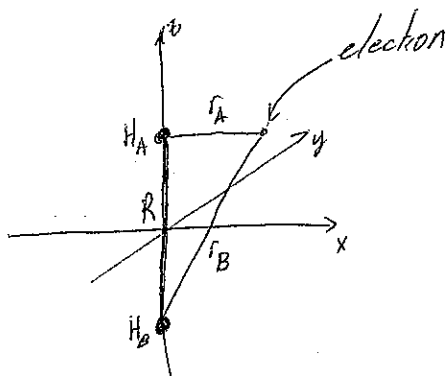


Molecular Structures

In this chapter, we will examine the quantum mechanical description of the covalent bond.

Let start with the hydrogen molecule ion, H_2^+ , the simplest molecular system



The hydrogen molecule ion has two protons and one electron, and has the full Hamiltonian expressed as.

$$\hat{H} = -\frac{\hbar^2}{2m_A} \nabla_A^2 - \frac{\hbar^2}{2m_B} \nabla_B^2 + \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{1}{R} +$$

← E.E. of the nuclei

$$-\frac{\hbar^2}{2m_e} \nabla_c^2 - \left(\frac{e^2}{4\pi\epsilon_0}\right) \left(\frac{1}{r_A} + \frac{1}{r_B}\right)$$

← n-n repulsion

E.E. of the electron

← n-e attractions.

\hat{H} depends on 6 degrees of freedom of the nuclei and 3 degrees of freedom of the electron. To simplify the problem we start to make approximations!!!

① The Born-Oppenheimer approximation

since the nuclei are much heavier than the electron, they move much slower. In other words, motions of the electron around the nuclei see the nuclei as if they are nearly fixed.

The Born-Oppenheimer approximation assumes that the nuclei are fixed while solving the Schrödinger equation for the electronic motion. This allows us to separate the nuclei motions from the electronic motions. The Hamiltonian operator for the H_2^+ molecule within the BO approximation is given by

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla^2 + \frac{e^2}{4\pi\epsilon_0} \left(-\frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right)$$

↑
↑
↑
 K.E. of the e^- n-e attraction n-n repulsion

There are no K.E. terms for the nuclei since the nuclei are fixed within the BO approximation. Furthermore, since R is constant

$$\frac{e^2}{4\pi\epsilon_0} \frac{1}{R} = \text{constant} = V_{n-n}$$

$$\hat{H}_e = -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi\epsilon_0} \left(-\frac{1}{r_A} - \frac{1}{r_B} \right) \quad ; \text{ the electronic Hamiltonian}$$

Solving the electronic Schrödinger equation

$$H_e \psi_e = E_e \psi_e$$

for E_e and ψ_e , the total BO energy is defined by

$$E_{BO} = E_e + V_{n-n}$$

B. The molecular orbital approximation

In principle, we can solve the H_2^+ electronic Schrödinger equation for exact solutions. However, the molecular orbital wavefunctions have very complicated-looking functions which do not provide useful insights. Here, we introduce a new approximation, called Linear Combination of Atomic Orbitals (LCAO), for the molecular orbitals.

Notice that
$$V = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_A} + \frac{1}{r_B} \right)$$

$$\rightarrow -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r_A} \quad \text{as } r_A \rightarrow 0, \text{ thus } \psi_e \rightarrow \psi_{1s}(A)$$

$$\rightarrow -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r_B} \quad \text{as } r_B \rightarrow 0, \text{ thus } \psi_e \rightarrow \psi_{1s}(B)$$

It is then reasonable to approximate the molecular orbitals as linear combinations of atomic orbitals

$$\psi = c_A \psi_{1s}(A) + c_B \psi_{1s}(B) \quad \text{where } \psi_{1s}(A) = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r_A/a_0}$$

Since the nuclei are identical in the H_2^+ system, we expect $c_A = c_B = N$. Consequently, we can form two combinations from two individual atomic orbitals.

$$\psi_+ = N_+ \{ \psi_{1s}(A) + \psi_{1s}(B) \}$$

$$\psi_- = N_- \{ \psi_{1s}(A) - \psi_{1s}(B) \}$$

where N_{\pm} are the normalization constants ensuring that

$$\int \psi_+^* \psi_+ d\tau = 1 \quad \text{and} \quad \int \psi_-^* \psi_- d\tau = 1$$

If we define the overlap integral as

$$S = \int \psi_{1s}(A) \psi_{1s}(B) d\tau$$

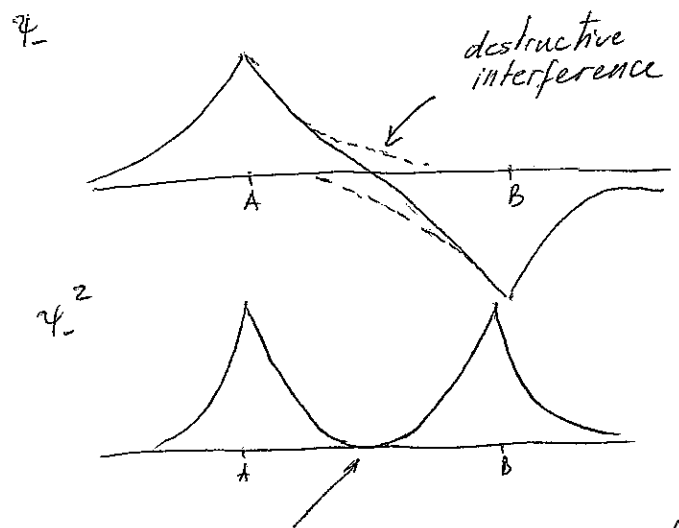
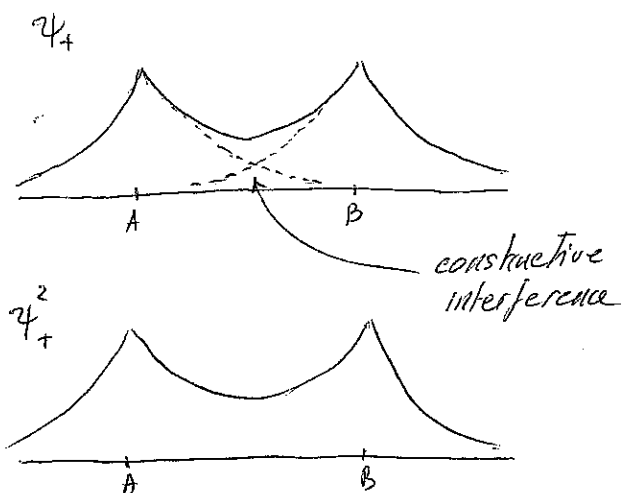
N_{\pm} normalization constants can be obtained as

$$N_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}}$$

Let take a closer look at these LCAO molecular orbitals.

Since the probability density of the electron is proportional to the square of the wavefunction

$$\psi_{\pm}^2 = N_{\pm}^2 \{ \psi_{1s}(A) \pm \psi_{1s}(B) \}^2 = N_{\pm}^2 \{ \psi_{1s}^2(A) + \psi_{1s}^2(B) \pm 2\psi_{1s}(A)\psi_{1s}(B) \}$$



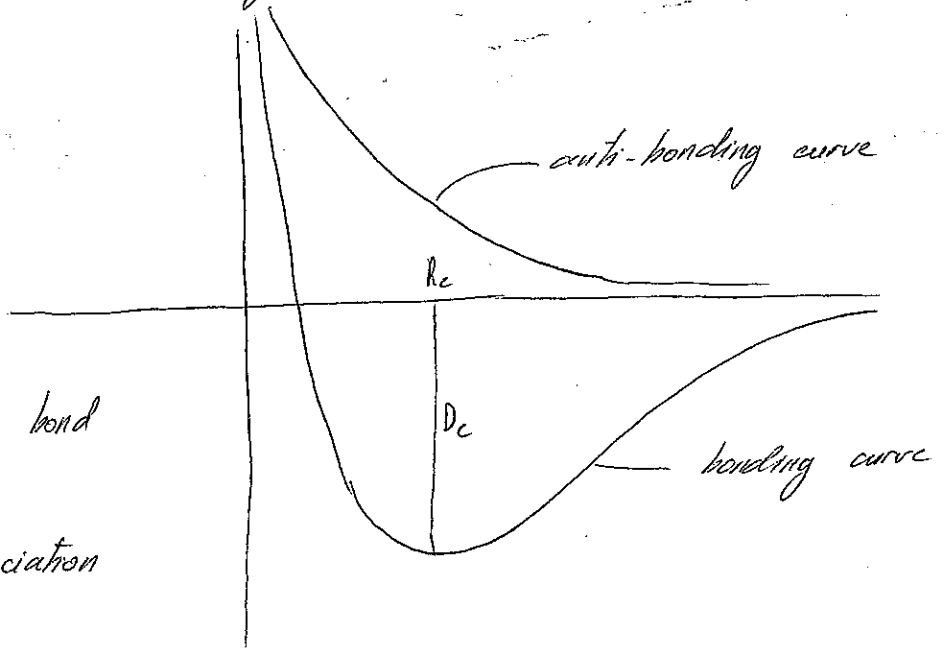
There is a build up of e^- density in the internuclear region due to the constructive interference in ψ_+ . ψ_+ is called bonding orbital. It is also referred to as σ orbital since it resembles the s orbital when viewing along the internuclear axis

Depletion of electron density in the internuclear region. ψ_- is called anti-bonding orbital, and is labeled with a $*$. Thus, ψ_- is labeled as σ^* .

Having approximated the molecular orbitals, we can then calculate the average energies ~~with~~

$$\langle E_+ \rangle = \int \psi_+^* \hat{H} \psi_+ d\tau \quad \text{and} \quad \langle E_- \rangle = \int \psi_-^* \hat{H} \psi_- d\tau$$

as functions of the internuclear distance R , and obtain the bonding and anti-bonding molecular potential energy curves.



R_e : equilibrium bond length.

D_e : bond dissociation energy

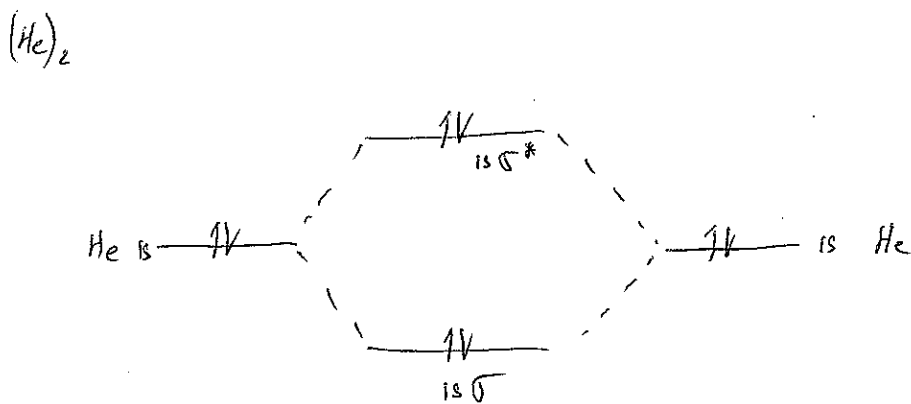
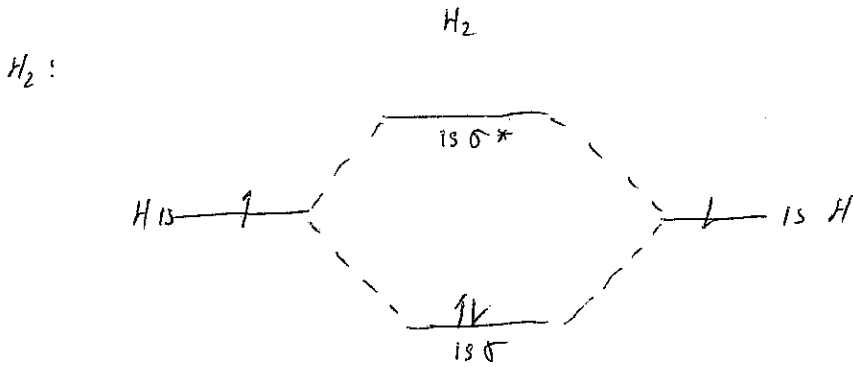
$$R_e = 1.3 \text{ \AA} \quad (\text{experimental } R_e = 1.06 \text{ \AA})$$

$$D_e = 1.77 \text{ eV} \quad (\text{experimental } D_e = 2.6 \text{ eV})$$

Although our ECAO approximation is quantitatively inaccurate, it provides simple descriptions of chemical bonding

Structures of diatomic molecules

Similar to the Aufbau principle for deducing the ground-state electronic configuration for many-electron atoms, we also assign electrons to MO's which are constructed by linear combinations of the constituent atomic orbitals. To do this we construct the molecular orbital energy diagram



$$\text{bond order} = \frac{1}{2} (\# e \text{ in bonding orbitals} - \# e \text{ in anti-bonding orbitals})$$

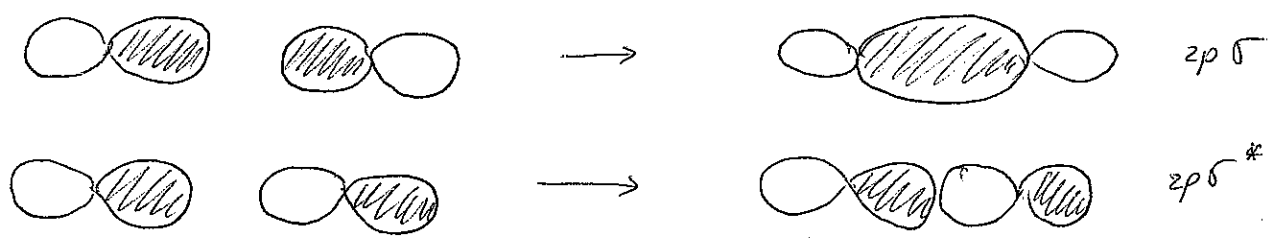
H₂: B.O. = $\frac{1}{2} (2 - 0) = 1$ single bond

(He)₂: B.O. = $\frac{1}{2} (2 - 2) = 0$ no-bonding, unstable

∴ Greater the bond order, the greater the bond strength.

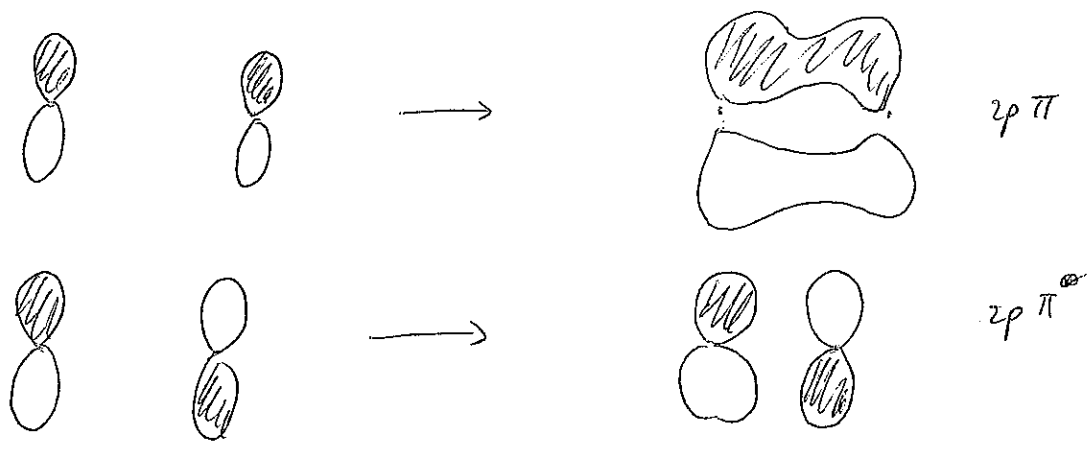
2p σ orbitals

If the diatomic molecule lies along the z-axis, the two p_z orbitals can form a bonding and an anti-bonding σ orbitals



2p π orbitals

For the p_x and p_y orbitals, we can form the π and π^* orbitals



Question - then which one $2p \sigma$ or $2p \pi$ has the lower energy?

$$2S+1 = \text{spin multiplicity} = \begin{matrix} 1 & \rightarrow & \text{singlet} \\ 2 & \rightarrow & \text{doublet} \\ 3 & \rightarrow & \text{triplet} \end{matrix}$$

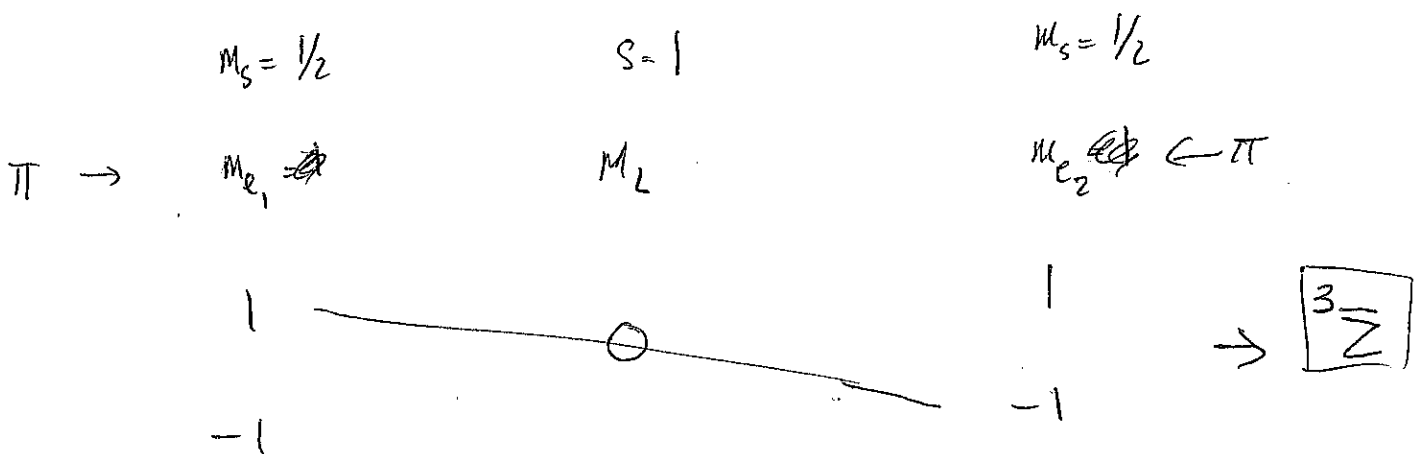
$$H_2: (1s)^2 \quad \left. \begin{matrix} m_{e_1} = m_{e_2} = 0 \\ S = 0 \end{matrix} \right\} \begin{matrix} \rightarrow M_L = 0 \\ \rightarrow 2S+1 = 1 \end{matrix} \quad \left. \right\} \quad {}^1\Sigma$$

For B_2 : $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^1 (1\pi_u)^1$

$M_L = 0, S = 0$
 so term symbols only arise from $(1\pi_u)^1 (1\pi_u)^1$

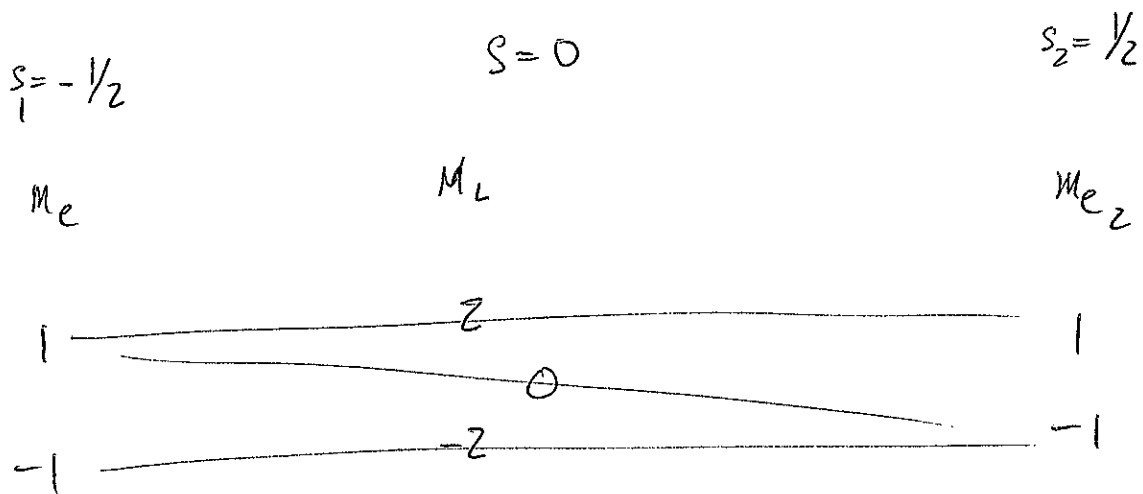
we need to consider when 2 \bar{e} have parallel spins and opposite spin cases.

parallel-spin:



- pauli exclusion principle → cannot have ~~same~~ the same m_{e_1} and m_{e_2} .
- \bar{e} are indistinguishable → $(1, -1) \equiv (-1, 1)$.

Opposite-spin.

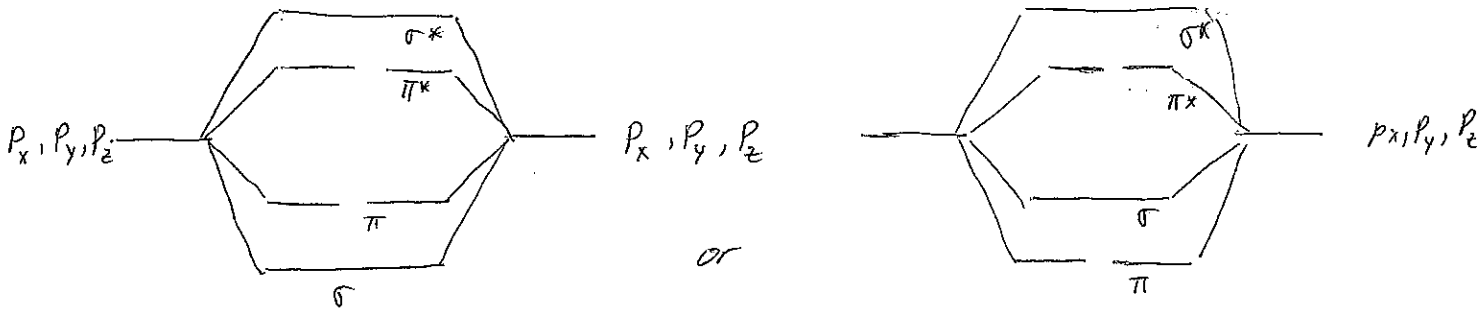


$$\Rightarrow |M_L| = 0 \text{ and } 2$$

$$\Rightarrow {}^1\Sigma \text{ and } {}^1\Delta$$

$$\Rightarrow 3 \text{ terms : } {}^3\Sigma, {}^1\Sigma \text{ and } {}^1\Delta$$

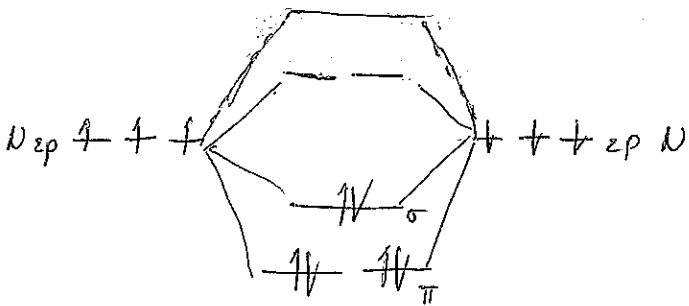
Hund's rule is also applied here $\rightarrow {}^3\Sigma$ is the lowest energy state, i.e. the ground state.



Since the $2p\sigma$ orbital has the maximum overlap in the internuclear region, intuitively we may expect the $2p\sigma$ has lower orbital energy. This is only true for O_2 , F_2 and Ne_2 whereas the reverse order is true for Li_2 , Be_2 , B_2 , C_2 and N_2 .

Let take a look at N_2 and O_2 .

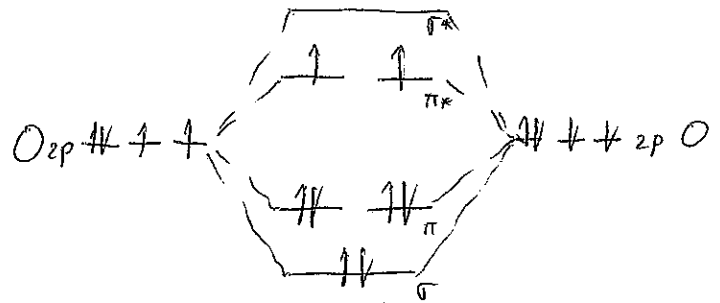
N_2



$$\dots (2p\pi)^4 (2p\sigma)^2$$

$$N_2: (1s\sigma)^2 (1s\sigma^*)^2 (2s\sigma)^2 (2s\sigma^*)^2 (2p\pi)^4 (2p\sigma)^2$$

$$B.O. = 3.$$



$$\dots (2p\sigma)^2 (2p\pi)^6 (2p\pi^*)^2$$

$$O_2: (1s\sigma)^2 (1s\sigma^*)^2 (2s\sigma)^2 (2s\sigma^*)^2 (2p\sigma)^2 (2p\pi)^6 (2p\pi^*)^2$$

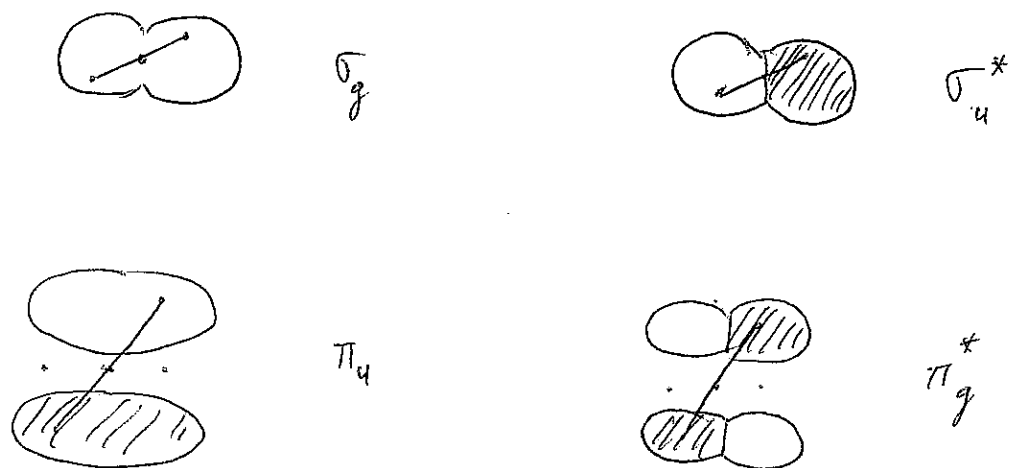
$$B.O. = 2.$$

Note: $2p\sigma$ orbital lies lower than the $2p\pi$ when we start to fill the anti-bonding orbitals.

Also, the two electrons in the $2p\pi^*$ orbitals in O_2 can have either parallel or opposite spins. Similar to Hund's rule, the triplet state (parallel spins) has the lower energy. Therefore, we expect O_2 to have a net spin angular momentum, and thus should be paramagnetic. Note paramagnetism arises when molecules have unpaired electron spins.

Parity

We also labeled the MO's of the homonuclear diatomic molecules by the subscript g (gerade) for orbitals which are symmetric under the inversion operation through the center of the molecule, and by the subscript u (ungerade) for the anti-symmetric case.



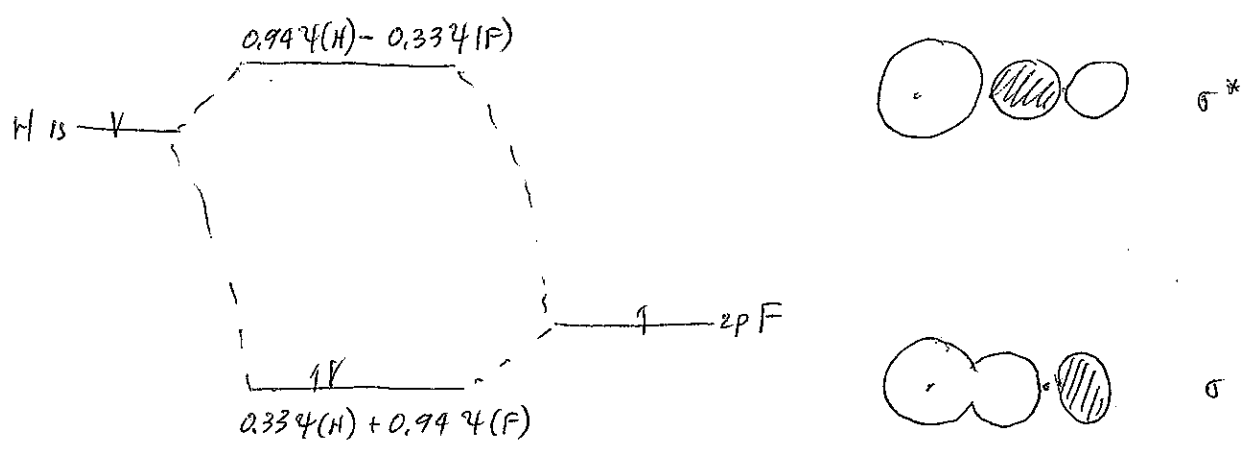
Heteronuclear diatomic molecules

are molecules formed by two different atoms. Thus, we expect

$$\psi^{LCAO} = c_A \psi(A) + c_B \psi(B)$$

to have unequal coefficients c_A and c_B .

For example: HF molecule



Since the ground-state σ bonding orbital of HF has mostly F 2p character, we expect the 2 electrons are likely to be found in the F 2p orbital. Hence, there is a partial negative charge on the F atom and a partial positive charge on the H atom.

How did one get these coefficients c_A and c_B ?

We use the Variational principle

For any approximate wavefunction, the calculated average energy is never less than the true energy.

$$\langle E \rangle = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \geq E_{\text{exact}}$$

Thus, for ψ^{LCAO} molecular orbitals, there exists an optimum set of coefficients, such that the average energy is the closest to the exact energy.

We can find these coefficients by minimizing the average energy

$$\frac{\partial E}{\partial c_i} = 0$$

Let take an example of a diatomic molecule.

$$\psi = c_A \psi(A) + c_B \psi(B)$$

where $\psi(A)$ and $\psi(B)$ are normalized.

$$\int \psi^2(A) d\tau = \int \psi^2(B) d\tau = 1$$

$$\begin{aligned} \int \psi^* \psi d\tau &= \int \{c_A \psi(A) + c_B \psi(B)\}^2 d\tau \\ &= c_A^2 + c_B^2 + 2c_A c_B S \end{aligned}$$

$$\text{recall } S = \int \psi(A) \psi(B) d\tau.$$

$$\int \psi H \psi d\tau = \int \{c_A \psi(A) + c_B \psi(B)\} \hat{H} \{c_A \psi(A) + c_B \psi(B)\} d\tau.$$

$$= c_A^2 \int \psi(A) \hat{H} \psi(A) d\tau + c_B^2 \int \psi(B) \hat{H} \psi(B) d\tau + 2c_A c_B \int \psi_A \hat{H} \psi_B d\tau$$

let define

$$\int \psi(A) \hat{H} \psi(A) d\tau = \alpha_A \quad (\text{Coulomb integral})$$

similarly for α_B , and

$$\int \psi(A) \hat{H} \psi(B) d\tau = \beta \quad (\text{resonance integral})$$

The average energy is then given by

$$E = \frac{c_A^2 \alpha_A + c_B^2 \alpha_B + 2c_A c_B \beta}{c_A^2 + c_B^2 + 2c_A c_B S}$$

By taking

$$\frac{\partial E}{\partial c_A} = 0 \quad \text{and} \quad \frac{\partial E}{\partial c_B} = 0$$

we obtain

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

For non-trivial solutions, the secular determinant

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

$$\text{or } (d_A - E)(d_B - E) - (\beta - ES)^2 = 0$$

we can solve this quadratic equation for the bonding orbital energy (the lower root) and the anti-bonding orbital energy (the larger root).

For each orbital energy, we can substitute it back into the secular equation and use the normalization condition

$$\int \psi \psi d\tau = c_A^2 + c_B^2 + 2c_A c_B S = 1$$

to obtain the coefficients for the corresponding MO.

For, H_2^+ :

$$d_A = d_B = d$$

so

$$(d - E)^2 - (\beta - ES)^2 = 0 \Rightarrow E_+ = \frac{d + \beta}{1 + S} \quad \text{and} \quad E_- = \frac{d - \beta}{1 - S}$$

From the secular equations, we obtain.

$$c_A = c_B \quad \text{for } E_+$$

$$c_A = -c_B \quad \text{for } E_-$$

From the normalization condition,

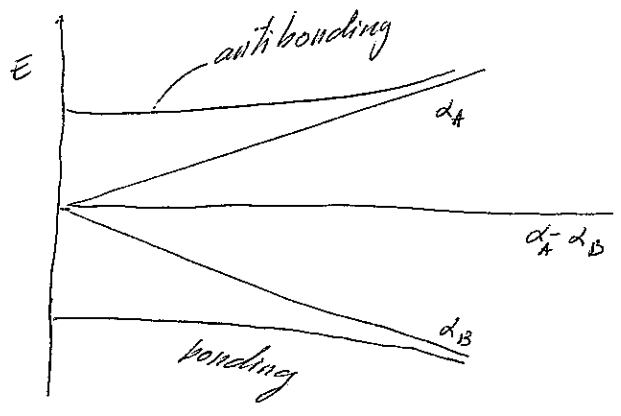
$$c_A = \sqrt{\frac{1}{2(1+S)}} \Rightarrow \psi_+ = \sqrt{\frac{1}{2(1+S)}} \{ \psi(A) + \psi(B) \} \quad \text{for } E_+ = \frac{d + \beta}{1 + S}$$

$$c_A = \sqrt{\frac{1}{2(1-S)}} \Rightarrow \psi_- = \sqrt{\frac{1}{2(1-S)}} \{ \psi(A) - \psi(B) \} \quad \text{for } E_- = \frac{d - \beta}{1 - S}$$

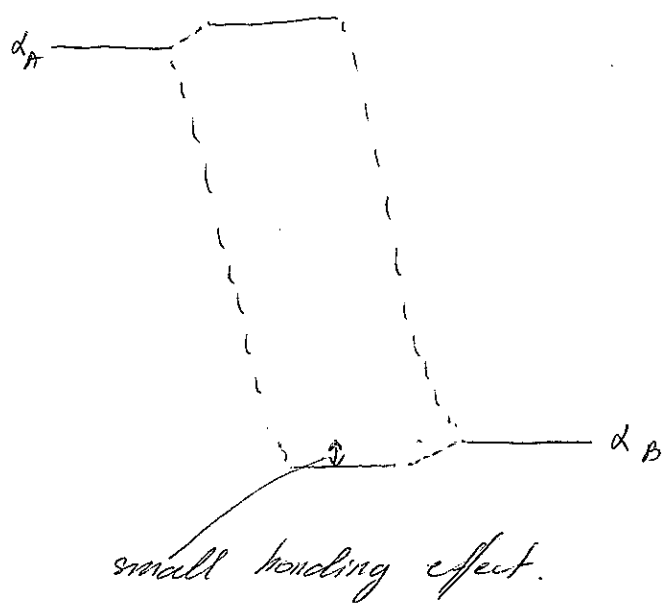
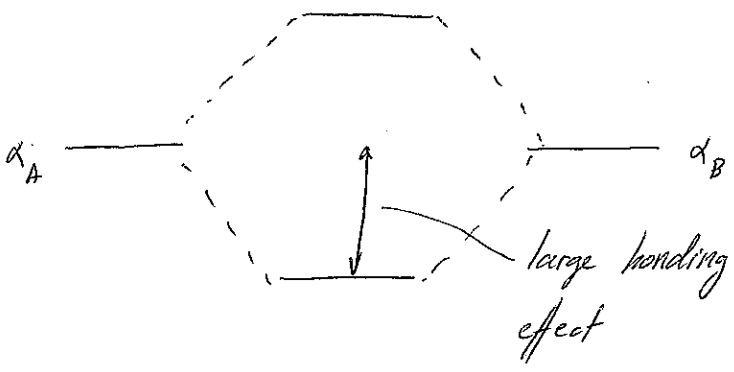
If we neglect the overlap, $S=0$, in the secular determinant, then

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

we can solve the quadratic equation for the bonding and antibonding orbital energies. If these orbital energies are plotted versus the difference, $d_A - d_B$, we found



The largest bonding and antibonding effects when $d_A = d_B$ or when two contributing atomic orbitals have similar energies



Molecular Term symbols for electronic states of molecules

Similar to atomic term symbols, electronic states of molecules are also designated by term symbols

where M_L is the total orbital angular momentum (the z projection)

$$M_L = m_{l_1} + m_{l_2} + \dots \leftarrow \text{sum over } \bar{e} \text{ occupying the MO.}$$

$$m_l = 0 \text{ for } \sigma$$

$$m_l = \pm 1 \text{ for } \pi$$

| $ M_L $ | Letter |
|---------|----------|
| 0 | Σ |
| 1 | π |
| 2 | Δ |

Similarly,

$$M_S = m_{s_1} + m_{s_2} + \dots$$

Again, M_S is the z -projection of the spin angular momentum

$$S=0 \quad M_S=0$$

$$S=1/2 \quad M_S=\pm 1/2$$

$$S=1 \quad M_S=\pm 1, 0$$