Molecular Structure 1

Ch. 11

Techniques of approximation (ch. 9, pp 310-)

(7판 ch.12, pp 355-)

Born-Oppenheimer approximation

Valence-bond theory

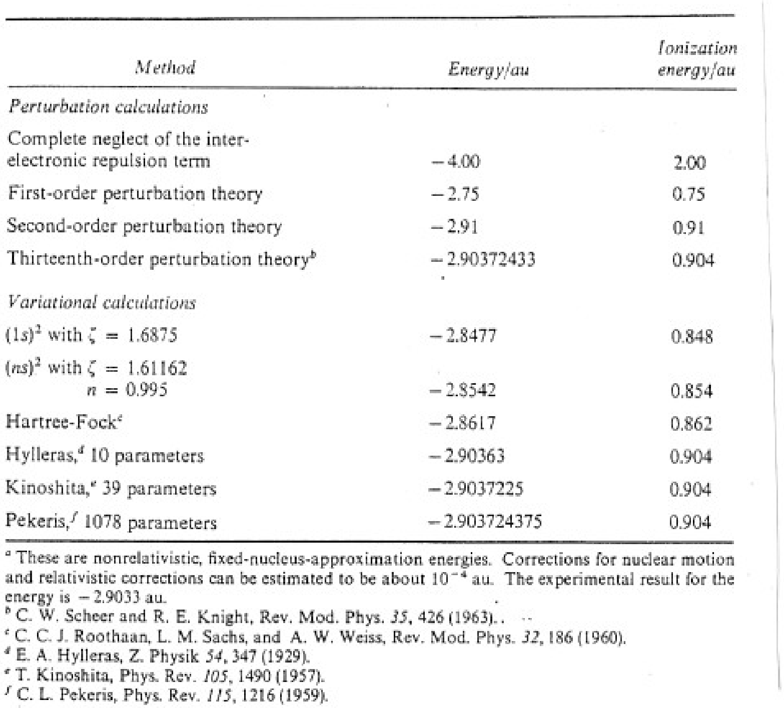
Molecular orbital theory

Molecular orbitals for polyatomic systems

Approximation Methods

He (Z = 2), $E \propto Z^2$

Table. Ground state energies of He atom by various methods



Method	*Energy/au*	*Ionization energy/au*
Perturbation calculations		
Complete neglect of the inter-electronic repulsion term	−4.00	2.00
First-order perturbation theory	−2.75	0.75
Second-order perturbation theory	−2.91	0.91
Thirteenth-order perturbation theory[b]	−2.90372433	0.904
Variational calculations		
$(1s)^2$ with $\zeta = 1.6875$	−2.8477	0.848
$(ns)^2$ with $\zeta = 1.61162$ $n = 0.995$	−2.8542	0.854
Hartree-Fock[c]	−2.8617	0.862
Hylleras,[d] 10 parameters	−2.90363	0.904
Kinoshita,[e] 39 parameters	−2.9037225	0.904
Pekeris,[f] 1078 parameters	−2.903724375	0.904

[a] These are nonrelativistic, fixed-nucleus-approximation energies. Corrections for nuclear motion and relativistic corrections can be estimated to be about 10^{-4} au. The experimental result for the energy is −2.9033 au.

[b] C. W. Scheer and R. E. Knight, Rev. Mod. Phys. *35*, 426 (1963).

[c] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. *32*, 186 (1960).

[d] E. A. Hylleras, Z. Physik *54*, 347 (1929).

[e] T. Kinoshita, Phys. Rev. *105*, 1490 (1957).

[f] C. L. Pekeris, Phys. Rev. *115*, 1216 (1959).

1. Perturbation theory

$\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$: exactly solved

$\rightarrow \hat{H}\psi = E\psi$, where $\underline{\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}}$

assume $\hat{H}^{(1)}$ is small

$\underline{\psi = \psi^{(0)} + \Delta\psi}$, $\underline{E = E^{(0)} + \Delta E}$ $\Rightarrow$ $\hat{H}\psi = E\psi$

$$\cancel{\hat{H}^{(0)}\psi^{(0)}} + \hat{H}^{(1)}\psi^{(0)} + \hat{H}^{(0)}\underset{\substack{0\\ \downarrow\\ \text{too small}}}{\cancel{\Delta\psi}} + \hat{H}^{(1)}\underset{\substack{0\\ ''}}{\cancel{\Delta\psi}} = \cancel{E^{(0)}\psi^{(0)}} + \Delta E\psi^{(0)} + E^{(0)}\Delta\psi + \Delta E\underset{\text{too small}}{\cancelto{0}{\Delta\psi}}$$

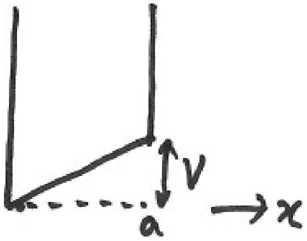
$\hat{H}^{(0)}\Delta\psi + \hat{H}^{(1)}\psi^{(0)} = E^{(0)}\Delta\psi + \Delta E\psi^{(0)}$: 1st order perturbation

multiply $\psi^{(0)*}$ and integrate

$$\int \psi^{(0)*}\underset{\substack{\parallel\\ 0}}{[\hat{H}^{(0)} - E^{(0)}]}\Delta\psi\, d\tau + \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}d\tau = \Delta E \underset{\substack{\parallel\\ 1}}{\int \psi^{(0)*}\psi^{(0)}d\tau}$$

$$\therefore \underline{\underline{\Delta E = \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}d\tau}}$$

$\therefore$ $E = E^{(0)} + \int \psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}d\tau$ + higher order term e.g., particle-in-a-box



$$\psi^{(0)} = \left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi x}{a}, \quad E^{(0)} = \frac{n^2h^2}{8ma^2}$$

$$\hat{H}^{(1)} = \frac{V}{a}x$$

$$\Rightarrow \Delta E = \int_0^a \psi^{(0)*}\left(\frac{V}{a}x\right)\psi^{(0)}\,dx = \frac{2V}{a^2}\int_0^a x\sin^2\frac{n\pi x}{a}\,dx$$

$$= \frac{a^2}{4}\cdot\frac{2V}{a^2} = \frac{V}{2}$$

$$\therefore E \cong \frac{n^2h^2}{8ma^2} + \frac{V}{2}, \quad n=1,2,3\dots$$

2. Variation method

ground state : $\hat{H}\psi_0 = E_0\psi_0$

$$E_0 = \frac{\int \psi_0^* \hat{H} \psi_0 \, d\tau}{\int \psi_0^* \psi_0 \, d\tau}$$

arbitrary wavefunction or "trial function"

$$E_\phi = \frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau}$$

$$\Rightarrow \quad E_\phi \geq E_0$$

$\therefore$ minimized $E_\phi = E_0$

$$\xrightarrow[\text{differentiation}]{} \frac{\partial E_\phi}{\partial c} = 0 \Rightarrow c = ?$$

general form $\phi = \sum_{n=1}^{N} c_n f_n$

consider $\phi = c_1 f_1 + c_2 f_2$

$$\Rightarrow \int \phi \hat{H} \phi \, d\tau = \int (c_1 f_1 + c_2 f_2) \hat{H} (c_1 f_1 + c_2 f_2) \, d\tau$$

$$= c_1^2 \int f_1 \hat{H} f_1 \, d\tau + c_1 c_2 \int f_1 \hat{H} f_2 \, d\tau + c_1 c_2 \int f_2 \hat{H} f_1 \, d\tau + c_2^2 \int f_2 \hat{H} f_2 \, d\tau$$

$$= c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22} \quad (\because H_{12} = H_{21})$$

where $\underline{H_{ij} = \int f_i \hat{H} f_j \, d\tau}$

$$\int \phi^2 d\tau = c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22}$$

where $S_{ij} = S_{ji} = \int \phi_i \phi_j \, d\tau$

$$\Rightarrow E(c_1, c_2) = \frac{c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22}}$$

$$E(c_1, c_2) \left[c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22} \right] = c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22}$$

- $\frac{\partial E}{\partial C_1} = 0$ (minimizing)

$$(2C_1S_{11} + 2C_2S_{12})E + \frac{\partial E}{\partial C_1}(C_1^2S_{11} + 2C_1C_2S_{12} + C_2^2S_{22}) = 2C_1H_{11} + 2C_2H_{12}$$

$$\underline{C_1(H_{11} - ES_{11}) + C_2(H_{12} - ES_{12}) = 0}$$

- $\frac{\partial E}{\partial C_2} = 0 \Rightarrow \underline{C_1(H_{12} - ES_{12}) + C_2(H_{22} - ES_{22}) = 0}$

$$\Rightarrow \begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

secular determinant

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = 0 \Rightarrow ad - bc = 0$$

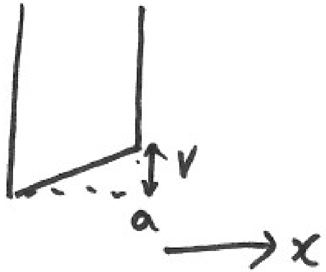
General

$$\begin{vmatrix} H_{11}-ES_{11} & \cdots & H_{N1}-ES_{N1} \\ \vdots & \ddots & \vdots \\ H_{1N}-ES_{1N} & \cdots & H_{NN}-ES_{NN} \end{vmatrix} = 0$$

orthonormal : $S_{ii}=1$, $S_{ij}=0$

$$\begin{vmatrix} H_{11}-E & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22}-E & & \\ \vdots & & \ddots & \\ H_{N1} & & & H_{NN}-E \end{vmatrix} = 0$$

e.g., particle-in-a-box



if $a=1$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + Vx \qquad 0 \leq x \leq 1$$

$$\phi = c_1\psi_1 + c_2\psi_2 = c_1\left(\frac{2}{a}\right)^{1/2}\sin\frac{\pi x}{a} + c_2\left(\frac{2}{a}\right)^{1/2}\sin\frac{2\pi x}{a}$$

$$\Rightarrow H_{11} = \int_0^1 dx\, \psi_1 \hat{H} \psi_1 = \frac{\pi^2\hbar^2}{m}\int_0^1 dx \sin^2\pi x + 2V\int_0^1 dx\cdot x\sin^2\pi x = \frac{h^2}{8m} + \frac{V}{2}$$

$$H_{22} = \frac{h^2}{2m} + \frac{V}{2}, \quad H_{12} = -\frac{16V}{9\pi^2}$$

$$S_{11} = S_{22} = 1, \quad S_{12} = S_{21} = 0$$

$$\Rightarrow \begin{vmatrix} \frac{h^2}{8m} + \frac{V}{2} - E & -\frac{16V}{9\pi^2} \\ -\frac{16V}{9\pi^2} & \frac{h^2}{2m} + \frac{V}{2} - E \end{vmatrix} = 0 \Rightarrow E = \frac{h^2}{8m} + \frac{V}{2} \; //$$

Molecular Structure 1

Reading: Atkins, Ch. 14.

- Question: Why molecule forms?

Shape?  $O=C=O$

Bond strength? $N\equiv N$ $O=O$ $H-H$

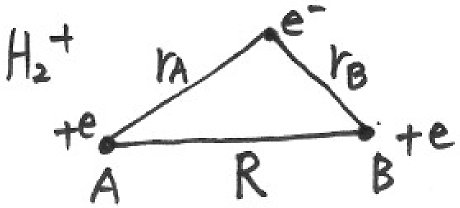
- Quantum mechanical theories → Molecular electronic structure

(1) **Valence-bond theory**: shared electronic pair → σ,π-bond, promotion, hybridization….

(2) **Molecular orbital theory**: extended from atomic orbital → solid properties, conduction, semiconductor…..

1. Born-Oppenheimer approximation

Nuclei: heavier than electron → move relatively slow → “fixed”



$$\hat{H}=\hat{T}+\hat{V}=\underset{\underset{\text{proton}}{\uparrow}}{-\frac{\hbar^2}{2M}}\underset{0}{\cancel{\left(\nabla_A^2+\nabla_B^2\right)}}\underset{\underset{e^-}{\uparrow}}{-\frac{\hbar^2}{2m}}\nabla_r^2-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A}+\frac{1}{r_B}-\underset{\underset{\text{Const.}}{\Downarrow}}{\frac{1}{R}}\right)$$

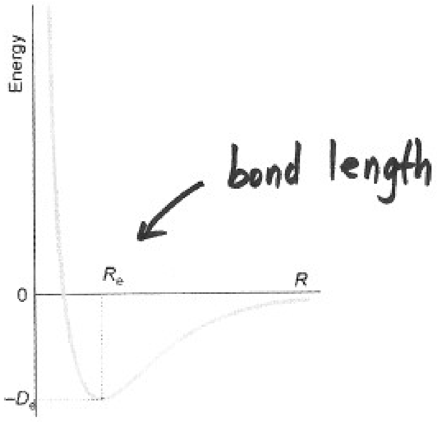
$$M \approx 1830 \cdot m$$

⇒ nuclei as being fixed : B-O approximation

separation of nuclei motion from e^- motion

→ reduced to one particle problem for H_2^+

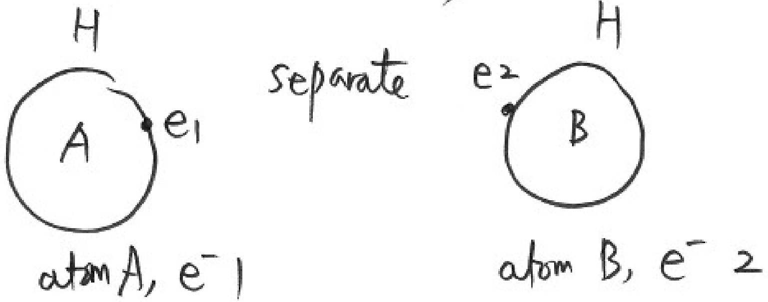
$$\hat{H}=-\frac{\hbar^2}{2m}\nabla^2-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A}+\frac{1}{r_B}\right)$$

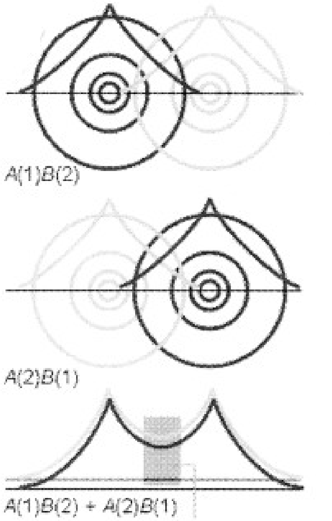


2. Valence-bond theory

- widely used in chemistry, especially organic compound: spin-pair, σ,π-bond, promotion, hybridization
- pairing of the electrons: accumulation of electron density in the internuclear region from pairing

1) Hydrogen molecule (H_2)



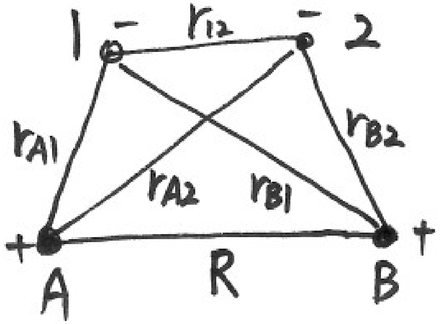


$$\Psi = \psi_{H1sA}(r_1)\,\psi_{H1sB}(r_2) = A(1)\,B(2)$$

$\xrightarrow[\text{close}]{}$ indistinguishable electrons 1, 2

$$\Rightarrow \psi_\pm = A(1)B(2) \pm A(2)B(1)$$: not normalized

ψ_+ : lower energy



$$V = -\frac{e^2}{4\pi\varepsilon_0}\underbrace{\left(\frac{1}{r_{A1}} + \frac{1}{r_{A2}} + \frac{1}{r_{B1}} + \frac{1}{r_{B2}}\right)}_{\text{attractive between electron and nuclei}} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_{12}}}_{\text{repulsion between two electrons}}$$

$$H = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 + V + \underbrace{\frac{e^2}{4\pi\varepsilon_0 R}}_{\text{nucleus-nucleus repulsion (const.)}}$$

$$\psi_1 = A(1)B(2), \quad \psi_2 = A(2)B(1)$$

$$\psi = c_1\psi_1 + c_2\psi_2$$

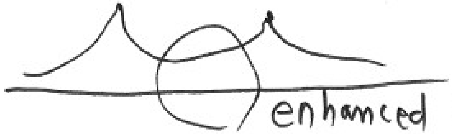
$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$\Delta E_{\pm} = \frac{J \pm K}{1 \pm S^2}$$

S: overlap integral, J: Coulomb integral
K: exchange integral

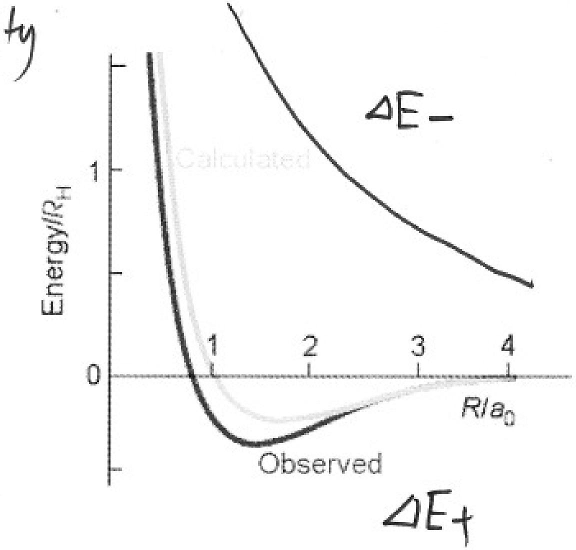
J, K: negative

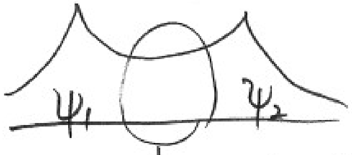
ΔE_{+}: stable chemical bond



(∵ E is less than that of two isolated H-atoms)

$\psi_{+} = A(1)B(2) + A(2)B(1)$ has lower E than ψ_{-}





↳ overlap ⇒ bind them together!

- the role of electron spin

pauli principle : $\psi(2,1) = -\psi(1,2)$ should be

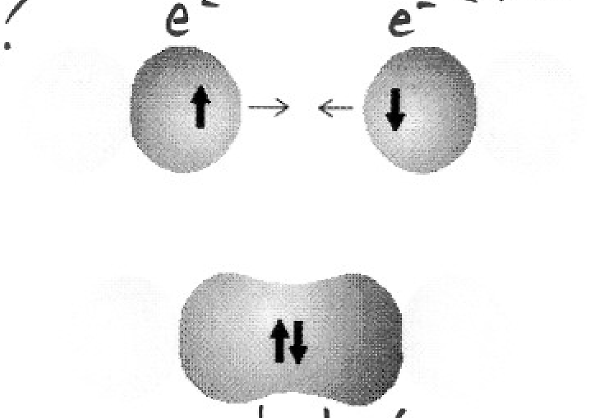
$$\psi(1,2) = [\,A(1)B(2) + A(2)B(1)\,]\,\sigma(1,2)$$

$$\psi(2,1) = [\,A(2)B(1) + A(1)B(2)\,]\,\sigma(2,1)$$

For $\psi(2,1) = -\psi(1,2) \Rightarrow \sigma(2,1) = -\sigma(1,2)$ $\left(\because [A(1)B(2) + A(2)B(1)] = [A(2)B(1) + A(1)B(2)]\right)$

$\therefore \sigma_-(1,2) = \frac{1}{2^{1/2}}\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$ allowed !

(paired electrn spins (opposite spins))



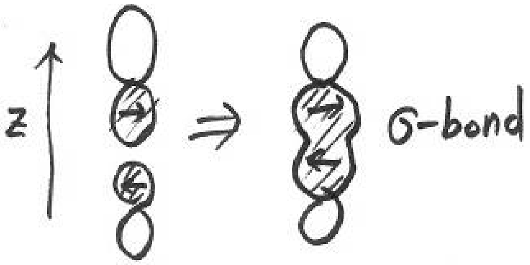
bonding !

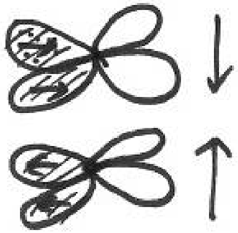
2) Homonuclear diatomic molecules

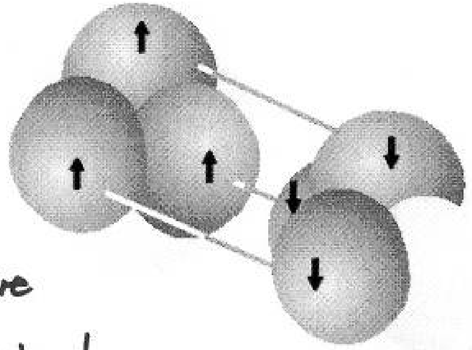
· valence bond theory : pairing of the electrons

e.g., N_2 $\quad N : 2s^2 2p_x^1 2p_y^1 2p_z^1$

z-axis : internuclear axis , x, y axis





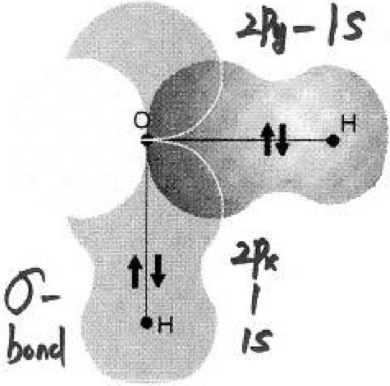


N_2 : 1-σ bond
2-π bonds } ⇒ $:N\equiv N:$
↓ Lewis structure

e.g., Cl_2 $\quad Cl : (Ar) 3s^2 3p_x^2 3p_y^2 3p_z^1$ $\quad :\underset{..}{\ddot{Cl}}:\underset{..}{\ddot{Cl}}:$ σ-bond

3) Polyatomic molecules

- H_2O $O: 2s^2 2p_x^2 2p_y^1 2p_z^1 \leftrightarrow 2H\ 1s$



$2p_y - 1s$, σ-bond

$\Rightarrow 90° \Rightarrow$ actual 104.5° ?

$2p_x$ | $1s$

σ-bond

- NH_3 $N: 2s^2 2p_x^1 2p_y^1 2p_z^1 \leftrightarrow 3H\ 1s$

  90° e.a ⇒ actual 107° ?

- CH_4 $C: 2s^2 2p_x^1 2p_y^1 \rightarrow$ 2bonds, actual 4 bonds ?

(i) Promotion

$C: 2s^2 2p_x^1 2p_y^1 \longrightarrow 2s^1 2p_x^1 2p_y^1 2p_z^1$: 4 unpaired electons $+ 4H\ 1s \Rightarrow CH_4$

3σ : p ↔ s, 4th C2s ↔ H1s ⇒ ?

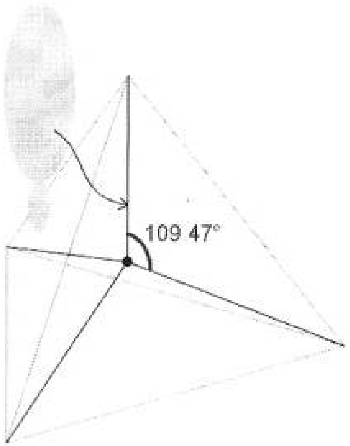
(ii) Hybridization: formation of hybrid orbital → equal electron density distribution

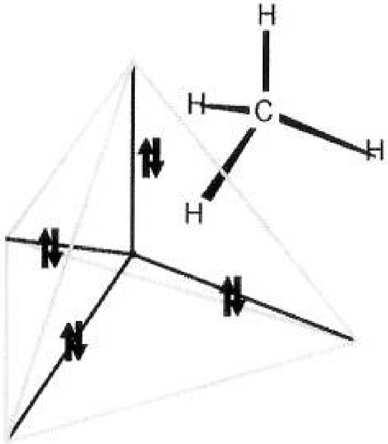
1-s + 3-p orbitals → sp^3 hybrid orbital "

$$\left.\begin{array}{l} h_1 = s + p_x + p_y + p_z \,, \quad h_2 = s - p_x - p_y + p_z \\ h_3 = s - p_x + p_y - p_z \,, \quad h_4 = s + p_x - p_y - p_z \end{array}\right\} \Rightarrow \text{equivalent hybrid orbitals}$$

CH_4 → tetrahedral (4 equivalent C–H bonds)

CH_4



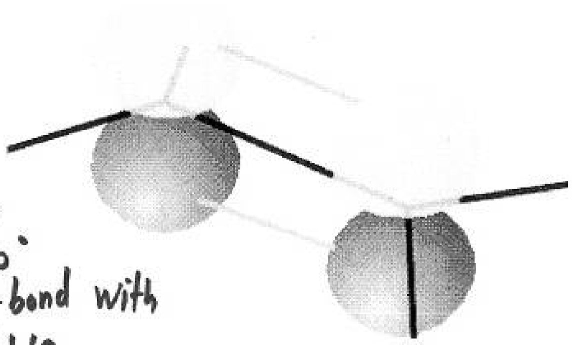


Ethene, $CH_2{=}CH_2$, sp^2 hybrid orbitals
(planar)

$$2s^1 2p_x^1 2p_y^1 \left[\begin{array}{l} h_1 = s + \sqrt{2}\, p_y \\ h_2 = s + \left(\frac{3}{2}\right)^{1/2} p_x - \left(\frac{1}{2}\right)^{1/2} p_y \\ h_3 = s - \left(\frac{3}{2}\right)^{1/2} p_x - \left(\frac{1}{2}\right)^{1/2} p_y \end{array} \right\} \rightarrow$$

120°
σ-bond with
H1s

$2p_z$: unhybridized → π-bond



Ethyne, ($HC\equiv CH$, linear), sp hybridized

$$\left. \begin{array}{l} h_1 = s + p_z \\ h_2 = s - p_z \end{array} \right\} \rightarrow \sigma\text{-bonds}$$

2 unhybridized p orbitals ⇒ π-bond

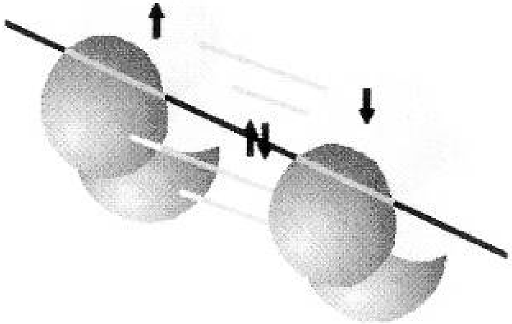


Table 14.1. Some hybridization schemes

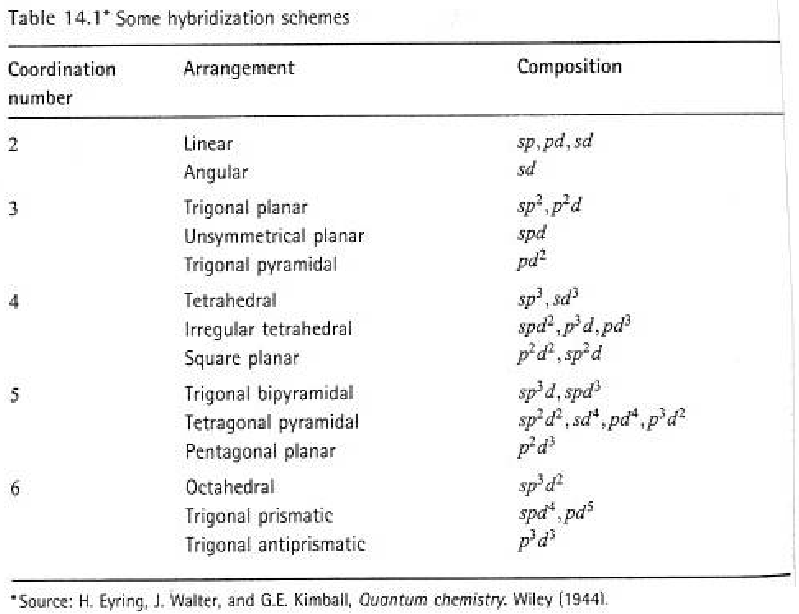


Table 14.1* Some hybridization schemes

Coordination number	Arrangement	Composition
2	Linear	*sp*, *pd*, *sd*
	Angular	*sd*
3	Trigonal planar	sp^2, p^2d
	Unsymmetrical planar	*spd*
	Trigonal pyramidal	pd^2
4	Tetrahedral	sp^3, sd^3
	Irregular tetrahedral	spd^2, p^3d, pd^3
	Square planar	p^2d^2, sp^2d
5	Trigonal bipyramidal	sp^3d, spd^3
	Tetragonal pyramidal	sp^2d^2, sd^4, pd^4, p^3d^2
	Pentagonal planar	p^2d^3
6	Octahedral	sp^3d^2
	Trigonal prismatic	spd^4, pd^5
	Trigonal antiprismatic	p^3d^3

*Source: H. Eyring, J. Walter, and G.E. Kimball, *Quantum chemistry*. Wiley (1944).

Molecular Structure 2

Ch. 11

Techniques of approximation

Born-Oppenheimer approximation

Valence-bond theory

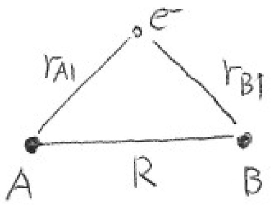
Molecular orbital theory

Molecular orbitals for polyatomic systems

3. Molecular orbital theory

- Electron should not be regarded as belonging to particular bonds but should be treated as spreading throughout the entire molecule.

1) Hydrogenic molecule-ion, H_2^+



$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 + \hat{V}, \quad \hat{V} = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R}\right)$$

$H\psi = E\psi \Rightarrow$ molecular orbital (MO)

$\rightarrow$ electron distribution in the molecule

- linear combinations of atomic orbitals (LCAO)

$$\psi_{\pm} = N(A \pm B), \quad A: \psi_{H1sA}, \quad B: \psi_{H1sB} \quad : \text{LCAO-MO}$$

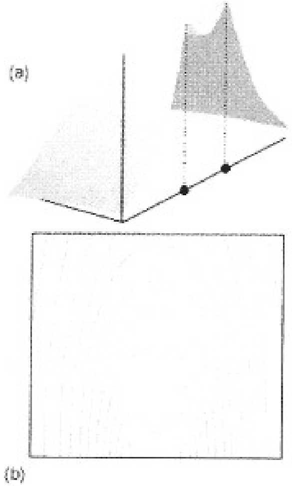
Normalized $\psi_+ : \int\psi^*\psi = 1 = N^2\left\{\int A^2 d\tau + \int B^2 d\tau + 2\int AB\, d\tau\right\} = N^2(1+1+2S)$

$$N = \frac{1}{\sqrt{2(1+S)}} \quad \text{where} \quad S = \int AB\, d\tau$$

$$\psi_- : N = \frac{1}{\sqrt{2(1-S)}}$$

- bonding orbital

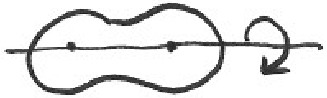
Probability density

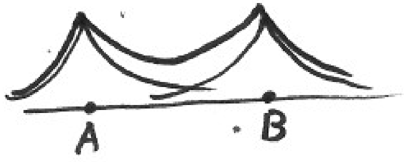


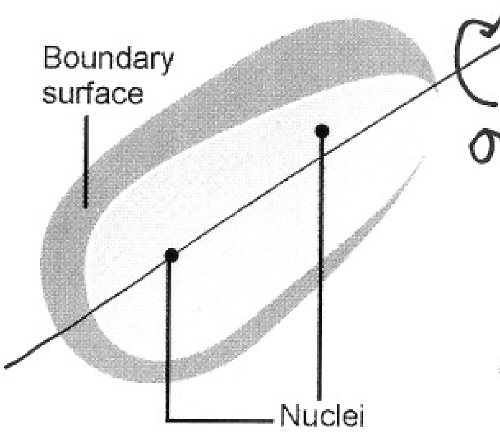
$\psi_+^2 = N^2(A^2+B^2+2AB)$

electron density in atomic orbital A — " B — **Overlap density** ⇓ e^- in the internuclear region

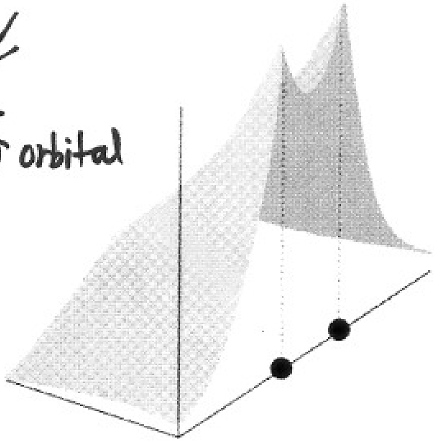
σ orbital ⇒ $1\sigma^1$

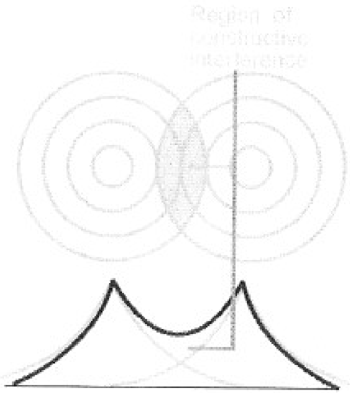






σ orbital

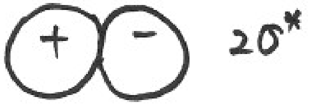


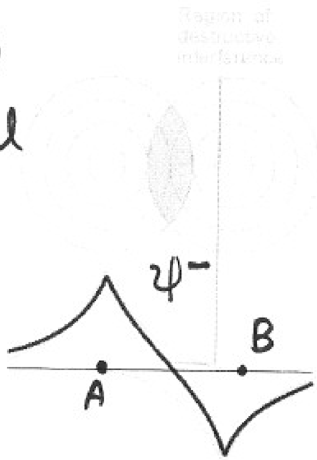


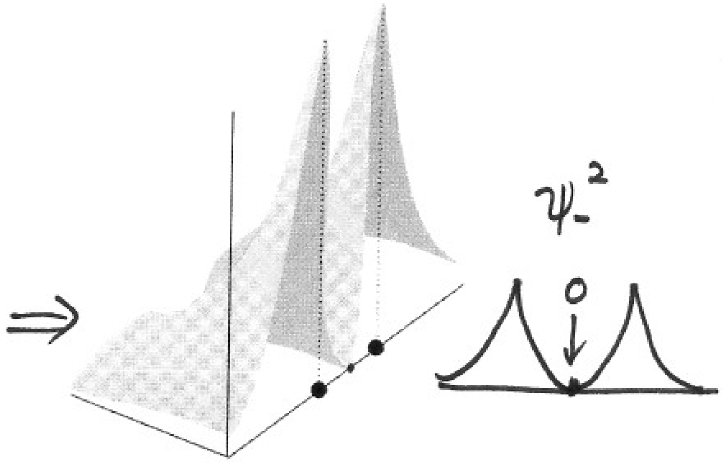
- antibonding orbital

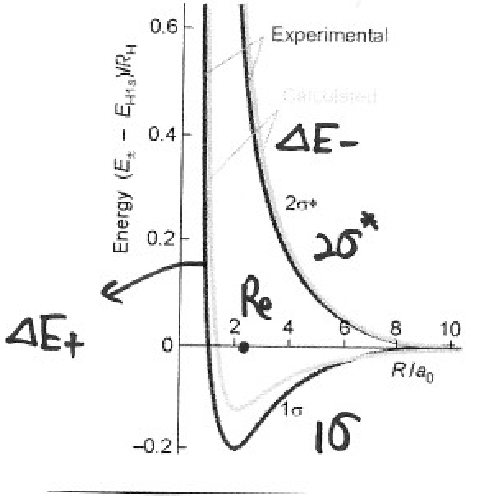
$$\psi_-^2 = N^2(A^2+B^2-2AB)$$

$\Rightarrow$ $2\sigma^*$: antibonding orbital









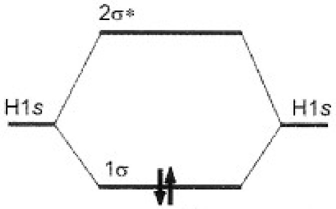
$$E_\pm = E_{H1s} + \frac{e^2}{4\pi\varepsilon_0 R} - \frac{j \pm k}{1 \pm S}$$

$$\left(\begin{aligned} S &= e^{-R}\left(1+R+\frac{R^2}{3}\right) \\ j &= e^{-2R}\left(1+\frac{1}{R}\right) \\ k &= \frac{S}{R} - e^{-R}(1+R) \end{aligned} \right.$$

2) Diatomic molecules

- build up many electron molecules using H_2^+ molecular orbitals
  "molecular configuration"

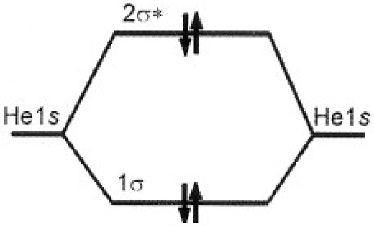
- H_2: $(1s\sigma)^2$



⇒ chemical bond

molecular orbital energy level diagram

- He_2:



$1\sigma^2 2\sigma^{*2}$

one-bond
one-antibond
antibond $\gtrsim$ bond ⇒ separated atoms

does not form diatomic molecules

- bond order $b = \frac{1}{2}(n - n^*)$

n: # of electrons in bonding orbitals
n^*: " in antibonding orbitals

$H_2 \Rightarrow b = 1$
$He_2 \Rightarrow b = 0$

$b\uparrow$ → shorter the bond, greater bond strength

Table 14.2* Bond lengths

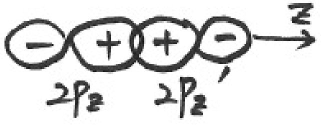
Bond	Order	R_e/pm
HH	1	74.14
NN	3	109.76
HCl	1	127.45
CH	1	*114*
CC	1	*154*
CC	2	*134*
CC	3	*120*

Table 14.3* Bond dissociation energies

Bond	Order	D_e/(kJ mol^{-1})
HH	1	432.1
NN	3	941.7
HCl	1	427.7
CH	1	*435*
CC	1	*368*
CC	2	*720*
CC	3	*962*

$2s \leftrightarrow 2s \Rightarrow 1\sigma,\ 2\sigma^*$: $\psi = c_{A2s}\psi_{A2s} + c_{B2s}\psi_{B2s}$

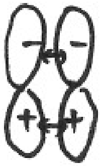
$2p_z \leftrightarrow 2p_z$



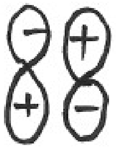
$\Rightarrow 3\sigma,\ 4\sigma^*$

$\psi = c_{A2p_z}\psi_{A2p_z} + c_{B2p_z}\psi_{B2p_z}$

$2p_x, 2p_y \leftrightarrow 2p_x, 2p_y$ p_x, p_y : degenerate

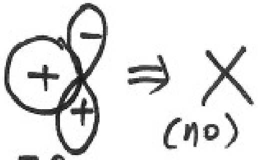


1π
π-orbital



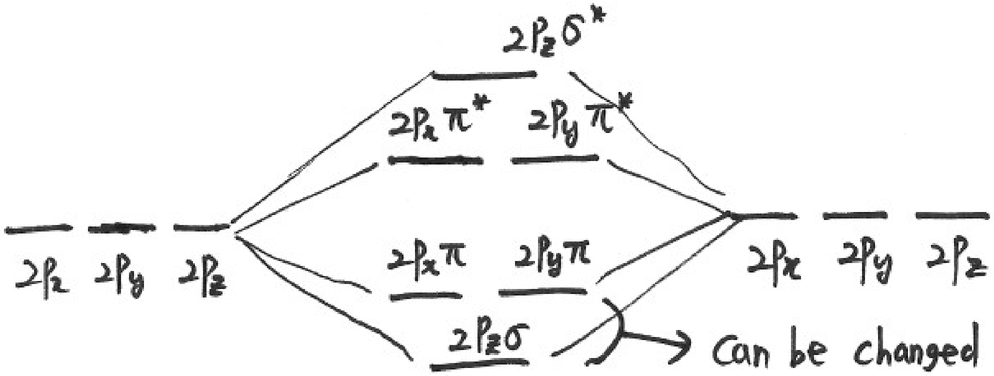
$2\pi^*$

※ $2s \leftrightarrow 2p_x$



zero

π-bond < σ-bond (∵ small overlap)



→ can be changed depending upon molecules

$C_2(12)$: $(1s\sigma)^2(1s\sigma^*)^2(2s\sigma)^2(2s\sigma^*)^2(2p_x\pi)^2(2p_y\pi)^2$ $b = 2$

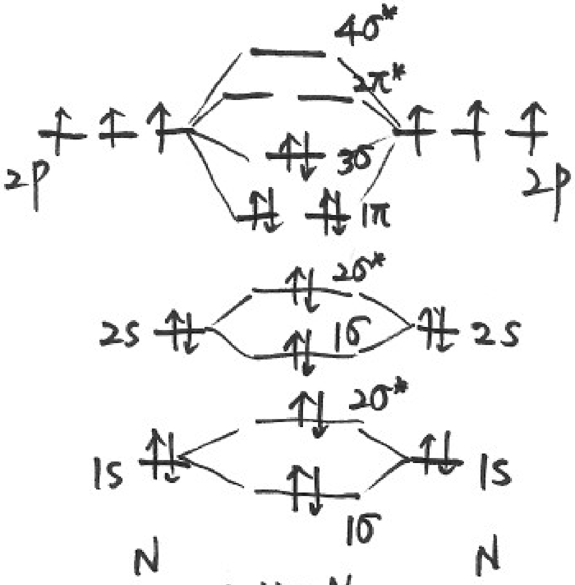
$N_2(14)$: " " " $(2p_z\sigma)^2$ $b = 3$

$O_2(16)$: " " " " $(2p_z\sigma)^2(2p\pi^*)^2$ $b = \frac{1}{2}(6-2) = 2$

O_2^+ : $\frac{1}{2}(6-1) = 2.5$: more stable than O_2

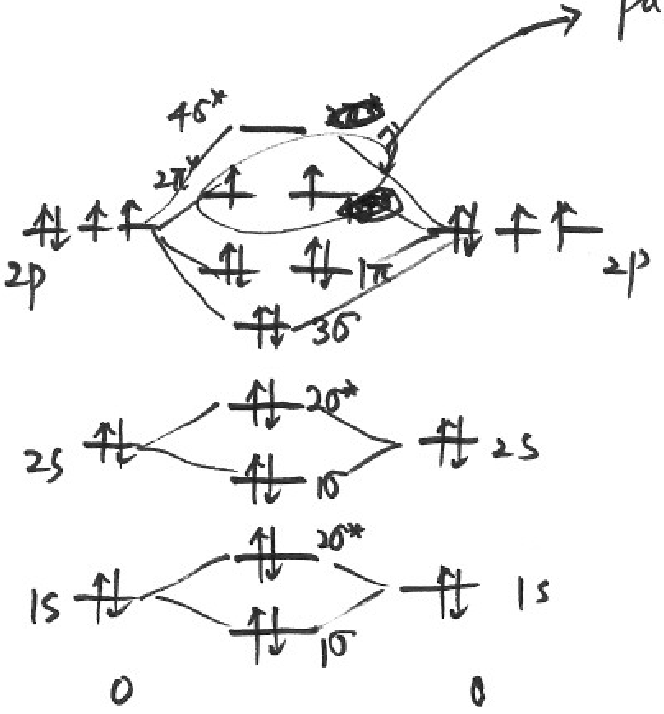
O_2^- : $\frac{1}{2}(6-3) = 1.5$

N_2



: N≡N:

O_2



parallel spins

↓

spin ang. momentum

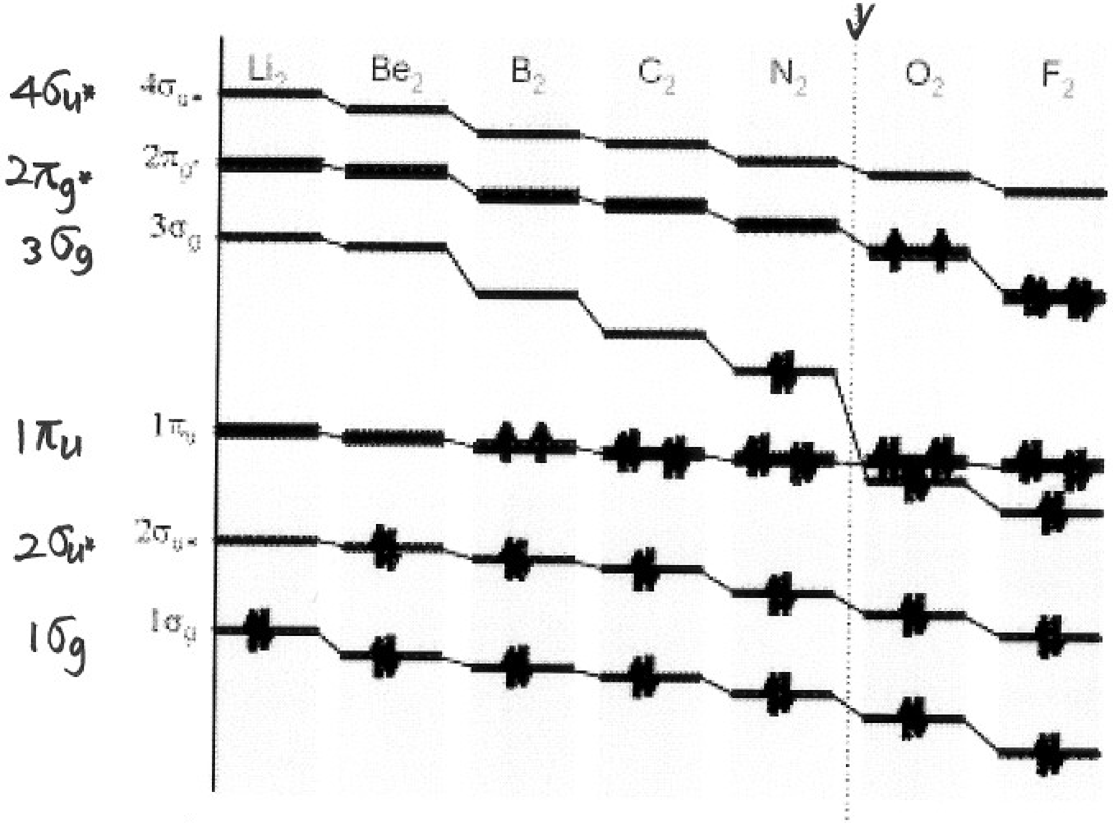
$S=1$

(triplet)

⇓

∴ paramagnetic

(move into a magnetic field)



F_2 : $b=1$

Ne_2 : $b=0$ → monatomic nature

3) Heteronuclear diatomic molecules e.g., CO, HCl

- inbalance electron distribution: polar bond

HF: e^- pair: close to the F

→ partial negative change (δ^-)

$\underset{\delta^+}{H}-\underset{\delta^-}{F}$

- Polar bonds 2e^- polar bond $\psi = C_A A + C_B B$

nonpolar bond: $|C_A|^2 = |C_B|^2$

pure ionic bond (A^+B^-), $C_A = 0$, $C_B = 1$

↳ lower energy atomic orbital → larger contribution to the bonding MO

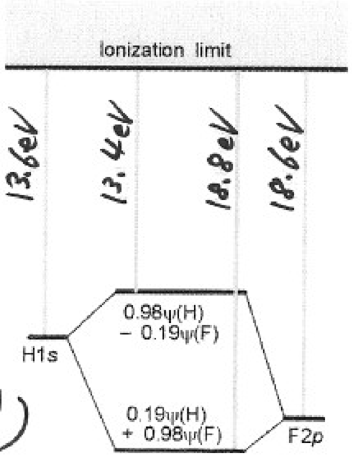
e.g., HF $\psi = C_H\psi_H + C_F\psi_F$

$\downarrow$ H1s orbital

$\downarrow$ F2p orbital

⇒ bonding σ orbital: mainly F2p (most electrons are in the F2p orbital)

$\underset{\delta^+}{H}\underset{\delta^-}{F}$



- Electronegativity (χ (chi)): charge distribution in bonds

(i) Pauling electronegativity (Valence bond argument) χ_p

: a measure of the power of an atom to attract electrons when it is part of a compound

$$|\chi_A - \chi_B| = 0.102\{D(A\text{-}B) - \tfrac{1}{2}[D(A\text{-}A) + D(B\text{-}B)]\}^{1/2}$$, D: bond dissociation E

	H	C	N	O	F	Cl	Cs
χ_p	2.2	2.6	3	3.4	4.0 ↑ most	3.2	0.79 ↓ least

$\Delta\chi\uparrow \rightarrow$ greater polar bond

ex) HF: $\Delta\chi = 1.78$ polar, C-H: 0.51 nonpolar

(ii) Mulliken electronegativity (χ_M)

$$\chi_M = \frac{1}{2}(\underset{\substack{\downarrow \\ \text{ionization} \\ \text{energy}}}{I} + \underset{\substack{\downarrow \\ \text{electron} \\ \text{affinity}}}{E_{ea}})$$

higher ionizat. E → $\chi\uparrow$
(it will not release e^- readily)
higher E_{ea} → $\chi\uparrow$

$$\chi_p = 1.35\chi_M^{1/2} - 1.37$$

bond polarity → find the coefficients in the linear combination

- <u>Variation principle</u>: if an arbitrary wavefunction is used to calculate the energy, the value calculated is never less than the true energy

trial function $\psi = c_A A + c_B B$

⇒ secular determinant

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

negative

$$\left(\text{cf. } \begin{matrix} \alpha_A = H_{11}, & \alpha_B = H_{22} \\ \beta = H_{12} & \end{matrix} \right)$$

$$S = \int AB \, d\tau = S_{ij}$$

- Homonuclear diatomic molecule : $\alpha_A = \alpha_B$

α: Coulomb integral
S: overlap integral
β: resonance integral

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0$$

$$\therefore E_\pm = \frac{\alpha \pm \beta}{1 \pm S}$$

E_+: lower E : bonding MO
E_-: upper E : antibonding MO

Normalized $\int \psi^2 d\tau = C_A^2 + C_B^2 + 2C_A C_B S = 1$,

$$E_+ = \frac{\alpha+\beta}{1+S} , \quad C_A = \frac{1}{\{2(1+S)\}^{1/2}} , \quad C_B = C_A$$

$$E_- = \frac{\alpha-\beta}{1-S} , \quad C_A = \frac{1}{\{2(1-S)\}^{1/2}} , \quad C_B = -C_A$$

bonding orbital $\psi_+ = \frac{A+B}{\{2(1+S)\}^{1/2}}$ antibonding orbital $\psi_- = \frac{A-B}{\{2(1-S)\}^{1/2}}$

- <u>heterogeneous diatomic molecule, but with $S=0$</u>

$$\begin{vmatrix} \alpha_A - E & \beta \\ \beta & \alpha_B - E \end{vmatrix} = (\alpha_A - E)(\alpha_B - E) - \beta^2 = 0$$

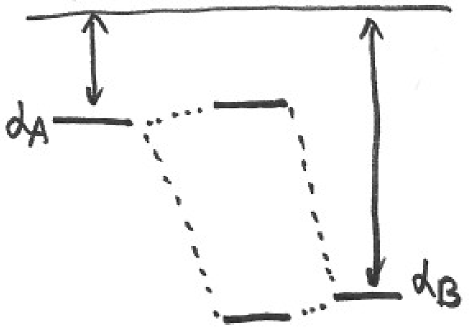
if ζ (zeta) $= \frac{1}{2}\arctan \frac{2|\beta|}{\alpha_B - \alpha_A}$ (cf. $\arctan x = \tan^{-1} x$)

$\Rightarrow E_- = \alpha_A - \beta \cot\zeta$, $\psi_- = -A\sin\zeta + B\cos\zeta$

$E_+ = \alpha_B + \beta\cot\zeta$, $\psi_+ = A\cos\zeta + B\sin\zeta$

$|\alpha_A - \alpha_B| \uparrow \rightarrow \zeta \downarrow$, $\zeta \ll 1 \rightarrow$ almost pure B, pure A

e.g.) A-B



e.g.) 14.5 σ orbital in HF, if $\beta = -1.0$ eV

H1s : 13.6 eV, F2p : 18.6 eV

$\Rightarrow \alpha_H \cong -13.6$ eV, $\alpha_F \cong -18.6$ eV

$\tan 2\zeta = 0.4 \Rightarrow \zeta = 10.9°$

$\Rightarrow E_- = -13.4$ eV, $\psi_- = 0.98\psi_H - 0.19\psi_F$

$E_+ = -18.8$ eV, $\psi_+ = 0.19\psi_H + 0.98\psi_F$

4. Molecular orbitals for polyatomic systems

The Hückel approximation

- conjugated molecules : σ, π orbitals
- Hückel approximation → π molecular orbital energy level diagrams

- Secular determinant : π orbitals as LCAO's of the C2p

- Ethene : $\psi = c_A A + c_B B$

  A: C2p orbital on atom A

  all C atoms identical → Coulomb integral

  $\alpha = \alpha_A = \alpha_B$, $\alpha = \int A H A d\tau$

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

- Butadiene : $\psi = c_A A + c_B B + c_C C + c_D D$

$$\begin{vmatrix} \alpha - E & \beta_{AB} - ES_{AB} & \beta_{AC} - ES_{AC} & \beta_{AD} - ES_{AD} \\ \beta_{BA} - ES_{BA} & \alpha - E & \beta_{BC} - ES_{BC} & \beta_{BD} - ES_{BD} \\ \beta_{CA} - ES_{CA} & \beta_{CB} - ES_{CB} & \alpha - E & \beta_{CD} - ES_{CD} \\ \beta_{DA} - ES_{DA} & \beta_{DB} - ES_{DB} & \beta_{DC} - ES_{DC} & \alpha - E \end{vmatrix} = 0$$

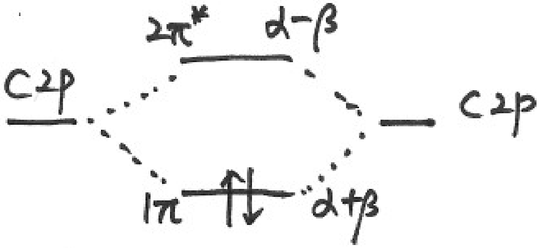
Complicated ?

The Hückel approximation

1. All overlap integrals are set equal to zero : all diagonal elements $\alpha - E$
2. All resonance integrals between non-neighbors → zero Off-diagonal btwn neighbors atoms : β
3. All remaining resonance integrals → β (equal)

- Ethene

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = (\alpha - E)^2 - \beta^2 = 0 \qquad E_\pm = \alpha \pm \beta \quad \left(\begin{array}{l} + : \text{bonding combination } (\beta < 0) \\ - : \text{anti- " "} \end{array} \right.$$



configuration : $1\pi^2$

HOMO (highest occupied molecular orbital) : 1π

LUMO (lowest unoccupied " ") : $2\pi^*$

- Butadiene

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & 0 & \alpha-E \end{vmatrix} = 0$$

$$= (\alpha-E)\begin{vmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix} - \beta\begin{vmatrix} \beta & \beta & 0 \\ 0 & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix}$$

$$= (\alpha-E)^2\begin{vmatrix} \alpha-E & \beta \\ \beta & \alpha-E \end{vmatrix} - \beta(\alpha-E)\begin{vmatrix} \beta & \beta \\ 0 & \alpha-E \end{vmatrix}$$

$$-\beta^2\begin{vmatrix} \alpha-E & \beta \\ \beta & \alpha-E \end{vmatrix} + \beta^2\begin{vmatrix} 0 & \beta \\ 0 & \alpha-E \end{vmatrix}$$

$$= (\alpha-E)^4 - (\alpha-E)^2\beta^2 - (\alpha-E)^2\beta^2 - (\alpha-E)^2\beta^2 + \beta^4$$

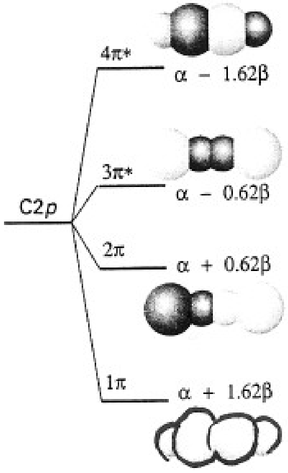
$$= (\alpha-E)^4 - 3(\alpha-E)^2\beta^2 + \beta^4 = 0$$

With $x = (\alpha-E)^2/\beta^2$, the expanded determinant has the form of a quadratic equation

$$x^2 - 3x + 1 = 0$$

The roots are $x = 2.62$ and 0.38. Therefore, the energies of the four LCAO-MOs are

$$\underline{E = \alpha \pm 1.62\beta}, \quad \underline{\alpha \pm 0.62\beta}$$



$$\therefore E = \alpha \pm 1.62\beta, \ \alpha \pm 0.62\beta$$

- ground state : $1\pi^2 2\pi^2$, HOMO : 2π , LUMO : 3π
- Total E :

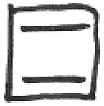
ethene : $E_\pi = 2(\alpha+\beta) = 2\alpha + 2\beta$

butadiene : $E_\pi = 2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) = 4\alpha + 4.48\beta$

$\Rightarrow$ 0.48β lower ($\approx$36 kJ/mol than 2 individual π bonds)

$\therefore$ delocalization energy

- Cyclobutadiene



now A–D are neighbors:

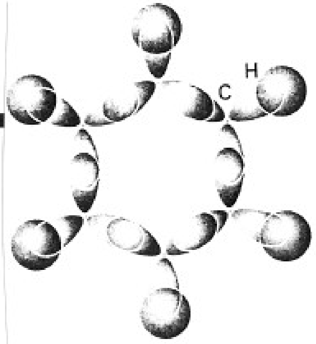
not 0, but β

$$\begin{vmatrix} \alpha-E & \beta & 0 & \beta \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ \beta & 0 & \beta & \alpha-E \end{vmatrix} = 0$$

when $x = \left(\frac{\alpha-E}{\beta}\right)^2$, $x(x-4) = 0$

$E = \underbrace{\alpha+2\beta}_{2e^-},\ \underbrace{\alpha}_{2e^-},\ \alpha,\ \alpha-2\beta$

total $E_\pi = 4\alpha + 4\beta$: delocalization $E = 0$



- Benzene

valence bond + MO

↓ six C atoms ↓ sp^2 ↓ σ bond

↓ six C2p ↓ 6π orbitals

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0$$

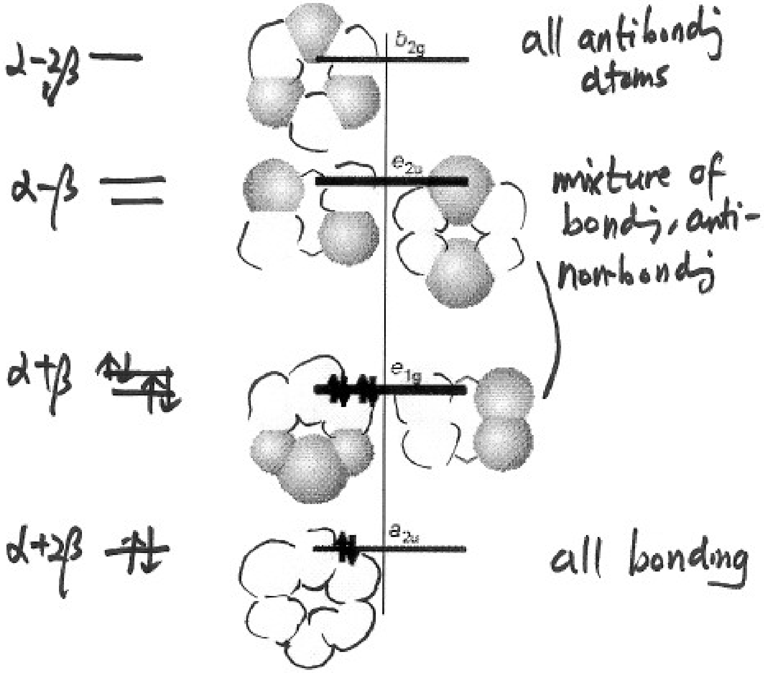
$E = \alpha \pm 2\beta,\ \alpha \pm \beta\ \ \alpha \pm \beta$

ground state configuration: $a_{2u}^2 e_{1g}^4$

total E (π electrons)

$E_\pi = 2(\alpha+2\beta)+4(\alpha+\beta) = 6\alpha+8\beta$

$\therefore 2\beta \simeq -150$ kJ/mol : delocalization E.



Extended Hückel theory (ETH)

1. ETH includes σ and π orbitals: not confined to conjugated hydrocarbons
2. ETH does not ignore overlap: calculate all the overlap integrals → matrix S

Diagonal elements of the hamiltonian matrix (α terms of Hückel theory): set equal to the negative of the ionization energy of the atom (H: 13.60 eV)

Off-diagonal elements (β and 0 of Hückel theory): assume to be proportional to the overlap integral

$$H_{ij} = \tfrac{1}{2}KS_{ij}(H_{ii} + H_{jj})$$

K: constant (= 1.75)

$S^{-1}HC = CE$

$C^{-1}S^{-1}HC = E$

Population analysis: where is the e^- density in a molecule?

$\Psi = c_A\Psi_A + c_B\Psi_B \rightarrow \Psi^2 = c_A{}^2\Psi_A{}^2 + c_B{}^2\Psi_B{}^2 + 2c_Ac_B\Psi_A\Psi_B \rightarrow 1 = c_A{}^2 + c_B{}^2 + 2c_Ac_BS_{AB}$

Atomic population: $\rho_i = c_i{}^2$, overlap population: $\rho_{ij} = 2c_ic_jS_{ij}$

ETH: inability to predict correct 3-D structures

Self-consistent field calculations (SFC)

(a) Hartree-Fock equations
Many-electron wavefunction which satisfy the Pauli principle

(b) semi-empirical and *ab initio* methods

The integrals estimated by experimental data
The *ab initio* methods: calculate all the integrals
→ complete neglect of differential overlap (CNDO)
Gaussian type orbital (GTO)

(c) Density functional theory (DFT)

To focus the elctron density (ρ), rather than waveftn Ψ
→ energy of molecule is ftn of ρ (E(ρ)) & ρ is ftn f position (ρ(r))

(d) Graphical output

Isodensity surface