

Molecular orbital theory

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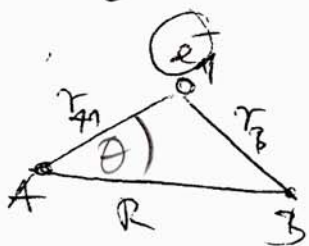
- electrons belong not to particular bonds but are treated as spreading throughout the entire molecule
- more fully developed than VB theory
- introduction by taking H atom as the fundamental species \rightarrow developing the description of atoms; analogy: using H_2^+ , the simplest molecular species

The hydrogen molecule ion

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
nuclei-electron

repulsive
nucleus-nucleus

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

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

- for H_2^+ -Ion: Schrödinger eq. can be solved 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: ~~from~~ results from superposition of 2 AO

$$\psi_{\pm} = N(A \pm B) \quad A = \psi_{1s_A} \quad B = \psi_{1s_B}$$

technical term: LCAO; approximate MO

from LCAO is called LCAO-MO

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

Normalization of ψ_{\pm} :

$\int \psi \psi^* d\tau$; find factor N

- substitute ~~into~~ LCAO ~~into~~ ~~the~~ ~~integral~~

- atomic orbitals are individually normalized

$$S = N^2 \left(\int A^2 d\tau + \int B^2 d\tau + 2 \int AB d\tau \right) = N^2 (1 + 1 + 2S)$$

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

Normalization

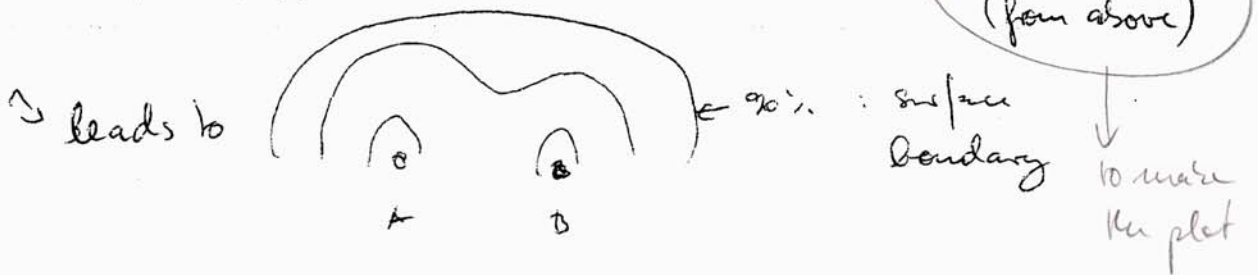
For the integrals to be equal to 1, one requires:

$$N = \frac{1}{\{2(1+S)\}^{1/2}} \quad \left[\begin{array}{l} \text{Comment} \\ H_2^+ : S \approx 0.55 \text{ \& } N = 0.56 \end{array} \right]$$

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

and r_A and r_B are not independent!

$$r_B = (r_A^2 + R^2 - 2r_A R \cos\theta)^{1/2}$$



b) Bonding orbitals

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

— probability density corresponds to the real wavefunction
 $\psi_+^2 = N^2 (A^2 + B^2 + 2AB)$ (from above!)

⇒ the total probability density proportional to the sum of

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

2) B^2 (" " B - AC)

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

overlap density: crucial: enhancement of the probability to find an electron between the nuclei!

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

- bonding orbital 1σ , σ of lowest energy

Calculation on H_2^+ : $R_e = 130 \text{ pm}$, $D_e = 177 \text{ eV}$
experimental 106 pm , 2.6 eV (LCAO ~~reflects~~ gives approximate values!)

Foll: justification p. 420



c) Antibonding orbitals

constructive interference: $1s$ orbitals overlap, form σ -orbital

ψ_- corresponds to higher energy than ψ_+

also a ~~sigma~~ σ orbital: $2\sigma^*$ antibonding orbital which raises the energy of a molecule

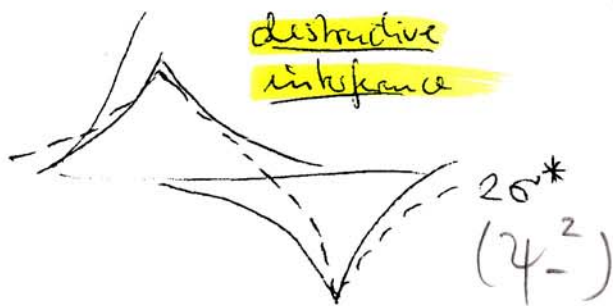
if occupied! (reaction in collision) often labelled

as $2\sigma^*$ ('two sigma star')

probability density:

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

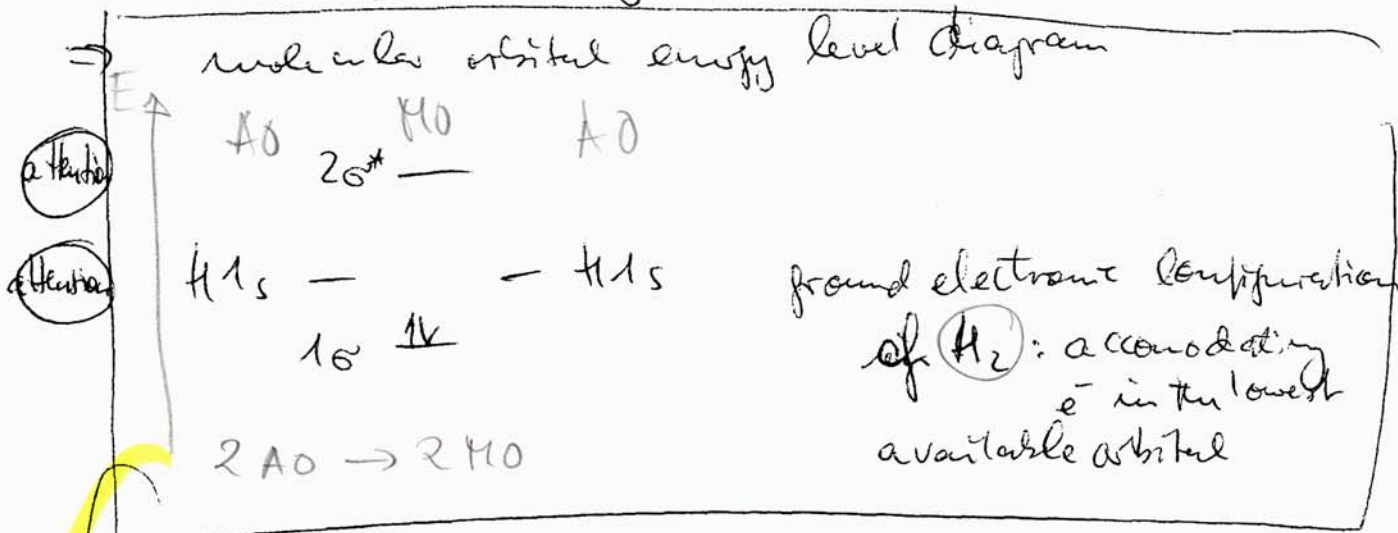
- antibonding e^- : excluded from the internuclear region
↳ pulls nuclei apart!



- $|E_- - E_{H1s}| > |E_+ - E_{H1s}|$ σ^* more antibonding than σ is bonding! presence of nuclei-repulsion! is partially the reason!

put the following below!

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Structure of diatomic molecules

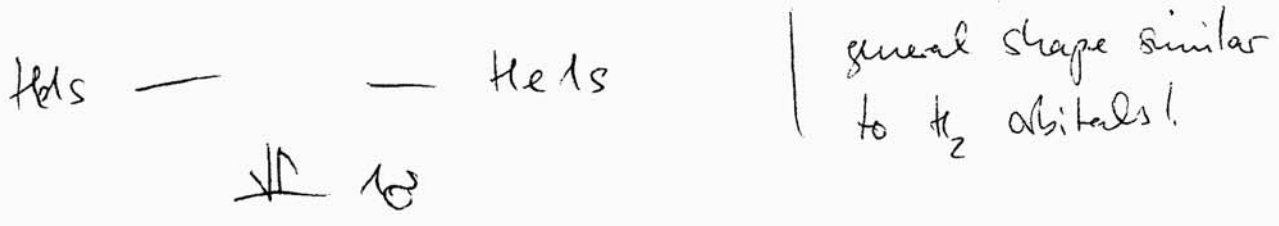
- $1s$ - atom orbitals used for deduction of ground electronic configuration of many-electron atoms
- analogy: H_2^+ MO \rightarrow many-electron diatomic molecules

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!
~~He 2s*~~



Higher energy than individual atoms \rightarrow unstable

b) bond order:

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

\uparrow \uparrow

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

greater bond order \rightarrow greater bond strength
smaller bond length

c) Period 2 diatomic molecules:

- only valence shell orbitals
 - 2s and 2p, MO theory considers all AO of appropriate symmetry, σ bonds: ~~span~~ cylindrical symmetry along internuclear axis: s + 2p_z 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

\rightarrow 4 MO of σ symmetry

- 2s and 2p_z : distinctively different energies,
 might be ~~also~~ treated separately \rightarrow 4 σ 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:

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

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

$$\rightarrow \Psi_{A2p_z} \pm \Psi_{B2p_z} \quad \text{and} \quad \Psi_{A2p_z} \pm \Psi_{B2p_z}$$

\downarrow

~~2005~~ overlap \rightarrow give
 1 σ and 2 σ^*

\downarrow

3 σ and 4 σ^*

Numbering follows increasing energy

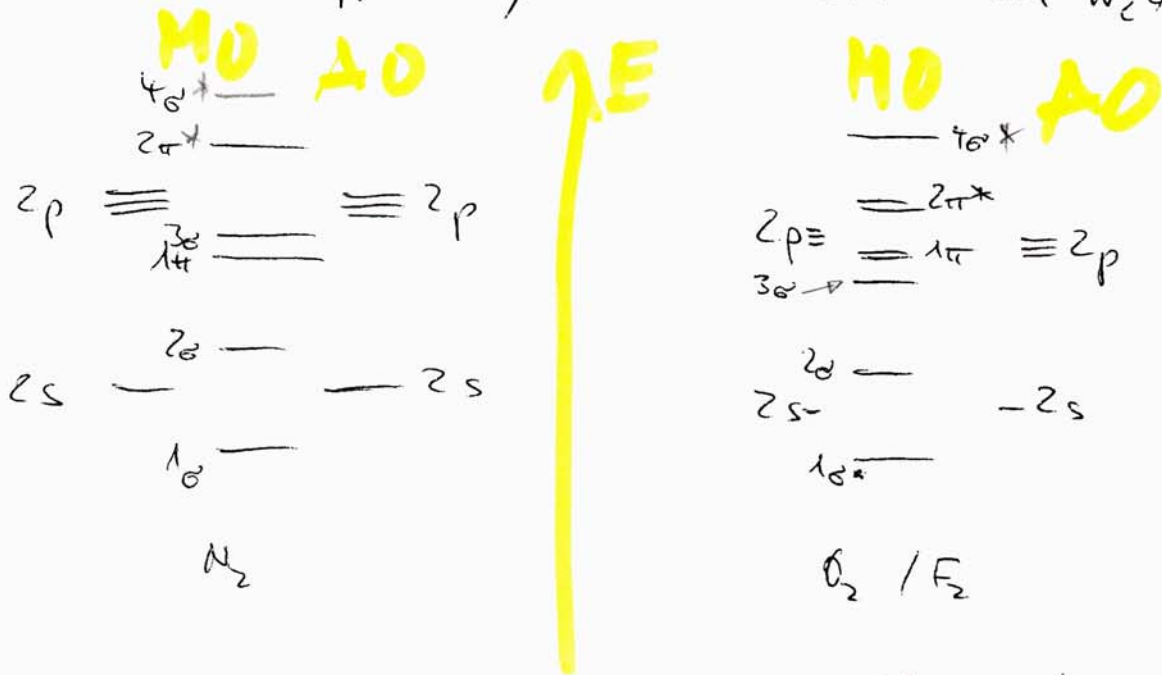
d) π - orbitals

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

\rightarrow π - orbitals, 1 ~~atypical~~ unit of
 (def as before) orbital angular momentum

\rightarrow 2 π_x and 2 π_y bonding / antibonding orbitals
 π_x and π_y , π_x^* and π_y^* : degenerate

- Some cases: π orbitals are less strongly bonding than σ : maximum overlap occurs off-axis, switch occurs between N_2 and O_2 -8-



⇒ evidence found by spectroscopy

e) The overlap integral

Attempt to find 2 atomic orbitals

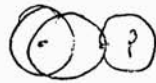
overlap: measured by the overlap integral S

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

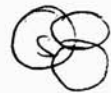
pictured



small overlap



large overlap



zero net overlap

$S = 0.53$ at r_0 in H_2^+

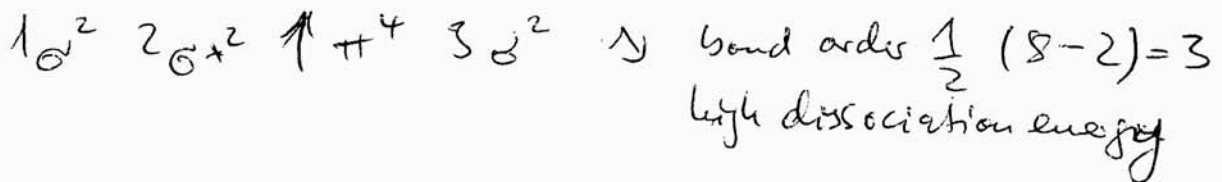
$S = 0.2-0.3$ for orbitals with $n=2$

f) structure of diatomic molecules:

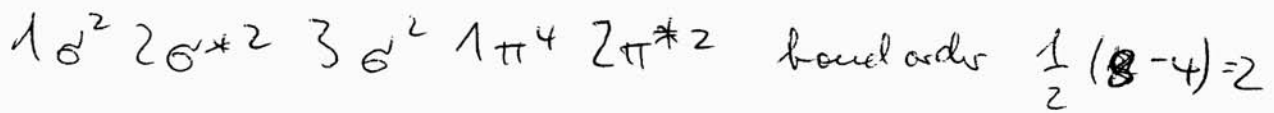
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building-up principle, using the electrons from unbound atoms

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



- O_2 : $12 e^-$



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

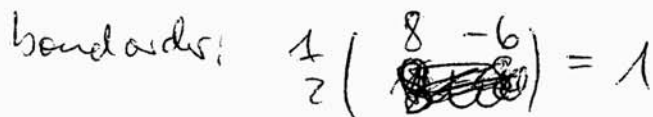
~ parallel spins, net spin angular momentum

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

confirmed by experiment (not predicted by

valence bond theory!)

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



low dissociation energy