In 2-dimensions, $\underset{\sim}{H} = \underset{\sim}{H}_x + \underset{\sim}{H}_y = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}$

separable into disjoint parts

$$\underset{\sim}{H}_x \psi_x = E_{n_x}\psi_x \quad ; \quad \underset{\sim}{H}_y \psi_y = E_{n_y}\psi_y$$

$$\underset{\sim}{H}\,\psi(x,y) = E\,\psi(x,y)$$

$$\psi(x,y) \equiv \psi_x \cdot \psi_y = \sqrt{\frac{2}{L_x}}\sin\left(\frac{n\pi x}{L_x}\right)\cdot\sqrt{\frac{2}{L_y}}\sin\left(\frac{n\pi y}{L_y}\right)$$

$$\underset{\sim}{H}\psi = \left(\underset{\sim}{H}_x + \underset{\sim}{H}_y\right)\psi_x\psi_y = \left(E_{n_x} + E_{n_y}\right)\psi_x\psi_y$$

If $\underset{\sim}{H}$ is a sum of separable, distinct parts,

then : $\psi$ is a <u>product</u> of the eigenfunctions of the parts of $\underset{\sim}{H}$

$E$ = <u>sum</u> of the eigenvalues of the parts of $\underset{\sim}{H}$

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]$$

degeneracy

n-dependence

sign of E

$\psi$ satisfies the Schrodinger/Dirac equation

$\psi$ is well behaved –

finite, continuous, single-valued

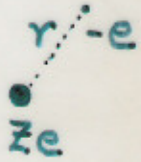
Boundary Conditions

$\psi^*\psi \, d\tau$ = Probability of finding the particle(s) in the volume element '$d\tau$'

## ATOMC ORBITALS

$$\hat{H}\psi = E\psi \; ; \quad \hat{H} = (K.E)_{op} + (P.E)_{op}$$

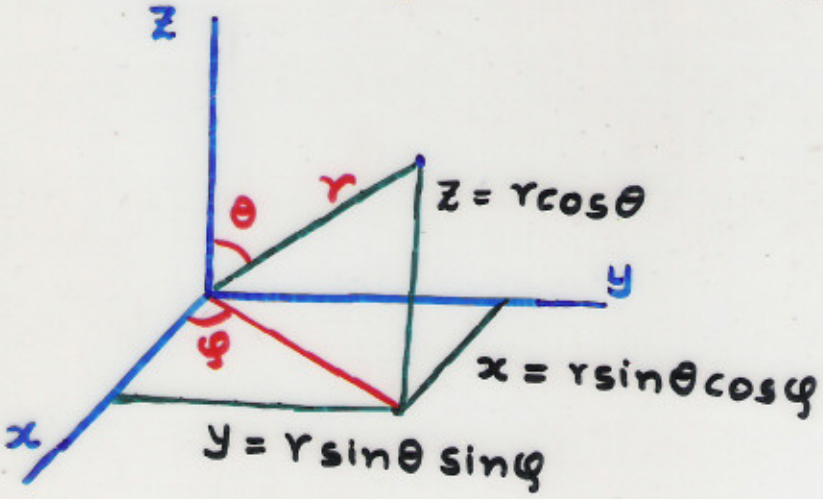
$p_x \to +\frac{\hbar}{i}\frac{\partial}{\partial x}$ Hydrogen-like atom: $= -\frac{h^2}{8\pi^2\mu}\nabla^2 - \frac{Ze^2}{r}$




Rewrite: $\nabla^2\psi + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{r}\right)\psi = 0$

$r = \sqrt{x^2 + y^2 + z^2}$, not separable as $f_1(x) + f_2(y) + f_3(z)$

$\therefore$ Change the coordinates from $x, y, z$ to $r, \theta, \varphi$




$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial x}\frac{\partial}{\partial \varphi}$$

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

Separation of variables : $\Psi(r,\theta,\varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi)$

$$F(r) + G(\theta) + H(\varphi) = 0 \quad , \quad r, \theta, \varphi \text{ independent}$$

$\Rightarrow$ Each term is a constant

$$\frac{d^2\Phi}{d\varphi^2} = -\underline{\underline{m_\ell^2}}\,\Phi$$

– sign for finite $\Phi$

$$\left(-\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta} + \frac{m_\ell^2}{\sin^2\theta}\right)\Theta = \underline{\underline{\ell(\ell+1)}}\,\Theta$$

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{2\mu}{\hbar^2}\frac{Ze^2}{r} - \frac{\ell(\ell+1)}{r^2}\right]R(r) = \underline{\underline{E}}\,R(r)$$

3 ordinary differential equations in variables $\varphi$, $\theta$ and $r$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$ in spherical polar coordinates

$$r = (x^2 + y^2 + z^2)^{1/2} \qquad x = r\sin\theta\cos\phi$$

$$\theta = \cos^{-1}\frac{z}{r} \qquad y = r\sin\theta\sin\phi$$

$$\phi = \tan^{-1}(y/x) \qquad z = r\cos\theta$$

$$x, y, z \longleftrightarrow r, \theta, \phi$$

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta} + \frac{\partial\varphi}{\partial x}\frac{\partial}{\partial\phi}$$ $|||^{ly}$ $\frac{\partial}{\partial r}$ in terms of $\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}$

$$\frac{\partial r}{\partial x} = \frac{x}{r}\ ; \quad \frac{\partial\theta}{\partial x} = \operatorname{cosec}\theta\,\frac{zx}{r^3}\ ; \quad \frac{\partial\phi}{\partial x} = \cos^2\phi\left(-\frac{y}{x^2}\right)$$

$$\frac{\partial}{\partial x}\cdot\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r}\left\{\sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right\}$$

$$+ \frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta}\left\{\ \text{''}\ \right\} + \frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}\left\{\ \text{''}\ \right\}$$

Similarly for $\frac{\partial}{\partial y}\frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}\frac{\partial}{\partial z}$

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

$$\vec{L} = \vec{r}\times\vec{p} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}\ ; \qquad \hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

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

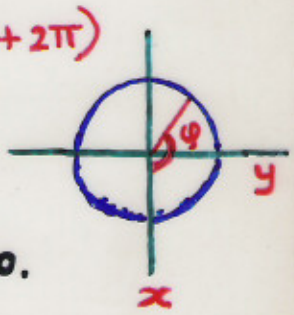
$$L_x = y p_z - z p_y$$

$$(L_x)_{op} = y\frac{\hbar}{i}\frac{\partial}{\partial z} - z\frac{\hbar}{i}\frac{\partial}{\partial y}\ ;$$

$\psi(r, \theta, \varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi)$ Separations of variables $r, \theta, \varphi$

$$\frac{\partial^2 \Phi(\varphi)}{\partial \varphi^2} + m^2 \Phi = 0$$

$\Phi(\varphi) = \Phi(\varphi + 2\pi)$




$\Phi = e^{\pm i m \varphi}$ , $m = 0, \pm 1, 2, 3 \cdots$

magnetic quantum no.

$L_z = -i\hbar \frac{\partial}{\partial \varphi}$ operator for z-component of $\vec{L}$

$L_z \Phi = \pm m\hbar \Phi$

Equation for $\Theta$ yields the constant $\beta = l(l+1)$

$m = -l, -l+1, \cdots 0, 1, 2, \cdots l$

Magnitude of angular momentum $\vec{L} = \sqrt{l(l+1)}\,\hbar$

Equation for R gives $E_n = \dfrac{-2\pi^2 \mu Z^2 e^4}{n^2 h^2}$

we require $\psi(r) \to 0$ as $r \to \infty$ for bound or stationary states

The spin quantum number $m_s = \pm 1/2$ (Relativistic)

Pauli's exclusion principle :

No two electrons can have identical values of $n$, $l$, $m_l$ and $m_s$

Connection between $\Psi$ and the Uncertainty Principle

# Plotting AOs and MOs using Hydrogenlike wavefunctions

$q = Zr/a_0$ , $(x, y, z) \leftrightarrow (R, \Theta, \Phi)$

$\rightarrow (r, \theta, \varphi)$

| Orbital | n | l | m | R | $\Theta\Phi$ |
|---|---|---|---|---|---|
| 1s | 1 | 0 | 0 | $2(Z/a_0)^{3/2} e^{-q}$ | $(4\pi)^{-1/2}$ |
| 2s | 2 | 0 | 0 | $(2\sqrt{2})^{-1}(Z/a_0)^{3/2}(2-q)e^{-q/2}$ | $(4\pi)^{-1/2}$ |
| $2p_x$ | 2 | 1 | 1 | $(2\sqrt{6})^{-1}(Z/a_0)^{3/2}\, q e^{-q/2}$ | $(3/4\pi)^{1/2} \sin\theta \cos\varphi$ |
| $2p_y$ | 2 | 1 | 0 | " " " | " $\sin\theta \sin\varphi$ |
| $2p_z$ | 2 | 1 | -1 | " " " | " $\cos\theta$ |
| 3s | 3 | 0 | 0 | $2/(81\sqrt{3})(Z/a_0)^{3/2}(27-18q+2q^2)e^{-q/3}$ | $(4\pi)^{-1/2}$ |
| $3p_x$ | 3 | 1 | 1 | $4/(81\sqrt{6})(Z/a_0)^{3/2}(6-q)\,q e^{-q/3}$ | $\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \cos\varphi$ |
| $3p_y$ | 3 | 1 | -1 | " " " | " $\sin\theta \sin\varphi$ |
| $3d_{z^2}$ | 3 | 2 | 0 | $4/(81\sqrt{30})(Z/a_0)^{3/2} q^2 e^{-q/3}$ | $\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$ |
| $3d_{xy}$ | 3 | 2 | -2 | " " | $\left(\frac{15}{4\pi}\right)^{1/2} \sin^2\theta \sin 2\varphi$ |
| $3d_{x^2-y^2}$ | 3 | 2 | 2 | " " | " $\sin^2\theta \cos 2\varphi$ |
| $3d_{yz}$ | 3 | 2 | -1 | " " | " $\sin\theta \cos\theta \sin\varphi$ |
| $3d_{xz}$ | 3 | 2 | 1 | " " | " $\sin\theta \cos\theta \cos\varphi$ |

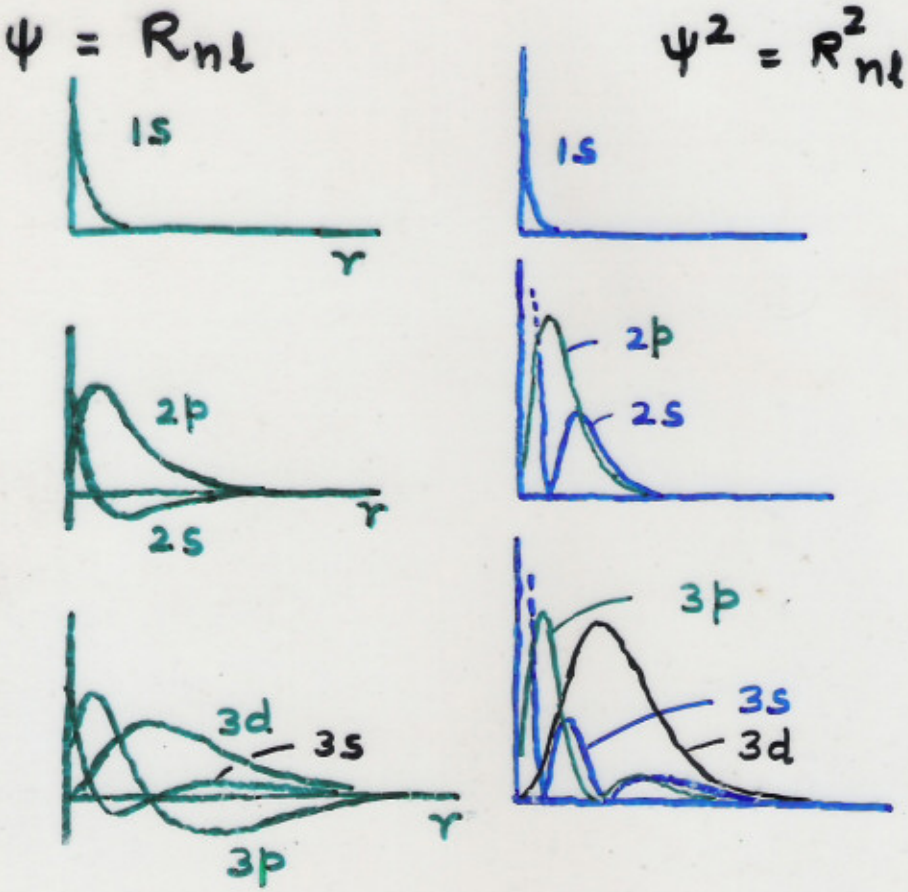
# Orbitals for hydrogen-like atoms

$$\sigma = Zr/a_0 \;, \quad a_0 = \frac{h^2}{4\pi^2 \mu e^2} = 0.529 \text{ Å}$$

| | Radial Part $R_{nl}(r)$ | | Angular Part $\Theta(\theta)\Phi(\varphi) = Y_l^m(\theta,\varphi)$ | Quantum No.s $n$ | $l$ | $m_l$ | $m_s$ |
|---|---|---|---|---|---|---|---|
| 1s | $\cdot\cdot\; e^{-\sigma}$ | | $(1/4\pi)^{+1/2}$ | 1 | 0 | 0 | $\pm 1/2$ |
| 2s | $\cdot\cdot\; (2-\sigma)e^{-\sigma/2}$ | | " | 2 | 0 | 0 | |
| 2p | $\cdot\cdot\; \sigma e^{-\sigma/2}$ | $p_x$ | $\cdot\cdot\; \sin\theta\cos\varphi$ | 2 | 1 | $\pm 1$ | |
| | | $p_y$ | $\cdot\cdot\; \sin\theta\sin\varphi$ | 2 | 1 | | |
| | | $p_z$ | $\cdot\cdot\; \cos\theta$ | 2 | 1 | 0 | |
| 3s | $\cdot\cdot\; (27-18\sigma+2\sigma^2)e^{-\sigma/3}$ | | $(4\pi)^{-1/2}$ | 3 | 0 | 0 | |
| 3p | $\cdot\cdot\; (6-\sigma)\sigma\, e^{-\sigma/3}$ | | same as $2p_x, 2p_y, 2p_z$ | 3 | 1 | | |
| 3d | $\cdot\cdot\; \sigma^2 e^{-\sigma/3}$ | $d_{z^2}$ | $\cdot\cdot\; (3\cos^2\theta - 1)$ | 3 | 2 | 0 | |

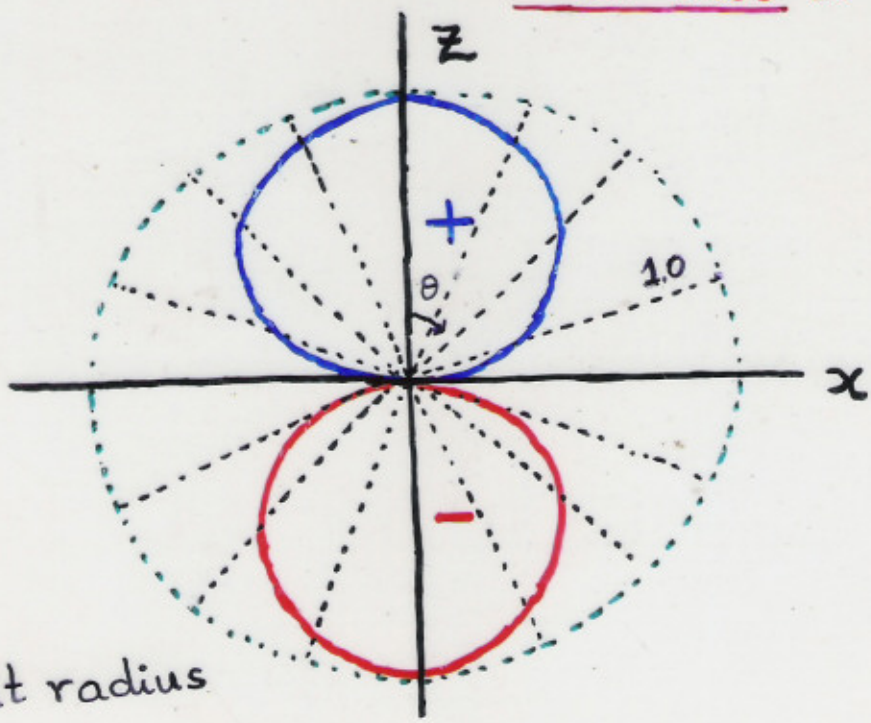
$\cdot\cdot$ Normalization Constants

$$\Psi(r, \theta, \varphi) = R_{nl}(r)\, Y_l^m(\theta, \varphi)$$




Radial Parts of hydrogen-like orbitals

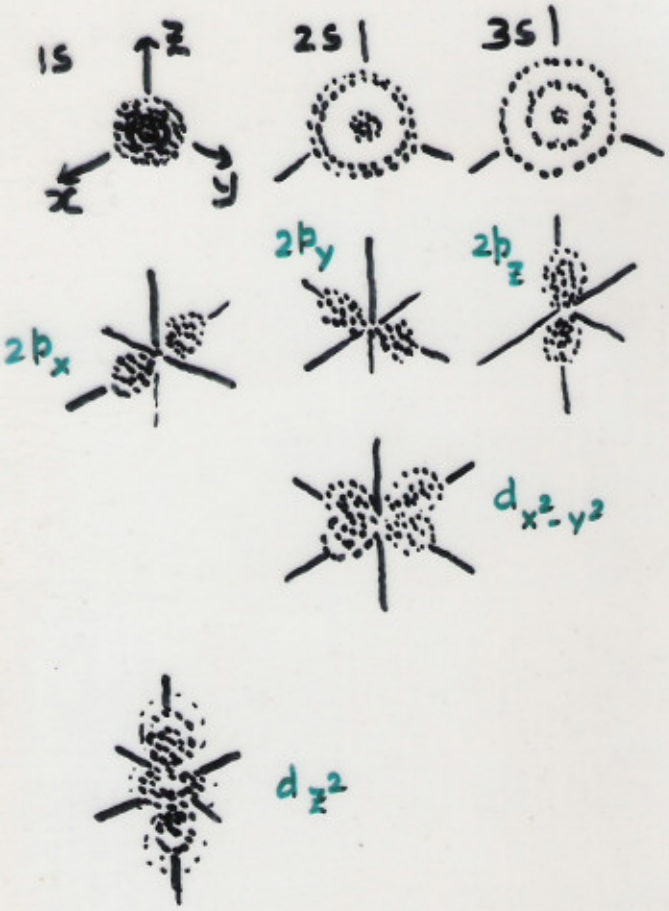
## Angular Part – Polar Plot of $p_z = -\cos\theta$



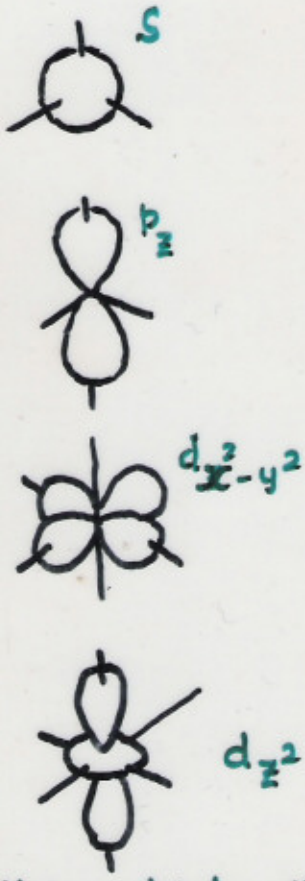

Unit radius

| θ | cos θ |
|---|---|
| 10 | 0.985 |
| 20 | 0.940 |
| 30 | 0.866 |
| 40 | 0.766 |
| 50 | 0.643 |
| 60 | 0.500 |
| 70 | 0.342 |
| 80 | 0.174 |
| 120 | −0.500 |
| 150 | −0.866 |
| 210 | −0.866 |
| 240 | −0.500 |

Electron Densities

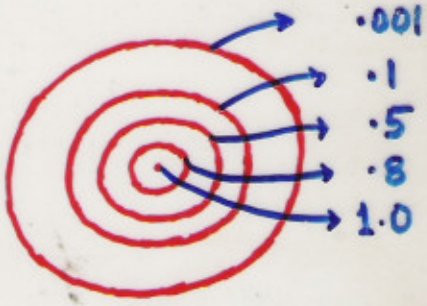



Boundary Surfaces




within which there is 90% probability of finding the electron

CONTOURS

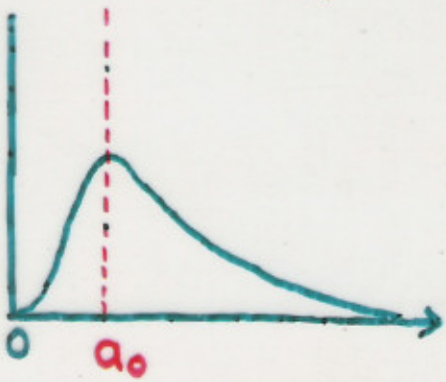



Contours of $\psi^2$ (Constant values) measured relative to $\psi^2$ at the origin (for 1s)

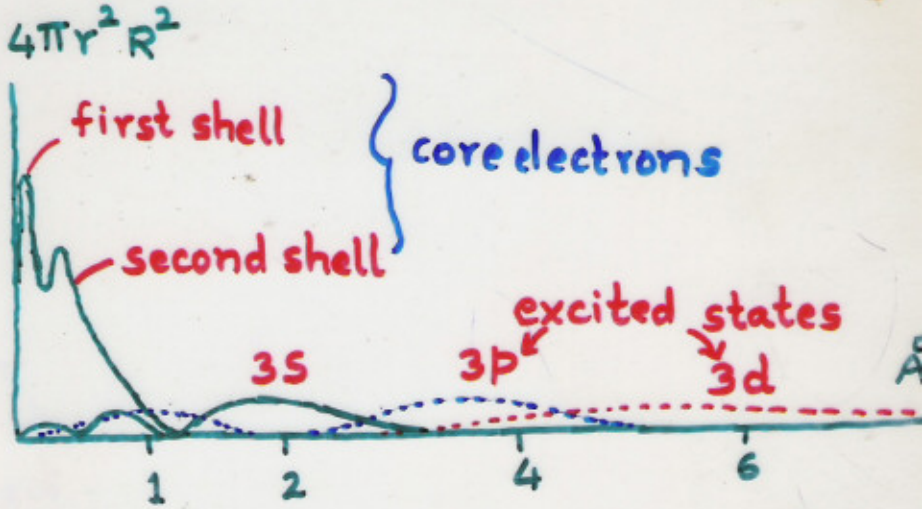
Radial Distribution Function $P(r) = 4\pi r^2|\psi|^2$

$P(r)\cdot dr$ = Probability of finding the electron anywhere in a shell of thickness $\underline{dr}$ at the radius $\underline{r}$

$P(r)$ for $1s_H$




Most probable radius




Radial electron density in Na

Size of Na = ? Size of $Na^+$ = ?

# Nodes of Different Orbitals

1 s — No node

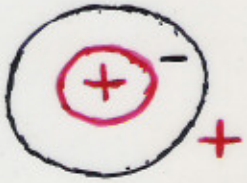
2 s — 1 spherical node


$\sigma = \frac{Zr}{a_0}$ ; $\sigma = 2$ : Node

2p — 1 planar node
due to angular functions

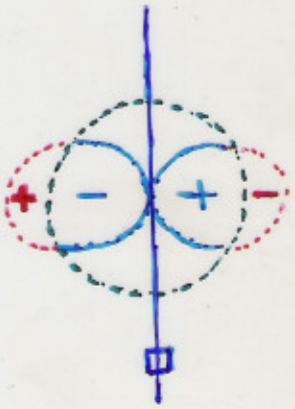
3s — 2 spherical nodes

$27 - 18\sigma + 2\sigma^2 = 0$




3p — $(6-\sigma)\sigma e^{-\sigma/3}$

1 spherical, 1 planar



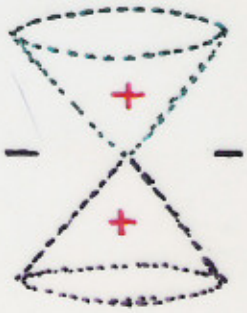

$3d_{xy}, 3d_{yz}, 3d_{zx}, 3d_{x^2-y^2}$

2 planar nodes

$3d_{z^2}$ : $(3\cos^2\theta - 1) = 0$

$\cos\theta = \pm\frac{1}{\sqrt{3}}$

$\theta = 54.74^\circ$
$125.26^\circ$



Effective Nuclear Charge $Z_{eff}$

Effective radius $r_e$

Useful Parameters : Not measurable quantities like < >

I.E. of H = $1.313 \times 10^6$ J/mol = 13.6 eV

I.E. of other atoms = I.E. of H $\times \dfrac{(Z-S)^2}{n^2}$

Z = charge, S = Screening Constant

n = principal quantum no.

"$e_1$"


"$e_2$"

recall $E = -\dfrac{2\pi^2 m e^4}{h^2}\dfrac{Z^2}{n^2}$

$$\boxed{Z_{eff} = Z - S}$$

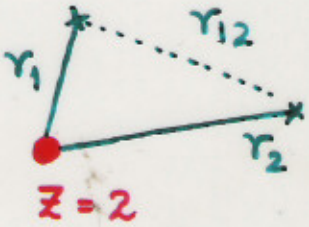
$$r_{eff} = \frac{n^2 h^2}{4\pi^2 m e^2 Z_{eff}}$$

$$r_H = \frac{n^2 h^2}{4\pi^2 m e^2 Z} = 0.529 \text{ Å}$$

$$= 52.9 \text{ pm}$$

# Atomic Structure

He atom




K.E P.E

$$\left[-\frac{h^2}{8\pi^2 m}\left(\nabla_1^2+\nabla_2^2\right) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}\right]\Psi = E\Psi$$

$$\Psi(\vec{r}_1, \vec{r}_2) \neq \phi_1(r_1)\cdot\phi_2(r_2)$$

Total wavefunction — Products of orbitals

$$\overset{?}{\approx} \phi_1(r_1)\cdot\phi_2(r_2)$$ An approximation

An orbital $\equiv$ ONE ELECTRON FUNCTION

$$r_{12} = \left[(x_2-x_1)^2 + (y_2-y_1)^2 + (z_2-z_1)^2\right]^{1/2}$$

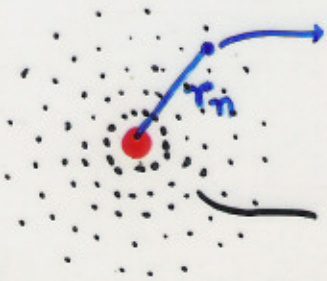
$$\frac{1}{r_{12}} \neq f_1\left(\frac{1}{r_1}\right) + f_2\left(\frac{1}{r_2}\right)$$

$\therefore$ $H_1\phi_1 = E_1\phi_1$ and $H_2\phi_2 = E_2\phi_2$ is not possible

$\therefore$ Energy depends on all quantum numbers $n, l, m_l, m_s$

The Aufbau Principle & electronic configuration of atoms ... $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < \ldots$

Solving for $\Psi$ using the notion of a Self Consistent Field (SCF method)



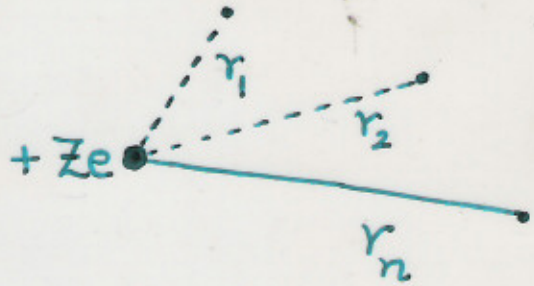

the $n^{th}$ electron ..... determine $\phi_n$

The field due to all the other $(n-1)$ electrons

# Atomic Structure

He atom : $\mathcal{H} = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - 2e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{r_{12}}$

N-electron atom




$$\mathcal{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 - Z\sum_i \frac{e^2}{r_i} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{e^2}{r_{ij}} \; ; \quad \vec{\nabla}_i = \hat{i}\frac{\partial}{\partial x_i} + \hat{j}\frac{\partial}{\partial y_i} + \hat{k}\frac{\partial}{\partial z_i}$$

$$\frac{1}{r_{ij}} \neq f\left(\frac{1}{r_i}\right) + g\left(\frac{1}{r_j}\right) \Rightarrow \text{Not separable}$$

$$\Psi(1,2,\ldots N) \approx \phi_1(\vec{r}_1)\,\phi_2(\vec{r}_2)\,\ldots\,\phi_N(\vec{r}_N)$$

Total Wavefunction

Product of orbitals

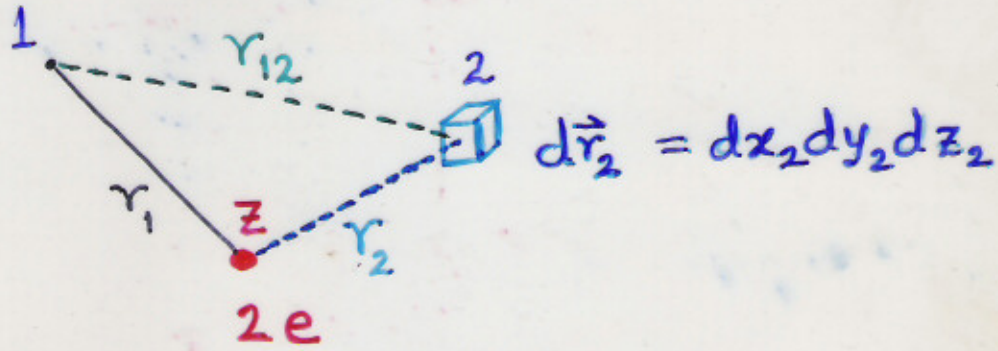
Orbital = Function of the coordinates of $\boxed{\text{one}}$ electron

$$\mathcal{H}_{eff}(i)\,\phi_i = \epsilon_i\,\phi_i$$

$\epsilon_i$ ↓ orbital energy

For He,

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{r_1} + V_{eff}(r_1)\right]\phi(r_1) = \epsilon_1\,\phi(r_1)$$




$$\int \phi_2^*(r_2)\,\frac{e^2}{r_{12}}\,\phi_2(r_2)\,d\vec{r}_2 = V_{eff}(r_1)$$

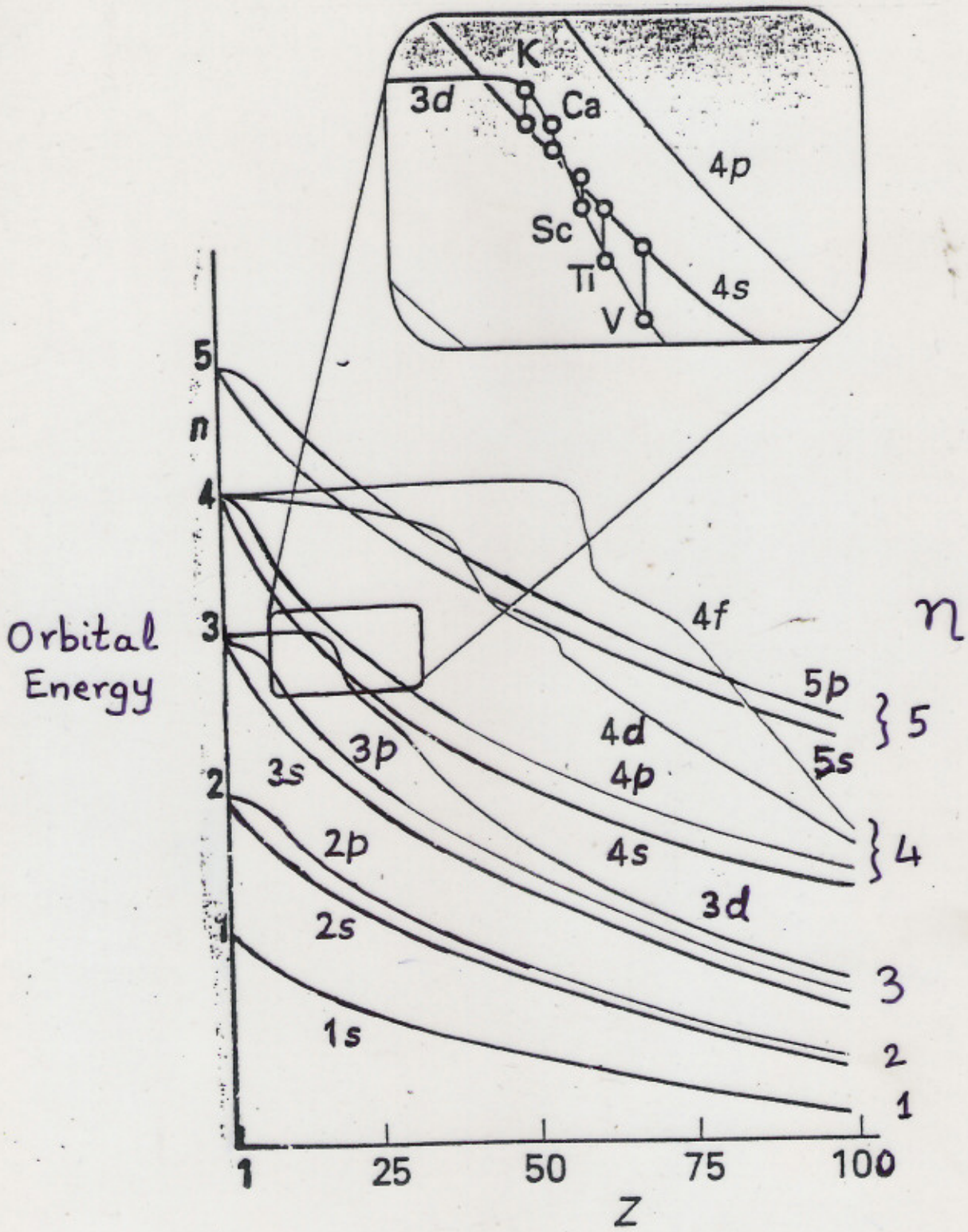
Electron 1 moves in an average or effective (not instantaneous) field due to electron 2, 3 .... N

$|||^{ly}$ $V_{eff}(r_2)$ for $\phi(r_2)$

Electrons move in "<u>self consistent fields</u>" that they mutually exert on one another

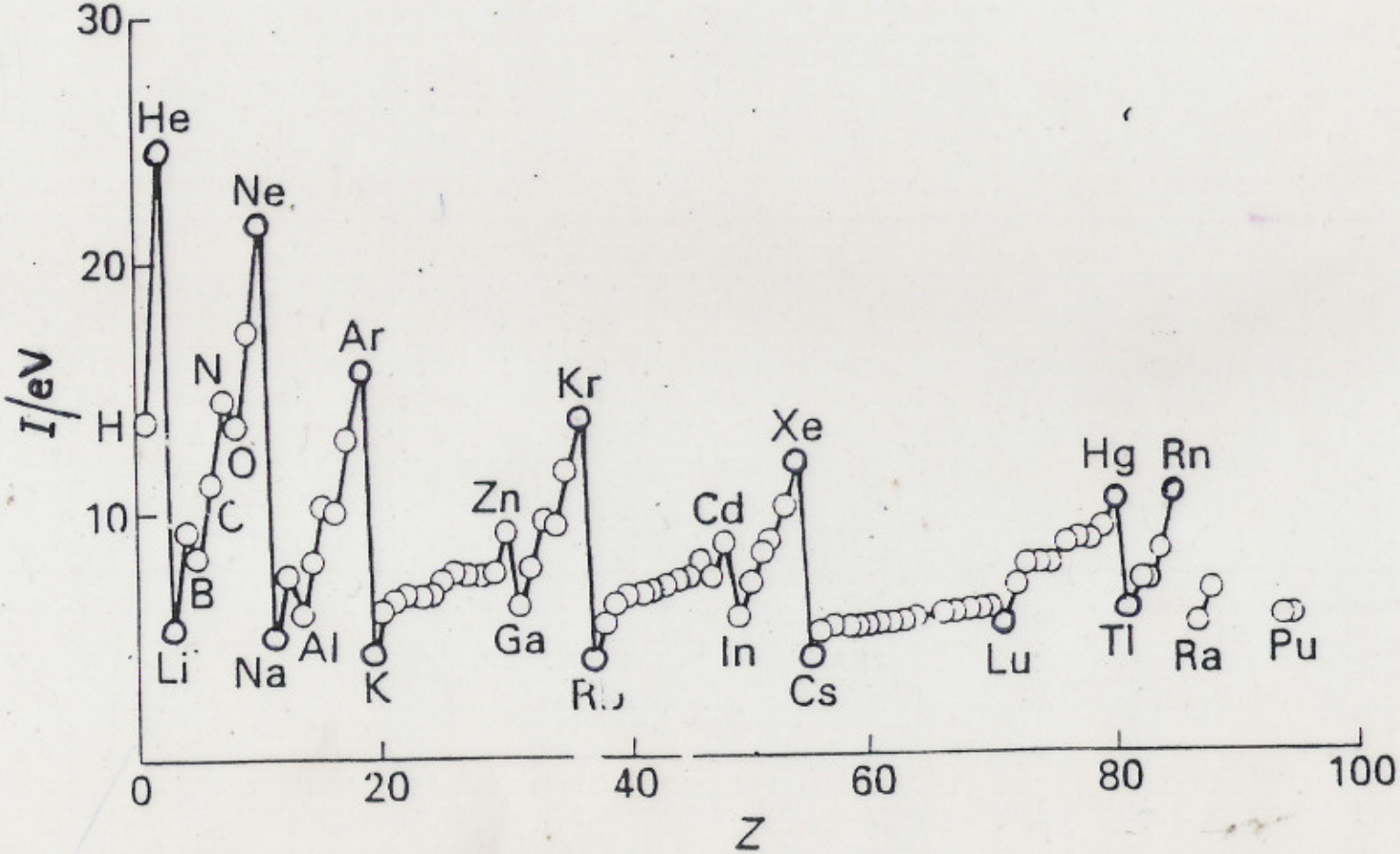
$$\phi_1^{(0)}\,\phi_2^{(0)} \longrightarrow \phi_1^{(1)}\,\phi_2^{(1)} \dashrightarrow \phi_1^{(n)}\,\phi_2^{(n)} \longrightarrow \phi_1\,\phi_2$$

converged SCF orbitals




Orbital energies as a function of Atomic Number

# Ionization Energies



# Electron Affinities

Energy released when $A + e^- \longrightarrow A^-$

or

$A^- \longrightarrow A + e^-$ , $\Delta E$ = Electron Affinity

= Ionization potential of $A^-$ = $E_{ea}$

Examples :

| Species | E.A. / (kJ mol$^{-1}$) |
|---|---|
| Cl | 349 |
| H | 73 |
| O | 141 |
| $O^-$ | -844 |

## Electronegativities, $\chi_M$, $\chi_P$

Power of an atom to attract electrons towards itself when it is part of a compound.

Polarity of a bond $\propto$ electronegativity difference between participating atoms

$$\chi_M = \frac{1}{2}(I + E_{ea})$$

$$\chi_P : |\chi_A - \chi_B| = 0.102 \left\{ D_{AB} - \frac{1}{2}(D_{AA} + D_{BB}) \right\}^{1/2}$$

D = dissociation energy

| Atom | $\chi_P$ | Atom | $\chi_P$ | Atom | $\chi_P$ |
|---|---|---|---|---|---|
| H | 2.2 | N | 3.0 | F | 4.0 |
| C | 2.6 | O | 3.4 | Cl | 3.2 |
| Cs | 0.79 | | | | |

# Electronic Configurations

$\Psi$ : Product of orbitals or a single determinant

He : $1s^2$ : $\psi_{1s}\alpha(1)\,\psi_{1s}\beta(2)$ ; $1s^1 2s^1$ : $\psi_{1s}(1)\,\psi_{2s}(2)\,\alpha(1)\alpha(2)$

N : $[He]\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$ Hunds rule

Aufbau Principle: $1s < 2s < 2p < 3s$ $3p, 4s, 3d, 4p,$
$5s, 4d, 5p, 6s, \cdots$

Spin Orbitals : $\phi_a(1)\alpha(1)$, $\phi_b(3)\beta(3)$

Pauli Principle: $\boxed{\psi(1,2) = -\psi(2,1)}$ Antisymmetric w.r.t. particle exchange

For two electrons, with orbitals $\phi_a(r_1)$ and $\phi_b(r_2)$,

$$\psi_S(1,2) = \frac{1}{\sqrt{2}}\left\{\phi_a(r_1)\phi_b(r_2) + \phi_a(r_2)\phi_b(r_1)\right\}\left\{\begin{matrix}\alpha(1)\beta(2) \\ -\alpha(2)\beta(1)\end{matrix}\right\}$$

$$\psi_T(1,2) = \frac{1}{\sqrt{2}}\left\{\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\right\}\left\{\begin{matrix}\bullet\ \alpha(1)\alpha(2) \\ \bullet\ \beta(1)\beta(2) \\ \bullet\ \alpha(1)\beta(2) + \alpha(2)\beta(1)\end{matrix}\right\}$$

triplet

$\psi_T$ vanishes when $r_1 = r_2$, $\Rightarrow$
parallel spins avoid each other

---

True electronic configuration of He

$c_1\,1s^2 + c_2\,1s\,2s + c_3\,1s\,2p + c_4\,1s\,3s + \cdots$

dominant

CONFIGURATION SUPERPOSITION

# Spin Orbitals : one electron functions

$$\Psi(\underset{\sim}{1}) = \Psi(\vec{r}_1, \sigma_1) = \Psi_{orb}(\vec{r}_1)\,\Psi_{spin}(\sigma_1)$$

He atom, ground state

$$\Psi(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) = \underset{\vec{r}_1}{1s(1)}\,\underset{\vec{r}_2}{1s(2)}\,\underset{\sigma_1}{\alpha(1)}\,\underset{\sigma_2}{\beta(2)}$$

Indistinguishability of elementary particles $\Rightarrow$ $\Psi(\underset{\sim}{1}, \underset{\sim}{2}) = \pm\Psi(\underset{\sim}{2}, 1)$

Possible Spin Functions

$$\left\{\begin{array}{ll} \alpha(1)\,\alpha(2) & \\ \beta(1)\,\beta(2) & \text{symmetric when } 1 \rightleftarrows 2 \\ \alpha(1)\beta(2) + \beta(1)\alpha(2) & \\ \alpha(1)\beta(2) - \beta(1)\alpha(2) & \text{Anti-symmetric} \end{array}\right.$$

He $1s^2$ $\quad 1s(1)\,1s(2)\,[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$ $\quad {}^1S$

He* $1s2s$

$$[1s(1)\,2s(2) + 2s(1)\,1s(2)]\,[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad {}^1S$$

$$[1s(1)\,2s(2) - 2s(1)\,1s(2)] \left\{\begin{array}{l} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) + \beta(1)\alpha(2) \end{array}\right. \quad {}^3S$$

# Term Symbols, Electronic Configurations

$^{2S+1}L_J$

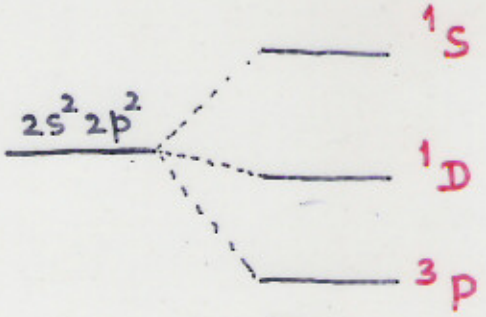
$J = L + S$

$L = \sum_i l_i$

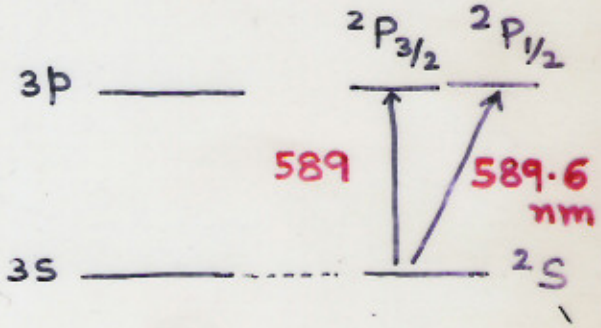
$S = \sum_i s_i$

| Conifuration | Atomic States |
|---|---|
| $p$ | $^2P$ |
| $p^2$ | $^1S$, $^1D$, $^3P$ |
| $p^3$ | $^2P$, $^2D$, $^4S$ |
| $d$ | $^2D$ |
| $d^2$ | $^1S$, $^1D$, $^1G$, $^3P$, $^3F$ |
| $d^3$ | $^2P$, $^2D(2)$, $^2F$, $^2G$, $^2H$, $^4P$, $^4F$ |

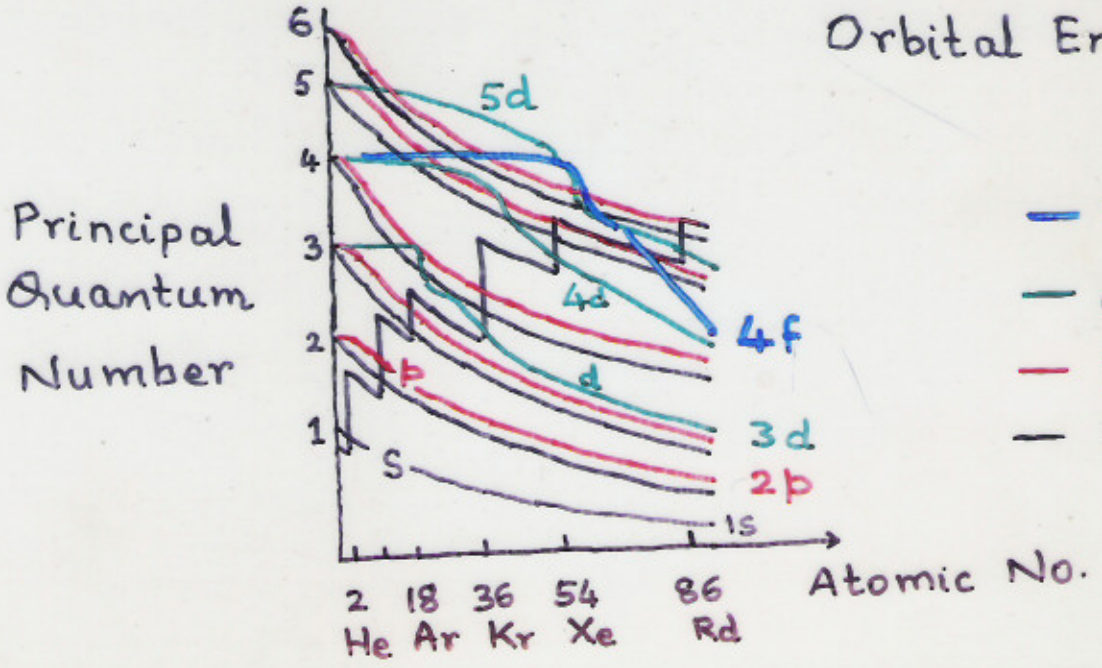
Carbon atom



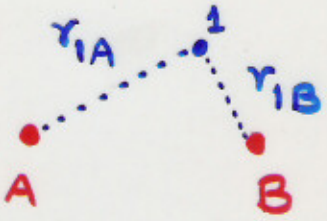

Sodium atom




Orbital Energies



eg: $H_2^+$




Nucleii assumed to be stationary

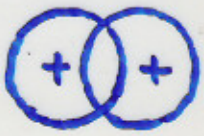
$$\left[-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}}\right]\psi = E\psi$$

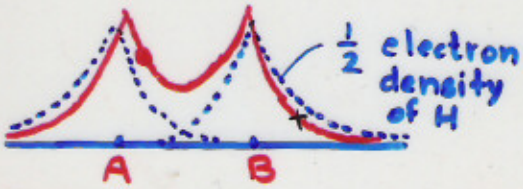
A MO [one electron function like an AO] spreads throughout the molecule

ie, it is a polycentric one electron function

eg: Linear Combination of Atomic Orbitals [LCAO-MO]

$\psi_{Bonding} = 1s_A + 1s_B$

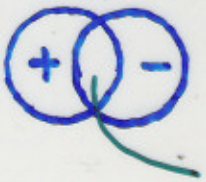


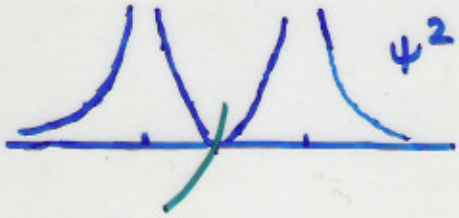




Electron density along Internuclear axis

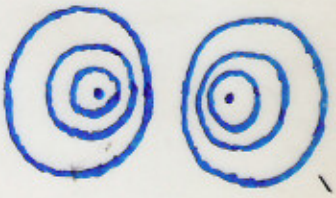
Contours of constant density

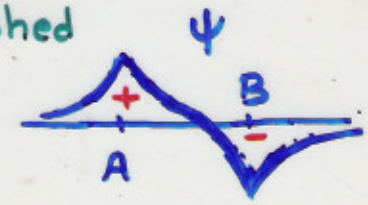
$\psi_{Antibonding} = 1s_A - 1s_B$



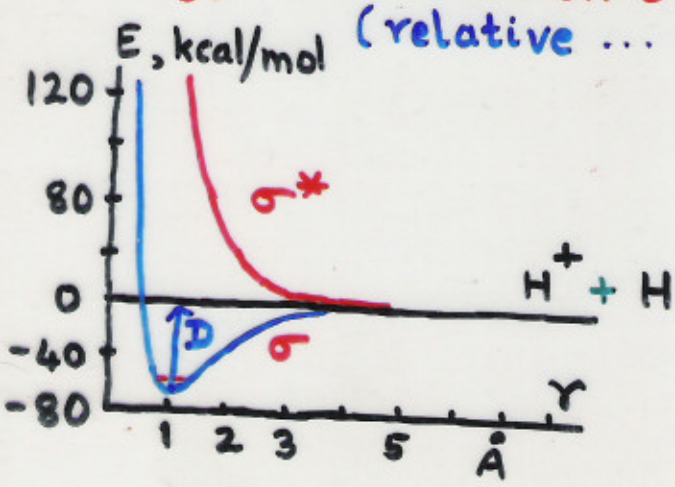




diminished






Energy as a function of internuclear distance (relative ... w.r.t. separated atoms/ions)



**The Variational Principle:** The energy calculated from an arbitrary wavefunction is never less than the true energy

Example of a Minimal Basis Set. HCl : H 1s $\psi_A$ Cl 3p $\psi_B$

$$E = \int \psi^* \hat{H} \psi \, d\tau \Big/ \int \psi^* \psi \, d\tau \; ; \quad \text{Let } \psi = c_A \psi_A + c_B \psi_B$$

Start with normalized $\psi_A$ and $\psi_B$

$$\int \psi^* \psi \, d\tau = c_A^2 + c_B^2 + 2 c_A c_B S \; ; \quad S = \int \psi_A \psi_B \, d\tau$$

overlap integral

$$\int \psi^* H \psi \, d\tau = c_A^2 \underbrace{\int \psi_A \hat{H} \psi_A \, d\tau}_{\alpha_A} + c_B^2 \underbrace{\int \psi_B \hat{H} \psi_B \, d\tau}_{\alpha_B} + 2 c_A c_B \underbrace{\int \psi_A H \psi_B \, d\tau}_{\beta}$$

Coulomb Integrals — Resonance Integral

$$E = [\alpha_A c_A^2 + \alpha_B c_B^2 + 2\beta c_A c_B] / [c_A^2 + c_B^2 + 2 c_A c_B S]$$

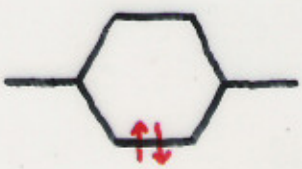
For the minimum in E, $\partial E / \partial c_A = 0$, $\partial E / \partial c_B = 0$

$$\left.\begin{aligned} (\alpha_A - E) c_A + (\beta - ES) c_B &= 0 \\ (\beta - ES) c_A + (\alpha_E - E) c_B &= 0 \end{aligned}\right\} \text{Secular Equations}$$

$$\begin{vmatrix} \alpha_A - E & \beta - ES \\ \beta - ES & \alpha_B - E \end{vmatrix} = 0$$

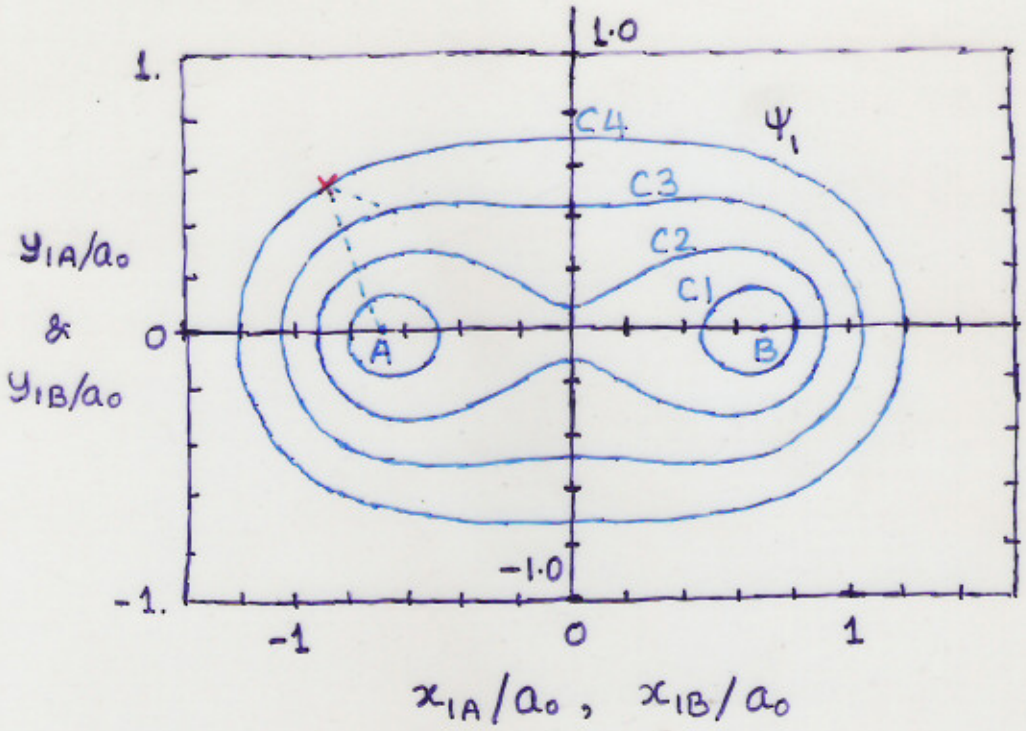
Secular determinant

For the case of two identical atoms, $\alpha_A = \alpha_B$



$$E_{\text{Antibonding}} = (\alpha - \beta)/(1 - S) \; ; \; c_A = -c_B = 1/[2 - 2S]^{1/2}$$

$$E_{\text{Bonding}} = (\alpha + \beta)/(1 + S) \; ; \; c_A = c_B = 1/[2 + 2S]^{1/2}$$



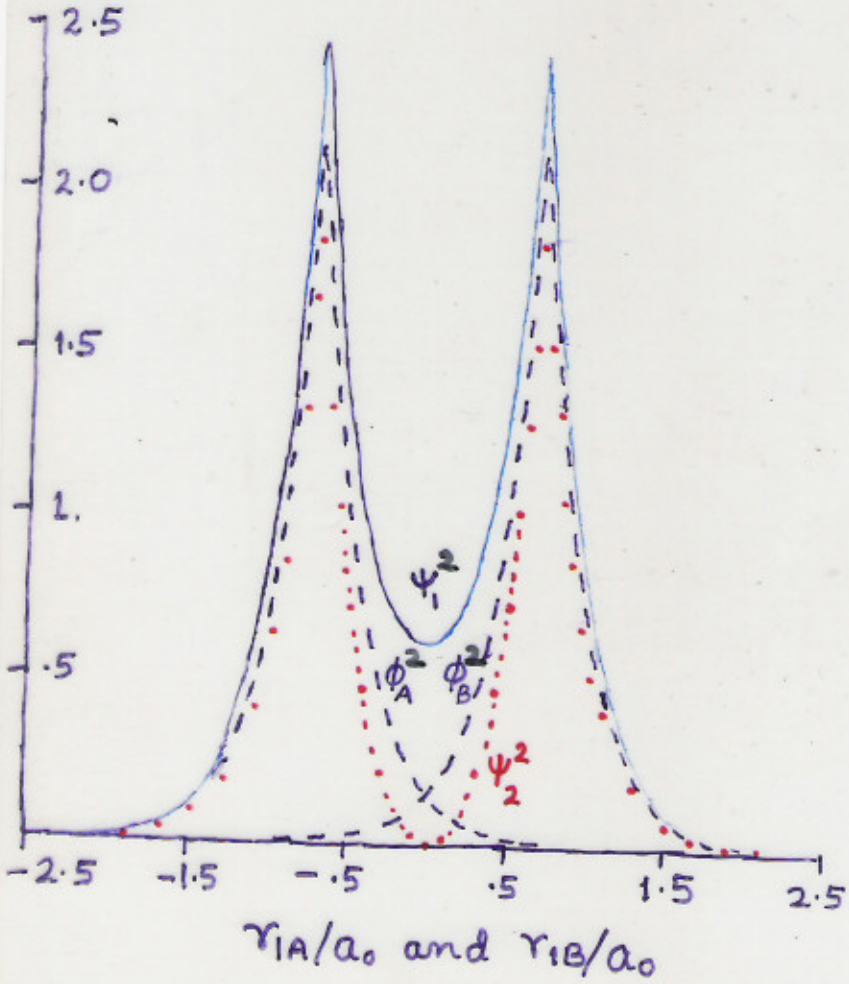

C1 : 1.66
C2 : 1.50
C3 : 1.29
C4 : ?

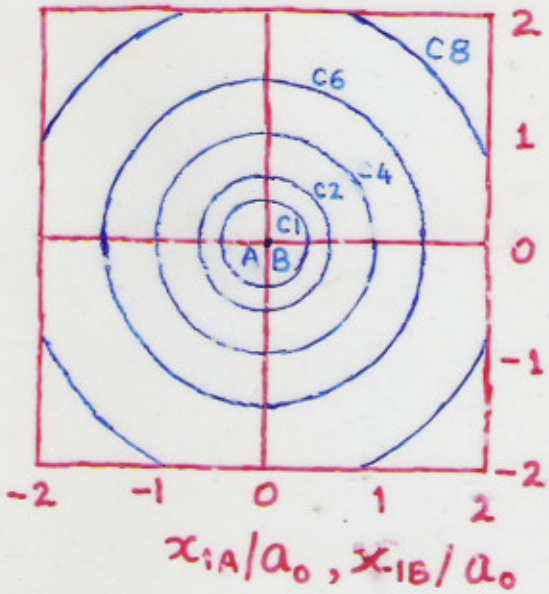
$ang^{-3/2}$

MOs:

$$\psi_1 = \phi_A(r_{1A}) + \phi_B(r_{1B})$$
$$\psi_2 = \phi_A(r_{1A}) - \phi_B(r_{1B})$$

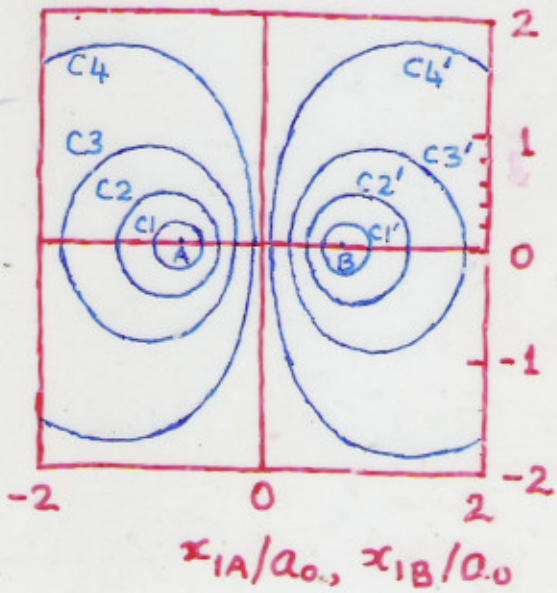
Function of the coordinates of <u>an</u> electron



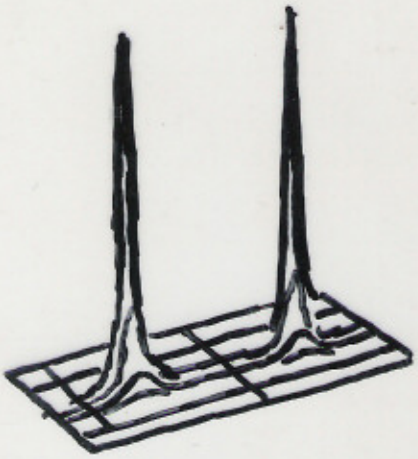



$y_{1A}/a_0$
and
$y_{1B}/a_0$

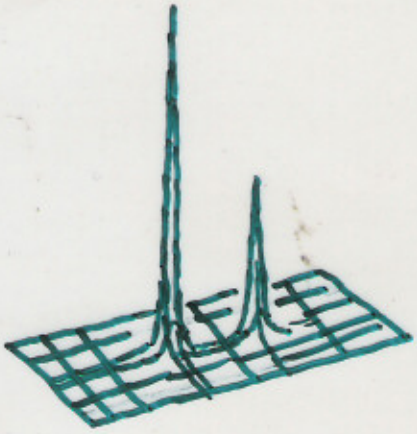
Axial Symmetry




$y_{1A}/a_0$
and
$y_{1B}/a_0$

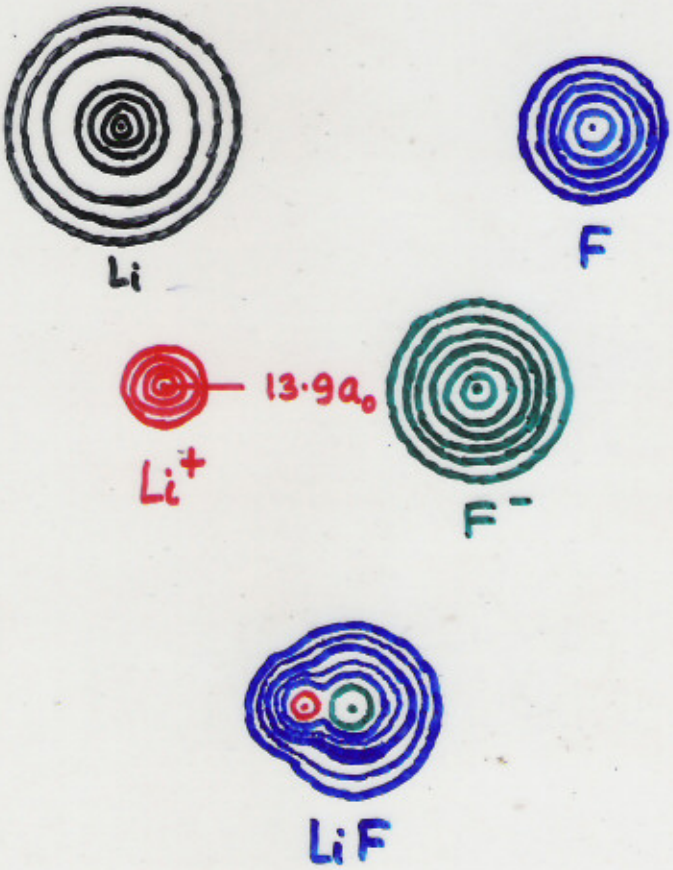


$Li_2$

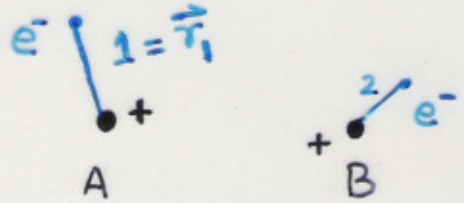


OC

Total Electron densities



# Valence Bond Theory




Electron Pair/Heitler-London/
Valence Bond functions:

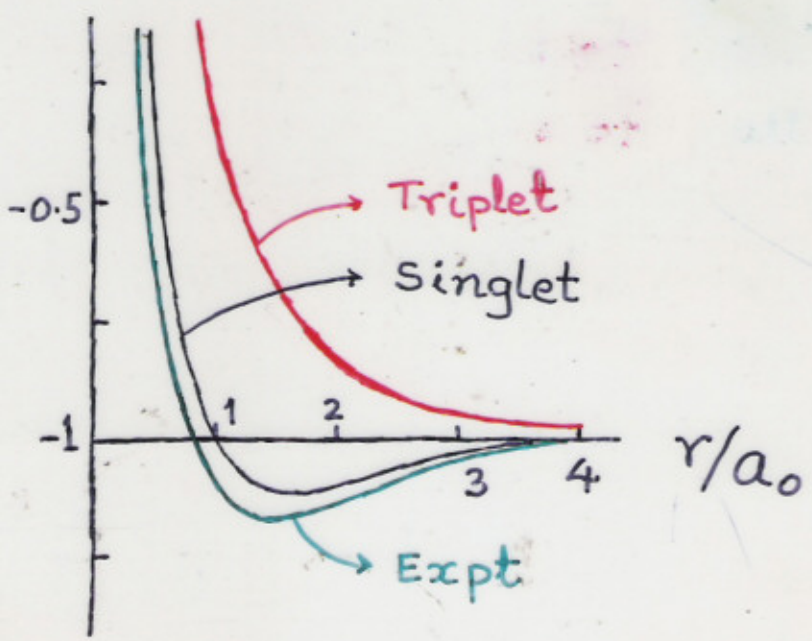
Products of AOs

$$\phi_1 = 1s_a(1)\cdot 1s_b(2)$$

$$\phi_2 = 1s_a(2)\cdot 1s_b(1)$$

$$\psi_1(VB) = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \times \underbrace{\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]}_{\text{singlet}}$$

$$\psi_2(VB) = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \times \underbrace{\begin{cases} \alpha(1)\alpha(2) \\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \alpha(2)\beta(1)\right] \\ \beta(1)\beta(2) \end{cases}}_{\text{triplet}}$$




$$\frac{E(H_2)}{\text{Hartree}}$$

1 hartree = 27·2 eV = $\dfrac{e^2}{4\pi\epsilon_0 a_0}$

# Comparison of MO and VB Theories

$$\Psi(VB) = \phi_a(1)\,\phi_b(2) + \phi_b(1)\,\phi_a(2)$$

$$\psi(MO) = \left[\phi_a(1) + \phi_b(1)\right]\left[\phi_a(2) + \phi_b(2)\right]$$

$$= \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2) + \phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)$$

$$= \Psi(VB) + \Psi(\text{Ionic terms})$$

Consider

$$\Psi'(MO) = \left[\phi_a(1) - \phi_b(1)\right]\cdot\left[\phi_a(2) - \phi_b(2)\right]$$

$$= -\,\Psi(VB) + \Psi\left[\text{Ionic Terms}\right]$$

"Best Wavefunction" $= c\,\psi(MO) - c'\,\psi'(MO)$

obtained by optimizing $c$ and $c'$

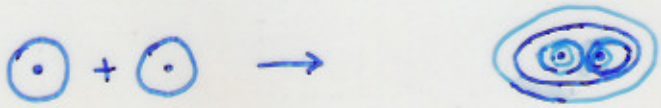
$c' = 0 \equiv \psi(MO)$; $c = c' = \frac{1}{2} \equiv \psi(VB)$

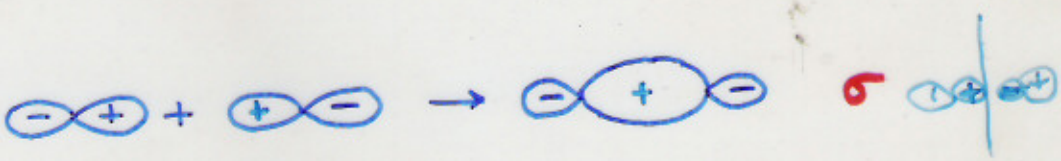
⇒ True theory involves features of all approximate theories ?

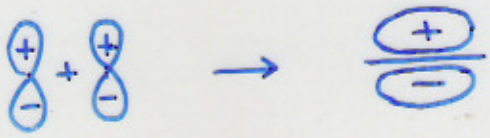
Comparison of Various Theories

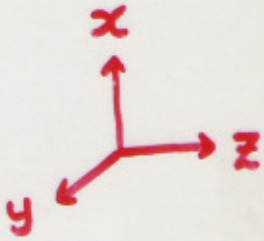
| Wavefunction | $R_e$ (pm) | $D_e$ (eV) |
|---|---|---|
| Simple MO | 85.0 | 2.70 |
| Simple VB | 87.0 | 3.14 |
| VB minimized wrt Z | 74.3 | 3.78 |
| James & Coolidge $\{r_{12}\}$ | 74.0 | 4.72 |
| Roothan [50 functions] | 74.1 | 4.7467 |
| **Experimental** | 74.1 | 4.747 |

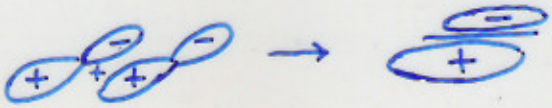
# Bonding Types

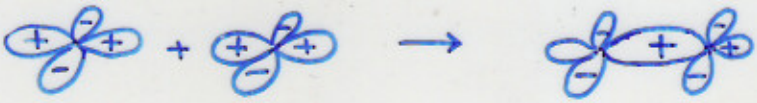
a) s  σ

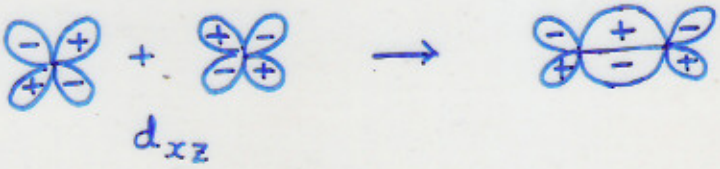
b) $p_z$  σ

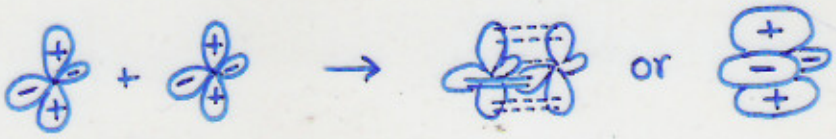
c) $p_x$  $\pi_x$




d) $p_y$  $\pi_y$

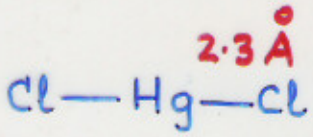
e)  σ

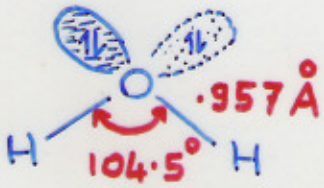
f) 
$d_{xz}$ π

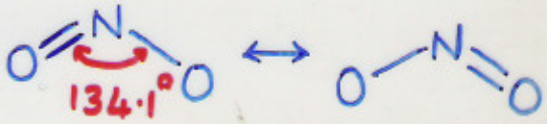
g) 

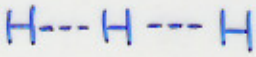
$d_{x^2-y^2}$ δ

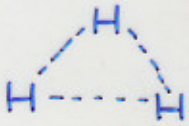
# Molecular Structures

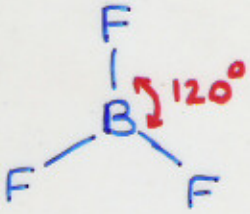


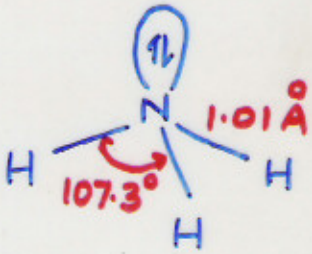



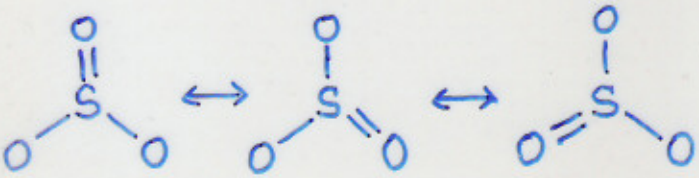



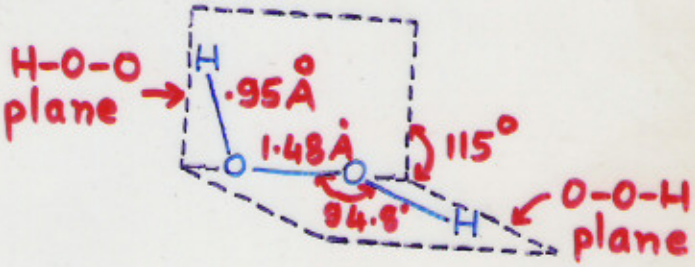



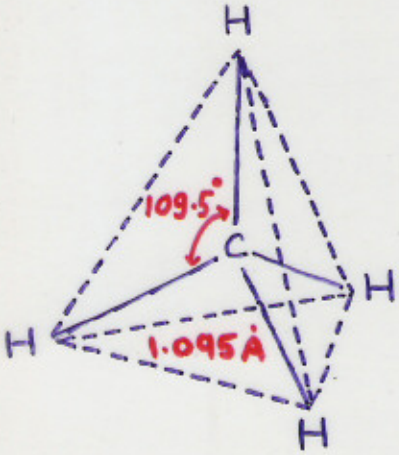



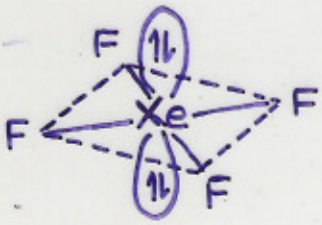



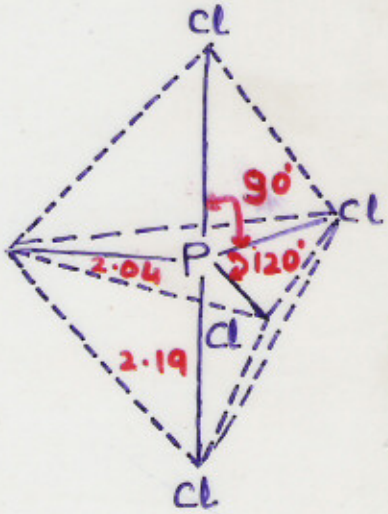



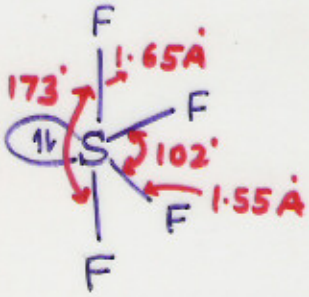



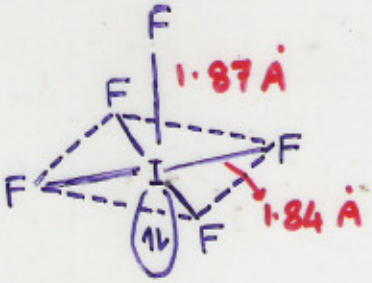



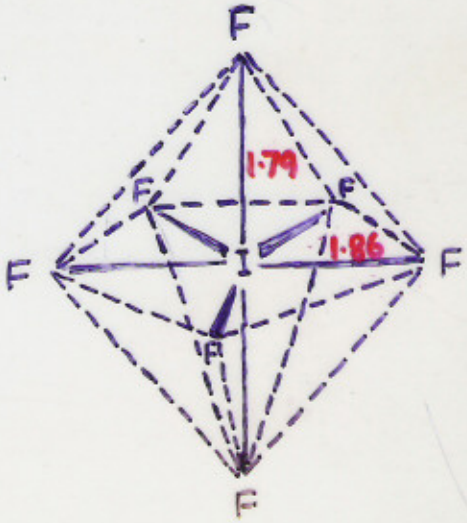



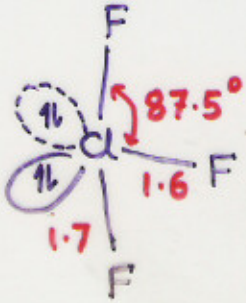



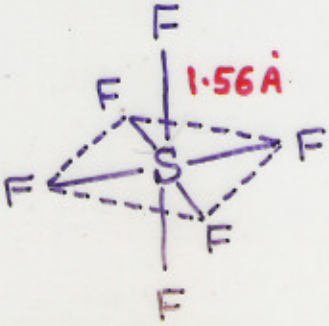



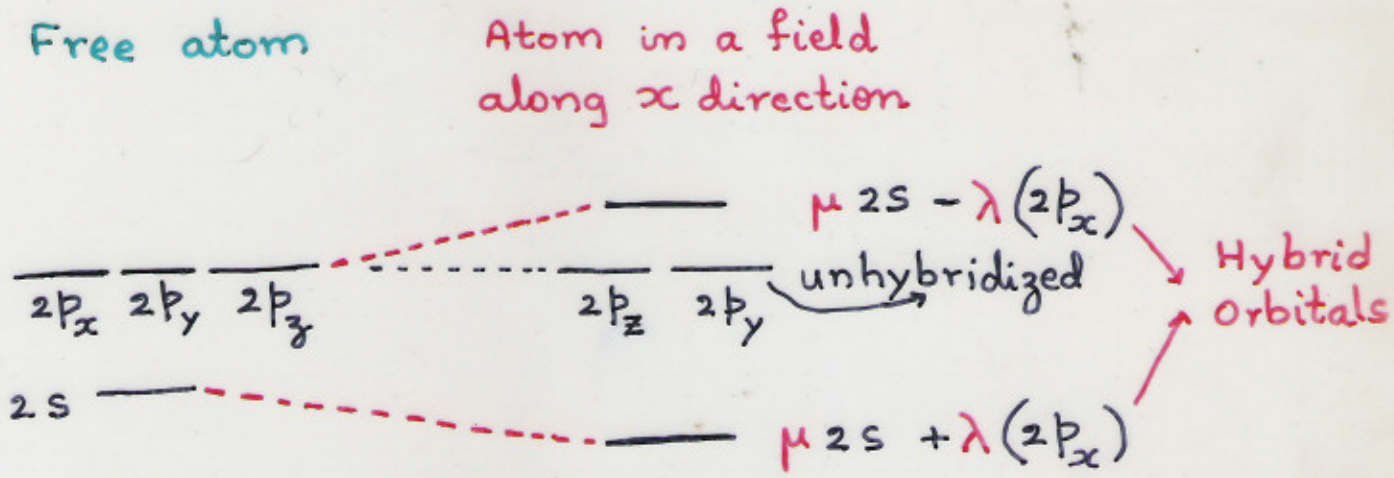



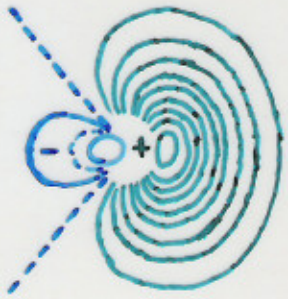
# Hybrid Orbitals

linear combination of atomic orbitals <u>within</u> an atom leading to more effective bonding




coefficients $\mu$ and $\lambda$ depend on field strength

## Linear Environment

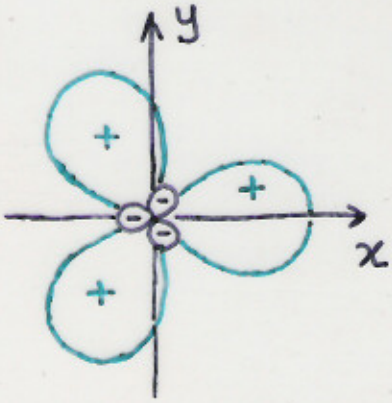



sp hybrid

$$h_1 = \frac{1}{\sqrt{2}}(s + p_x)$$

$$h_2 = \frac{1}{\sqrt{2}}(s - p_x)$$

## Triangular Environment:




Three $sp^2$ hybrids

$$h_1 = \frac{1}{\sqrt{3}} s + \sqrt{\frac{2}{3}}\, p_x$$

$$h_2 = \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x + \frac{1}{\sqrt{2}} p_y$$

$$h_3 = \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x - \frac{1}{\sqrt{2}} p_y$$

Contribution of an orbital to a hybrid $\equiv$ the square of the coefficient of that orbital in the hybrid.

# Hybridization

$p_x$ $p_y$ $p_z$

— s

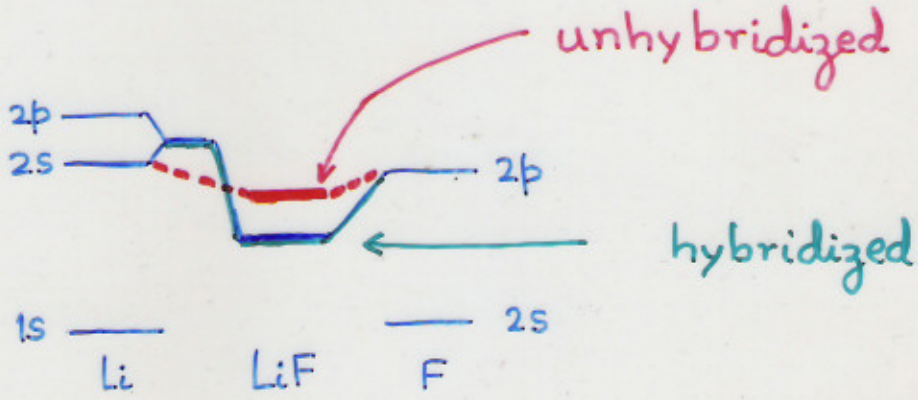
$h_1$ $h_2$ $h_3$ $h_4$

$sp^3$

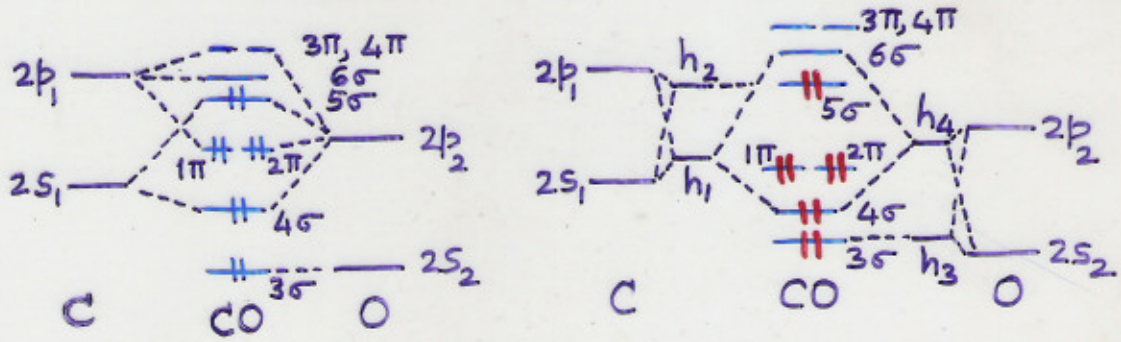
Tetrahedral Symmetry

$$h_1 = \tfrac{1}{2}(s + p_x + p_y + p_z)$$
$$h_2 = \tfrac{1}{2}(s + p_x - p_y - p_z)$$
$$h_3 = \tfrac{1}{2}(s - p_x - p_y + p_z)$$
$$h_4 = \tfrac{1}{2}(s - p_x + p_y - p_z)$$

## LiF

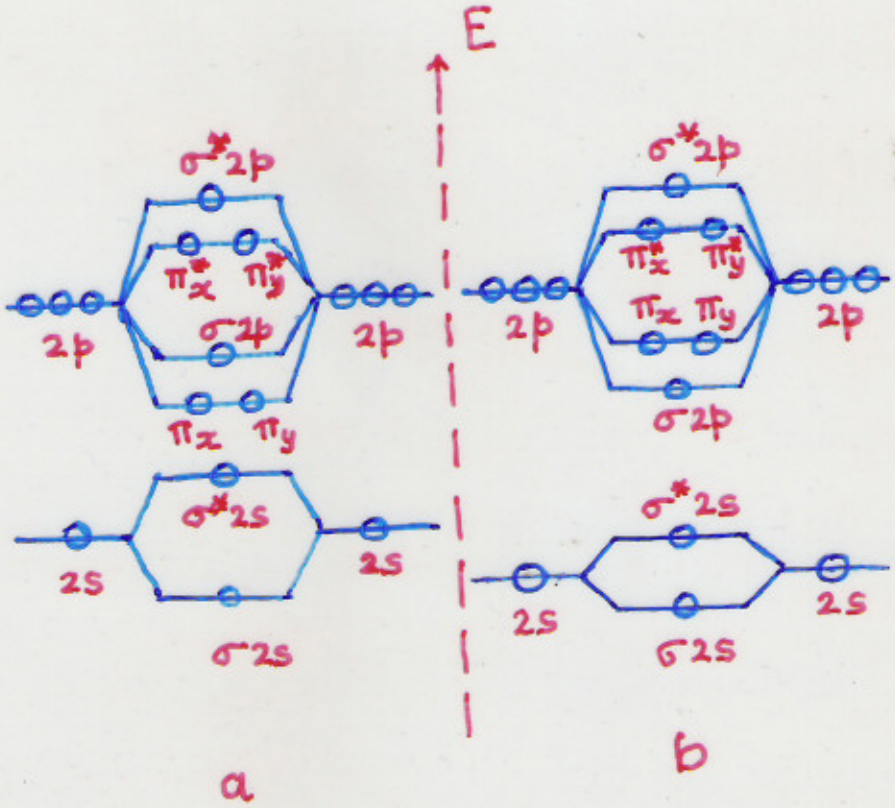



## CO




unhybridized hybridized

# Energy Level Diagram : Homonuclear Diatomics



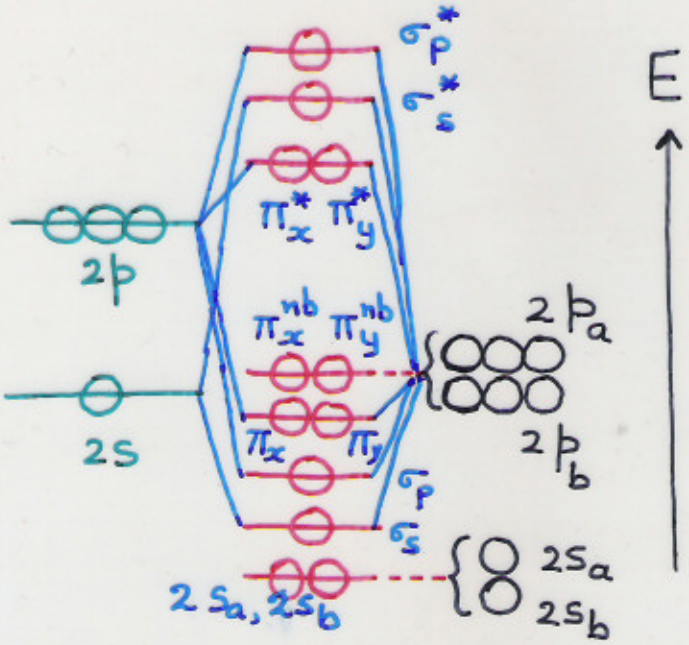

$Li_2 \cdots\cdots N_2$

$O_2, F_2,$

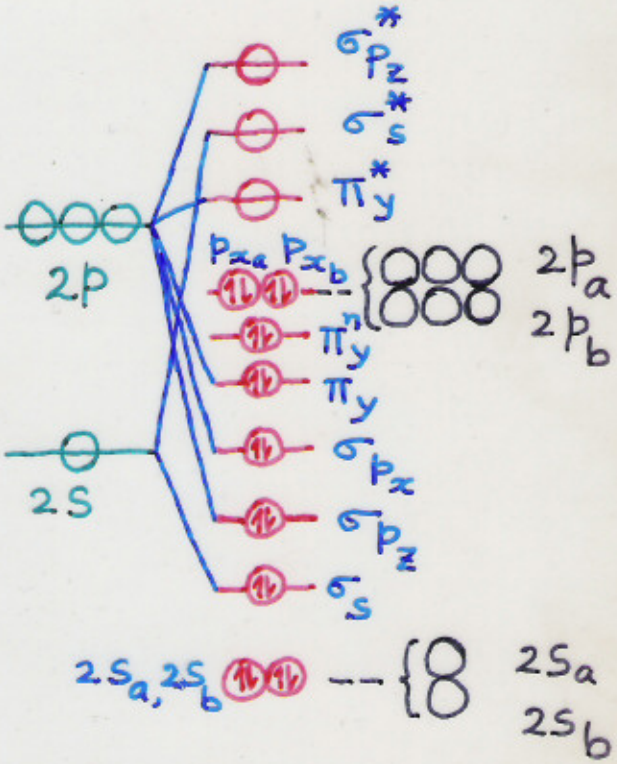
"Non Crossing Rule"

"Orbitals of same symmetry repel each other"

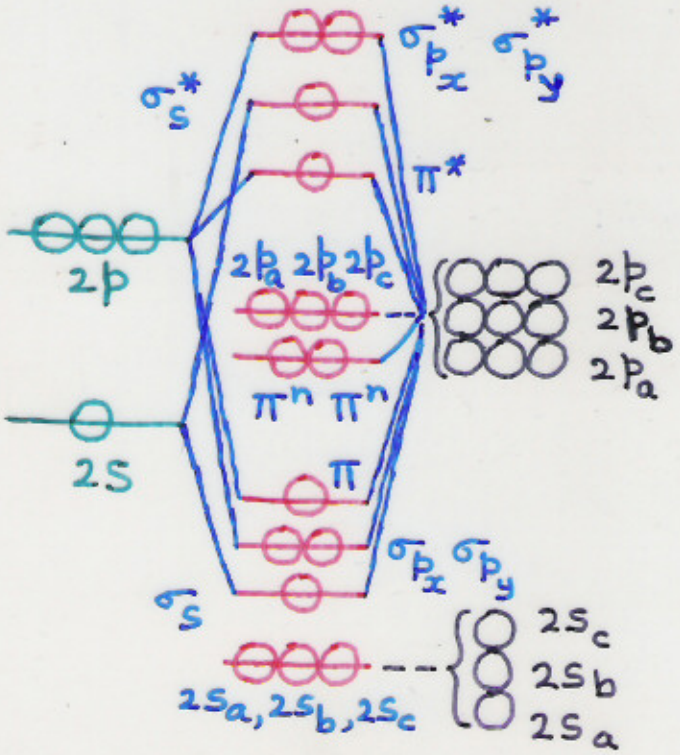
# MO Energy level Diagrams : Polyatomics

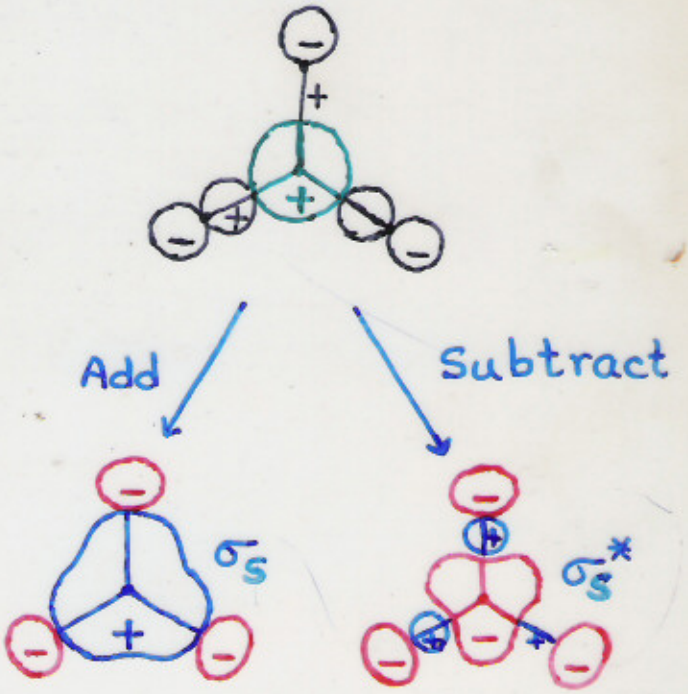



$CO_2$ (linear)

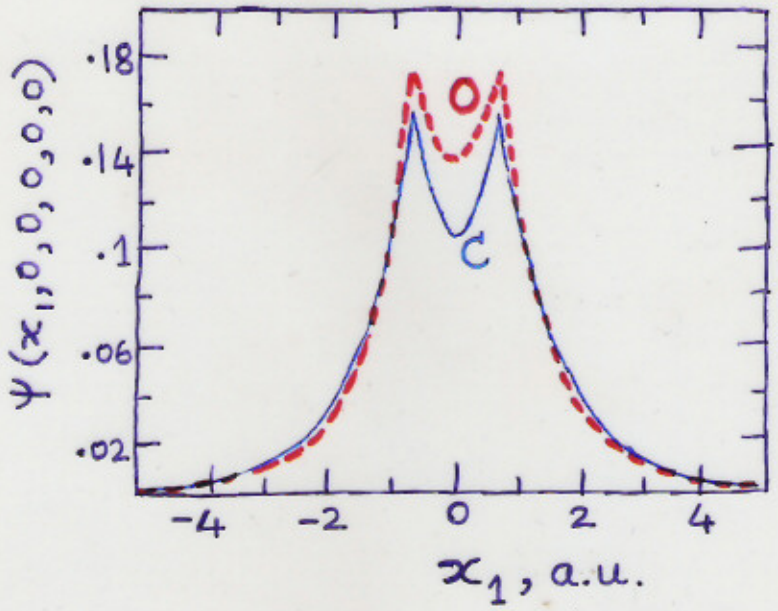



$O_3$, $NO_2^-$ (bent)
(18 electrons)




$NO_3^-$, $CO_3^{--}$, $SO_3$ (planar)




The effect of Electron Correlation

## The Variation Theorem

$$H\Psi = E\Psi \; ; \qquad E \geqslant E_{exact} = E_{experimental}$$

For $H_2$ :

$1\sigma^2$

$1\sigma^1 2\sigma^1$

$1\sigma^0 2\sigma^2$

$1\sigma^1 3\sigma^1$

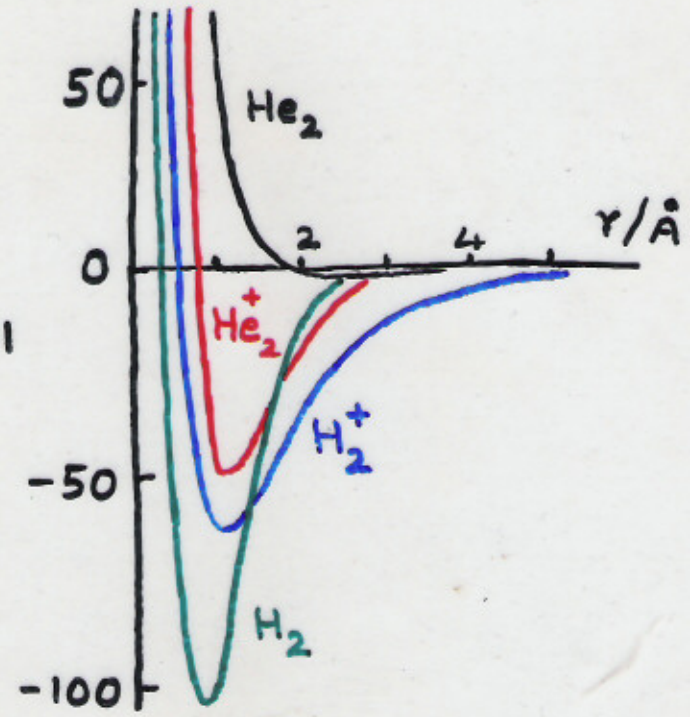
$\vdots$

Configuration Superposition

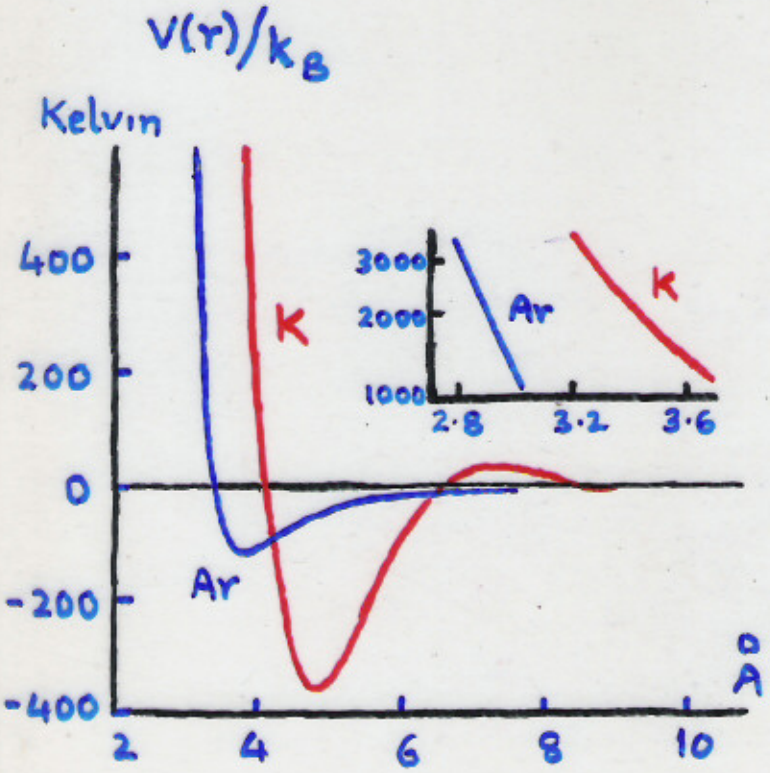
# Potential Energy as a function of $r$

Diatomics

E in kcal·mol$^{-1}$



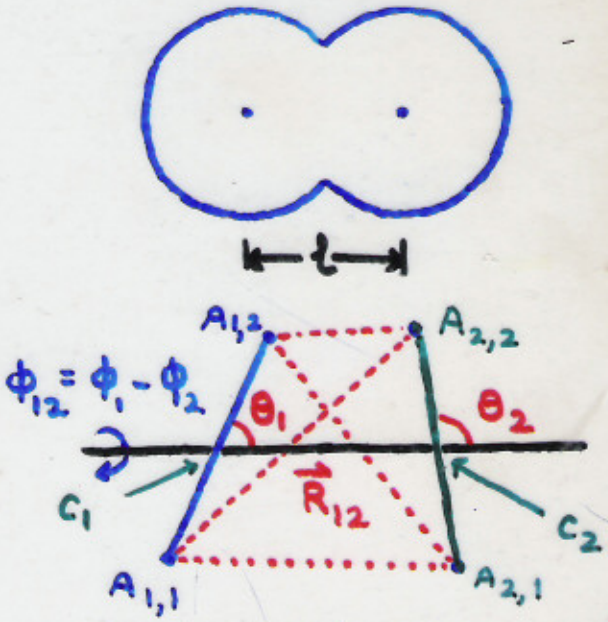

| | B.E. | $r_{eq}$ |
|---|---|---|
| $H_2$ | 104 | .74 |
| $H_2^+$ | 65 | 1.0 |




L-J Potential for Ar

Effective ion-ion potential for liquid potassium

Two diatomics approaching each other

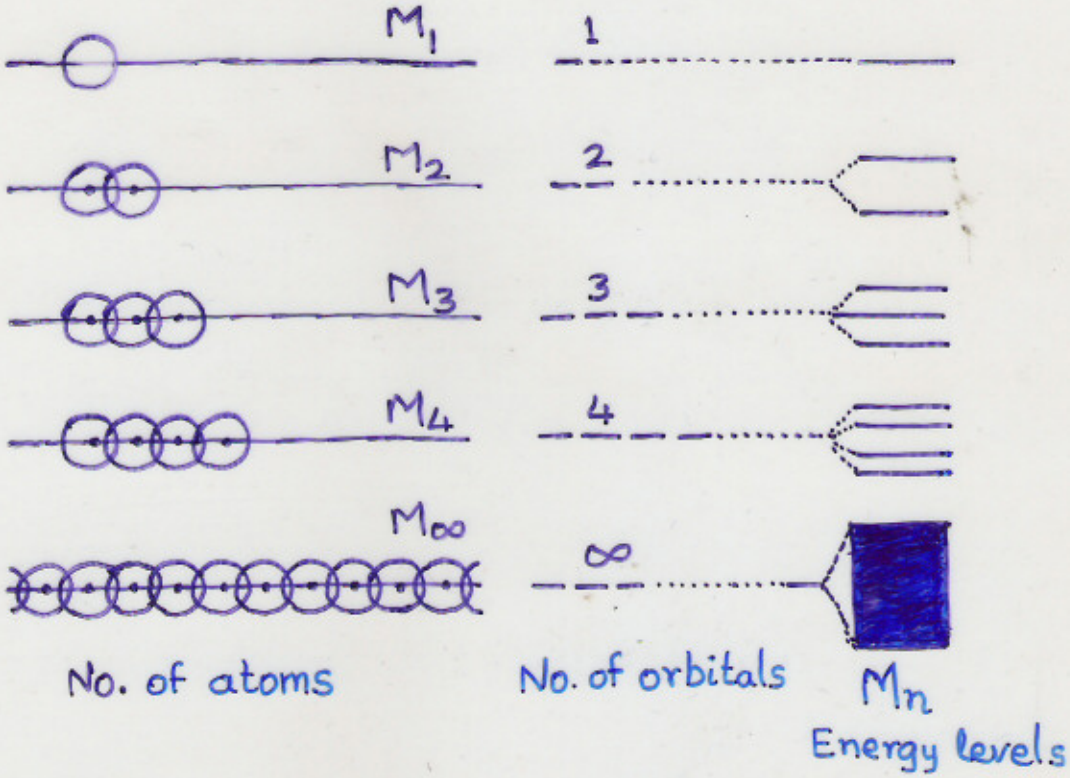


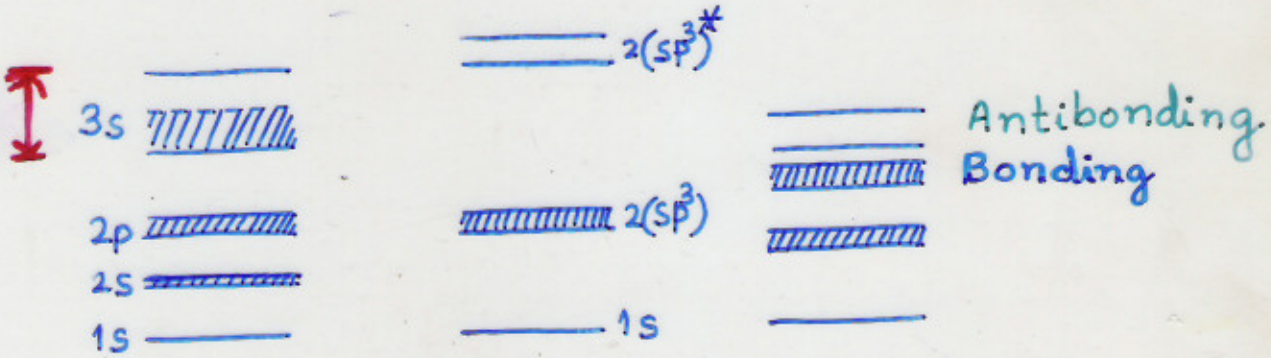

Centers of mass $C_1$, $C_2$

* INTERACTION SITE MODEL *

# Ordered Solids





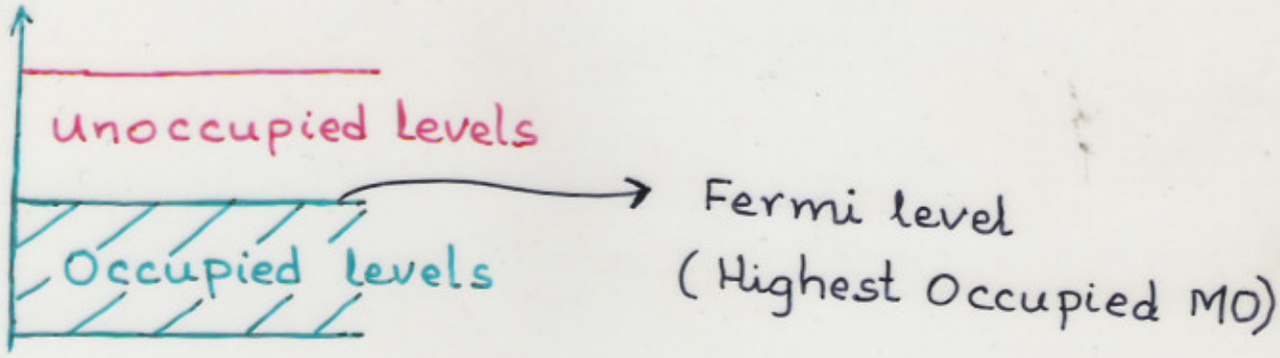




Na (Sodium) — **Conductor** — Half filled bands

C (diamond) — Insulator — Completely filled bands

Semiconductor — Si, Ge — Vacant band close to a filled band

$T = 0$, N electrons, $\frac{N}{2}$ MOs occupied



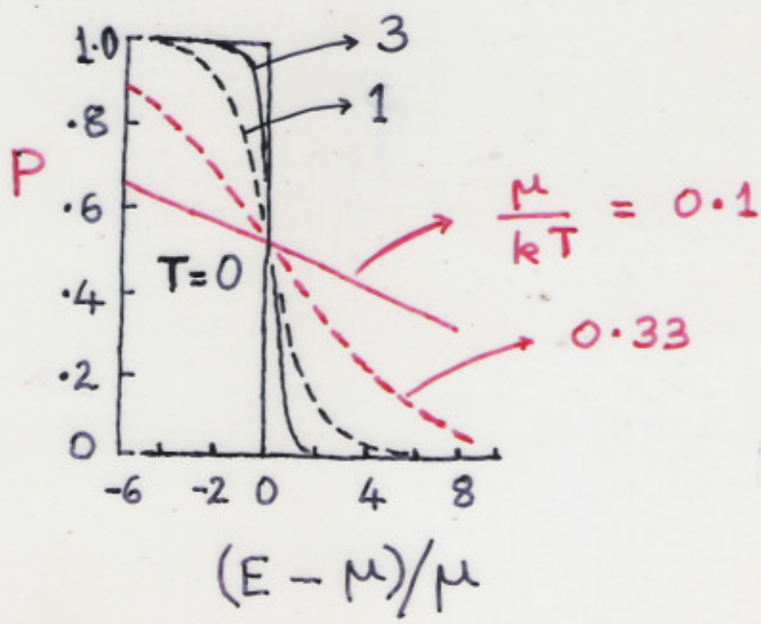

$T > 0$, Population of Orbitals

$$P = \frac{1}{e^{(E-\mu)/kT} + 1}$$

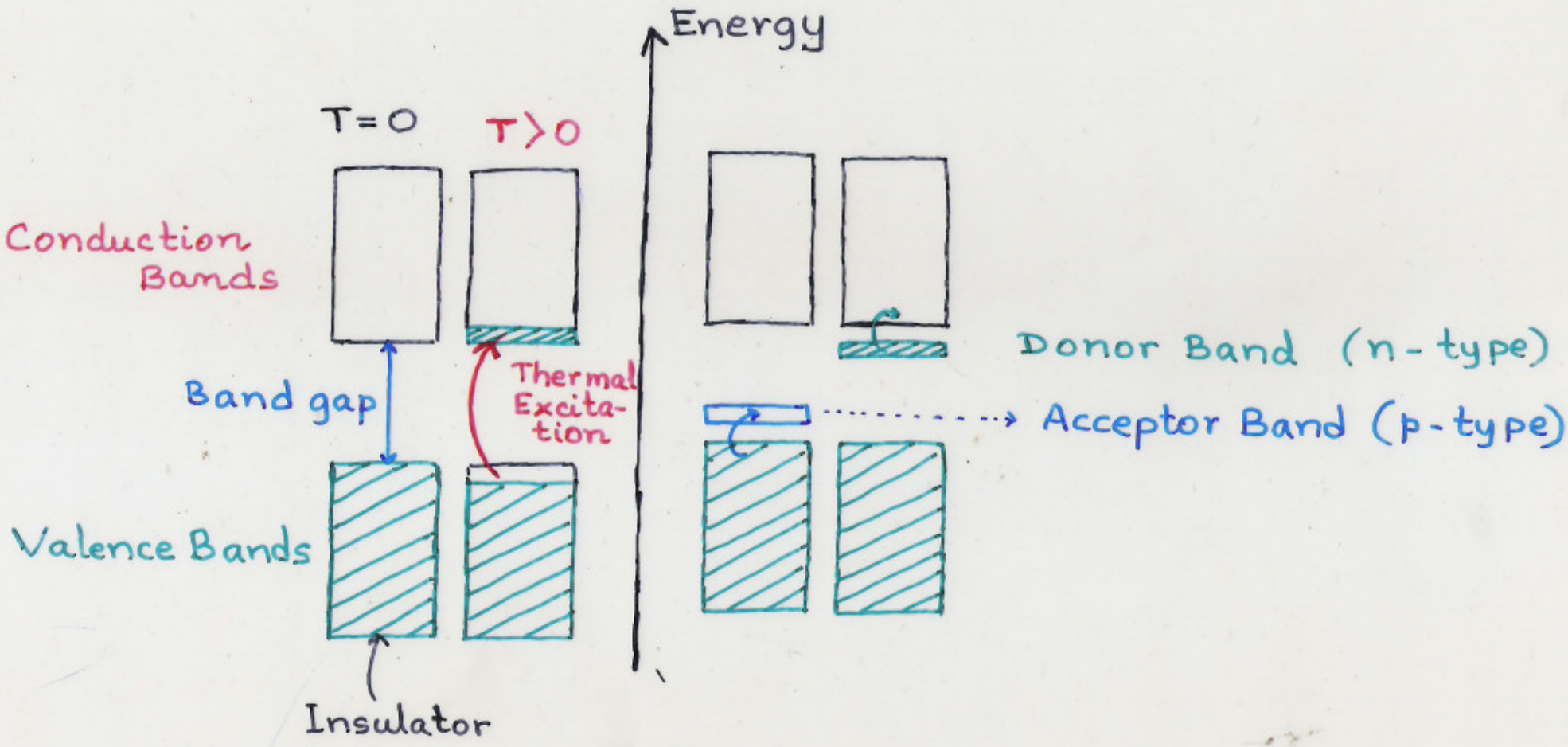
Fermi Dirac Distribution

$\mu$ = "Chemical Potential" $\equiv E$ when $P = \frac{1}{2}$

Temperature Dependence of P

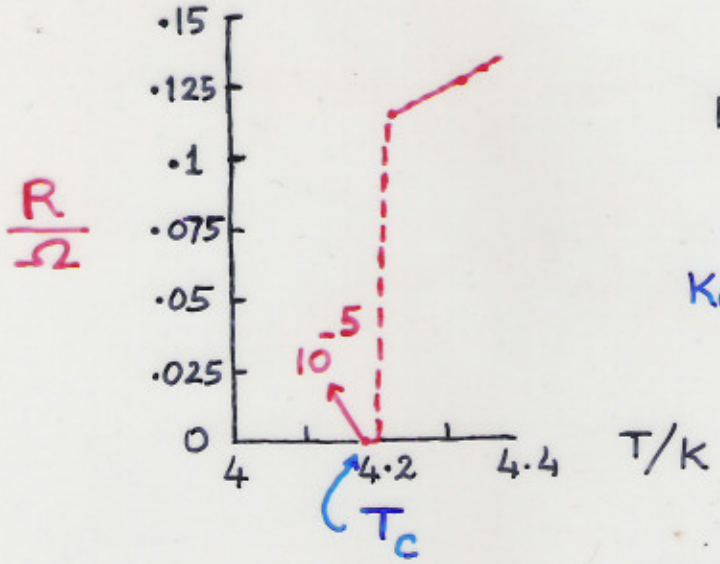


# Semiconductors




$\frac{N}{2}$ levels Occupied

# Superconductivity



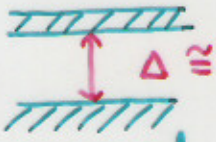

Resistance of Hg vs Temperature

Kamerlingh Onnes (1911)

Below $T_c$, a superconducting state/phase is attained

unusual magnetic and entropic behaviour

Bardeen Cooper Schrieffer (BCS) Theory 1957



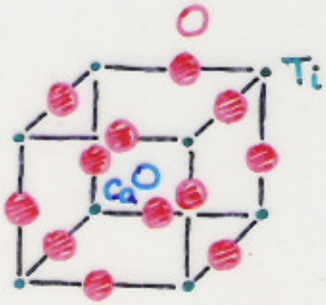

normal electrons

Ordered Pairs of $e^-$ due to interaction of electrons with lattice ions

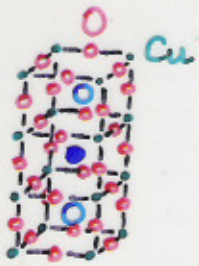
The "pairs" weakly interact with lattice and move freely

High $T_c$ Superconductors: $YBa_2Cu_3O_{7-x}$ ($x \leq 0.1$)

1986, $T_c \sim 90K$

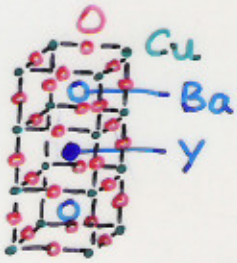



$CaTiO_3$




$YaBa_2Cu_3O_9$

Pervoskite substructure




1-2-3 Oxide

oxygen vacancy

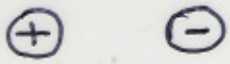
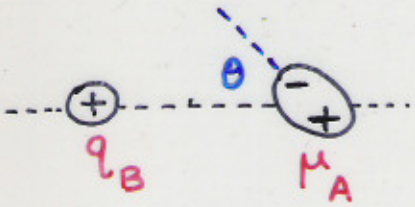
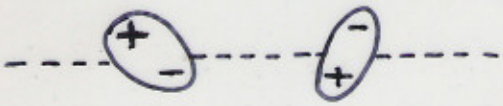
Nonstoichometry

# Intermolecular Forces.

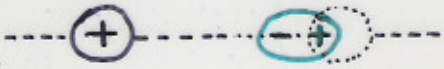
**Chemical Bonding:** Intramolecular, Covalent Solids

**Intermolecular forces:** Liquids, molecular solids, molecular motion, H-bonding

## Types of Intermolecular Forces

| | | Function |
|---|---|---|
| Ion-ion |  | $-1/r$ |
| Ion-Dipole |   | $-\dfrac{q_B \mu_A \cos\theta}{r_{AB}^2}$ |
| Dipole-dipole |  | $-\mu_A \cdot \mu_B / r_{AB}^3$ |

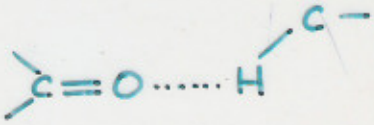
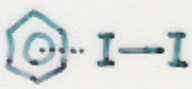
**Polar-nonpolar interactions**

| | | |
|---|---|---|
| Ion-induced-dipole |  | $-1/r^4$ |
| Dipole-induced dipole |  | $-1/r^6$ |

**Nonpolar Interactions**

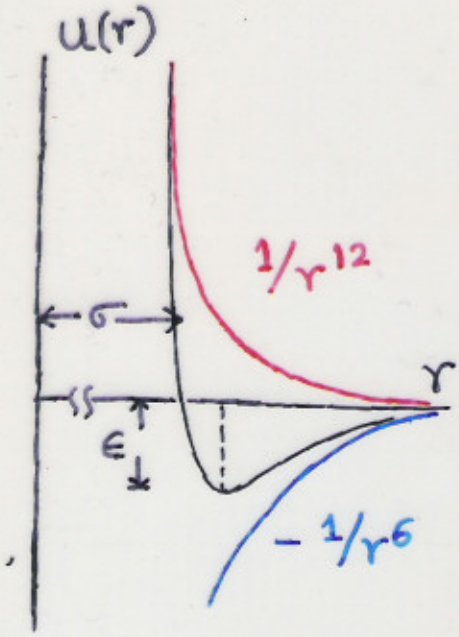
| | | |
|---|---|---|
| Induced dipole-Induced dipole | Dispersion<br>instantaneous dipole | $-1/r^6$ |

**Specific Interactions**

| | | |
|---|---|---|
| Hydrogen bonding |  | 3-8 $\frac{kcal}{mol}$ |
| Donor-Acceptor interaction (charge transfer) |  | 1-10 $\frac{kcal}{mol}$ |

# Lennard-Jones Potential






$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$u(r)$ is minimum at

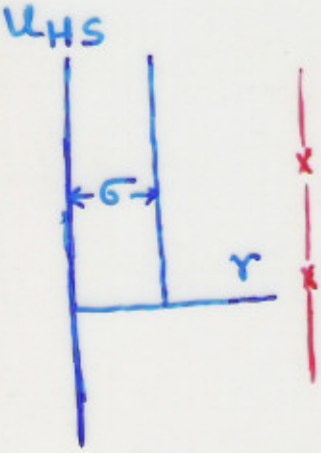
$$r = 2^{1/6}\,\sigma$$

## Some LJ parameters

| | $\sigma$/Å | $\epsilon/k_B$ in K |
|---|---|---|
| Ne | 2.79 | 36 |
| Ar | 3.42 | 120 |
| $N_2$ | 3.92 | 95 |
| $CH_4$ | 3.82 | 137 |
| $CCl_4$ | 6.24 | 377 |

Second virial coefficient, $pV = RT + BP + \cdots$

$$B(T) = -2\pi N_A \int_0^\infty \left(e^{-u(r)/k_BT} - 1\right) r^2 dr$$




$$\frac{B}{B_{HS}} = B^*$$

$$B_{HS} = \frac{2}{3}\pi N_A \sigma^3$$

$T^* = k_BT/\epsilon$