Chapter 6, Introduction of molecular orbital theory

I. Homonuclear diatoms

H_2^+ Hamiltonian

$$\begin{aligned}\hat{H} &= \hat{T}_n + \hat{T}_e + V_{en} + V_{nn} \\ &= -\frac{1}{2M_a}\nabla_a^2 - \frac{1}{2M_b}\nabla_b^2 - \frac{1}{2}\nabla_e^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R_{ab}}\end{aligned}$$

Born-Oppenheimer approximation:

$$|\Psi(\mathbf{r},\mathbf{R})\rangle = |\psi(\mathbf{r}:\mathbf{R})\rangle|\varphi(\mathbf{R})\rangle$$

Substituting to $\hat{H}|\Psi\rangle = E|\Psi\rangle$ and ignore the action of $\hat{T}_n$ on $|\psi(\mathbf{r}:\mathbf{R})\rangle$, we have

$$[\hat{T}_e + V_{en}]|\psi(\mathbf{r}:\mathbf{R})\rangle = E_e(\mathbf{R})|\psi(\mathbf{r}:\mathbf{R})\rangle \quad \text{(electronic)}$$

$$[\hat{T}_n + V_{nn} + E_e(\mathbf{R})]|\varphi(\mathbf{R})\rangle = E|\varphi(\mathbf{R})\rangle \quad \text{(nuclear)}$$

Because of the small mass of an electron, it can respond instantaneously to change of nuclear coordinates.

In B-O approximation, electronic Schrödinger equation is solved at a fixed nuclear framework. The nuclei Schrödinger equation is solved with potential energy surface ($V = V_{nn} + E_e$).

LCAO-MO:

$$\left|\Psi^{MO}\right\rangle = \sum_n c_n \left|\psi^{AO}\right\rangle$$

H_2^+

$$\left|\Psi\right\rangle = c_a\left|1s_a\right\rangle + c_b\left|1s_b\right\rangle$$

Schrödinger Eq. for $\hat{H}_e = \hat{T}_e + V_{en}$

$$\hat{H}_e\left|\Psi\right\rangle = E\left|\Psi\right\rangle$$

Multiplying $\left\langle 1s_a\right|$ on the left and integrate:

$$H_{aa}c_a + H_{ab}c_b = Ec_a + S_{ab}Ec_b$$

similarly with $\left\langle 1s_b\right|$,

$$H_{ab}c_a + H_{bb}c_b = ES_{ab}c_a + Ec_b$$

in which the Hamiltonian and overlap matrix elements are

$$H_{aa} = \left\langle 1s_a\middle|\hat{H}_e\middle|1s_a\right\rangle \qquad H_{bb} = \left\langle 1s_b\middle|\hat{H}_e\middle|1s_b\right\rangle$$

$$H_{ab} = \left\langle 1s_a\middle|\hat{H}_e\middle|1s_b\right\rangle = H_{ba}$$

$$S_{ab} = \left\langle 1s_a\middle|1s_b\right\rangle = S_{ba}$$

Matrix form:

$$\begin{pmatrix} H_{aa}-E & H_{ab}-ES_{ab} \\ H_{ab}-ES_{ab} & H_{bb}-E \end{pmatrix}\begin{pmatrix} c_a \\ c_b \end{pmatrix}=0$$

Solution of coupled linear equations:

$$\begin{vmatrix} H_{aa}-E & H_{ab}-ES_{ab} \\ H_{ab}-ES_{ab} & H_{bb}-E \end{vmatrix}=0$$

The same equations can be obtained by variational principle.

For homonuclear diatoms, $H_{aa}=H_{bb}=\alpha$, $H_{ab}=\beta$, $S_{ab}=S$

$$(\alpha-E)^2-(\beta-ES)^2=0$$

Solution:

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

and

$$c_a^+=c_b^+=\frac{1}{\sqrt{2(1+S)}}$$
$$c_a^-=-c_b^-=\frac{1}{\sqrt{2(1-S)}}$$

$|\Psi_+\rangle$, $|\Psi_-\rangle$ have 0 and 1 node, respectively.

Bonding and antibonding MOs

$$\left|\Psi_-\right\rangle = N_-[\left|1s_a\right\rangle - \left|1s_b\right\rangle]$$

$\left|1s_a\right\rangle$ $\left|1s_b\right\rangle$

$$\left|\Psi_+\right\rangle = N_+[\left|1s_a\right\rangle + \left|1s_b\right\rangle]$$

Bonding MO has extra e-density between nuclei (constructive interference). It lowers the energies of the AOs.

$$P_+ = N_+^2[1s_a^2 + 1s_b^2 + 2(1s_a 1s_b)]$$

Antibonding MO has node (destructive interference). It raises the energies of AOs.

$$P_- = N_-^2[1s_a^2 + 1s_b^2 - 2(1s_a 1s_b)]$$

Let’s take a closer look at the energy:

$$E_+ = \left\langle \Psi_+ \middle| \hat{H} \middle| \Psi_+ \right\rangle = \int \Psi_+^* \hat{H} \Psi_+ d\tau$$

$$= N_+^2 \left(\left\langle 1s_a \right| + \left\langle 1s_b \right| \right) \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} \right) \left(\left| 1s_a \right\rangle + \left| 1s_b \right\rangle \right)$$

Let’s define the atomic energy first

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} \right) \left| 1s_a \right\rangle = E_{1s} \left| 1s_a \right\rangle$$

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_b} \right) \left| 1s_b \right\rangle = E_{1s} \left| 1s_b \right\rangle$$

we have

$$E_+ = N_+^2 [\left(\left\langle 1s_a \right| + \left\langle 1s_b \right| \right) \left(E_{1s} - \frac{1}{r_b} + \frac{1}{R} \right) \left| 1s_a \right\rangle$$

$$+ \left(\left\langle 1s_a \right| + \left\langle 1s_b \right| \right) \left(E_{1s} - \frac{1}{r_a} + \frac{1}{R} \right) \left| 1s_b \right\rangle]$$

$$= N_+^2 [2E_{1s}(1+S)$$

$$+ \left\langle 1s_a \right| \left(-\frac{1}{r_b} + \frac{1}{R} \right) \left| 1s_a \right\rangle + \left\langle 1s_b \right| \left(-\frac{1}{r_b} + \frac{1}{R} \right) \left| 1s_a \right\rangle$$

$$+ \left\langle 1s_a \right| \left(-\frac{1}{r_a} + \frac{1}{R} \right) \left| 1s_b \right\rangle + \left\langle 1s_b \right| \left(-\frac{1}{r_a} + \frac{1}{R} \right) \left| 1s_b \right\rangle]$$

$$= N_+^2 [2E_{1s}(1+S) + 2J + 2K]$$

The Coulumb integral represents electrostatic interaction between the A electron and B nucleus (always >0):

$$J = \int 1s_a \left(-\frac{1}{r_b} + \frac{1}{R} \right) 1s_a d\tau = -\int \frac{1s_a 1s_a}{r_b} d\tau + \frac{1}{R}$$

and the exchange integral stems from the LCAO assumption

$$K = \int 1s_b \left(-\frac{1}{r_b} + \frac{1}{R} \right) 1s_a d\tau = -\int \frac{1s_b 1s_a}{r_b} d\tau + \frac{S}{R}$$

and is a quantum mechanical effect. *K* is usually negative and responsible for the binding energy.

Thus, chemical bond is a quantum mechanical phenomenon.

Substituting the normalization factor, we reach

$$E_+ = \frac{2E_{1s}(1+S) + 2J + 2K}{2(1+S)} = E_{1s} + \frac{J+K}{1+S}$$

Comparing with the energy expression earlier, it is easy to see

$\alpha = E_{1s} + J$, and $\beta = E_{1s} S + K$

The relative energy becomes:

$$\Delta E_+ = E_+ - E_{1s} = \frac{J+K}{1+S}$$

For the antibonding orbital

$$\Delta E_{-} = \frac{J - K}{1 - S}$$

The integrals can be obtained analytically for H_2^+:

$$S = e^{-R}\left(1 + R + R^2/3\right)$$

$$J = e^{-2R}\left(1 + \frac{1}{R}\right)$$

$$K = \frac{S}{R} - e^{-R}\left(1 + R\right)$$

Potential energy curve:

<u>Labeling MOs by λ (projection of angular momentum on internuclear distance):</u>

$\lambda = \lvert m \rvert$	0,	1,	2, …
Symbol:	σ,	π,	δ, …

For 1s AOs, $\lambda = 0$; and we have σ MOs.

For homonuclear diatoms:, the MOs can be further labels by parity (inversion symmetry).

	$\left|\Psi_+\right\rangle$	$\left|\Psi_-\right\rangle$
parity:	gerade	ungerade
	σ_g	σ_u

MO energy level diagram:

2nd period homonuclear diatoms:

Core electrons do not participate in bonding.

$3\sigma_u$

$2\sigma_u$ $1\pi_g$

2s 2s 2p 2p

$2\sigma_g$ $1\pi_u$

$3\sigma_g$

Electronic configuration determined by Aufbau principle:

H_2^+, $1\sigma_g^1$

H_2, $1\sigma_g^2$, spin paired (Pauli principle),
Bond order = (# bonding e^- - antibonding e^-)/2
= (2-0)/2 = 1, single bond.

He_2, $1\sigma_g^2 1\sigma_u^2$, unstable, energy gained in σ_g offset by energy loss in σ_u, bond order = 0

Li_2, $2\sigma_g^2$, single bond.

HOMO: highest occupied MO ($2\sigma_g$)
LUMO: lowest unoccupied MO ($2\sigma_u$).

These orbitals are called frontier orbitals and largely responsible for chemical and spectroscopic properties of the molecule.

N_2, $2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$,
Extremely stable because of 6 bonding e^- (triple bond).
Because of interaction with $2\sigma_u$, $3\sigma_g$ higher than $1\pi_u$.

O_2, $2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2$, two top electrons unpaired (Hund's rule), paramagnetic.

Term symbol of a molecular state:

$$^{2S+1}\Lambda_{parity}^{reflection}$$

S: total spin
Λ: total orbital angular momentum on the molecular axis
Σ, Π, Δ,... for Λ= 0, 1, 2, ...

Determined by occupied MOs

Overall parity:

$g \times g = g, \qquad u \times u = g, \qquad u \times g = u$

Reflection symmetry:

$+ \times - = -, \qquad + \times + = +, \qquad - \times - = +$

+/-: behavior of MO under the reflection of a plane containing the nuclei.

	σ_g	σ_u	π_u	π_g
reflection	+	+	-	-

H_2^+, $1\sigma_g^1$, $\Lambda = 0$ (Σ), $S = 1/2$, $2S+1 = 2$ (doublet), parity = g, reflection = +, so term symbol: ${}^2\Sigma_g^+$

H_2, $1\sigma_g^2$, $\Lambda = 0$ (Σ), $S = 0$, $2S+1 = 1$ (singlet), parity = g ($g \times g$), reflection = + ($+\times+$), so: ${}^1\Sigma_g^+$

II. Heteronuclear diatoms

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES_{ab} \\ H_{ab} - ES_{ab} & H_{bb} - E \end{vmatrix} = 0$$

Assuming:

$$H_{aa} = \alpha_a, \qquad H_{bb} = \alpha_b, \qquad H_{ab} = \beta, \qquad S_{ab} = 0$$

Solution can be expressed in terms of ζ:

$$E_+ = \alpha_a + \beta \tan \zeta$$
$$E_- = \alpha_b - \beta \tan \zeta$$

where

$$\tan 2\zeta = \frac{2|\beta|}{\alpha_b - \alpha_a}$$

ΔE of two AOs ($\alpha_b - \alpha_a$) determines the strength of MO.

Example: H-F bond

Energies (α) of AOs: H1s: -13.6 eV, F2p: -18.6 eV

Assume β = -1.0 eV, ζ = 10.9°,

$$E_+ = -18.6 - 1.0 \tan(10.9^\circ) = -18.8 \text{ eV}$$

$$E_- = -13.6 + 1.0 \tan(10.9^\circ) = -13.4 \text{ eV}$$

III. Walsh diagram

Let's look at H_2A system.

$$\begin{aligned}\Psi_{MO} &= c_1 1s(\mathrm{H}_a) + c_2 1s(\mathrm{H}_b) \\ &\quad + c_3 2s(\mathrm{A}) + c_4 2p_x(\mathrm{A}) + c_5 2p_y(\mathrm{A}) + c_6 2p_z(\mathrm{A})\end{aligned}$$

At linear geometry At bent geometry

Walsh diagram

Explains why BeH_2 is linear and H_2O is bent.

IV. Hückel theory

π system in conjugated molecules (alternating single and double bonds), such as $CH_2=CH-CH=CH_2$, benzene, etc.

Hückel approximation:

i. Only π MOs are treated and molecular frame is fixed by σ bonds.

ii. Coulomb integrals (α) are set equal.

iii. Overlap integrals (S) are set to zero.

iv. Resonance integrals (β) are equal for neighbors, but zero for non-neighbors.

Ethene:

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

Orbital energies

$$E = \alpha \pm \beta$$

Total energy (π electrons) is

$$E = 2(\alpha + \beta) = 2\alpha + 2\beta \qquad \text{(no extra stabilization)}$$

Butadiene: $CH_2=CH-CH=CH_2$

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

Energies are

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

Total energy:

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

Delocalization energy: extra stabilization energy due to delocalization ($E - E_\pi = 0.48\beta$).

Benzene:

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

Orbital energies

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

Total energy

$$\begin{aligned} E &= 2(\alpha + 2\beta) + 4(\alpha + \beta) \\ &= 6\alpha + 8\beta \end{aligned}$$

Delocalization energy is 2β (app. -150 kJ/mol), aromatic stability.

What about $C_6H_6^+$?

$$\begin{aligned} E &= 2(\alpha + 2\beta) + 3(\alpha + \beta) \\ &= 5\alpha + 7\beta \end{aligned}$$

Delocalization energy is 2β.