化學鍵

【本著作除另有註明，所有內容皆採用 創用CC 姓名標示-非商業使用-相 同方式分享 3.0 台灣 授權條款釋出】

Chemical Bonding

Part 1：Properties of Atom

☆ Schrödinger's Equation

☆ Description of Eigenfunctions

☆ Orbital Energy (Eigenvalues)

Part 2：Molecular orbitals (MO) from Atomic orbitals (AO)

☆ Linear Combination of Atomic Orbitals (LCAO)

☆ Dinuclear Molecules -- Homo-nuclear：H_2 ; A_2

-- Hetero-nuclear：AH ; AB

☆ Poly-nuclear：H_n ; AH_n ; n = 2, 3, 4

-- Localized / delocalized bond

-- Delocalized π bonding

-- Symmetry in bonding

-- introduction to point groups

Mid term exam

Part 3：Chemical Bonding of 3d Transition Metal Complexes, ML_n

☆ Application of symm in chemical bond; AX_n n=2-6

☆ Lewis Structure ; VSEPR ; Hybridization

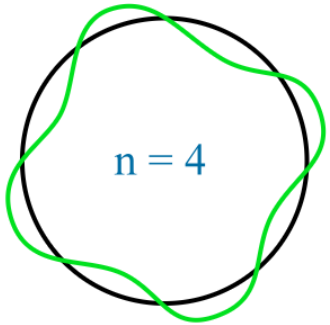
☆ Crystal Field Theory (CFT)

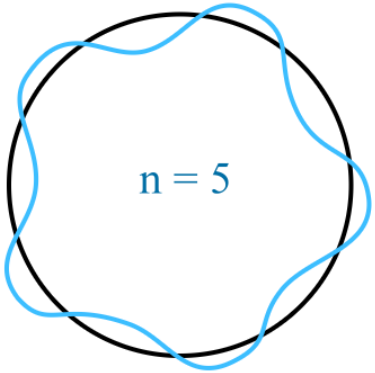
☆ Ligand Field Theory (LFT)

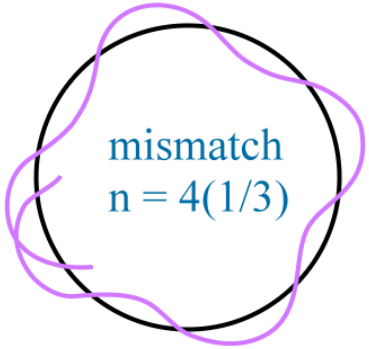
Reference:

1. "*An Introduction to Molecular Orbitals*" Oxford, Yves Jean; Francois Volatron; Jeremy Burdett
2. "*Chemical Applications of Group Theory*" Wiley, F. Albert Cotton
3. "*Molecular Symmetry and Group Theory*" 眾光出版社, Alan Vincent

Bohr Theory







Standing wave

$2\pi r = n\lambda$ (radius r)

$\lambda = h / mv$ (de Broglie's eq.)

$2\pi r = nh / mv$

Bohr assumption

$mvr = nh/2\pi$ (Quantized angular momentum)

$mv^2/r = Ze^2/r^2$ (balance of force)

Bohr orbital : $E = -K/n^2$; $R = n^2 a_0$

Heisenberg uncertainty priciple

$\Delta x \cdot \Delta p \geqq h/4\pi$

Yun-Chen Chien

Properties of Atom

☆ Schrödinger's Equation：

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

H：Hamiltonian (H=K.E.+P.E.)

Ψ：Eigenfunctions

E：Eigenvalues (Total Energy)

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(x,y,z)\right]\Psi(x,y,z) = E\Psi(x,y,z)$$

$$\mathbf{H}(\lambda\Psi) = \lambda\mathbf{H}(\Psi)$$

$$\mathbf{H}\Psi_i = \mathbf{E}_i\Psi_i$$

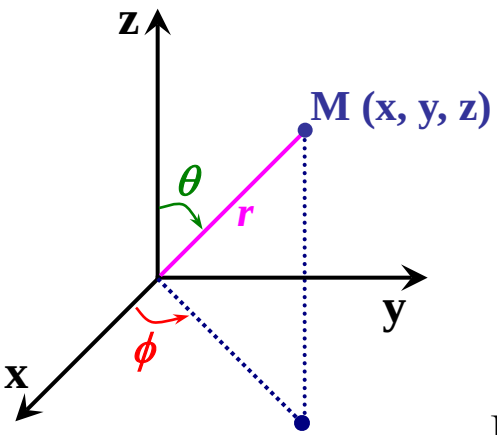
$$\int_{space}\Psi_i^2 d\tau = \mathbf{1}$$

$$\mathbf{H}(\lambda\Psi_i) = \lambda\mathbf{H}(\Psi_i) = \lambda\mathbf{E}_i\Psi_i = \mathbf{E}_i(\lambda\Psi_i)$$

$$\int_{space}(\lambda\Psi_i)^2 d\tau = \mathbf{1} \quad i.e. \quad \lambda^2\int_{space}\Psi_i^2 d\tau = \mathbf{1}$$

$$\lambda^2 = \mathbf{1}\ \mathbf{or}\ \lambda = \pm\mathbf{1}$$

☆ Description of the Eigenfunctions：



Orthogonal Coordinates → Spherical Coordinates
(x, y, z) **(r, θ, ϕ)**

$$x = r\sin\theta\cos\phi \qquad r \in [0, \infty]$$
$$y = r\sin\theta\sin\phi \qquad \theta \in [0, \pi]$$
$$z = r\cos\theta \qquad \phi \in [0, 2\pi]$$

$$H = -\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\left[\frac{\partial^2}{\partial\phi^2} + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right] - \frac{ze^2}{r}$$

Analytical Form

$$\Psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r)Y_{l,m_l}(\theta, \phi)$$

***Quantum Numbers*：**
n：Principal
l：Angular Momentum
m_l：Magnetic

The Angular Part：$\int_0^{\pi}\int_0^{2\pi} Y_{l,m_l}^2(\theta,\varphi)\sin\sum\theta\sum d\theta\, d\varphi = 1$

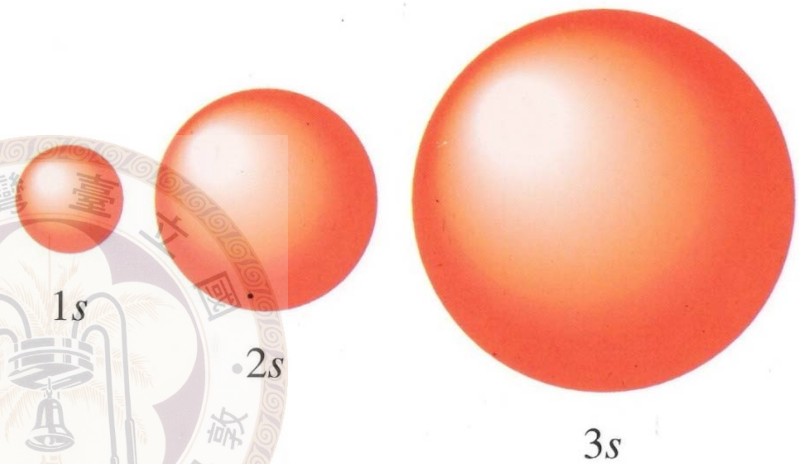
The Radial Part：$\int_0^{\infty} R_{n,l}^2(r)r^2 dr = 1$

Angular Functions, $Y_{l,m_l}(\theta,\phi)$

☆ **The *s* function ($l = 0$, $m_l = 0$)：**

Symbol：*s*

Angular Nodes = $l = 0$



Angular → $Y_{0,0}(\theta, \phi) = 1$

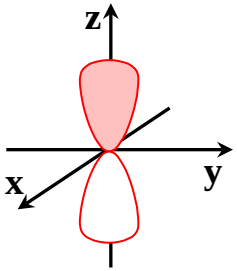
Spherical shape

☆ The *p* function ($l = 1$, $m_l = +1, 0, -1$) :

Symbol : *p*

Angular Nodes = $l = 1$

$m_l = 0$



p_z

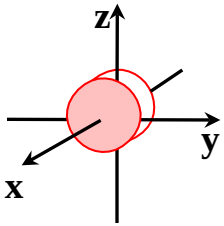
xy plane

p_z : $Y_{l,m_l}(\theta, \phi) = \cos\theta$

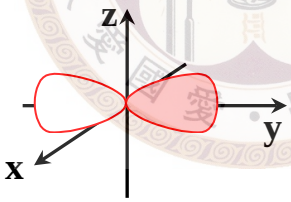
$Y_{1,0}(\theta, \phi) = 0$; when $\theta = 90°$

i.e. **xy plane**

$m_l = \pm 1$



p_x



p_y

$$Y_{1,1} = \sin\theta\, e^{i\varphi}$$

$$Y_{1,-1} = \sin\theta\, e^{-i\varphi}$$

$$p_x = \frac{i}{2}\left(Y_{1,1} + Y_{1,-1}\right)$$

$$p_y = \frac{i}{2}\left(Y_{1,1} - Y_{1,-1}\right)$$

p_x : $Y_{l,m_l}(\theta, \phi) = \sin\theta \cos\phi$

$Y_{l,m_l}(\theta, \phi) = 0$

$\theta = 0°, \phi = 90°$

yz plane

p_y : $Y_{l,m_l}(\theta, \phi) = \sin\theta \sin\phi$

$Y_{l,m_l}(\theta, \phi) = 0$

$\theta = 0°, \phi = 0°$

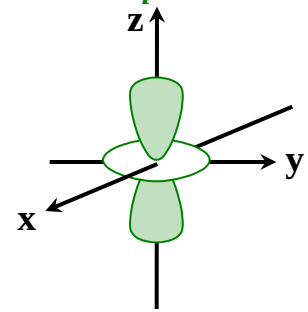
xz plane

☆ The *d* function ($l = 2$, $m_l = +2, +1, 0, -1, -2$) :

Symbol : *d*

Angular Nodes = $l = 2$

$m_l = 0$

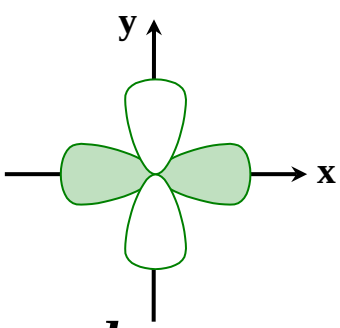


d_{z^2}

$Y_{l,m_l}(\theta, \phi) = 3\cos^2\theta - 1$

when $\cos\theta = \pm\sqrt{1/3}$

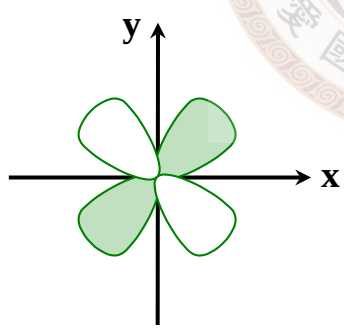
$m_l = \pm 2$



$d_{x^2-y^2}$

$Y_{l,m_l}(\theta, \phi) = \sin^2\theta \cos 2\phi$

$\theta = 0°, \phi = \pm 45°$

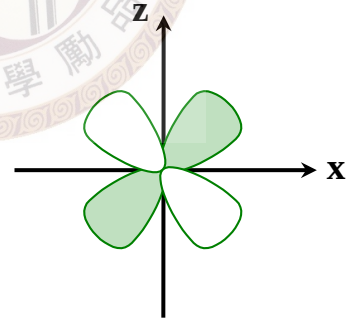


d_{xy}

$Y_{l,m_l}(\theta, \phi) = \sin^2\theta \sin 2\phi$

$\theta = 0°, \phi = 0°$ or $90°$

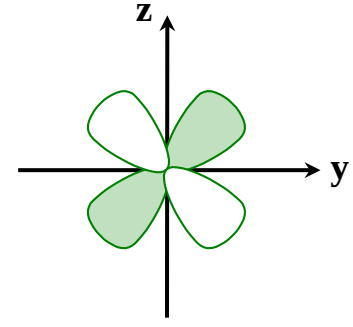
$m_l = \pm 1$



d_{xz}

$Y_{l,m_l}(\theta, \phi) = \sin\theta \cos\theta \sin\phi$

$\theta = 0°$ or $90°, \phi = 0°$



d_{yz}

$Y_{l,m_l}(\theta, \phi) = \sin\theta \cos\theta \cos\phi$

$\theta = 0°$ or $90°, \phi = 90°$

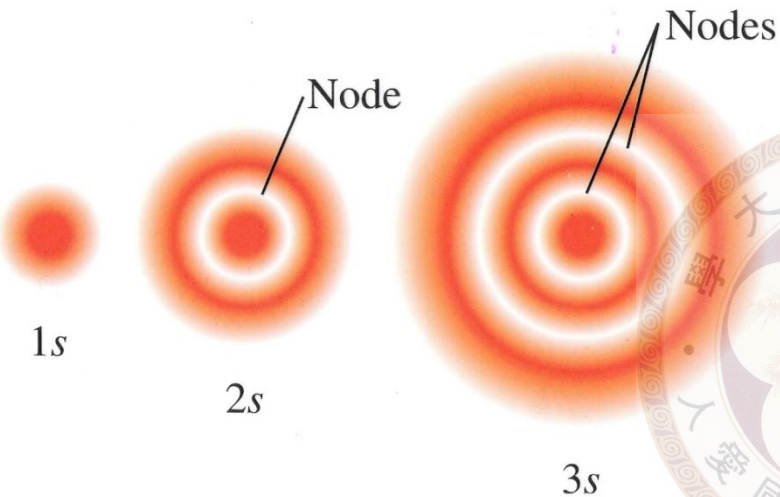
Radial Functions, $R_{n,l}(r)$

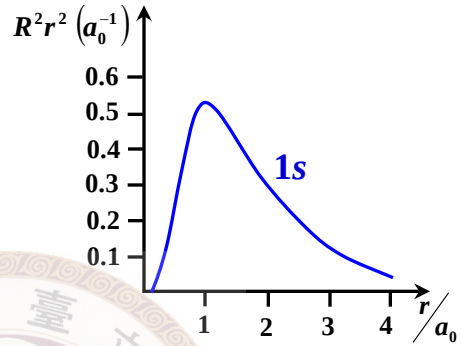
Radial Nodes = $n - l - 1$
Total Nodes = $n - 1$

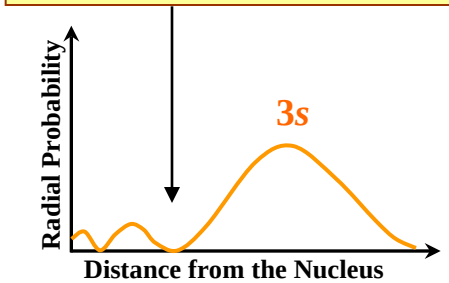
Node:

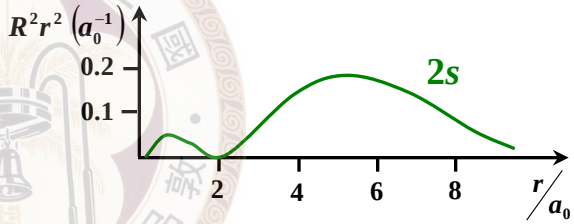
Electron density = 0

$$R_{n,l}(r) = \left(\sum_{i=0}^{n-l-1} a_i r^i \right) e^{-\xi r}$$

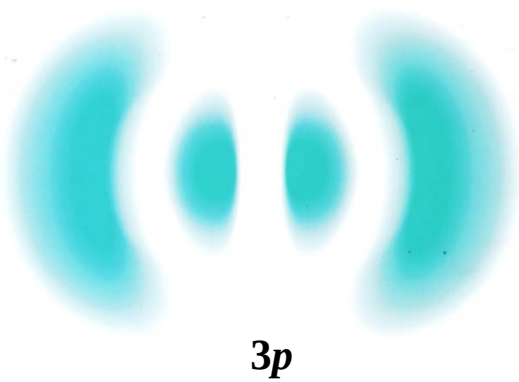


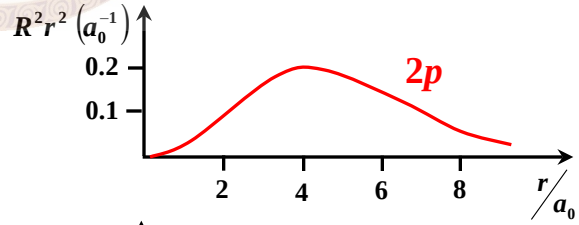


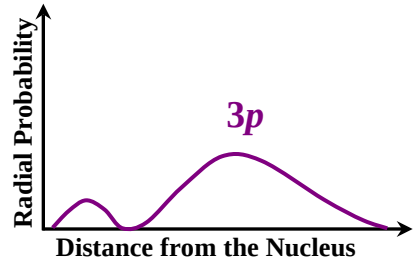




Combine angular and radial nodes







Nomenclature for the Eigenfunctions, Ψ_i

$l = 0, 1, 2, 3, \ldots$
$\downarrow\downarrow\downarrow\downarrow$
$s \quad p \quad d \quad f$

The Principal Quantum Number n	The Angular Quantum Number l	The Magnetic Quantum Number M_l	
$n = 1, 2, 3, \ldots$	$0 \le l < n$	$-l \le m_l \le +l$	
$n = 1$	$l = 0$	$m_l = 0$	$1s$
$n = 2$	$l = 0$	$m_l = 0$	$2s$
	$l = 1$	$m_l = +1$	$2p_{+1}$
		$m_l = 0$	$2p_0$
		$m_l = -1$	$2p_{-1}$
$n = 3$	$l = 0$	$m_l = 0$	$3s$
	$l = 1$	$m_l = +1$	$3p_{+1}$
		$m_l = 0$	$3p_0$
		$m_l = -1$	$3p_{-1}$
	$l = 2$	$m_l = +2$	$3d_{+2}$
		$m_l = +1$	$3d_{+1}$
		$m_l = 0$	$3d_0$
		$m_l = -1$	$3d_{-1}$
		$m_l = -2$	$3d_{-2}$

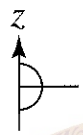
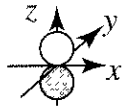
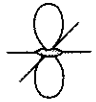
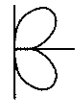
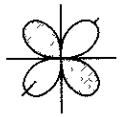
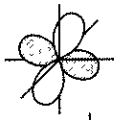
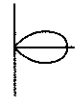
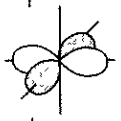
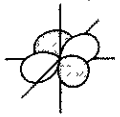
Quantum Numbers and Their Properties

Symbol	*Name*	*Values*	*Role*
n	Principal	$1, 2, 3, \ldots$	Determines the major part of the energy
l	Angular momentum	$0, 1, 2, \ldots, n-1$	Describes angular dependence and contributes to the energy
m_l	Magnetic	$0, \pm 1, \pm 2, \ldots, \pm l$	Describes orientation in space (angular momentum in the z direction)
m_s	Spin	$\pm \frac{1}{2}$	Describes orientation of the electron spin (magnetic moment) in space

Orbitals with different l values are known by the following labels, derived from early terms for different families of spectroscopic lines:

l	0	1	2	3	4	5, . . .
Label	*s*	*p*	*d*	*f*	*g*	continuing alphabetically

Hydrogen Atom Wave Functions: Angular Functions

		Angular factors			Real wave functions			
		Related to angular momentum		Functions of θ	In Polar coordinates	In Cartesian coordinates	Shapes	Label
l	m_l	Φ	Θ		$\Theta\Phi(\theta, \phi)$	$\Theta\Phi(x, y, z)$		
$0(s)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$		$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{2\sqrt{\pi}}$		s
$1(p)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r}$		p_z
	$+1$	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{x}{r}$		p_x
	-1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{y}{r}$		p_y
$2(d)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{2}\sqrt{\frac{5}{2}}(3\cos^2\theta - 1)$		$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\frac{(2z^2 - x^2 - y^2)}{r^2}$		d_{z^2}
	$+1$	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{xz}{r^2}$		d_{xz}
	-1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{yz}{r^2}$		d_{yz}
	$+2$	$\frac{1}{\sqrt{2\pi}}e^{2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{(x^2 - y^2)}{r^2}$		$d_{x^2-y^2}$
	-2	$\frac{1}{\sqrt{2\pi}}e^{-2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\sin 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{xy}{r^2}$		d_{xy}

☆ Orbital Energy (Eigenvalues)：

For H $E_n = - Ry / n^2$

Degeneracy = n^2; *e.g.: 2s; $2p_x$，$2p_y$，$2p_z$*

Degenerate states : different orbitals. Have same eigenvalue

Hydrogen-like Atoms

$$\text{Eigenvalues} \rightarrow E_{n,l} = -\frac{RyZeff^2}{n^2}$$

He^+ (Z = 2), Li^{2+} (Z = 3), and Be^{3+} (Z = 4)…

Slater's Rules for The Calculation of The Screening Constant

$$Zeff = Z - S$$

- S is the screening constant.
- The nucleus are screened (or shielded) by inner electrons, so valence electrons actually "see" only part of the total charge.
- Screening constants are very penetrating and somewhat less shielded by inner shell electrons than orbitals with larger values of *l*, and then to shield somewhat better than other orbitals.
- Orbitals with high *l* values, such as *d* and *f* orbitals, are much less penetrating and are far poorer at shielding.

	$n' < n - 1$	$n' = n - 1$	$n' = n$	$n' > n$
1*s*	–	–	0.30	0
ns, *np*	1	0.85	0.35	0
nd, *nf*	1	–	0.35	0

Emission Spectrum of H Atom

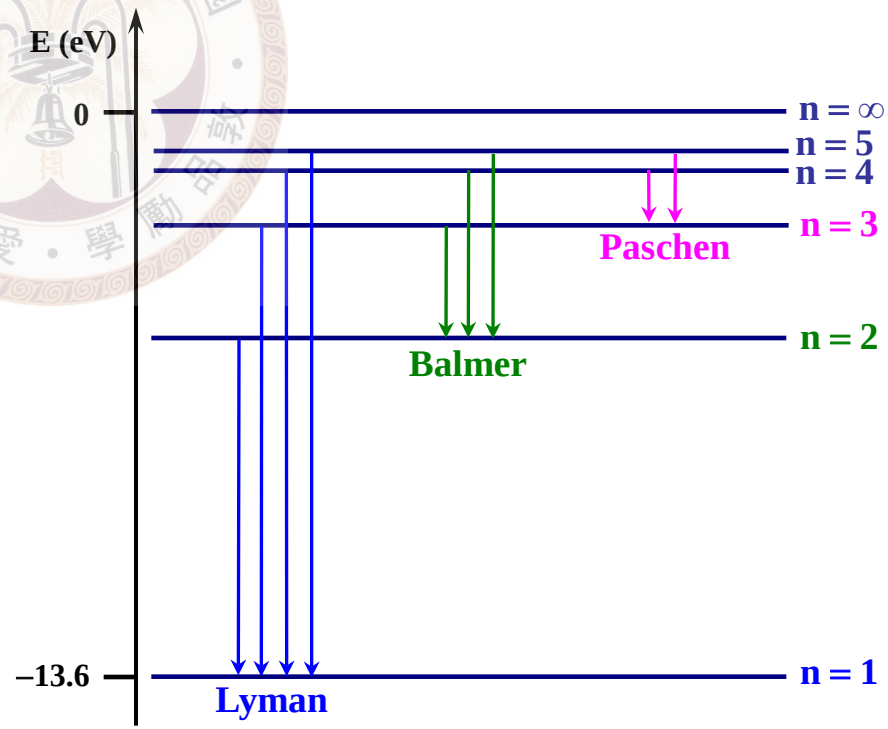
$$E_n = -\frac{Ry}{n^2} \qquad n = 1, 2, 3, \ldots$$

$E_1 = -Ry$	$(n = 1)$	ground state
$E_2 = -Ry/4$	$(n = 2)$	first excited state
$E_3 = -Ry/9$	$(n = 3)$	second excited state
etc.		

$$\Delta E = -\frac{Ry}{n^2} - \left(-\frac{Ry}{1^2}\right) = Ry\left(1 - \frac{1}{n^2}\right) = h\nu$$

$$\nu = \frac{Ry}{h}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

$$\Delta E_\infty = Ry = 13.6\,\text{eV}$$



Effect of Z_{eff};

Orbital E is fn. of n+l :

E (n,l)

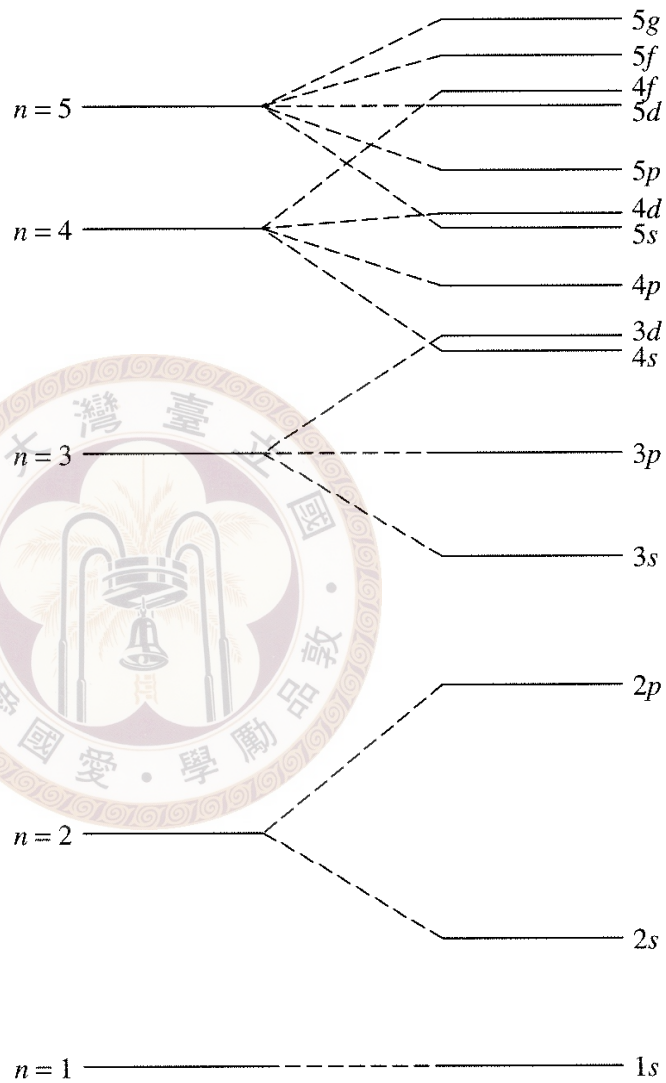
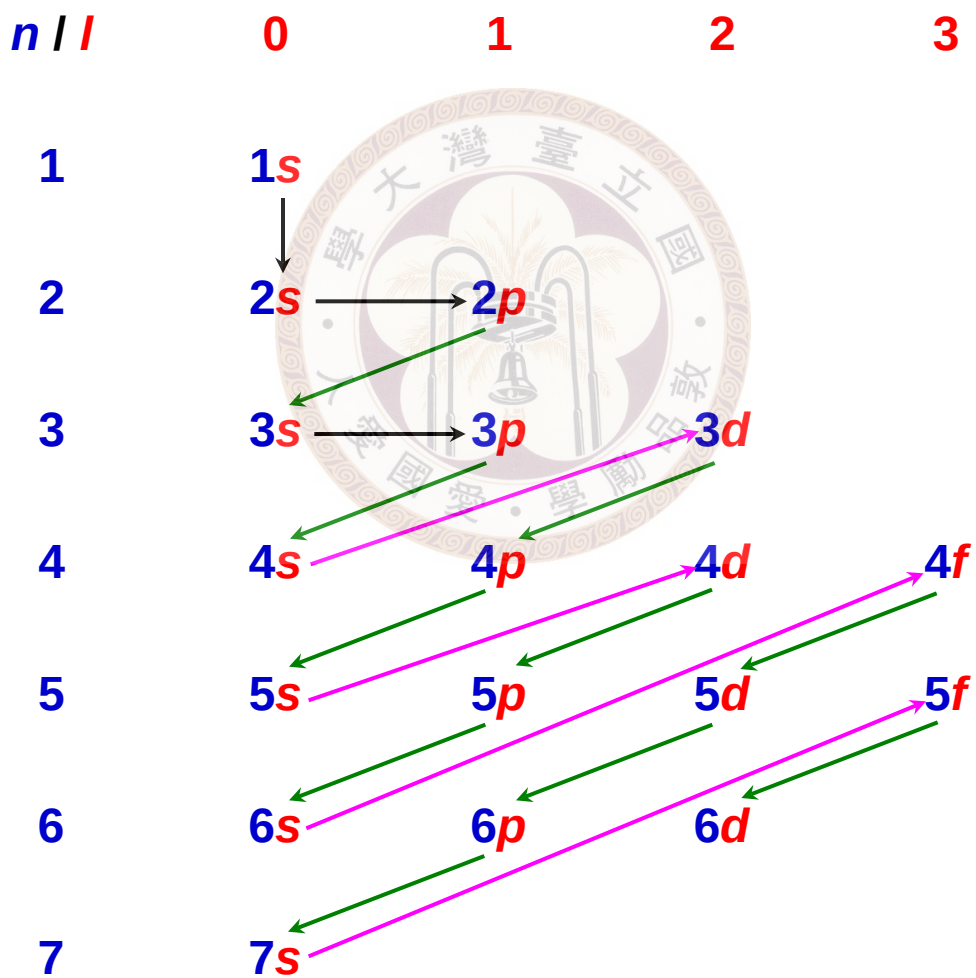


FIGURE 2-10 Energy Level Splitting and Overlap. The differences between the upper levels are exaggerated for easier visualization.

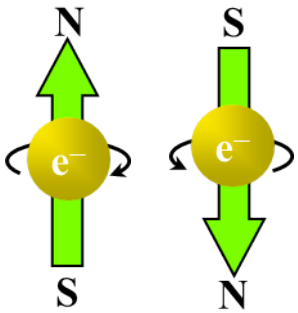
The Aufbau Process — Klechkowsky's Rule

	1*s*	<	2*s*	<	2*p*	<	3*s*	<	3*p*	<	4*s*	<	3*d*	<	4*p*	…
n + *l*	1		2		3		3		4		4		5		5	…



Pauli Exclusion Principle

☆ 4th Quantum Number：Spin Quantum → $m_s = \pm \frac{1}{2}$



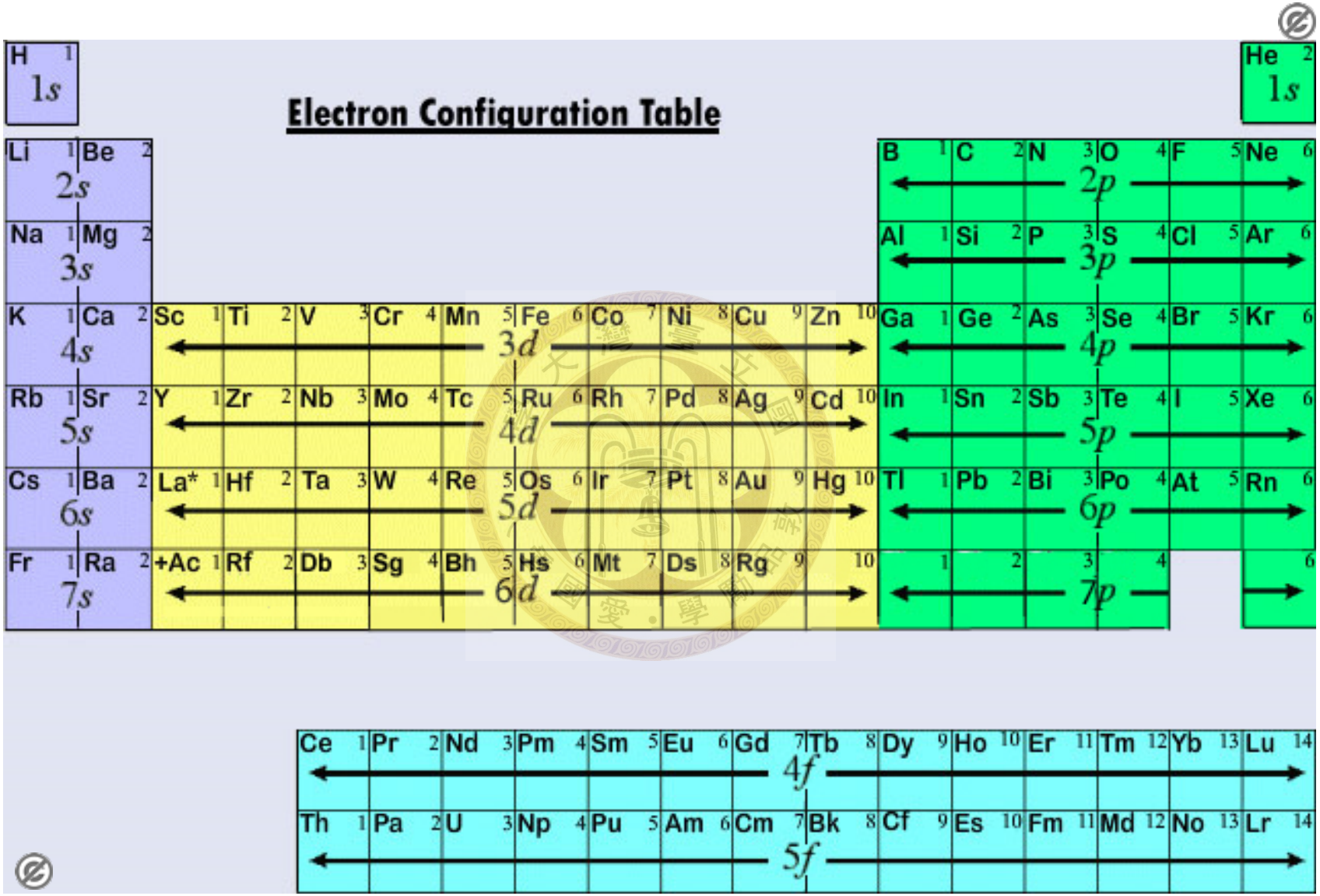
Two electrons can be populated on each orbital.

Each electron is identified with unique quantum # $\underbrace{n, l, m_l}_{\text{orbital}}, \underbrace{m_s}_{\text{electron}}$

Hund's Rule

For degenerate states, the electron is filled in with the same spin to set the maximum total spin quantum *S*.

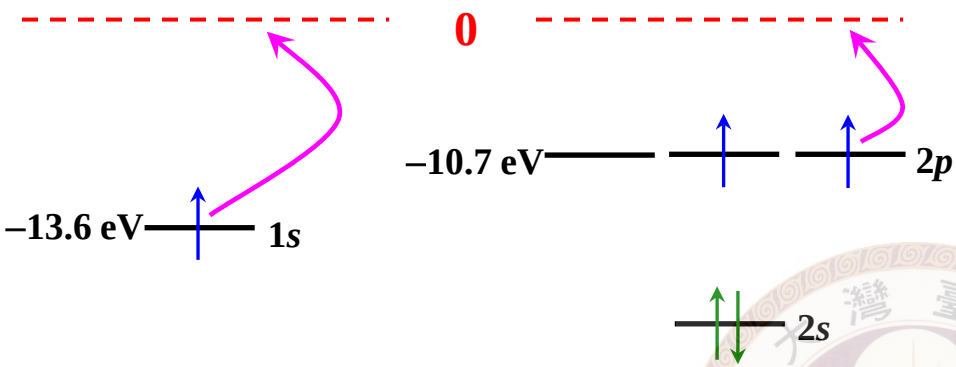
$$S = \sum m_s$$

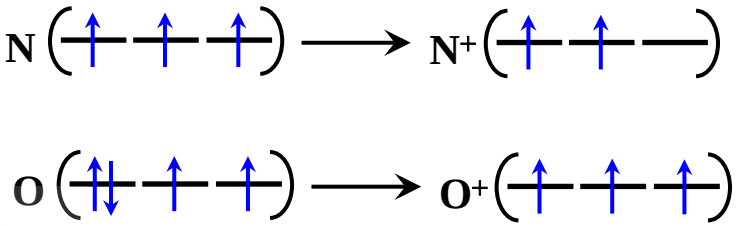


http://commons.wikimedia.org/wiki/File:Electron_Configuration_Table.jpg

Ionization Potential (IP)

$A \rightarrow A^+ + e^-$ $\Delta H = IP = -\text{orbital energy}$





Successive Ionization Energies in Kilojoules per Mole for the Elements in Period 3

General Increase →

General Decrease ↓

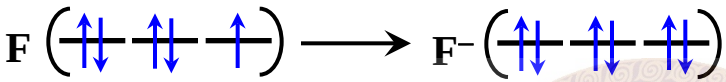
Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4560					
Mg	735	1445	7730				
Al	580	1815	2740	11,600			
Si	780	1575	3220	4350	16,100		
P	1060	1890	2905	4950	6270	21,200	
S	1005	2260	3375	4565	6950	8490	27,000
Cl	1255	2295	3850	5160	6560	9360	11,000
Ar	1527	2665	3945	5770	7230	8780	12,000

Core electrons*

*Note the large jump in ionization energy in going from removal of valence electrons to removal of core electrons. (kJ/mol)

Electron Affinity (EA)

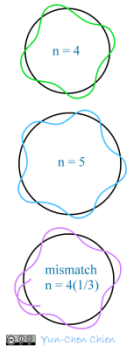
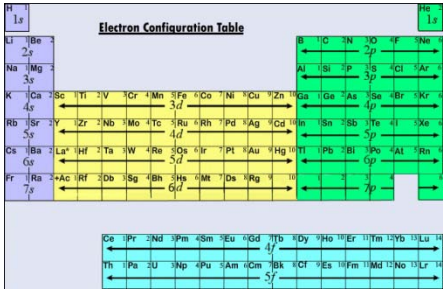
$$X_{(g)} + e^- \rightarrow X^-_{(g)} \qquad \Delta H = -B.E.$$



Electron Affinities of the Halogens

Atom	Electron Affinity (kJ/mol)
F	– 327.8
Cl	– 348.7
Br	– 324.5
I	– 295.2

版權聲明

作品	授權條件	作者
		Yun-Chen Chien
		Wiki USGS http://commons.wikimedia.org/wiki/File:Electron_Configuration_Table.jpg 2012/04/02 visited