

# Molecular orbital theory

- electrons belong not to particular bonds but are treated as spreading throughout the entire molecule
- more fully developed than VB theory
- introduction by taking H atom as the fundamental species  $\rightarrow$  developing the description of atoms; analogy: using  $H_2^+$ , the simplest molecular species

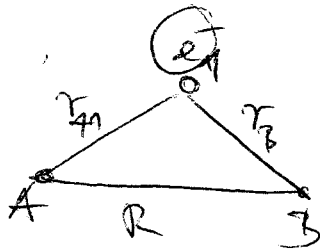
hydrogen molecule ion

## The hydrogen molecule ion

the Hamiltonian of  $H_2^+$

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 + V$$

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



attraction nucleus-electron

repulsive nucleus-nucleus

Solving Schrödinger eq.  $H\psi = E\psi$

$\rightarrow$  one electron wavefunction called MO (molecular orbitals)  
 MO  $\psi$  gives via  $|\psi|^2$  the  $e^-$  distribution in the molecule

- for  $H_2^+$ -Ion: Schrödinger eq. can be solved <sup>-2-</sup> within the Born-Oppenheimer approximation

- Complicated wavefunctions, solutions can not be extended to polyatomic systems  $\Rightarrow$  simpler procedure adopted

a) Linear combination of atomic orbitals

- 1 electron found in an AO belonging to A AND in an AO belonging to B

- overall wavefunction: ~~for~~ results from superposition of 2 AO

$$\Psi_{\pm} = N(A \pm B) \quad A = \Psi_{H1s_A} \quad B = \Psi_{H1s_B}$$

technical term: LCAO; approximate MO

from LCAO is called LCAO-MO

$\rightarrow$   $\sigma$  orbital, (same definition as in VB-theory is an MO (cylindrical symmetry along internuclear axis))

Normalization of  $\Psi_{\pm}$ :

$$\int \Psi \Psi^* d\tau; \text{ find factor } N$$

$$S = \int AB d\tau$$

- substitute ~~rule~~ LCAO ~~in~~ ~~the~~ ~~integral~~
  - atomic ~~orb~~ orbitals are ~~all~~ individually normalized
- $$\rightarrow = N^2 \left( \int A^2 d\tau + \int B^2 d\tau + 2 \int AB d\tau \right) = N^2 (1 + 1 + 2S)$$

## Normalization

For the integral to be equal to 1, one requires:

$$N = \frac{1}{\left\{ 2(1+S) \right\}^{1/2}} \quad \left[ \begin{array}{l} \text{Comment} \\ H_2^+ : S \approx 0.59 \quad N = 0.56 \end{array} \right]$$

$$\text{Example: } A = \frac{e^{-r_A/a_0}}{\left( \pi a_0^3 \right)^{1/2}} \quad B = \frac{e^{-r_B/a_0}}{\left( \pi a_0^3 \right)^{1/2}}$$

and  $r_A$  and  $r_B$  are not independent!

$$r_B = \left( r_A^2 + R^2 - 2r_A R \cos \theta \right)^{1/2} \quad N^2 = 0.31 \quad (\text{from above})$$



## b) Bonding orbitals

Basic interpretation: probability density is proportional to the square modulus of its wavefunction.

— probability density  $\psi^2$  corresponds to the real wavefunction  $\psi_+$  in eq. 7  $\psi_+^2 = N^2 (A^2 + B^2 + 2AB)$

⇒ the total probability density proportional to

1)  $A^2$  (electron would be confined to A - AO)

2)  $B^2$  ( " " " " B - AO)

3)  $2AB$  (extra contribution to the density)

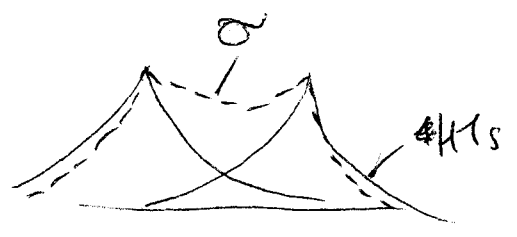
overlap density: crucial: enhancement of the prob. density

→ electrons accumulate where orbitals overlap and interfere constructively. (reflecting interaction with both nuclei)

- bonding orbital  $1\sigma$ ,  $\sigma$  of lowest energy

Calculation on  $H_2^+$ :  $R_e = 130 \text{ pm}$ ,  $D_e = 177 \text{ eV}$   
experimental  $106 \text{ pm}$ ,  $2.6 \text{ eV}$

Foll: justification p. 420

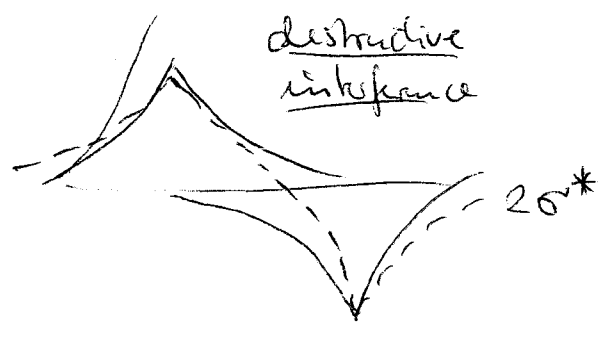


c) Antibonding orbitals

$\psi_-$  corresponds to higher energy than  $\psi_+$

also a  $\sigma$  orbital:  $2\sigma$  antibonding orbital which raises the energy of a molecule

if occupied! (reaction in collision) often labelled as  $2\sigma^*$  ('two sigma star')



- antibonding  $\bar{e}$ : excluded from the internuclear region  
↳ pulls nuclei apart!

-  $|E_- - E_{H1s}| > |E_+ - E_{H1s}|$   $\sigma^*$  more antibonding than  $\sigma$  is bonding! presence of nuclei-repulsion!

molecular orbital energy level diagram

2 He(1s)

He(1s)

$2s^*$  —

1s — — 1s

1s ~~1s~~

ground electronic configuration of  $H_2$ : accommodate  $e^-$  in the lowest available orbital

Structure of diatomic molecules

-  $n$ -atom orbitals used for deduction of ground electronic configuration of many-electron atoms

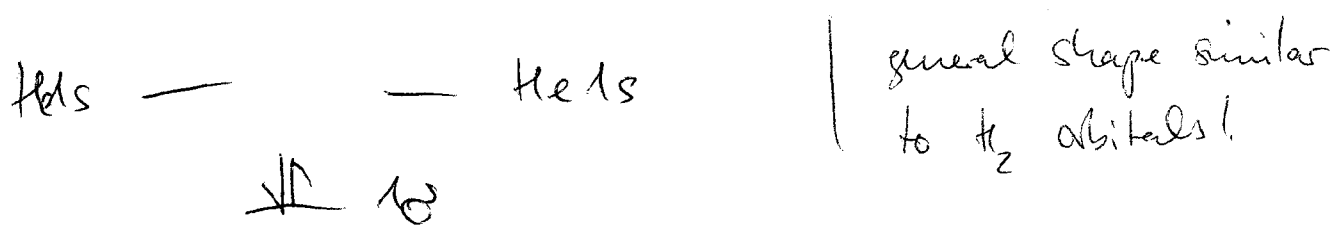
- analogy:  $H_2^+$  MO  $\rightarrow$  many-electron diatomic molecules

general procedure: - MO from LCAO

- electrons accommodated in the orbitals to achieve the lowest overall energy
- Pauli principle: no more than 2 electrons per orbital
- Hund's maximum multiplicity rule (parallel spin occupation of degenerate orbitals by electrons)

The hydrogen and helium molecules

He does not form diatomic molecules!  
 ~~$2s^*$~~



↑ higher energy than individual atoms → unstable

b) bond order:

measure of the net bonding in ~~the~~ a diatomic molecule:  $b = \frac{1}{2} (n - \overset{*}{n})$

$e^-$  in bonding orbitals       $e^-$  in antibonding orbitals

greater bond order → greater bond strength  
smaller bond length

c) Period 2 diatomic molecules:

- only valence shell orbitals

- 2s and 2p, no theory considers all AO

of appropriate symmetry, & bonds: ~~sp~~ cylindrical symmetry along intermolecular axis: s + 2p<sub>z</sub> orbitals!

general form:

$$\psi = C_{A2s} \psi_{A2s} + C_{B2s} \psi_{B2s} + C_{A2p_z} \psi_{A2p_z} + C_{B2p_z} \psi_{B2p_z}$$

C: appropriate coefficients

-  $2s$  and  $2p_z$ : distinctively different energies,  
 may be ~~also~~ treated separately  $\rightarrow$  4  $\sigma$  orbitals  
 fall into two sets: 1 consisting of 2 MO of the form:

$$\psi = C_{A2s}\psi_{A2s} + C_B\psi_{B2s}$$

and another consisting of two orbitals of the form:

$$\psi = C_{A2p_z}\psi_{A2p_z} + C_{B2p_z}\psi_{B2p_z} \quad (14, 16b)$$

- A, B identical,  $2s$  energies are the same  $\rightarrow$   
 coefficients are equal, same:  $2p_z$  orbitals

$$\downarrow \psi_{A2p_z} \pm \psi_{B2p_z} \quad \text{and} \quad \psi_{A2p_z} \pm \psi_{B2p_z}$$

$\downarrow$

~~20/15~~ overlap  $\rightarrow$  give  
 $1\sigma$  and  $2\sigma^*$

$\downarrow$

$3\sigma$  and  $4\sigma^*$

Numbering follows increasing energy

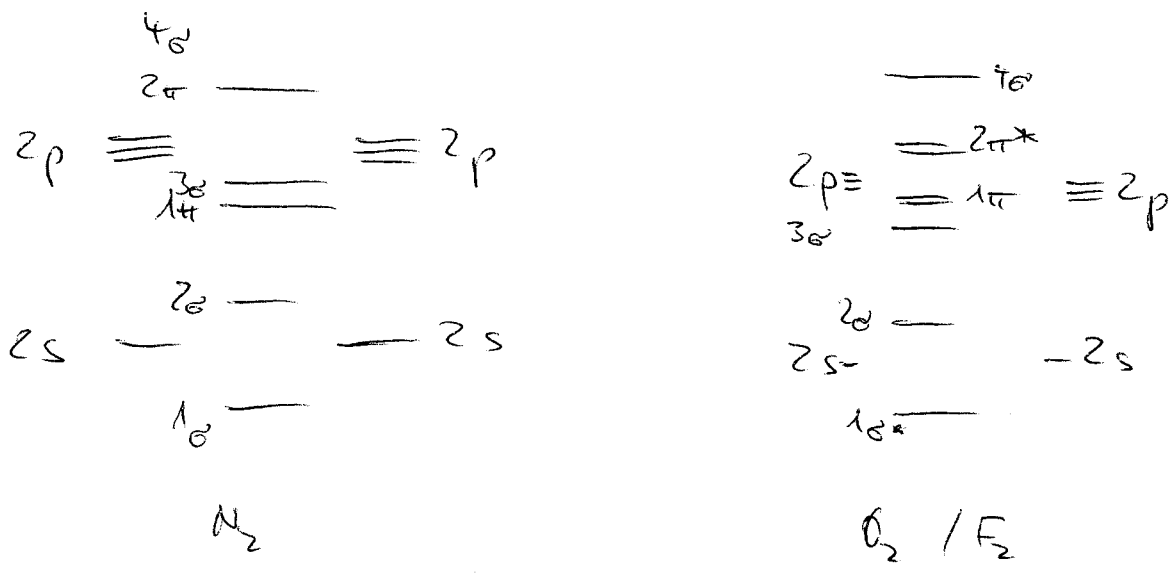
### d) $\pi$ - orbitals

- remaining  $2p_x$  and  $2p_y$  orbitals:  
 overlap broadside-on

$\rightarrow$   $\pi$  - orbitals, 1 ~~angular momentum~~ unit of  
 (def. as before) orbital angular momentum

$\rightarrow$   $2\pi_x$  and  $2\pi_y$  bonding / antibonding orbitals  
 $\pi_x$  and  $\pi_y$ ,  $\pi_x^*$  and  $\pi_y^*$ : degenerate

- Some cases:  $\pi$  orbitals are less strongly bonding than  $\sigma$ : maximum overlap occurs off-axis, match occurs between  $N_2$  and  $O_2$



e) The overlap integral

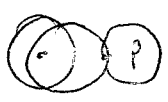
extent to which 2 atomic orbitals overlap: measured by the overlap integral  $S$

$$S = \int \psi_A^* \psi_B d\tau$$

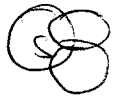
pictured



small overlap



large overlap



zero net overlap

$S = 0.53$  at  $r_0$  in  $H_2^+$

$S = 0.2-0.3$  for orbitals with  $n=2$



f) Structure of diatomic molecules:

building-up principle, using the electrons from unbound atoms

ground state configuration of  $N_2$ :  $10 e^-$

$$1\sigma^2 2\sigma^{*2} \uparrow\uparrow 2\pi^4 3\sigma^2 \quad \rightarrow \quad \text{bond order } \frac{1}{2}(8-2) = 3$$

high dissociation energy

-  $O_2$ :  $12 e^-$

$$1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*2} \quad \text{bond order } \frac{1}{2}(8-4) = 2$$

→  $2\pi^*$  electrons occupy 2 orbitals,  $1 2\pi_x^* 1 2\pi_y^*$

↳ parallel spins, net spin angular momentum

$S=1$  triplet state!  $O_2 = \text{paramagnetic!}$

confirmed by experiment (not predicted by valence bond theory!)

-  $F_2$ :  $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*4}$  :  $14 e^-$

$$\text{bond order: } \frac{1}{2}(8-6) = 1$$

low dissociation energy