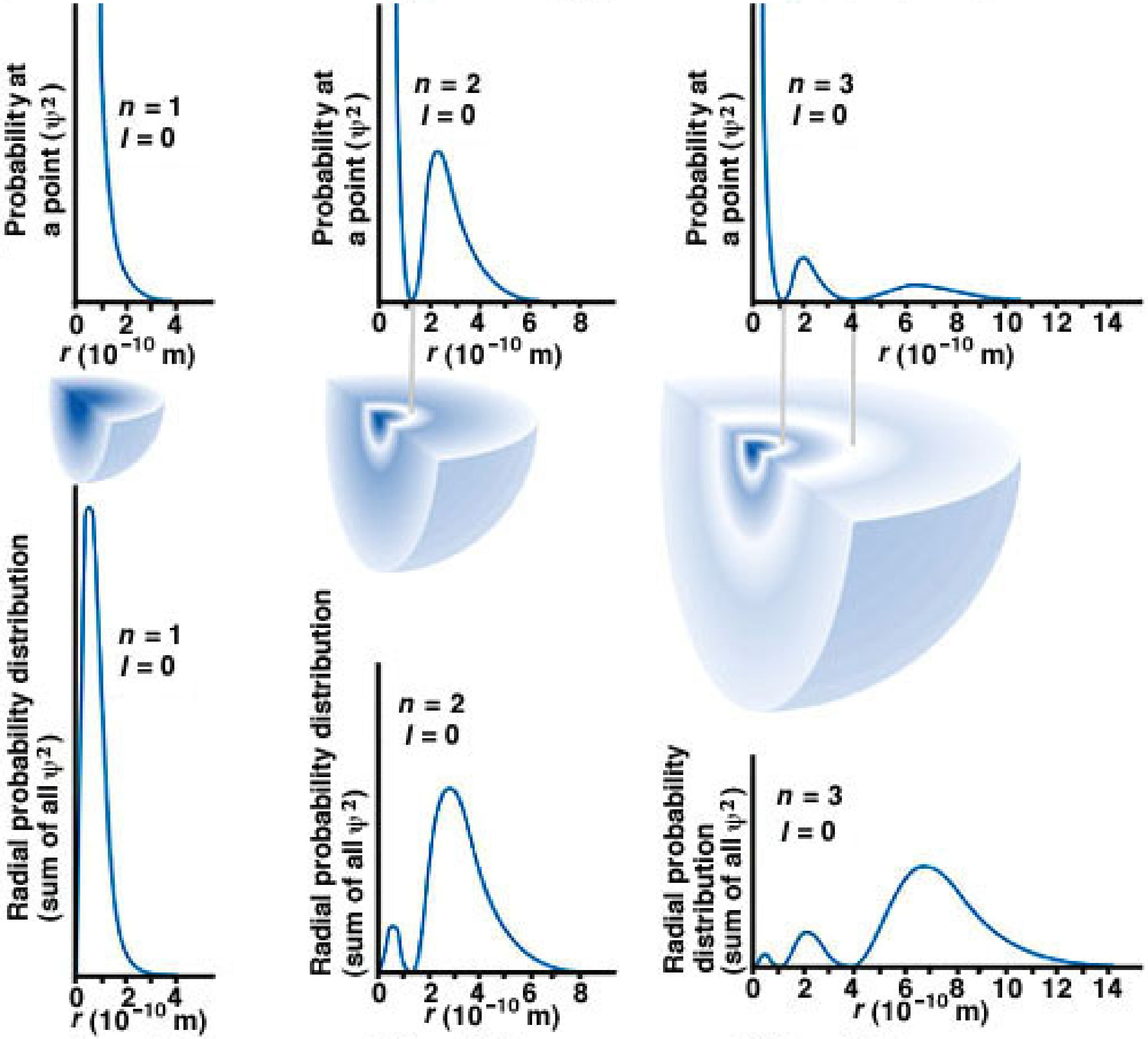
$$D(r)_{1s} = \int_0^{2\pi} \int_0^{\pi} |\psi_{1s}|^2 \, r^2 dr \sin\theta d\theta d\phi = 4\pi r^2 |\psi_{1s}|^2 = \frac{4r^2}{a_0^3} e^{\frac{-2r}{a_0}}$$

To derive the radium of its maximum, we have

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

$$\because \ \mathrm{r} \neq 0, \ \therefore \ 1 - \frac{r}{a_0} = 0 \ \Rightarrow \ \mathrm{r} = \mathrm{a}_0$$

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



A 1*s* orbital **B** 2*s* orbital **C** 3*s* orbital

- 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

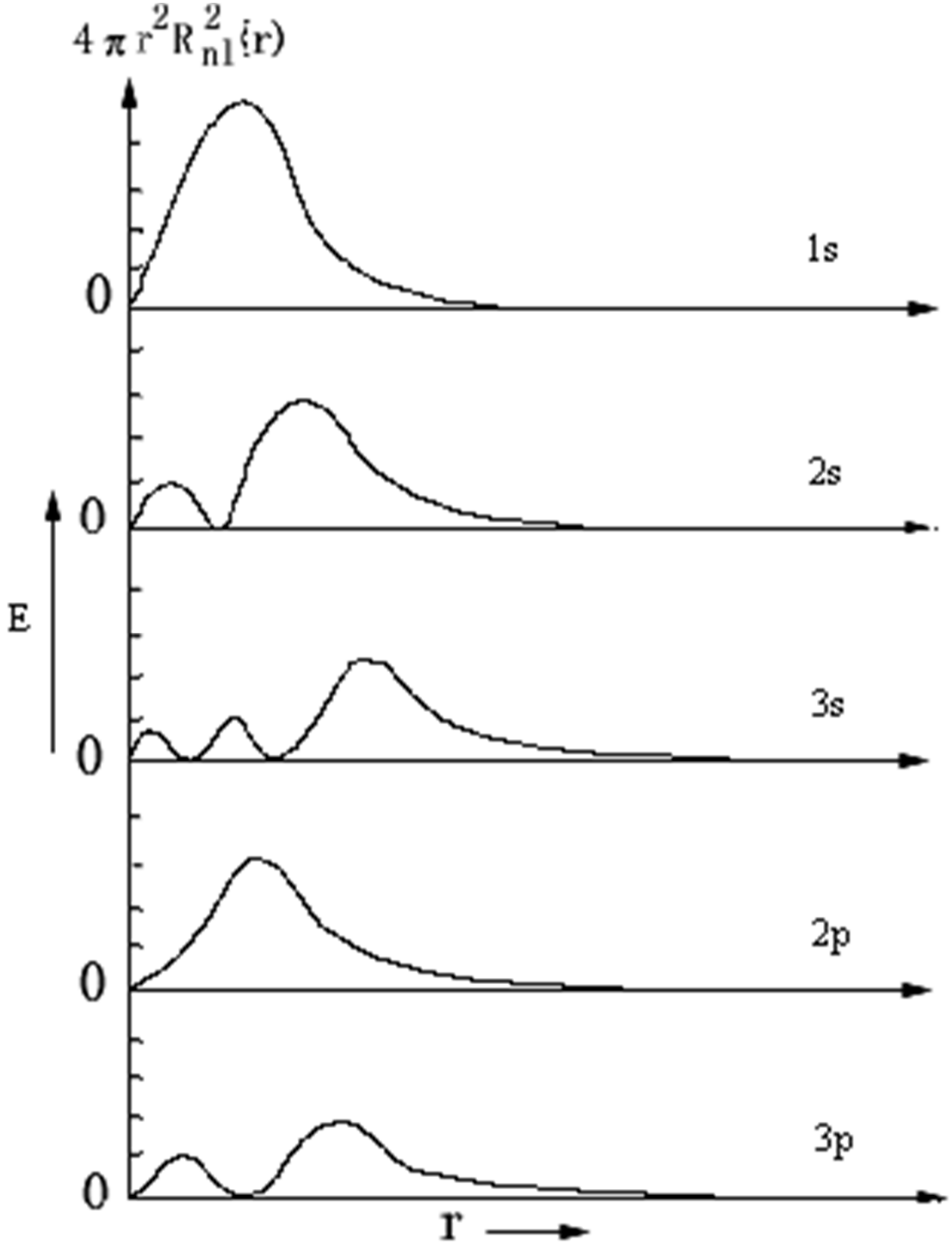
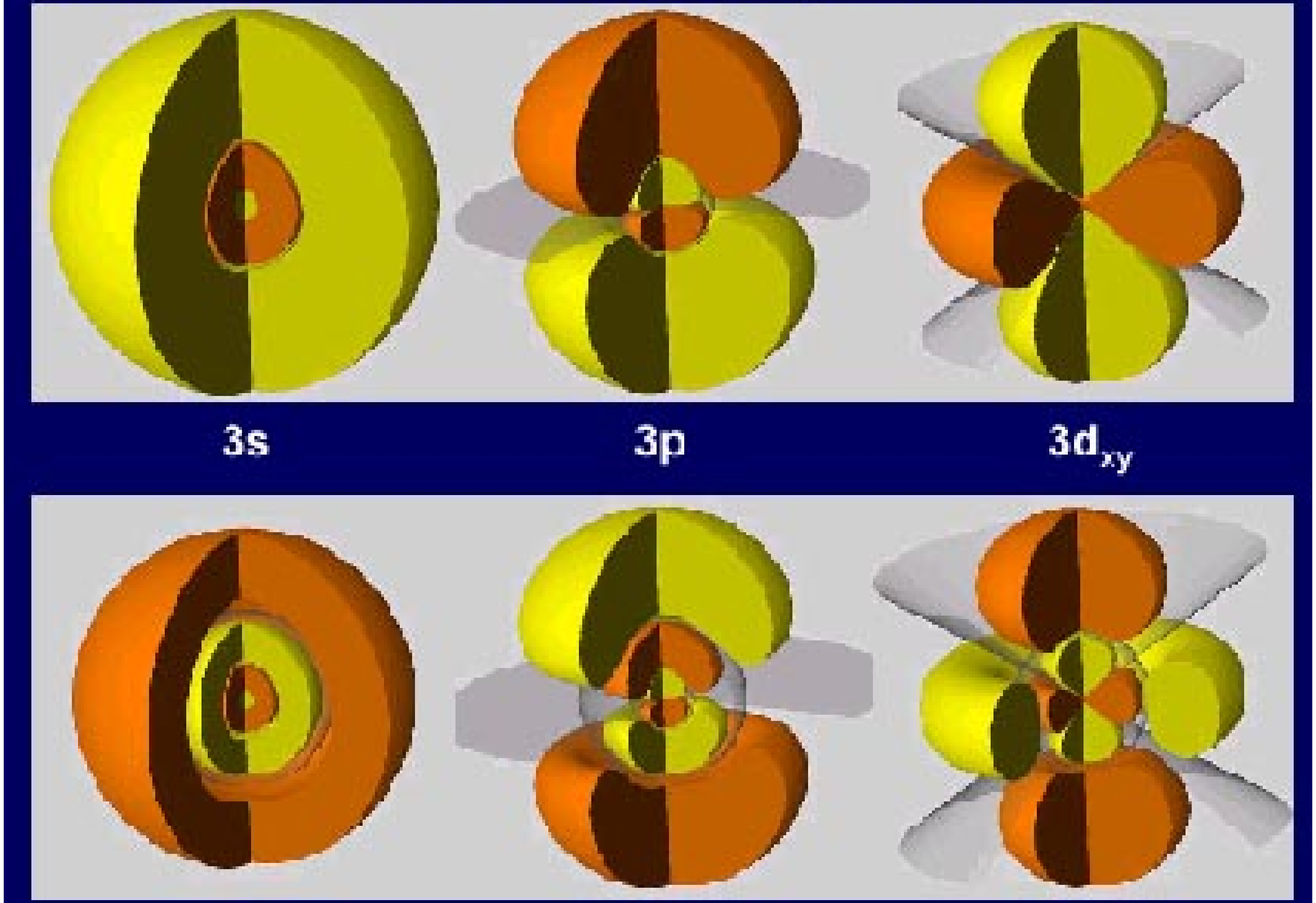


Fig. The radial distribution diagram (D(r) - r)

Nodes (cont)

There are a number of radial nodes equal to n – l –1:



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

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

- **Angular part**

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

It indicates the angular distribution function of an atomic orbital and is the eigenfunction of M^2 and M_z operators.

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

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

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

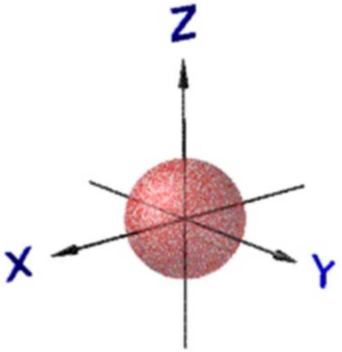
Angular function ($Y_{lm}(\theta,\varphi)$)

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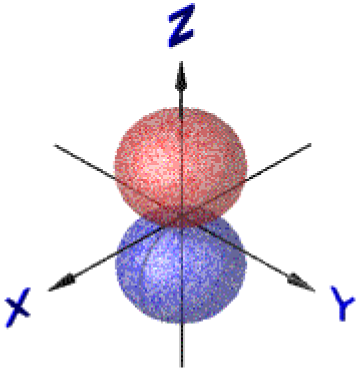
p-Orbital (l=1, 2l+1=3)

Y_{10}

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

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



$Y_{1\pm1}$

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

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

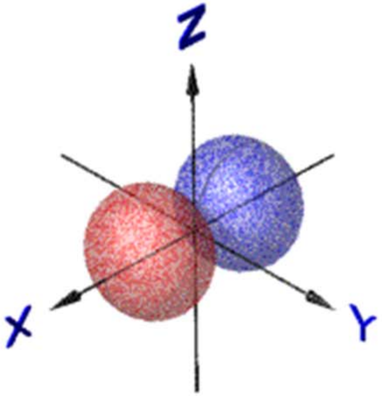
$$p_x=\sqrt{\frac{3}{4\pi}}\sin\theta\cos\varphi$$

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

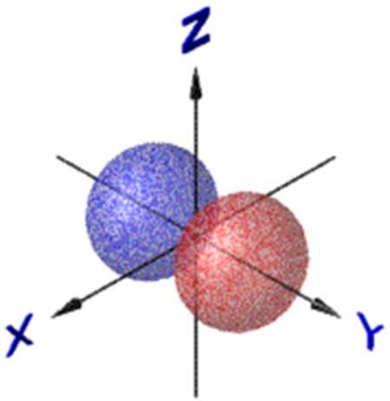
$$\frac{1}{\sqrt{2}}(Y_{1,1}+Y_{1,-1})=\frac{\sqrt{3}}{4\sqrt{\pi}}\sin\theta(e^{i\varphi}+e^{-i\varphi})$$

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

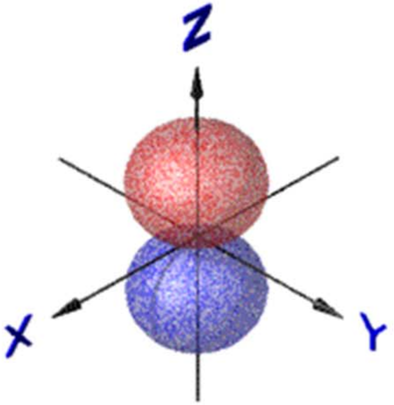
p-Orbital



p_x



p_y



p_z

---

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

Y_{20}

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

$Y_{2\pm1}$

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

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

$Y_{2\pm2}$

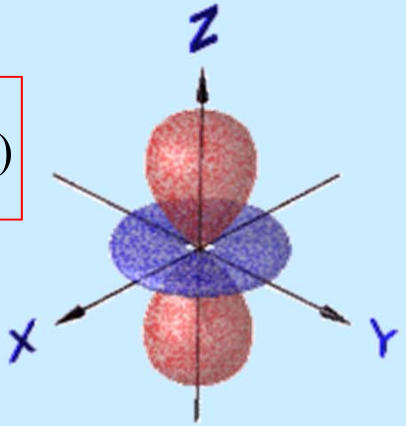
$$d_{x^2-y^2} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta \cos 2\varphi$$

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

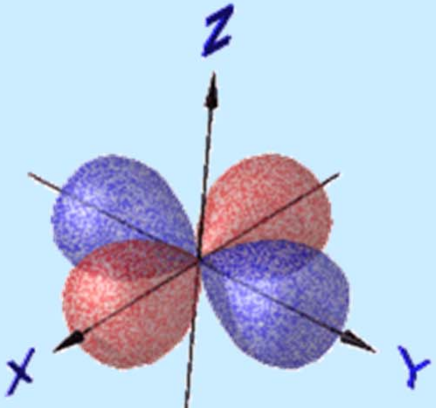
l	m_l	orbital
0	0	s
1	0	p_z
	± 1	p_x
	± 1	p_y
2	0	$d_{2z^2-x^2-y^2} = d_{z^2}$
	± 1	d_{xz}
	± 1	d_{yz}
	± 2	$d_{x^2-y^2}$
	± 2	d_{xy}

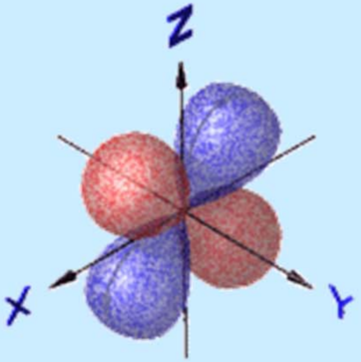
d-Orbital

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

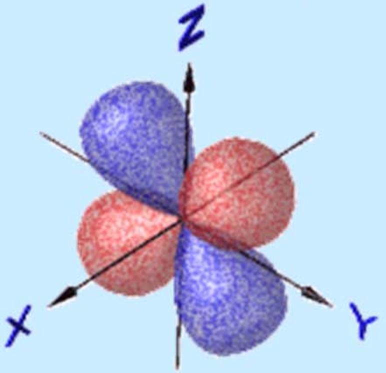


$$d_{x^2-y^2} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos 2\varphi$$



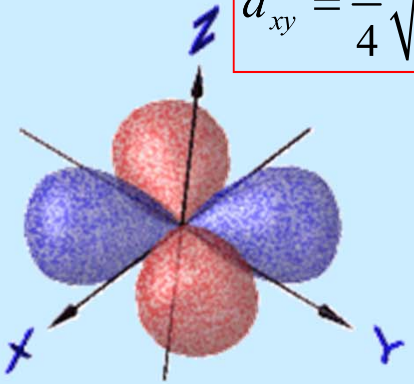


$$d_{xz} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin 2\theta\cos\varphi$$



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

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

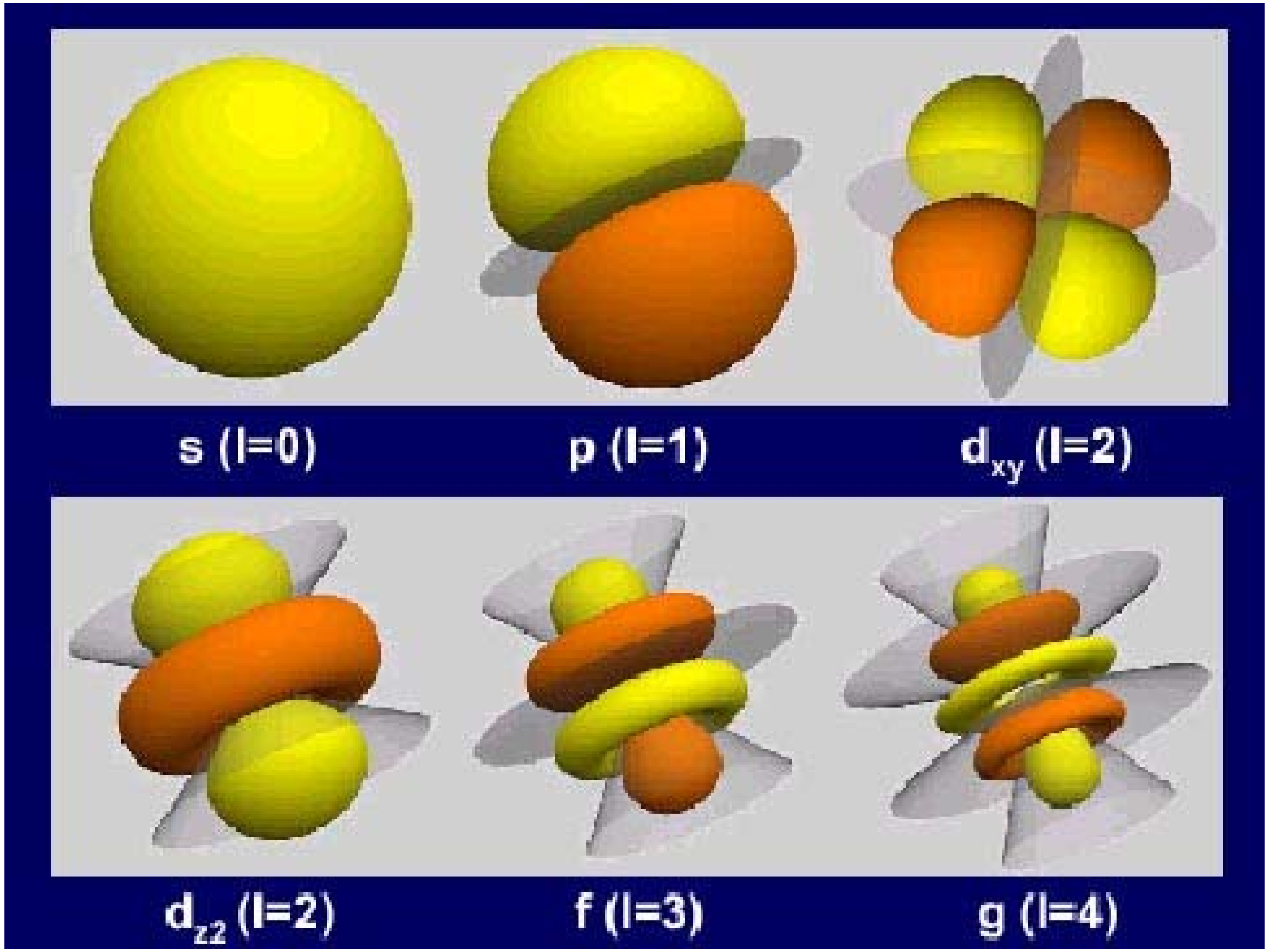


Nodes

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:

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

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

in atom unit (a.u.)

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

$m_e = 1 \quad a.u.$

$e = 1 \quad a.u.$

$a_0 = 1 \quad a.u.$

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

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

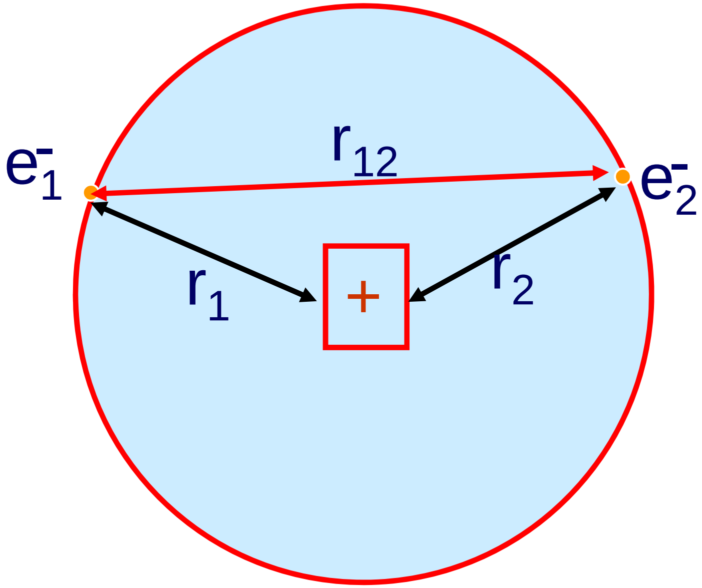
for He atom

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

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

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

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



$$for \quad many-electron \quad atoms$$

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

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

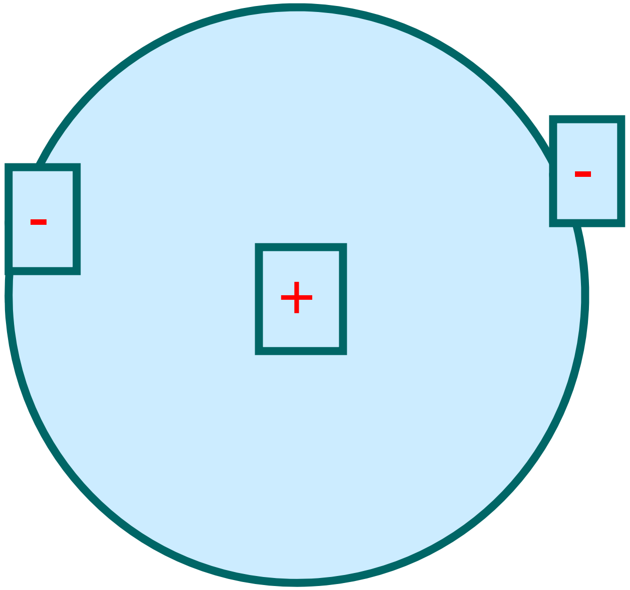
$$\hat{H} = \sum_{i} \left(-\frac{1}{2}\nabla_{i}^{2} - \frac{Z}{r_i}\right) = \sum_{i} \hat{H}_{i}$$

$$\Psi = \psi_{1} \cdot \psi_{2} \cdot \psi_{3} \cdots \psi_{n} = \prod_{i=1} \psi_{i}$$

$$E = E_{1} + E_{2} + E_{3} + \cdots = \sum_{i} E_{i}$$

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

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

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

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

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

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)

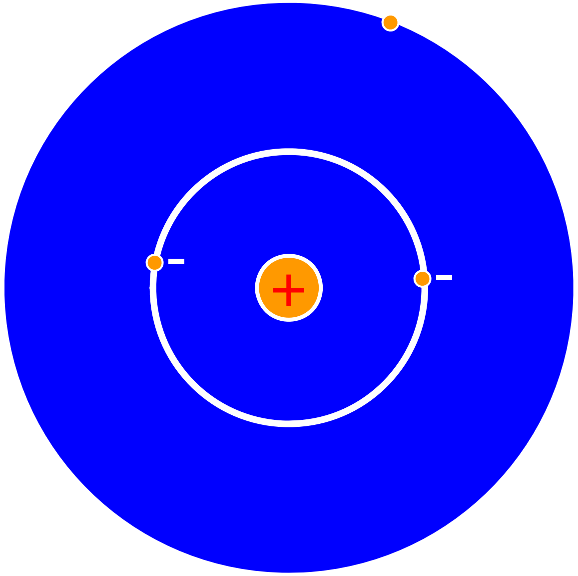
n*=4.0 (when n = 5)

How about n > 5 ???

Lithium , $Z = 3$

Predicted: $E_1 = -30.6$ eV

Actual: $E_1 = -5.4$ eV



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

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

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

$Z^* = 1.26$

$1.26 = 3 - \sigma$

$\sigma = 1.74$

a. Screen (shielding) constant

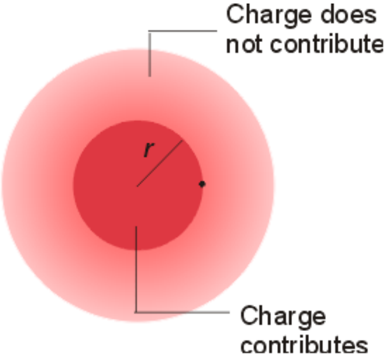
Slater's rules for the prediction of σ for an electron:

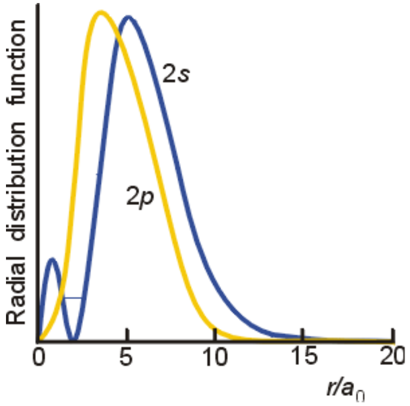
1. Group electron configuration as follows:
   (1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p) etc.
2. Electrons in the right shells (in higher subshells and shells) of an electron do not shield it.
3. For **ns** or **np** valence electrons:
   a) each other electron in the same group contributes **0.35**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

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

Example : O, $Z = 8$

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

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

b) $\sigma = \underbrace{(2 * 0.85)}_{\mathbf{1s}} + \underbrace{(5 * 0.35)}_{\mathbf{2s,\ 2p}} = 3.45$

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

$Z^* = Z - \sigma$

$Z^* = 8 – 3.45 = 4.55$

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

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:

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

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

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

For a 4s electron:

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

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

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).

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

The first ionization energy

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

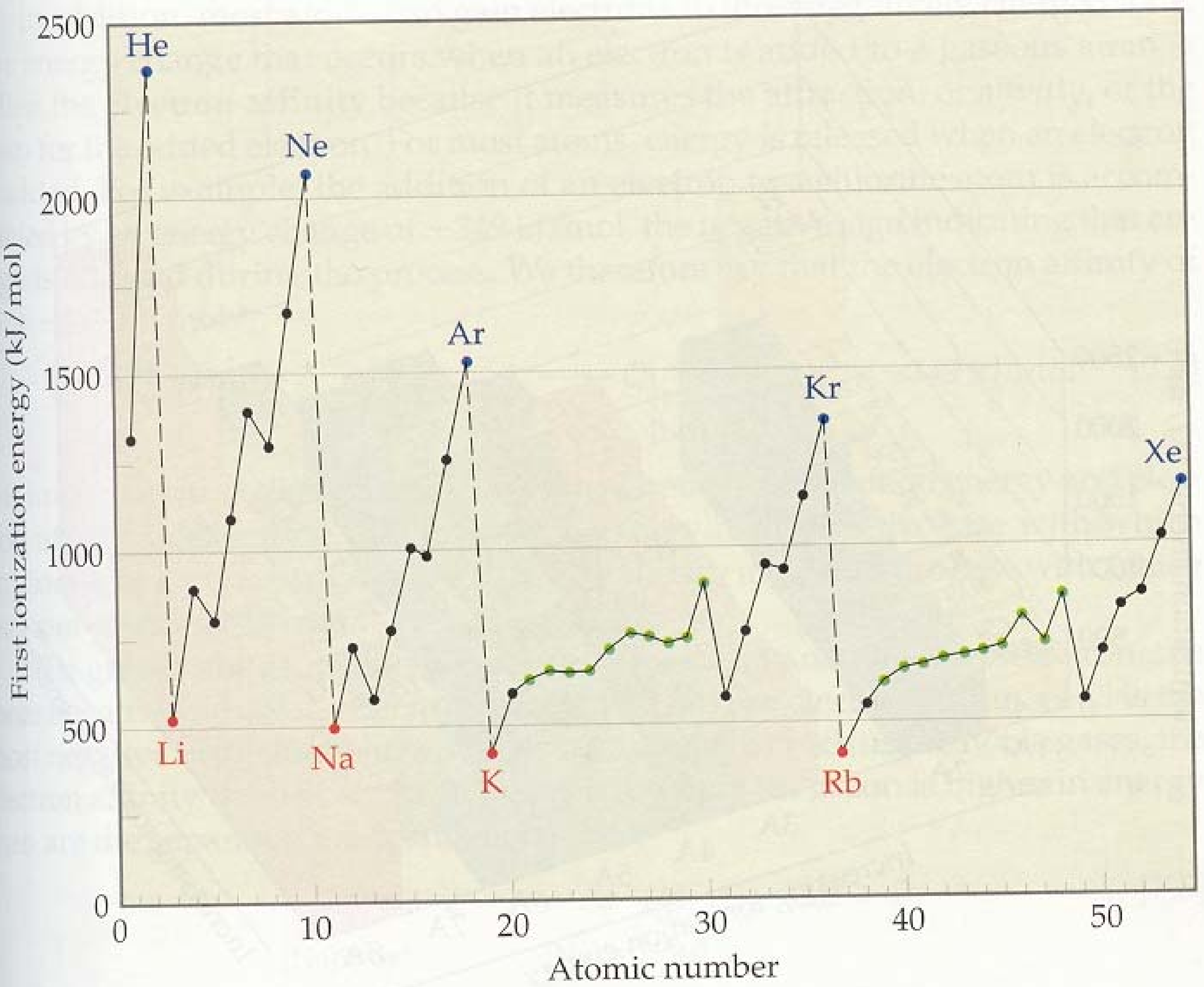
The second ionization energy

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

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			(Inner-shell electrons)		
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

Periodic Trends in Ionization Potentials



II. Estimation of ionization energy

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

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

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

$$E(C^+) = 2E_{1S} + 3E'_{2S,2P}$$

$$E(C) = 2E_{1S} + 4E_{2S,2P}$$

$$for \;\; C^+$$

$$Z^*_{2S,2P} = Z - \sigma = 6 - (2 \times 0.35 + 2 \times 0.85) = 3.60$$

$$for \;\; C$$

$$Z^*_{2S,2P} = Z - \sigma = 6 - (3 \times 0.35 + 2 \times 0.85) = 3.25$$

$$I_1 = 3E'_{2S,2P} - 4E_{2S,2P} = [3 \times (\frac{3.6}{2})^2 - 4 \times (\frac{3.25}{2})^2] \cdot R = 11.44eV$$

$$I_{actual} = 11.22eV$$

Example: Fe^+ for lacking of a K electron, $Z = 26$

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

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

1s: $26 - 0*0.30 = 26.00$

$Z^* = Z - \sigma$

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

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

1s: 26 –0.30 = 25.70

$Z^* = Z - \sigma$

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: $Fe \rightarrow Fe^{+}$

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

	$Fe(Z^*)$	$Fe^{+}(Z^*)$
$(1s)^{2-1}$:	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

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

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

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

$$I_{1K} = \Delta E = E(Fe^{+})-E(Fe)$$
$$= -1965.4+2497.3=531.9\ \text{eV}\ (524.0\ \text{expt})$$

III. Electron Affinity

The electron affinity is the energy change that occurs when an electron is <u>added</u> 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.

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!

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 the 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:

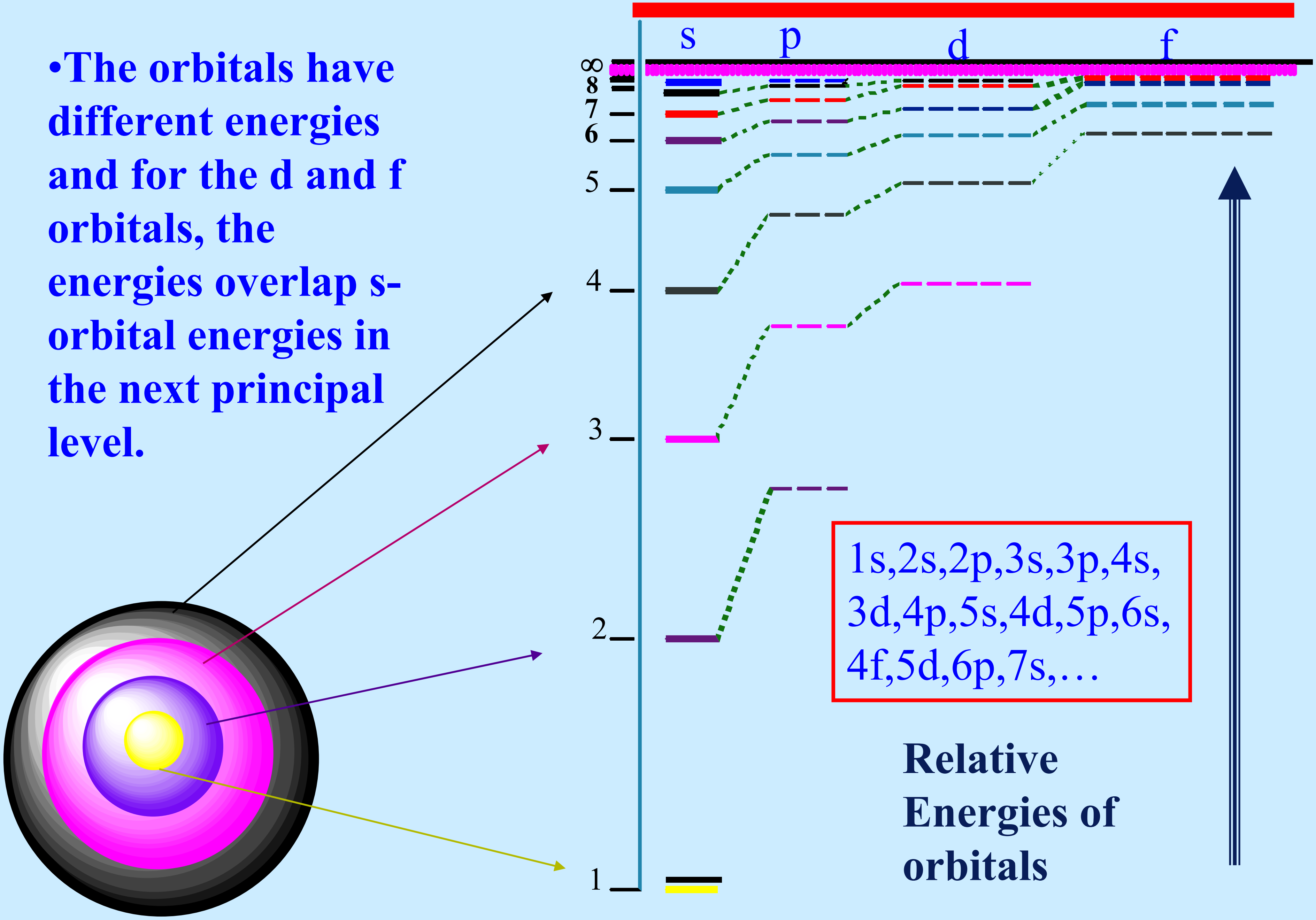
The energy level can be estimated by n+0.7*l*. *(G.X. Xu proposed.)*

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

Relative Energies for Shells and Orbitals

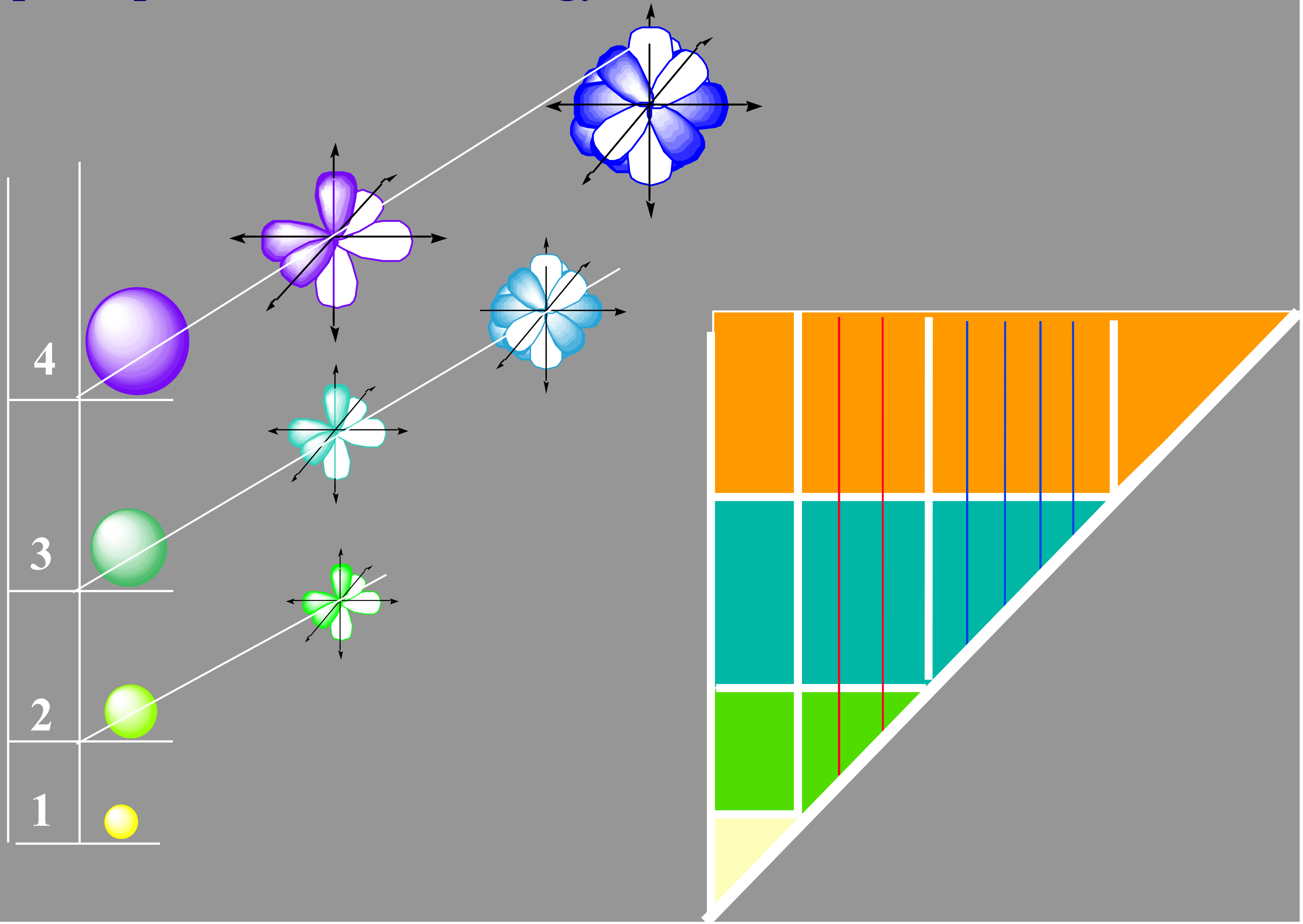
- The orbitals have different energies and for the d and f orbitals, the energies overlap s-orbital energies in the next principal level.



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

Relative Energies of orbitals

The principle of minimum energy



I. The building up principle (for the ground state)

a. **Pauli exclusion principle.**

Every orbital may contain only two electrons of opposite spins.

b. **The principle of minimum energy.**

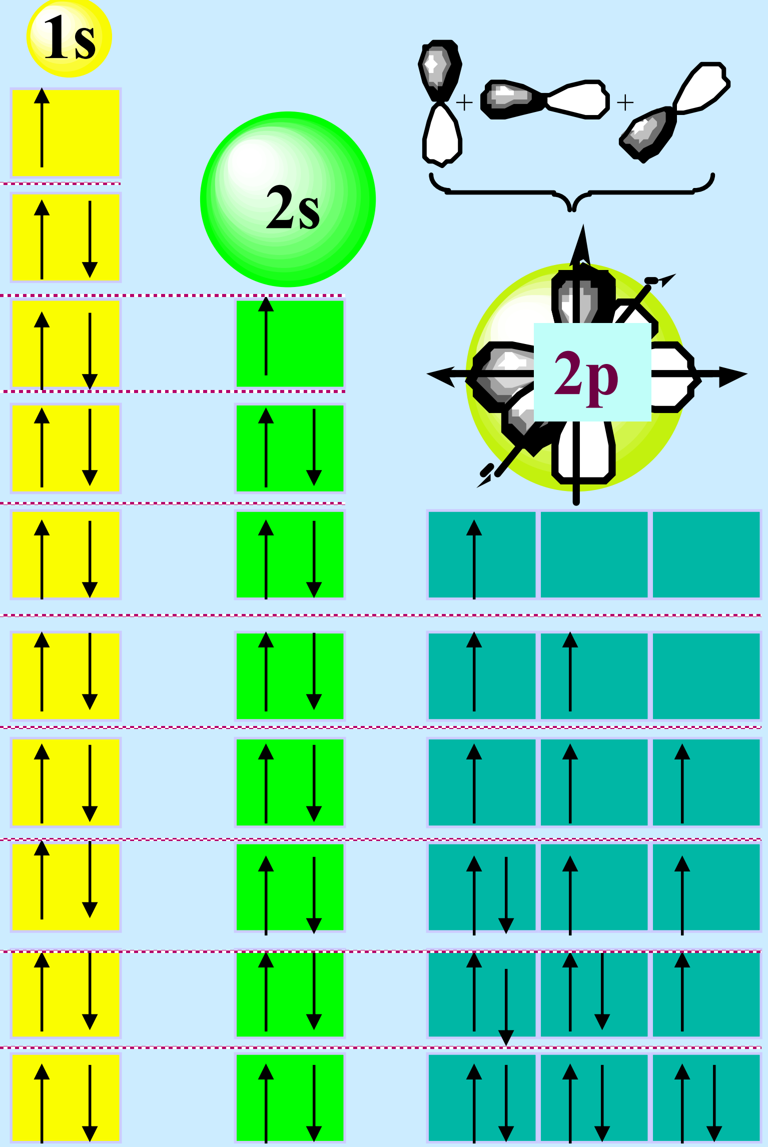
Whilst being compatible with the Pauli principle, electrons occupy the orbital with the lowest energy first.

c. **Hund's rule.**

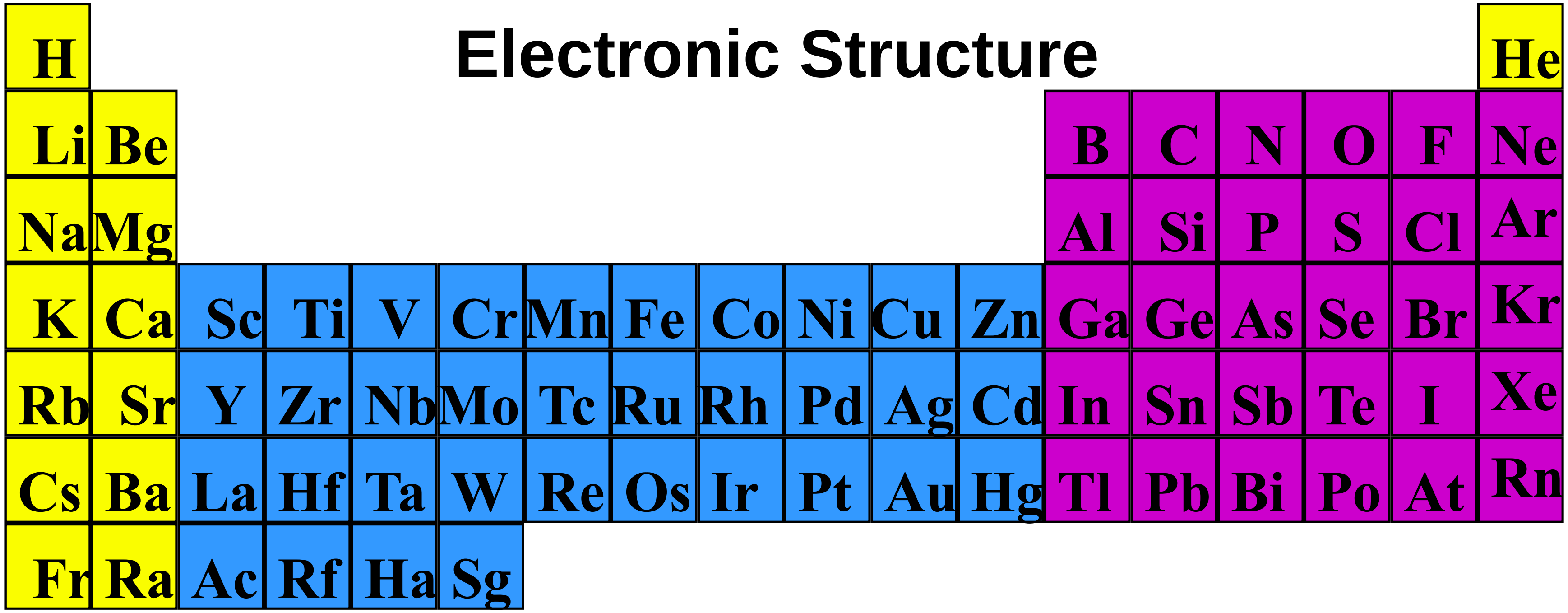
In degenerate energy states, electrons tend to occupy as many degenerate orbitals as possible. (The number of unpaired electrons is a maximum)

II. The electronic configuration (for the ground state)

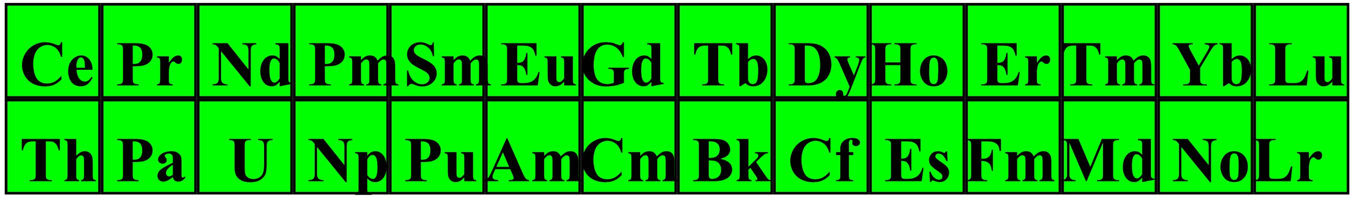
- H = $1s^1$
- He = $1s^2$
- Li = $1s^2\,2s^1$
- Be = $1s^2\,2s^2$
- B = $1s^2\,2s^2\,2p^1$
- C = $1s^2\,2s^2\,2p^2$
- N = $1s^2\,2s^2\,2p^3$
- O = $1s^2\,2s^2\,2p^4$
- F = $1s^2\,2s^2\,2p^5$
- Ne = $1s^2\,2s^2\,2p^6$



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

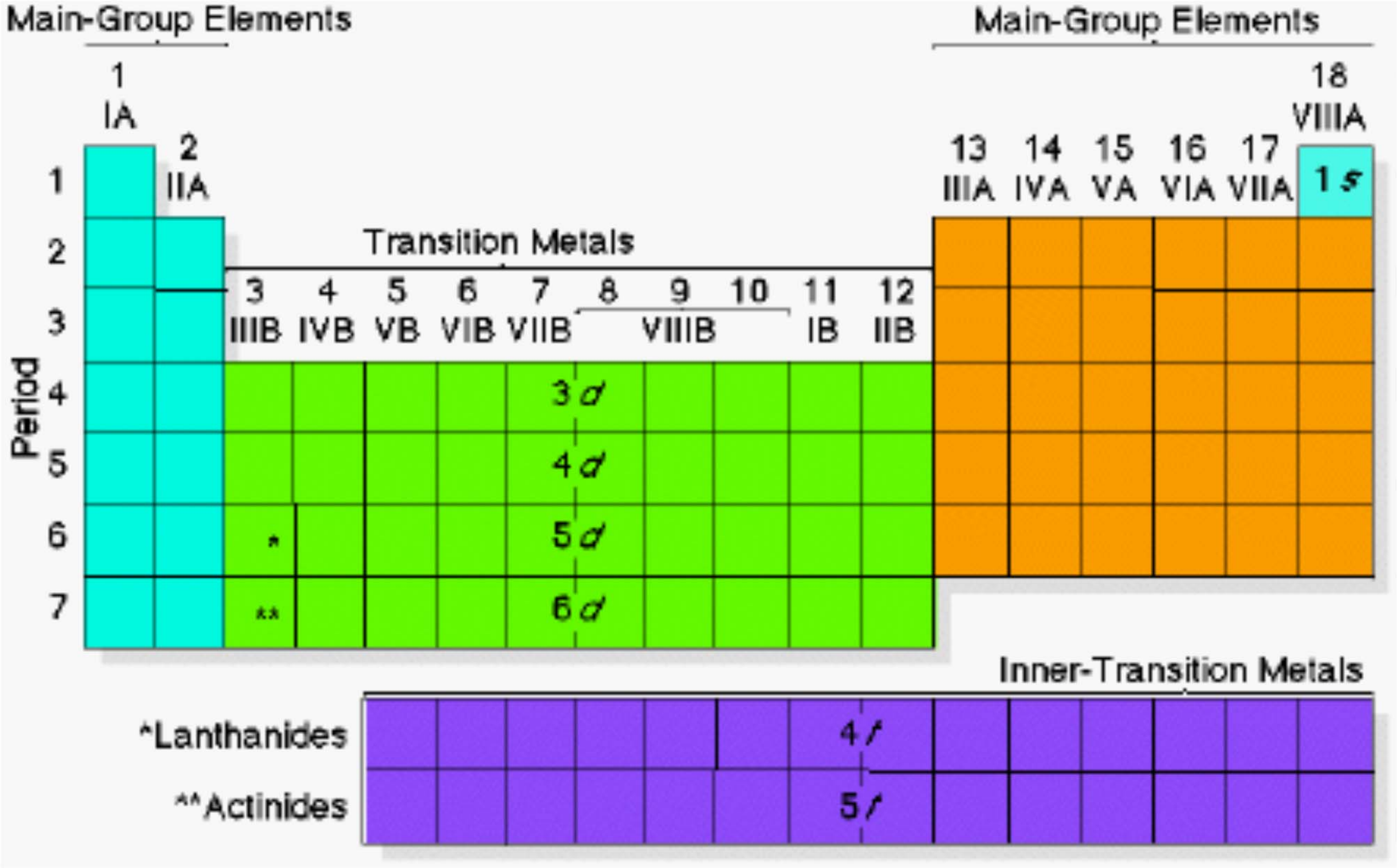
🟨 “ s” Orbitals

🟪 “ p” Orbitals

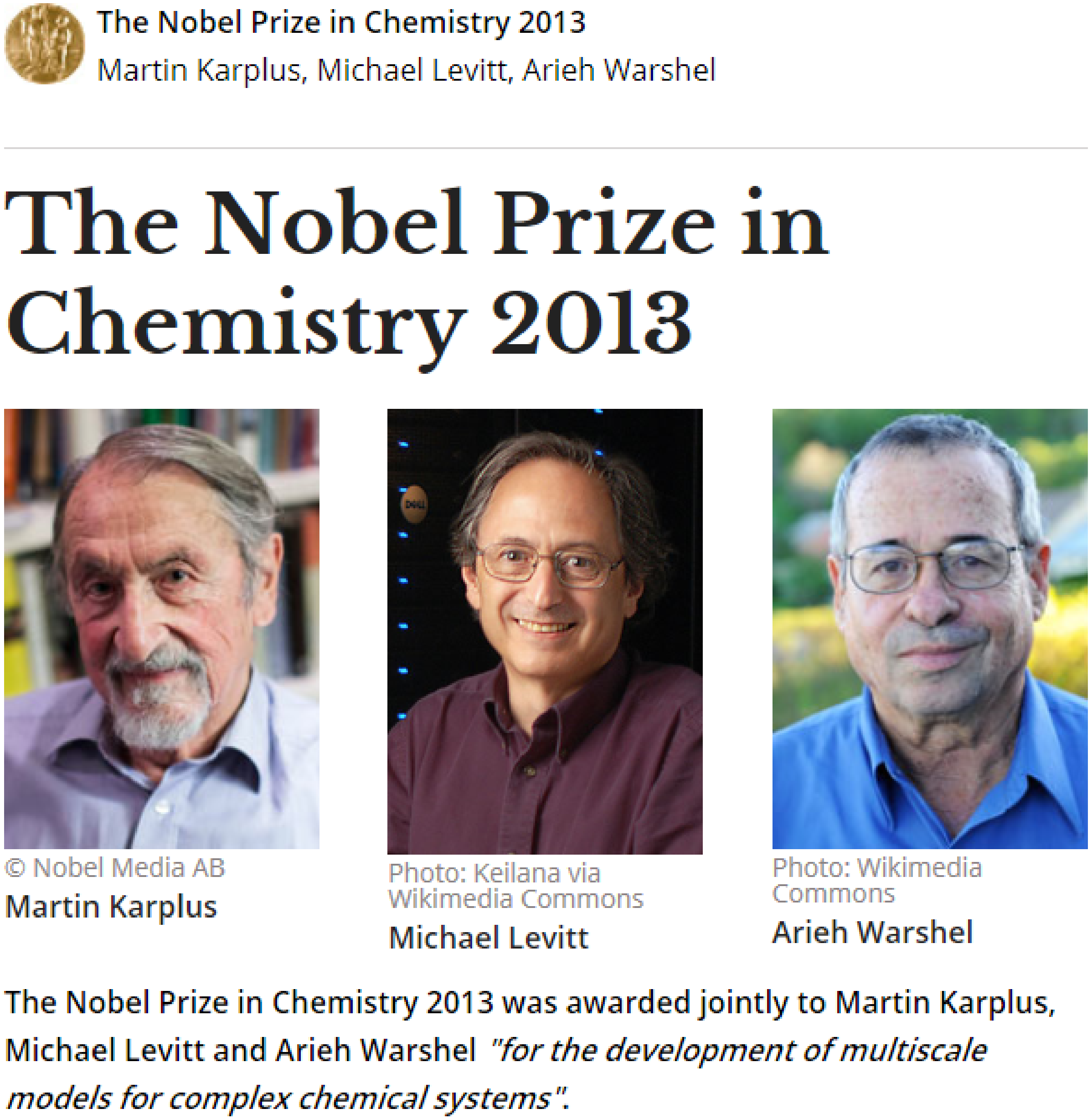
🟦 “ d” Orbitals

🟩 “ f ” Orbitals

Electron Configuration using the Periodic Table



2.5 Atomic spectra and spectral term



The Nobel Prize in Chemistry 2013
Martin Karplus, Michael Levitt, Arieh Warshel

The Nobel Prize in Chemistry 2013

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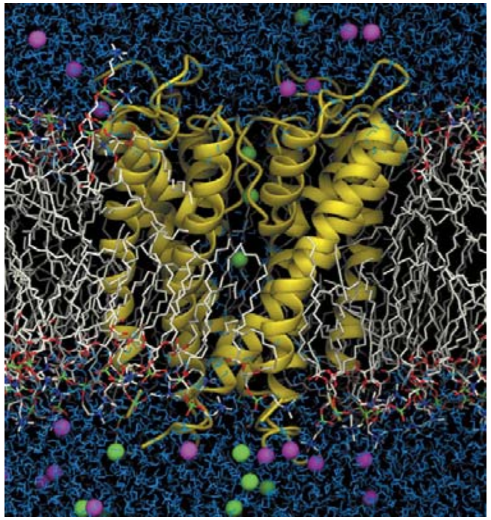
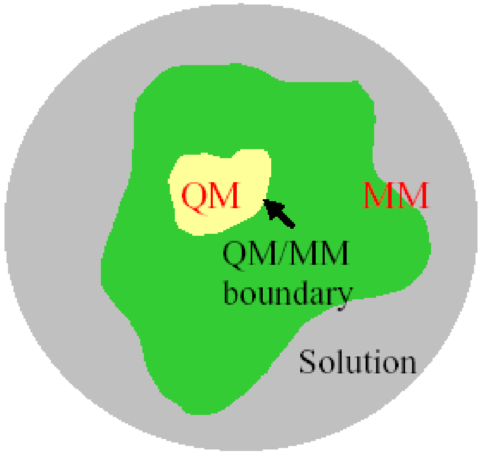
Martin Karplus

Photo: Keilana via Wikimedia Commons
Michael Levitt

Photo: Wikimedia Commons
Arieh Warshel

The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus, Michael Levitt and Arieh Warshel *"for the development of multiscale models for complex chemical systems".*





2013年诺贝尔化学奖获奖理由：多尺度模型

表彰他们发展了复杂化学体系中的多尺度模型，该研究把计算机模型应用于化学研究，开拓了崭新研究领域。

化学家们常常会利用塑料短杆和小球来表示分子结构。今天，化学家们早已开始使用电脑来展示各种模型。在上世纪70年代，**Martin Karplus, Michael Levitt** 和**Arieh Warshel**的工作为这项强大工具的应用奠定了基础，帮助我们加深对化学过程的理解与预测。时至今日，化学领域所取得的大部分重要进展都离不开先进计算机模型的帮助。

化学反应极为迅速，在数百万分一秒间，电子已经完成从一个原子核向另一个原子核的迁移。经典化学已经难以跟上这样的步伐，要想借助实验方法去描绘化学过程中的每一个小步骤几乎已经是不可能的任务。借助本次化学奖所奖励的科学家们发展的方法，科学家们得以在计算机的帮助下揭示一些精妙过程的细节，如废气的催化净化，或是植物绿叶中发生的光合作用过程。

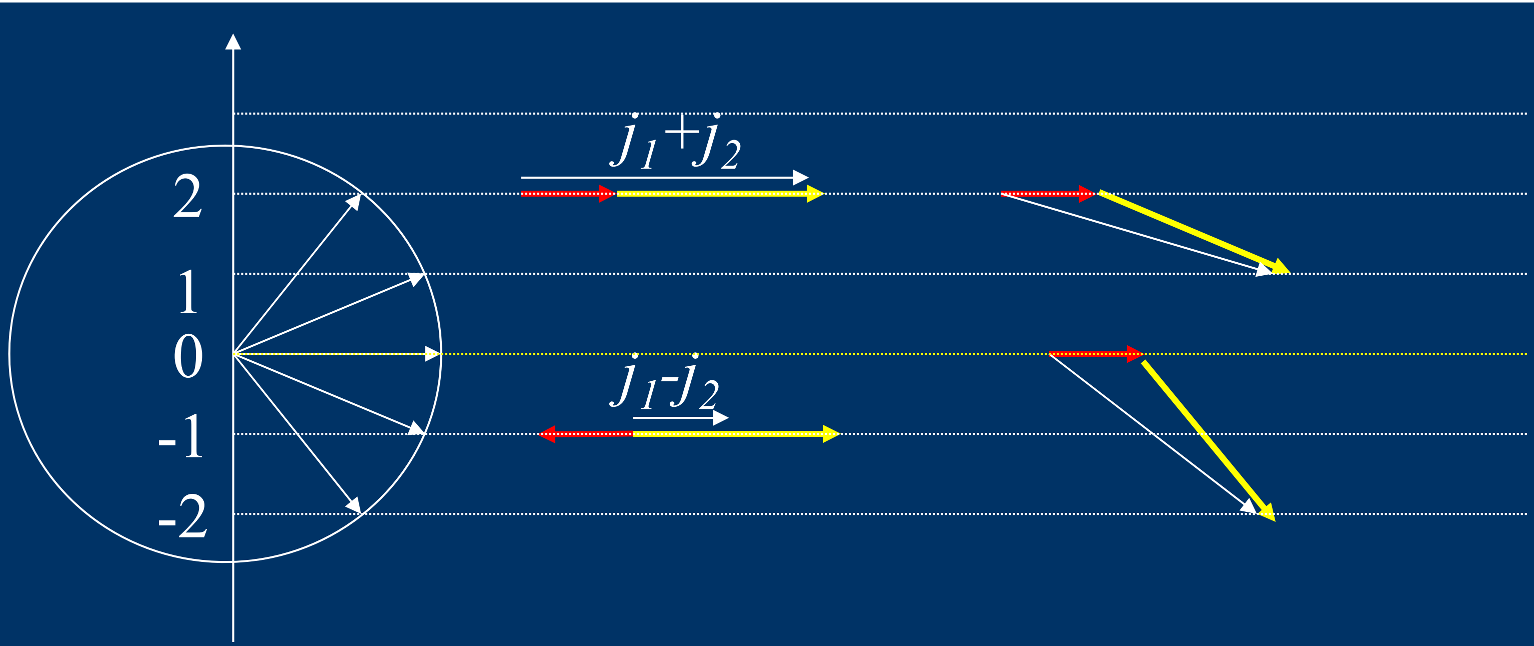
今年的诺贝尔化学奖成果简单来说便是综合了这两个不同领域方法的精华，设计出了基于经典物理与量子物理学方法两大领域的方法。举例而言，为了模拟药物如何在人体内与其靶标蛋白相结合，计算机会利用量子物理方法计算靶标蛋白质原子与药物发生反应的过程。而这一大型蛋白质的其余部分则会被借助基于经典物理学的方法进行模拟。

2.5.1 Total Electronic Orbital and Spin Angular Momenta

a. Addition of two angular momenta:

The coupling 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:

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



Example: **Find the possible values of the total-angular-momentum quantum number resulting from the addition of two angular momenta with the quantum numbers $j_1 = 2$ 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 momentum of the individual electron:

$$\vec{L} = \sum_i \vec{l}_i; \quad M_L = \sum_i m_i$$

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 $1s^2 2s^2 2p3d$.

Solution:

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

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

2p electrons: $m_s = \frac{1}{2}$ ***3d electrons:*** $m_s = \frac{1}{2}$

Addition of two angular momenta rule

$S = 1, 0$

D. The total angular momentum

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

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

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

$(np)^1\,(nd)^1$

$l_1=1,\ l_2=2$ $\quad$ $L=\ 3, 2, 1$

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

$^3F,\ ^1F,\ ^3D,\ ^1D,\ ^3P,\ ^1P$

c. Equivalent electrons.

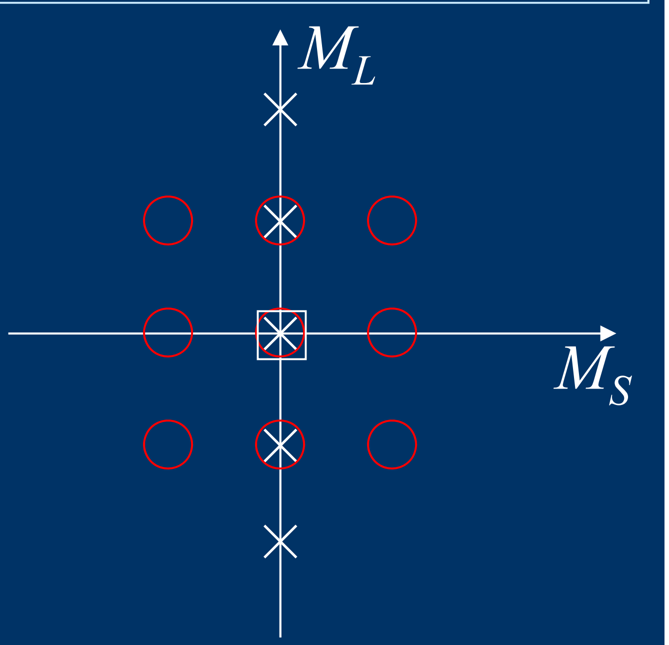
$1s^22s^22p^2$ → np^2 (two electrons in the same subshell)

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:

$$C_6^2 = 15$$

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



^1D, ^3P, ^1S

5 9 1 -> 15

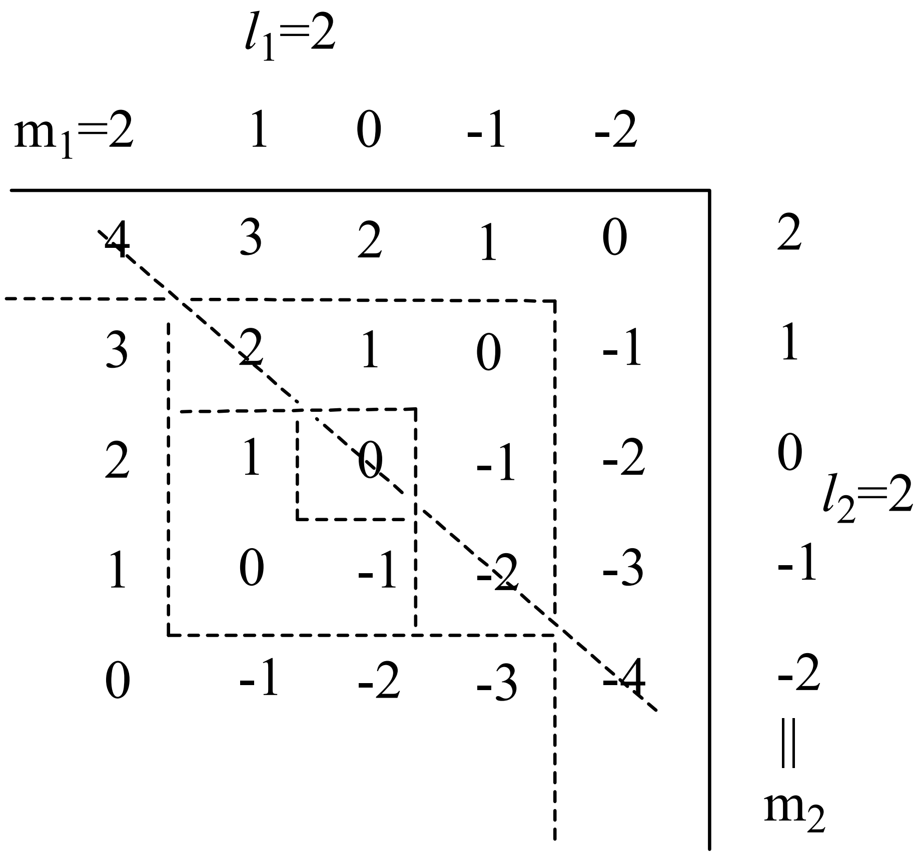
- **The terms arising from a subshell containing N electrons are the same as the terms for a subshell that is N electrons short of being full.**

Term : p^0 === p^6

p^1 === p^5

p^2 === p^4

$(nd)^2$



$l_1=2$

$m_1=2$	1	0	-1	-2	m_2
4	3	2	1	0	2
3	2	1	0	-1	1
2	1	0	-1	-2	0
1	0	-1	-2	-3	-1
0	-1	-2	-3	-4	-2

$l_2=2$

S=1

Take off-diagonal numbers:

3, 2, 1, 0, -1, -2, -3 ^{3}**F**
1, 0, -1 ^{3}**P**

S=0

Take diagonal and off-diagonal numbers:

4, 3, 2, 1, 0, -1, -2, -3, -4 ^{1}**G**
2, 1, 0, -1, -2 ^{1}**D**
0 ^{1}**S**

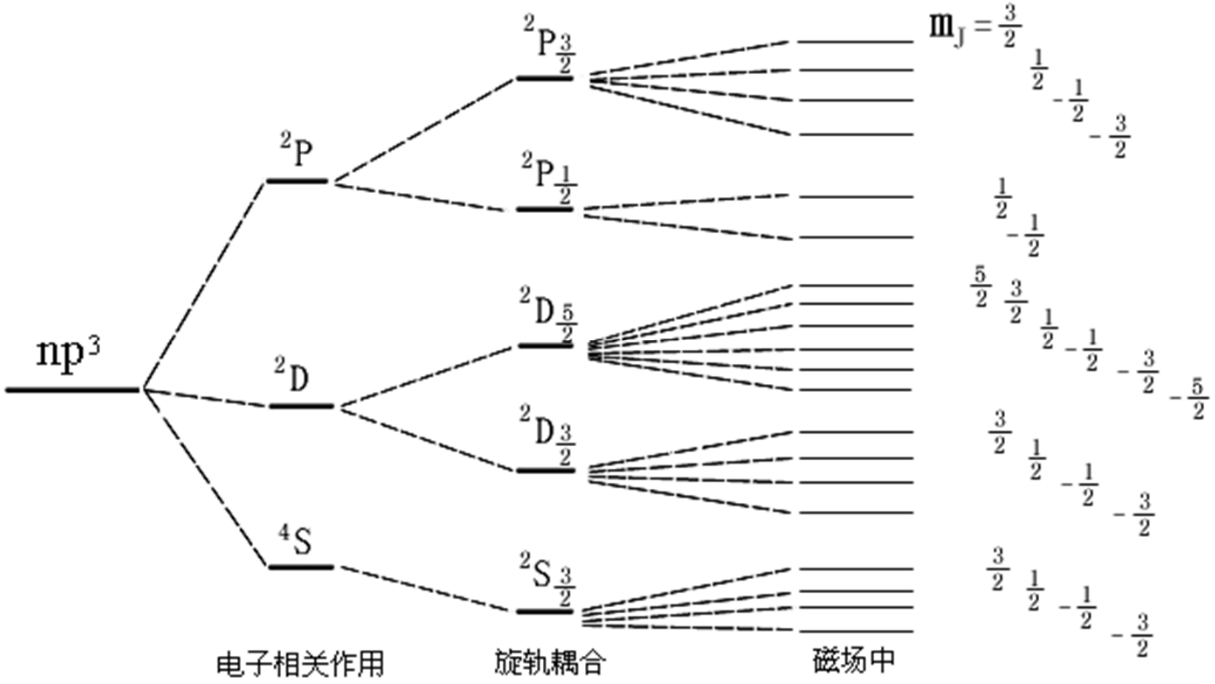
d. Energy level of microstates: (terms).

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, …, |L-S|

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

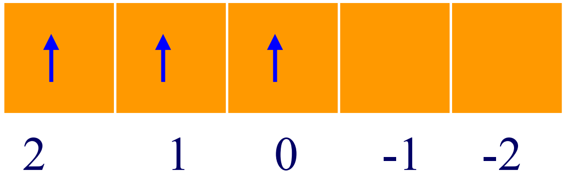
$^4S \rightarrow {}^4S_{3/2}$, $^2D \rightarrow {}^2D_{5/2}$, $^2D_{3/2}$,

f. The ground state of terms

Hund’s Rule:

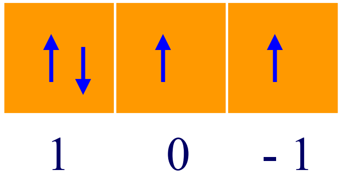
3. For the same **L** and **S** values, when the number of electrons is half-filled or less, the term with the smallest J lies lowest; whereas when the number of electrons is more than half-filled, the term with the largest J lies lowest.

nd^3



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

np^4



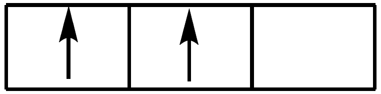
L=1, S=1 $\rightarrow {}^3P_2$

The ground-state term

Refer to Page 55

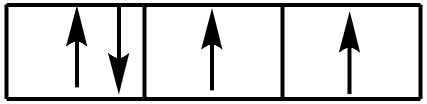
$(np)^2$ $^3P_0$

m_l 1 0 -1



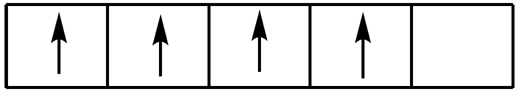
$(np)^4$ $^3P_2$

m_l 1 0 -1



$(nd)^4$ $^5D_0$

m_l 2 1 0 -1 -2



Hund's Rules

less than half-filled:

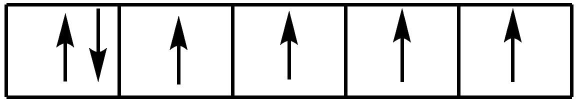
Large S;Large L;Small J

more than half-filled:

Large S;Large L;Large J

$(nd)^6$ $^5D_4$

m_l 2 1 0 -1 -2



$s^1s^1s^1$

s^1s^1： ^3S， ^1S

s^1： $L=0$； $S=1/2$

$\{^3S$： $L=0$； $S=1$； s^1： $L=0$； $S=1/2\}\rightarrow$

$\rightarrow\{L=0$； $S=3/2$， $1/2\}\rightarrow\{^4S\rightarrow{}^4S_{3/2}$, $^2S\rightarrow{}^2S_{1/2}\}$

$\{^1S$： $L=0$； $S=0$； s^1： $L=0$； $S=1/2\}\rightarrow$

$\rightarrow\{L=0$； $S=1/2\}\rightarrow\{^2S\rightarrow{}^2S_{1/2}\}$

$p^1p^1p^1$

p^1p^1： ^3D， ^1D， ^3P， ^1P， ^3S， ^1S

p^1： L=1； S=1/2

{^3D： L=2， S=1； p^1： L=1， S=1/2}→{L=3， 2， 1； S=3/2,1/2}→

→{^4F， ^2F； ^4D， ^2D； ^4P， ^2P}

{^1D： L=2， S=0； p^1： L=1， S=1/2}→{L=3， 2， 1； S=1/2}→

→{^2F； ^2D； ^2P}

{^3P： L=1， S=1； p^1： L=1， S=1/2}→{L=2， 1， 0； S=3/2,1/2}→

→{^4D， ^2D； ^4P， ^2P； ^4S， ^2S； }

{^1P： L=1， S=0； p^1： L=1， S=1/2}→{L=2， 1， 0； S=1/2}→

→{^2D； ^2P； ^2S }

{^3S： L=0， S=1； p^1： L=1， S=1/2}→{L=1； S=3/2， 1/2}→

→{ ^4D； ^2P}

{^1S： L=0， S=0； p^1： L=1， S=1/2}→{L=1； S=1/2}→{^2P}

$p^1p^1p^1$ {$^4F(1)$, $^4D(2)$,$^4P(3)$, $^4S(1)$, $^2F(2)$,$^2D(4)$,$^2P(6)$, $^2S(2)$ }

$p^1p^1d^1$

p^1p^1：^{3}D，^{1}D，^{3}P，^{1}P，^{3}S，^{1}S

d^1：L=2；S=1/2

{^{3}D：L=2，S=1；d^1：L=2，S=1/2}→{L=4, 3，2，1, 0 ; S=3/2，1/2}→{^{4}G ,^{4}F, ^{4}D,^{4}P, ^{4}S; ^{2}G ,^{2}F ,^{2}D,^{2}P,^{2}S }

{^{1}D：L=2，S=0；d^1：L=2，S=1/2}→{L=4, 3，2，1, 0 ;S=1/2}→ →{^{2}G ,^{2}F ,^{2}D,^{2}P,^{2}S }

{^{3}P：L=1，S=1；d^1：L=2，S=1/2}→{L=3, 2，1；S=3/2，1/2}→ →{^{4}F, ^{4}D,^{4}P ; ^{2}F ,^{2}D, ^{2}P }

{^{1}P：L=1，S=0；d^1：L=2，S=1/2}→{L=3, 2, 1；S=1/2}→ →{^{2}F , ^{2}D, ^{2}P}

{^{3}S：L=0，S=1；d^1：L=2，S=1/2}→{L=2；S=3/2，1/2}→ →{ ^{4}D；^{2}D}

{^{1}S：L=0，S=0；d^1：L=2，S=1/2}→{L=2；S=1/2}→{^{2}D}

$p^1p^1d^1$ ^{4}G ,^{4}F(2), ^{4}D(3),^{4}P(2), ^{4}S;^{2}G(2) ,^{2}F(4) ,^{2}D(6),^{2}P(4),^{2}S(2)

$p^1d^1d^1$

p^1d^1： $^3F,^3D,^3P,\ ^1F,^1D,^1P$

d^1： L=2； S=1/2

{^3F： L=3， S=1； d^1： L=2， S=1/2}→{L=5, 4, 3， 2， 1, 0 ; S=3/2， 1/2}→{$^4H,^4G\ ,^4F,\ ^4D,^4P$; $^2H\ ,^2G\ ,^2F\ ,^2D,^2P$}

{^3D： L=2， S=1； d^1： L=2， S=1/2}→{L=4, 3， 2， 1, 0 ; S=3/2， 1/2}→{$^4G\ ,^4F,\ ^4D,^4P,\ ^4S$; $^2G\ ,^2F\ ,^2D,^2P,^2S$ }

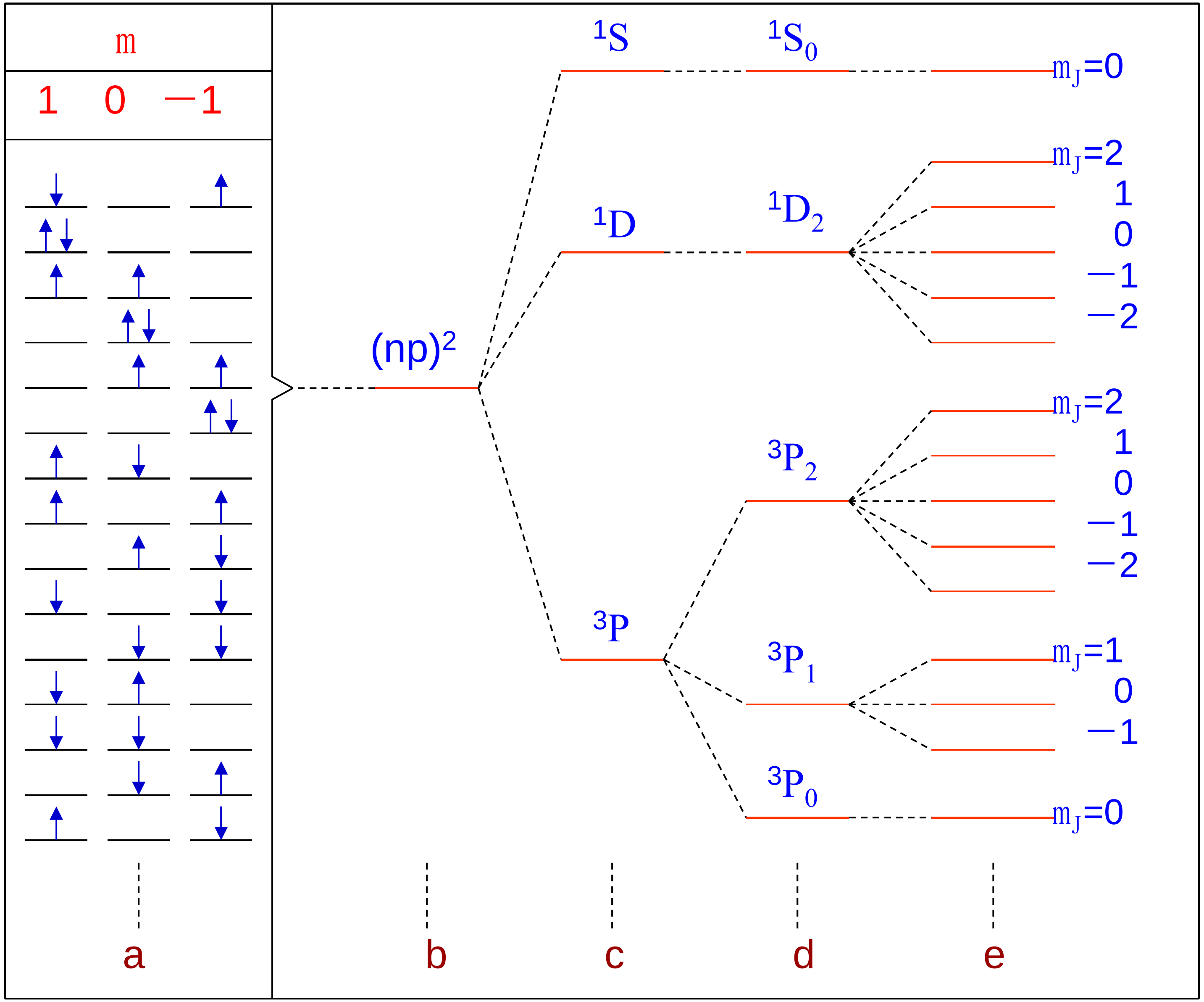
{^3P： L=1， S=1； d^1： L=2， S=1/2}→{L=3, 2， 1； S=3/2， 1/2}→ →{$^4F,\ ^4D,^4P$; $^2F\ ,^2D,\ ^2P$ }

{^1F： L=3， S=0； d^1： L=2， S=1/2}→{L=5,4,3,2,1; S=1/2} → →{$^2H\ ,^2G\ ,^2F\ ,^2D,^2P$}

{^1D： L=2， S=0； d^1： L=2， S=1/2}→{L=4,3,2,1, 0 ;S=1/2} → →{$^2G\ ,^2F\ ,^2D,^2P,^2S$ }

{^1P： L=1， S=0； d^1： L=2， S=1/2}→{L=3, 2, 1； S=1/2}→ →{^2F , ^2D, ^2P}

**$p^1d^1d^1$ {$^4H(1)\ ,^4G(2)\ ,^4F(3),\ ^4D(3),^4P(3),\ ^4S(1)$;
$^2H(2)\ ,^2G(4),^2F(6),^2D(6),^2P(6),^2S(2)$ }**


m
1 0 −1
$(np)^2$
^1S
^1D
^3P
$^1S_0$
$^1D_2$
$^3P_2$
$^3P_1$
$^3P_0$
$m_J=0$
$m_J=2$
1
0
−1
−2
$m_J=2$
1
0
−1
−2
$m_J=1$
0
−1
$m_J=0$
a
b
c
d
e