

# Chapter 12. The Chemical Bond in Diatomic Molecules

## I. Born-Oppenheimer approximation

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

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

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

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

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

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

## Molecular Orbital Theory

### Hydrogen molecular ion

$\text{H}_2^+$  electronic Hamiltonian

$$\hat{H}_e = \hat{T}_e + V_{en} = -\frac{\hbar^2}{2m_e} \nabla_e^2 + \frac{e^2}{4\pi\epsilon_0} \left( -\frac{1}{r_a} - \frac{1}{r_b} \right)$$

LCAO (linear combination of atomic orbitals):

$$\Psi^{MO} = \sum_n c_n \psi^{AO}$$

Let's assume that only the 1s orbitals are involved:

$$\Psi = c_a 1s_a + c_b 1s_b$$

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

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

Substituting LCAO-MO, we have

$$c_a \hat{H}_e 1s_a + c_b \hat{H}_e 1s_b = c_a E 1s_a + c_b E 1s_b$$

Multiply  $1s_a$  on the left and integrate:

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

We define the Coulomb integrals:

$$H_{aa} = \int 1s_a \hat{H}_e 1s_a d\tau, \quad H_{bb} = \int 1s_b \hat{H}_e 1s_b d\tau$$

the resonance integral:

$$H_{ab} = \int 1s_a \hat{H}_e 1s_b d\tau = H_{ba}$$

and the overlap integral:

$$S_{ab} = \int 1s_a 1s_b d\tau = S_{ba}$$

Similarly with  $1s_b$ ,

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

Matrix form of the secular equation:

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

Solution of coupled linear equations requires the secular determinant to be zero:

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

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

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

Solution:

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

Bonding and antibonding MOs

$\Psi_-$

$1s_a$

$1s_b$

$\Psi_+$

Substituting energy back to secular equation, we have

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

Wavefunctions

$$\Psi_+ = \frac{1}{\sqrt{2(1+S)}}(1s_a + 1s_b), \quad \Psi_- = \frac{1}{\sqrt{2(1-S)}}(1s_a - 1s_b)$$

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

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

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

Antibonding MO has a node (destructive interference). It raises the energy of MO relative to AOs.

Chemical bond is possible because of the interference, thus a quantum phenomenon.

Dependence on  $R$  (potential energy curves)

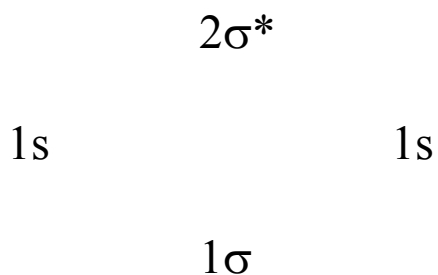
$$R_e = 1.3 \text{ \AA}$$
$$D_e = 1.77 \text{ eV}$$

## **Homonuclear diatoms**

H<sub>2</sub>:

MOs are essentially the same as in H<sub>2</sub><sup>+</sup>.

MOs formed by s-type AOs are called σ orbitals, because they are cylindrically symmetric about internuclear axis with zero angular momentum.

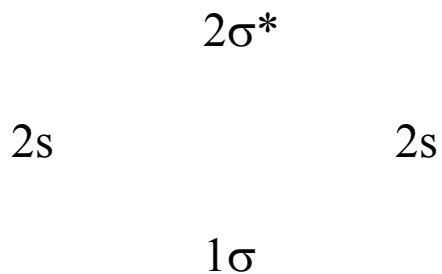


Both electrons are in the bonding orbital.

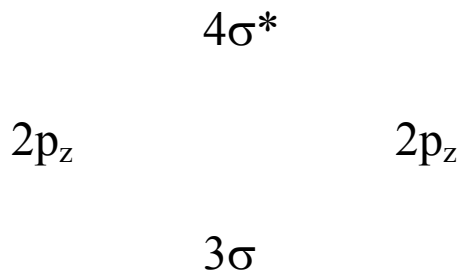
2<sup>nd</sup> period homonuclear diatoms:

1s electrons are in the core and do not interact strongly.

Valence electrons:

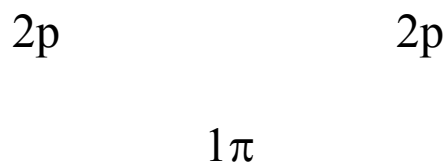


Head-on overlap between p orbitals:



Sideway overlap between p orbitals:

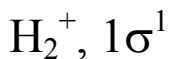




$\pi$  MOs have 1 unit of angular momentum around the axis.  
Both  $\pi$  MOs are doubly degenerate.

### MO energy level diagram

Electronic configuration determined by Aufbau principle:



$\text{H}_2, 1\sigma^2$ , spin paired (Pauli principle),

$$\begin{aligned}
 \text{Bond order} &= (\# \text{ bonding } e^- - \# \text{ antibonding } e^-)/2 \\
 &= (2-0)/2 = 1, \text{ single bond.}
 \end{aligned}$$

$\text{He}_2, 1\sigma^2 2\sigma^{*2}$ , unstable, energy gained in  $\sigma$  offset by energy loss in  $\sigma^*$ , bond order = 0

$\text{Li}_2$ ,  $1\sigma^2$ , single bond.

HOMO: highest occupied MO ( $1\sigma$ )

LUMO: lowest unoccupied MO ( $2\sigma^*$ ).

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

$\text{N}_2$ ,  $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$ ,

Extremely stable because of 6 bonding  $e^-$  (triple bond).

Because of interaction with  $2\sigma^*$ ,  $3\sigma$  is higher than  $1\pi$ . This is confirmed by photoelectron spectrum.

Relative bond strength:

$\text{N}_2$ ,  $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$ , bond order =  $(8-2)/2=3$

$\text{N}_2^+$ ,  $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^1$ , bond order =  $(7-2)/2=2.5$

$\text{N}_2^-$ ,  $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2 2\pi^{*1}$ , bond order =  $(8-3)/2=2.5$

$\text{O}_2$ ,  $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*2}$ , bond order = 2, two top electrons unpaired (Hund's rule), paramagnetic.



F<sub>2</sub>, 1σ<sup>2</sup>2σ\*<sup>2</sup>3σ<sup>2</sup>1π<sup>4</sup>2π\*<sup>4</sup>, bond order = 1.

Ne<sub>2</sub>, 1σ<sup>2</sup>2σ\*<sup>2</sup>3σ<sup>2</sup>1π<sup>4</sup>2π\*<sup>2</sup>4σ\*<sup>2</sup>, bond order = 0, unstable.

## Heteronuclear diatoms

Secular determinant:

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

Assuming:

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

Solution can be expressed in terms of  $\zeta$ :

$$\begin{aligned} E_+ &= \alpha_a + \beta \tan \zeta \\ E_- &= \alpha_b - \beta \tan \zeta \end{aligned}$$

where

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

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

Example: H-F bond

Energies ( $\alpha$ ) of AOs: H1s: -13.6 eV, F2p: -18.6 eV

Assume  $\beta = -1.0$  eV,  $\zeta = 10.9^\circ$ ,

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

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

CO:

NO:

$1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$   
Triple bond, very stable.

$1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2 \pi^{*1}$   
Free radical