

Molecules/I.

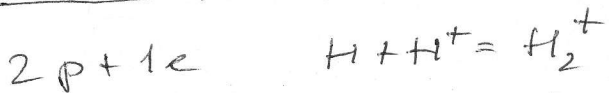
H_2^+ , bonding and anti-bonding molecular orbitals

Question: Why are the molecules such as they are?

What is a molecule?

- group of nuclei surrounded by electrons in a stable arrangement?
- individual atoms held together by some interactions?

H_2^+ Hydrogen molecule ion

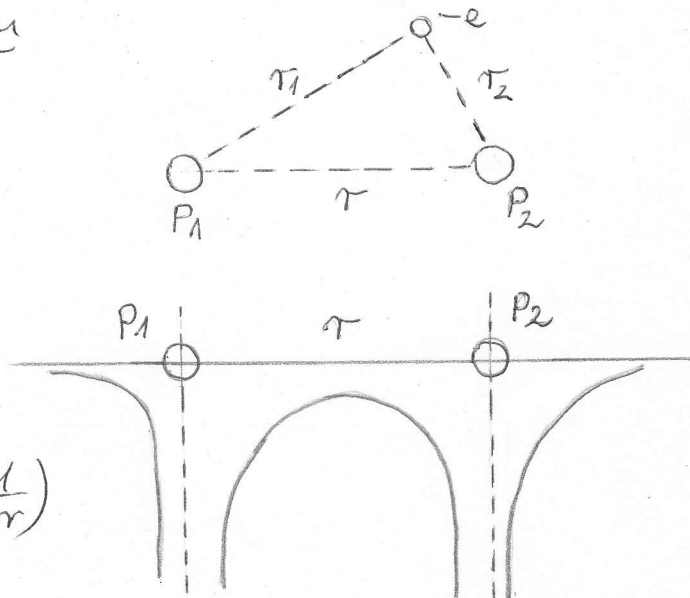


The electron does not "know" which proton it belongs to

Stationary states:

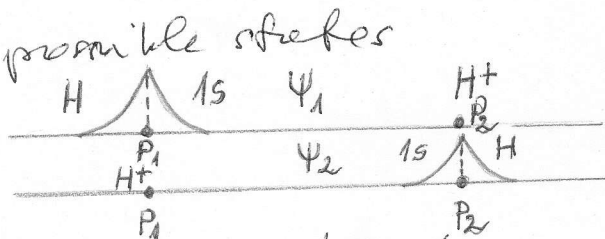
Schrodinger equation

Potential $E_p = \frac{e^2}{4\pi\epsilon_0} \left(-\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r} \right)$



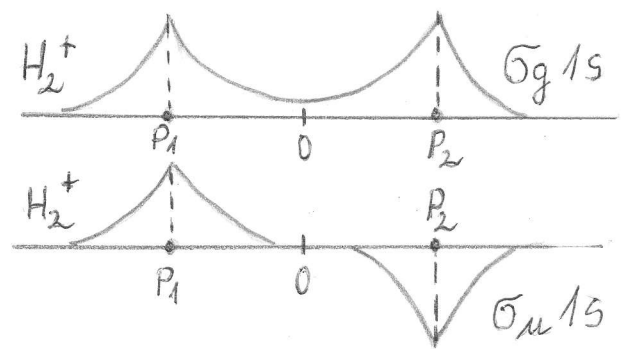
The wavefunctions

- 2 protons far away, 2 possible states
 el. around P_1 : 1s H atom, P_2 far
 el. around P_2 : 1s H atom, P_1 far



- Approaching the 2 protons: the free proton tries to pull the electron

- 2 protons close by
 ψ_{el} must follow the symmetry of the potential

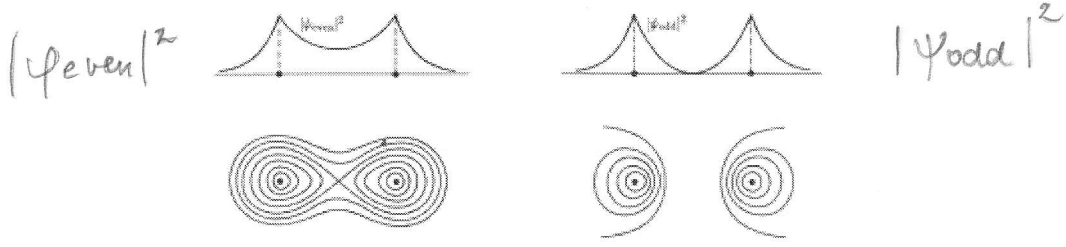


$\psi_{\text{even}} \approx \psi_1 + \psi_2 = \sigma_g 1s$

$\psi_{\text{odd}} \approx \psi_1 - \psi_2 = \sigma_u 1s$

Generation of molecular orbitals by linear combination of atomic orbitals

The probability distribution $|\psi|^2$



The energy of the two states are different, because
 Electron between 2p - helps to pull the 2p together against the repellent Coulomb force
 Electron outside 2p - they further pull the 2p away

$\sigma_g 1s$ has lower energy

Approaching 2p!

- $\sigma_g 1s$ energy decreases until r_0 , increases closer due to Coulomb repulsion
- $\sigma_u 1s$ increases all the way

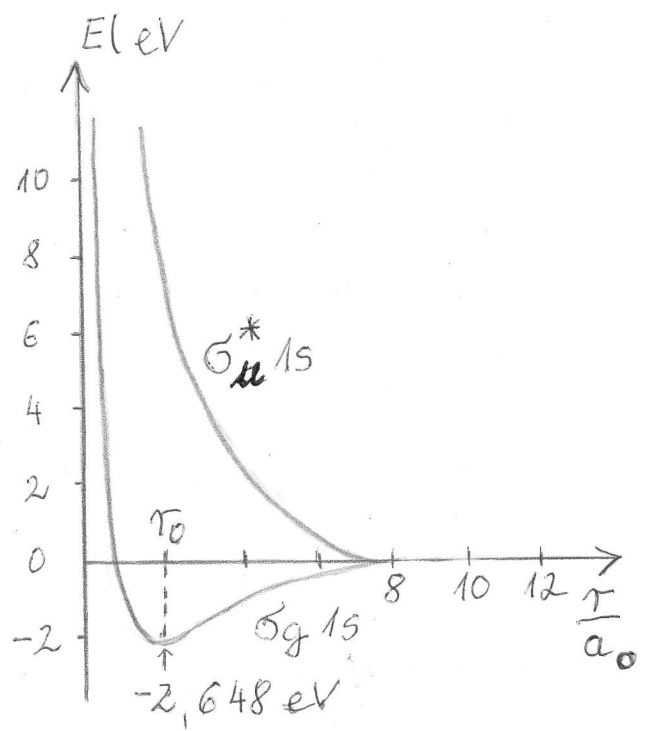
$r = r_0 \rightarrow$ minimum in potential energy for $\sigma_g 1s$

Stable H_2^+ configuration

$\sigma_g 1s$ bonding wavefunction

$\sigma_u 1s$ antibonding wavefunction (no energy minimum)

Denotation $\sigma_u 1s^*$



$r_0 = 1,06 \text{ \AA}$

The energy of these states:

$$E = \int \psi^* \hat{H} \psi d\tau \quad \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \frac{e^2}{4\pi\epsilon_0} \left(-\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r} \right)$$

The result is

$$E = E_a + \frac{e^2}{4\pi\epsilon_0 r} - \frac{A \pm B}{1 \pm S}$$

$\psi = \psi_g$ even
 $\psi = \psi_u$ odd

Let ψ_1 and ψ_2 atomic wavefunctions belonging to the same E_a energy. (ψ are linear combinations of ψ_1 and ψ_2)

$\frac{e^2}{4\pi\epsilon_0 r} \rightarrow$ repellent potential of the 2 protons

$$A = \frac{e^2}{4\pi\epsilon_0} \int \frac{\psi_1^2}{r_2} d\tau = \frac{e^2}{4\pi\epsilon_0} \int \frac{\psi_2^2}{r_1} d\tau$$

This is the attractive potential between the electron near to one of the protons and the other proton

$$B = \frac{e^2}{4\pi\epsilon_0} \int \frac{\psi_1 \psi_2}{r_1} d\tau = \frac{e^2}{4\pi\epsilon_0} \int \frac{\psi_1 \psi_2}{r_2} d\tau$$

B and S are quantum-mechanical terms

$$S = \int \psi_1 \psi_2 d\tau$$

B and S are related to the overlap of the atomic wavefunctions

No overlap $B = S = 0$

$$E = E_a + \frac{e^2}{4\pi\epsilon_0 r} - A$$

- no minima

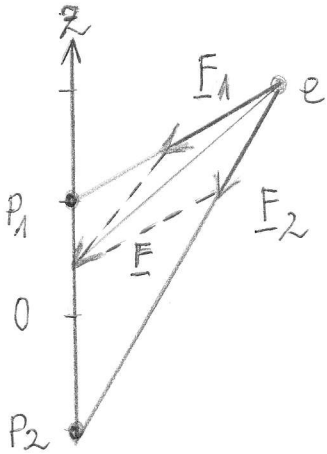
The stable molecule can be explained with the overlap of the wavefunctions and the symmetry of the wavefunction.

Molecular orbital of diatomic molecules

(17)

$H_2 \rightarrow 2$ electrons

Exclusion principle \uparrow : spin plays a role beside orbital



the force is not centrally but axially symmetric
 $\rightarrow L$ is not constant of motion

Since the force F always intersects with the z axis, the torque on the electron is \perp to the axis $\rightarrow L_z = \text{constant}$

$$L_z = m_l \hbar \quad m_l = 0, \pm 1, \pm 2, \dots$$

The energy depends on $|m_l| = \lambda$ only
 (direction of rotation does not play a role)

The states

m_l	0	± 1	± 2	$\pm 3, \dots$	
λ	0	1	2	3	
denotation	σ	π	δ	φ	
number of states	2	4	4	4	$m_s = \pm \frac{1}{2}$

Denotation of molecular orbitals: $\lambda n l$

$$\lambda = \sigma, \pi, \delta, \dots$$

n, l quantum numbers of the atomic orbitals which are combined for the molecular orbital

Homonuclear molecules: identical atoms

e.g. H_2

Potential symmetric to center \rightarrow

ψ is symmetric too

Two kinds of ψ : even and odd (g, u)

$\sigma_g, \sigma_u, \pi_g, \pi_u$ etc.

Chemical bond: approaching two atoms

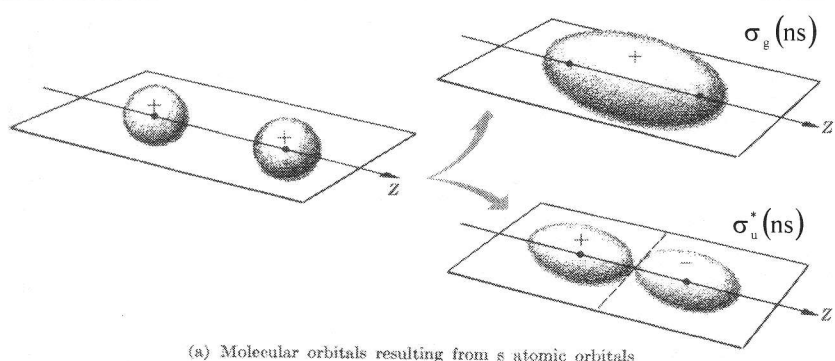
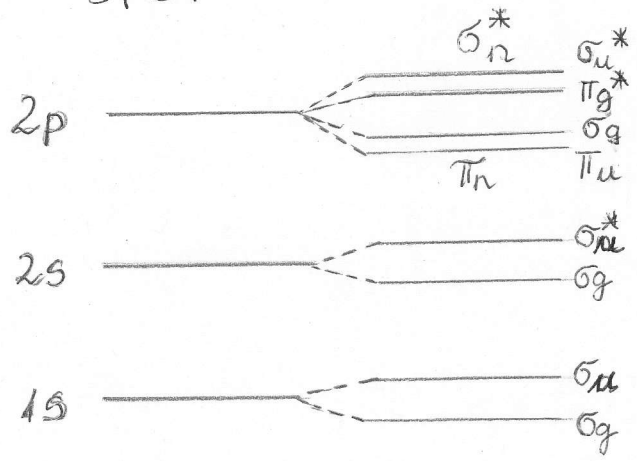
$$\psi_1 \pm \psi_2$$

Angular distributions:

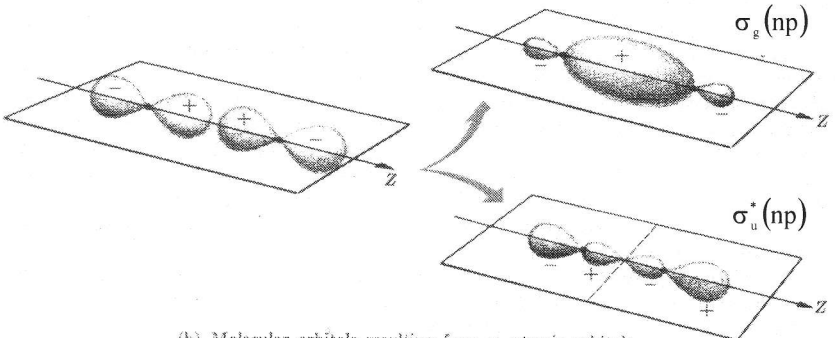
nodal planes - - -

antibonding states (*)

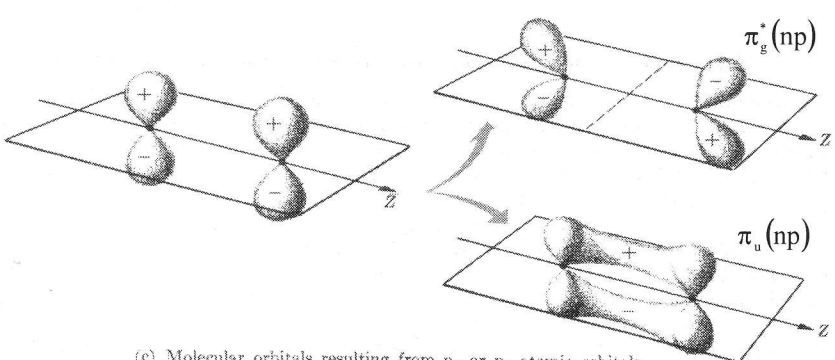
The energy levels of individual states



(a) Molecular orbitals resulting from s atomic orbitals



(b) Molecular orbitals resulting from p_z atomic orbitals

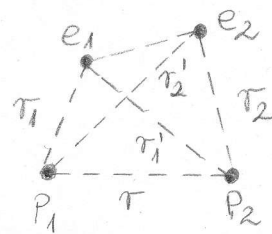
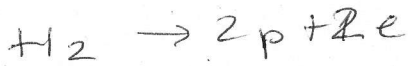


(c) Molecular orbitals resulting from p_x or p_y atomic orbitals

The actual energy levels, and energy differences depend on the particular molecule

Molecules / 2.

Homonuclear molecules



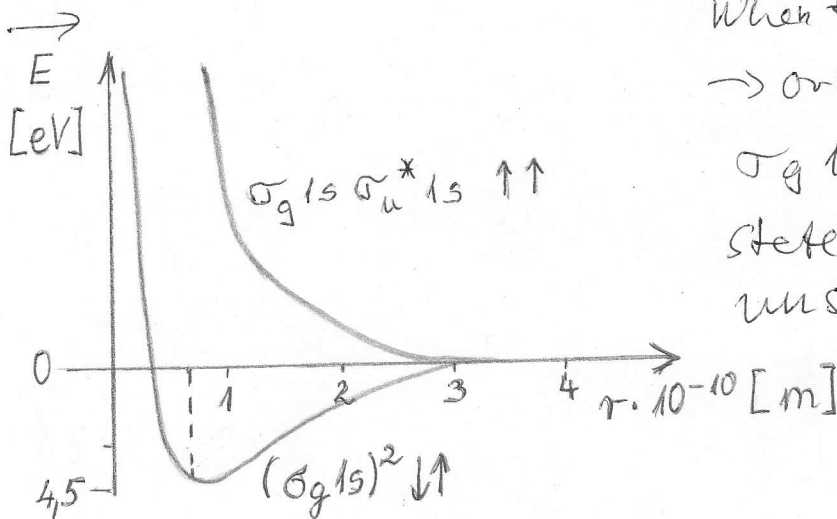
$$E_p = \frac{e^2}{4\pi\epsilon_0} \left(-\frac{1}{r_1} - \frac{1}{r_1'} - \frac{1}{r_2} - \frac{1}{r_2'} + \frac{1}{r_{12}} + \frac{1}{r} \right)$$

One can not tell which electron belongs to which proton

Exclusion principle: spin must be taken into account

→ 2 electrons on σ_g 1s bonding state → $\uparrow\downarrow$ spins

$(\sigma_g 1s)^2$ configuration → stable molecule



When the two spins are $\uparrow\uparrow$
 → orbital must be antisymmetric
 $\sigma_g 1s \sigma_u^* 1s$ → the antibonding state dominates
 unstable

He_2^+ molecule

3 electrons

$(\sigma_g 1s)^2 \sigma_u^* 1s$ configuration: stable

Total orbital angular momentum M_L is

$$M_L = \sum_i m_{l_i}$$

The energy depends on $\Lambda = |M_L|$

$\Lambda = 0, 1, 2, \dots$ $\Sigma, \Pi, \Delta, \Phi, \dots$ states

$2S+1 \Lambda$ $S = \text{total spin}$

Electron configuration of homonuclear diatomic molecules

	$\sigma_g 1s$	$\sigma_u^* 1s$	$\sigma_g 2s$	$\sigma_u^* 2s$	$\pi_u 2p$	$\sigma_g 2p$	$\pi_g^* 2p$	$\sigma_u^* 2p$	
H_2^+	↑								2, 0.5
H_2	↑↓								4, 4.8
He_2^+	↑↓	↑							3, 1
He_2	↑↓	↑↓							instab.
Li_2	↑↓	↑↓	↑↓						1, 0.3
Be_2	↑↓	↑↓	↑↓	↑↓					instab.
B_2	↑↓	↑↓	↑↓	↑↓	↑↑...				3, 6
C_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓				3, 6
N_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓			7, 3.7
O_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓	↑↑..		5, 0.8
F_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓	↑↑↓↓		2, 8
Ne_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓	↑↑↓↓	↑↓	instab.

The orbitals are filled sequentially with increasing energy

- Molecular bond: when electrons with opposite spins stay with high probability between the nuclei bonding states → covalent bond
- Exceptions: B_2, O_2 ↑↑ spins! Reason: π orbitals but only 2 electrons (instead of 4); due to repulsion the antisymmetric orbital is energetically optimal → spins ↑↑ → permanent magnetic moment ⇒ paramagnetic
- He_2, Be_2 : equal no. of bonding and antibonding orbitals → they are unstable
- N_2, O_2, F_2, Ne_2 : dissociation energy (stability) decreases monotonously because the difference in the number of bonding and antibonding pairs is 3, 2, 1, 0

Heteronuclear molecules

e.g. HCl, CO, NaCl ...

No center of symmetry!

Orbitals: σ, π, δ but no g and u combinations
Electrons on the unfilled shells participate in the bond only

- E.g. NaCl Na: 11e, Cl: 17e but
outside the closed shells, the number of unpaired electrons:
Na 1el: 3s Cl 1el 3p

The nuclear charges are different $Z_{Na} = 11, Z_{Cl} = 17$

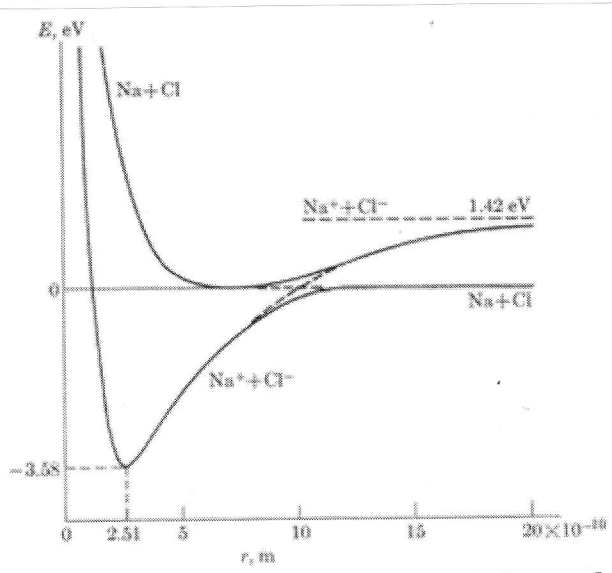
\rightarrow the negative charge shifts toward the Cl
polarization \rightarrow electric dipole moment: $3 \cdot 10^{-29}$ Cm

If the electron of Na was shifted completely to the position of Cl
 $e = 1.6 \cdot 10^{-19}$ C $d = 2.5 \cdot 10^{-10}$ m $e \cdot d = 4 \cdot 10^{-29}$ Cm

\rightarrow The electron of Na can be found with 75% probability at the position of Cl

\Rightarrow They can be considered ions Na^+, Cl^-

Electric attraction \rightarrow ionic bond



The wavefunctions
 $\psi = \psi_A + \lambda \psi_B$
 ψ_A and ψ_B atomic wavefunctions
 $\lambda \rightarrow$ from experiments

Most intermolecular molecules' bond is between covalent and ionic bond

e.g. CO - more covalent than ionic $e \cdot d = 4 \cdot 10^{-31}$ Cm