Molecules

PURPOSE / LEARNING OBJECTIVES:

- Familiarize with **Molecular Orbital (MO) Theory.**

- Understand **bonding** in simple diatomic molecules

- Sketch **energy level diagrams** for molecules using LCAO-MO and identify the **bonding orbitals** and **antibonding orbitals.**

- Describe important **molecule properties** from the energy level diagrams.

OUTLINE

- The hydrogen molecule-ion
- MO diagrams
- Sigma and pi orbitals
- Heteronuclear molecules
- Polyatomic molecules
- Conjugated molecules
- Molecular rotation
- Molecular vibration
- Electronic transition in molecules

What is a molecule?

- ▶ Group of atoms bound together by some kind of interaction?
- ▶ Group of nuclei surrounded by electrons according to the laws of quantum-mechanics?

Both explanations are true!

When two atoms combine to form a molecules the inner electrons of each atom are practically undisturbed, only the outermost, or valence, electrons in the unfilled shells are affected and form a chemical bond.

The Hydrogen molecule ion H_2^+

► Simplest of all molecules (two protons + one electron). It comes from a H atom reacting with a proton:

$$H + H^+ \rightarrow H_2^+$$
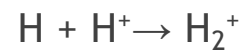
► Once the molecule is formed one cannot say anymore which was originally the atom or the proton: it can be described as an electron moving in the electric field of 2 protons separated by a distance r.
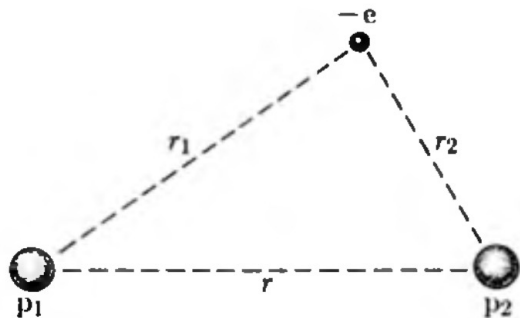
P_1 and P_2 are the two protons
r, r_1 and r_2 the relative distances
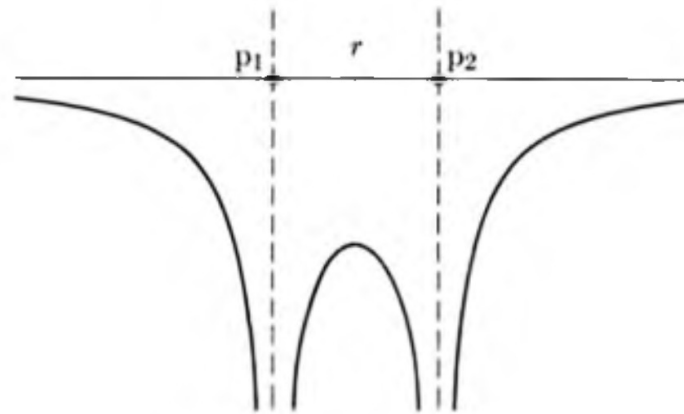e^- is the electron

Stationary states of H_2^+

▶ Potential energy E_p:

Attractive potential energy between electron and the protons

Repulsive potential energy between two protons

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

▶ Variation of electronic potential energy along the line joining the two protons

Molecular Orbitals

▶ Case (a): electron orbiting around P_1, forming a H atom in its ground state 1s, and the proton P_2 is very far away. In this case, the wave function of the electron is practically undisturbed by P2 and it coincides with the H-1s function.

▶ Case (b): electron orbiting around P2. H-1s function around P2.

▶ As the separation between the two protons decreases and **the molecule is formed**, the wave function of the electron is disturbed by the approaching proton.

▶ The symmetry of the electron potential energy suggests that the probability distribution of the electron must also be symmetric.

▶ Two possible wavefunctions with required symmetry for the probability distribution are (c) and (d)
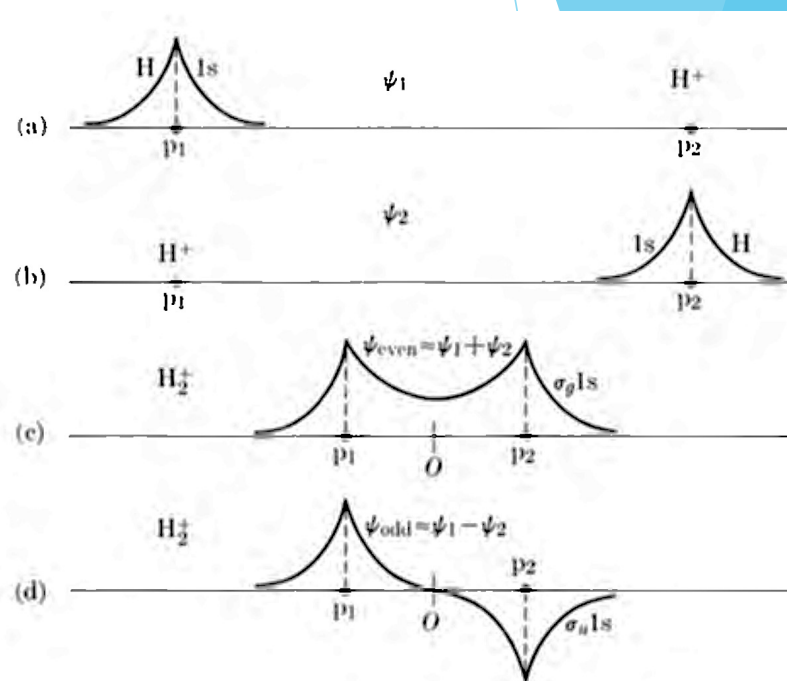
Probability distribution of the electron in the H_2^+ molecule

Even and odd molecular wave functions

▶ The case (c) in previous slide represents the even wave function, the case (d) shows the odd wave function relative to the center of the molecule.

▶ We can express their wave functions as **linear combination of atomic orbitals (LCAO)**:

$$\psi_{even} \approx \psi_1 + \psi_2 \qquad \psi_{odd} \approx \psi_1 - \psi_2$$

▶ These wave functions are called **molecular orbitals (MO).**

▶ In this specific case, they are the sigma orbitals: $\sigma_g 1s$ and $\sigma_u 1s$

▶ ψ_{even} has the max probability of finding the electron in the region between the protons, while ψ_{odd} has zero probability there
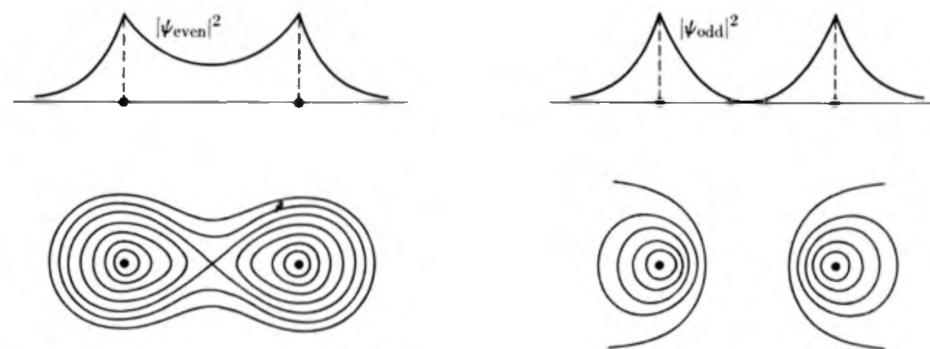
Probability density for even and odd MO of H_2^+ molecule along the lines joining the protons (top) and in a plane containing the two protons.

The energy of $\sigma_g 1s$ and $\sigma_u 1s$

Suppose we start with a hydrogen atom and a proton H⁺ far apart

▶ Since the negative attractive potential energy of the electron dominates the positive repulsive potential energy of the proton in the state $\sigma_g 1s$, the net energy decreases as r decreases.

▶ However, for distances smaller than a certain value r_0, the protons are so close that even in state $\sigma_g 1s$ their repulsive potential energy begins to dominate the attractive potential energy of the electron. Thus for distances less than r_0 the energy corresponding to ψ_{even} increases as r decreases.

▶ The energy curve for $\sigma_g 1s$ or ψ_{even} has a minimum at r_0, corresponding to the equilibrium separation of the two protons, which makes a stable configuration for H_2^+ possible. But the energy curve for $\sigma_u 1s$ or ψ_{odd} has no minimum; thus no stable configuration (or molecule) results.
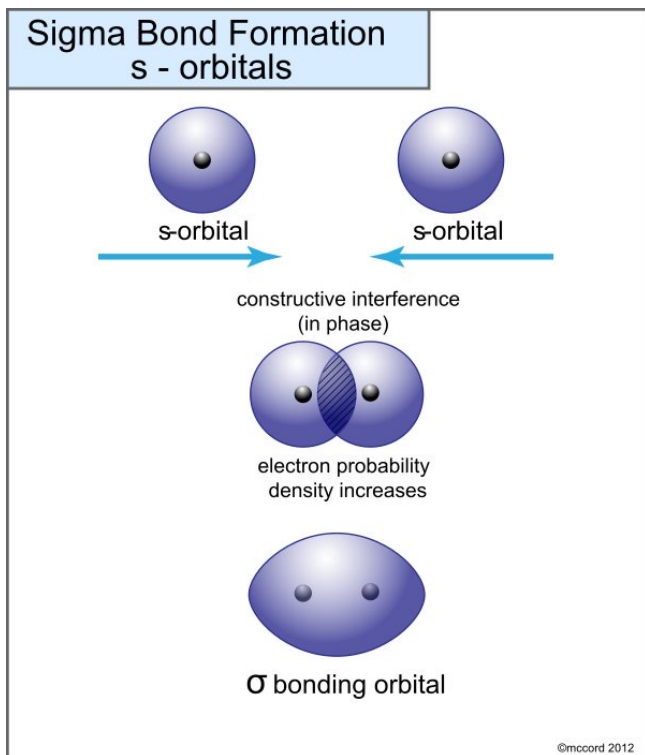
Which one do you think has the lower energy, $\sigma_g 1s$ or $\sigma_u 1s$?
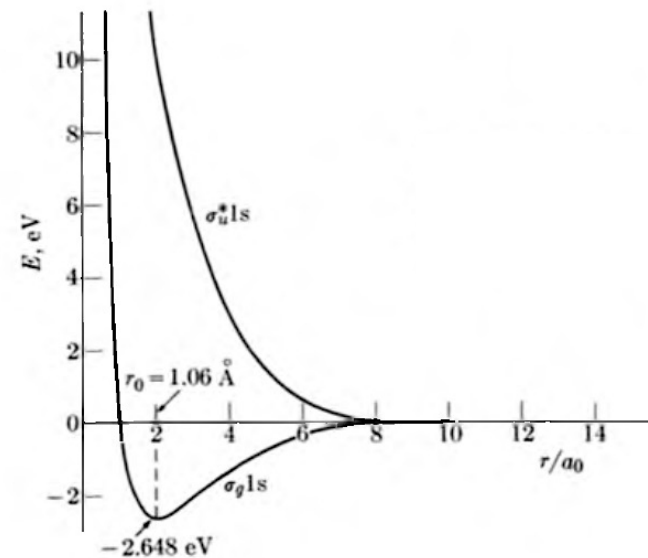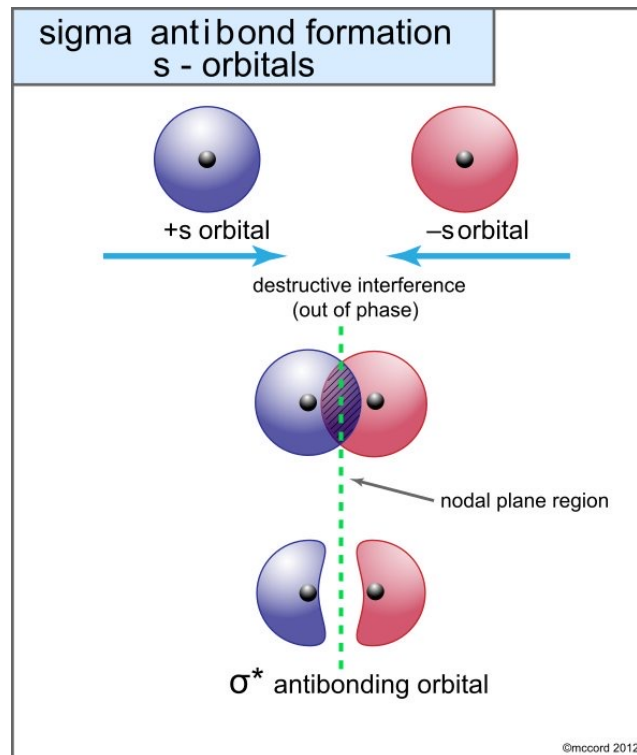
σ and σ* orbitals

When the electron is between the two protons it pulls them together: BONDING (σ_g)

When there is no electron between the protons: ANTI-BONDING ($\sigma_u \ or \ \sigma^*$)

Sigma Bond Formation
s - orbitals

s-orbital   s-orbital

constructive interference
(in phase)

electron probability
density increases

σ bonding orbital

©mccord 2012

sigma antibond formation
s - orbitals

+s orbital   −s orbital

destructive interference
(out of phase)

nodal plane region

σ* antibonding orbital

©mccord 2012

http://ch301.cm.utexas.edu/imfs/#mo/

Exercise 1:
charge-exchange collision H + H$^+$ → H$^+$ + H

Suppose that a beam of fast protons passes through hydrogen gas in the atomic state. It has been found that the probability of electron capture by the incoming protons varies with the energy of the protons, showing pronounced maxima periodically spaced. Why?

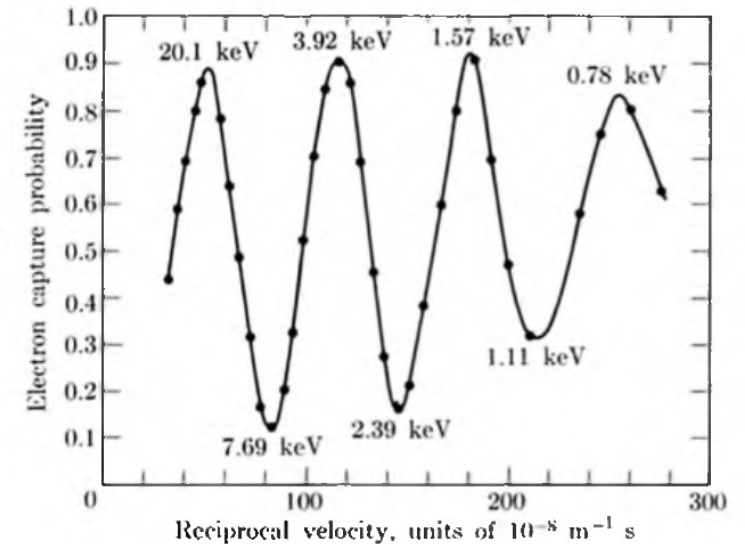At t=0 the H is very far from H$^+$, therefore the electron wavefunction is:

$$\psi(t=0) = \psi_1 \approx \frac{1}{2}\left(\psi_{even} + \psi_{odd}\right)$$

While the time-dependent wavefunction is:

$$\psi(t) = \frac{1}{2}\left(\psi_{even}e^{-\frac{iEt}{\hbar}} + \psi_{odd}e^{-\frac{iE't}{\hbar}}\right) = \frac{1}{2}\left(\psi_{even} + \psi_{odd}e^{-\frac{i\Delta Et}{\hbar}}\right)e^{-\frac{iEt}{\hbar}}$$

with $\Delta E = E' - E$

$$\psi\left(t = \frac{\pi\hbar}{\Delta E}\right) = \frac{1}{2}\left(\psi_{even} - \psi_{odd}\right)e^{-\frac{iEt}{\hbar}} \approx \psi_2\, e^{-\frac{iEt}{\hbar}}$$

i.e., the electron jumps on H$^+$. After again the same time, the electron goes back to the original H. Periodic oscillation with period = $\frac{2\pi\hbar}{\Delta E} = \frac{h}{\Delta E}$

Exercise 2:
calculation of the ground state energy of H_2^+, using the variational method

The Hamiltonian operator of the moving electron plus the two protons, assumed at rest is:

$$\widehat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{4\pi\epsilon_0}\left(-\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r}\right)$$

The molecular orbital wave function is a linear combination of the two atomic 1s orbitals:

$$\Psi_{MO} \approx c_1 1s_A(r) + c_2 1s_B(r)$$

The variational principle says that to find the values of c_1 and c_2 we need to minimize the expectation value of the energy:

$$E = \frac{\int \psi^* \widehat{H}\psi d\tau}{\int \psi\psi^* d\tau}$$

$$\frac{\partial E}{\partial c_1^*} = 0 \ \ and \ \ \frac{\partial E}{\partial c_2^*} = 0$$

Case of H_2^+, energy minimization

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$H_{12} = H_{21} = V_{12}$$

$$H_{11} = H_{22} = \varepsilon$$
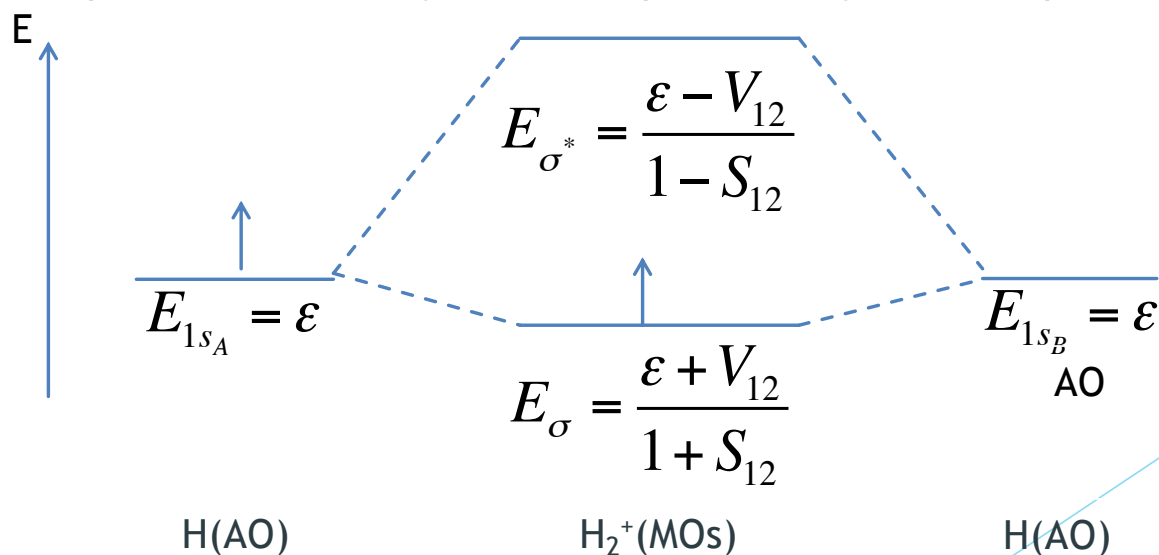
$$S_{11} = S_{22} = 1$$

$$\begin{pmatrix} \varepsilon & V_{12} \\ V_{12} & \varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} 1 & S_{12} \\ S_{21} & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Case of H_2^+, MO diagrams

Possible solutions are $c_1 = \pm c_2$:

$$E = \frac{\varepsilon \pm V_{12}}{1 \pm S_{12}}$$

$$\Psi = \frac{1}{\sqrt{2}}(1s_A \pm 1s_B)$$

We can incorporate these energies in a simple MO diagram or sequence of energy levels:

E

$$E_{1s_A} = \varepsilon$$

$$E_{\sigma^*} = \frac{\varepsilon - V_{12}}{1 - S_{12}}$$

$$E_{\sigma} = \frac{\varepsilon + V_{12}}{1 + S_{12}}$$

$$E_{1s_B} = \varepsilon$$

AO

H(AO)

H_2^+(MOs)

H(AO)

Molecular orbitals of diatomic molecules

▶ When there is more than one electron, the exclusion principle takes place, which requires we consider the spin of the electrons and their orbital motion.

▶ Line passing through the two nuclei is the Z-axis. The component of the angular momentum parallel to the Z-axis has values $L_Z = m_l \hbar$, where $m_l = 0, \pm 1, \pm 2, \ldots$ The sign determines the sense of rotation, but the energy is the same. Depending on m_l we define the following molecular orbitals:

| m_l	0	± 1	± 2	± 3
Symbol	σ	π	δ	ϕ

▶ In each of the above states, the electron may have spin up or down. Thus, except for σ -states, all other angular momentum states are doubly degenerate because of the double sign of m_l.

Molecular Orbital Theory

▶ To understand how two atoms bond to form a molecule, it is essential to know the space variation of the electron probability distribution corresponding to each electron angular momentum state.

▶Method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but treated as moving under the influence of the nuclei in the whole molecule.

▶ MOs are linear combinations of AOs:

▶ Method for predicting whether molecules should exist or not

- Why He_2 is unstable?

▶ Important molecule properties can be also predicted:

- O_2 paramagnetism

- Why CO is a poison?

$$\Psi^{MO} = \sum_i c_i \psi_i^{AO}$$

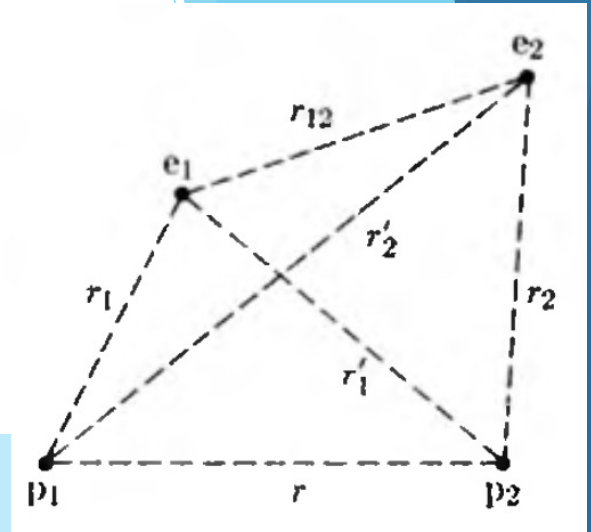# LCAO-MOs of axial p- orbitals
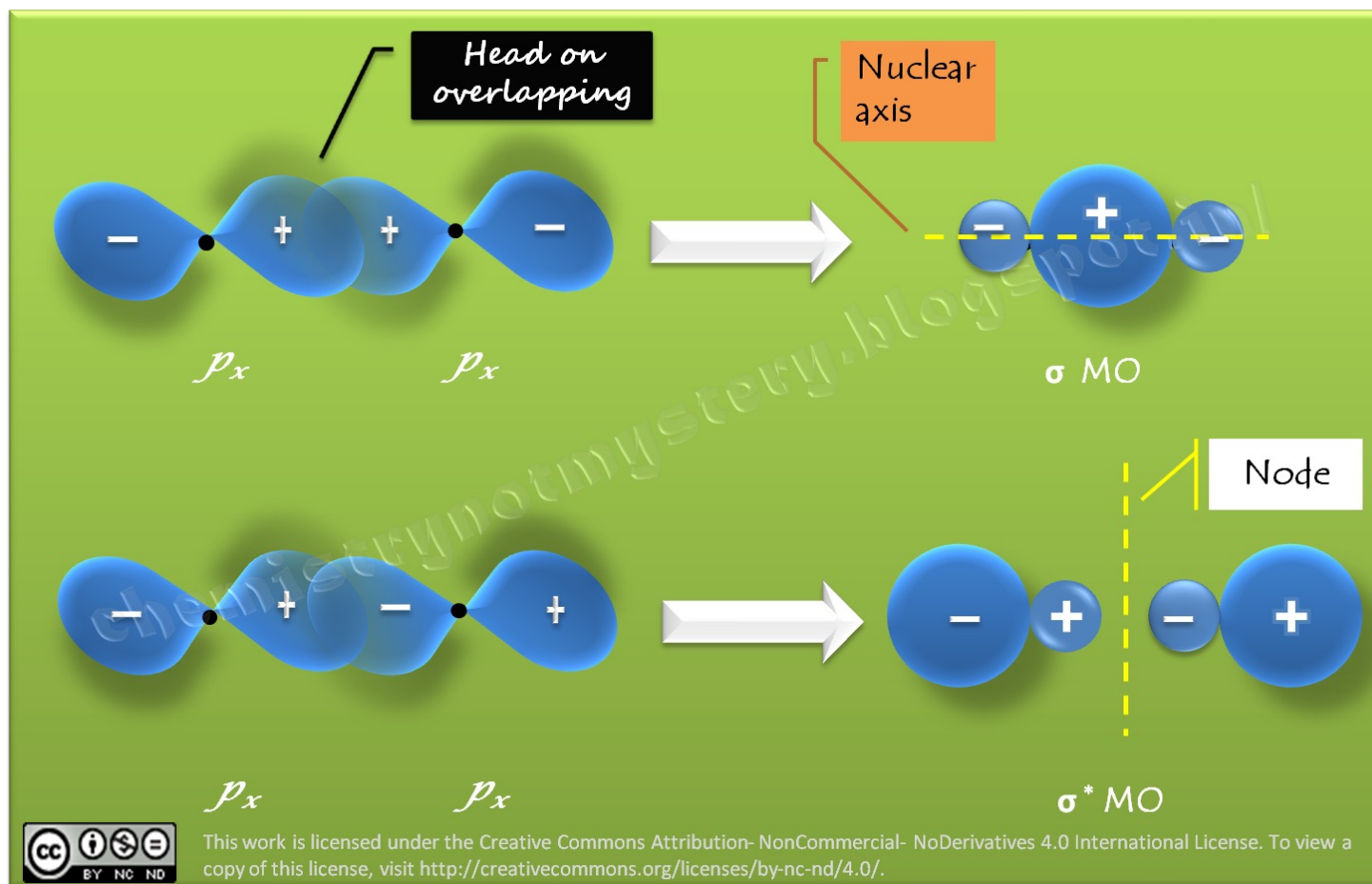
LCAO-MOs of longitudinal p orbitals
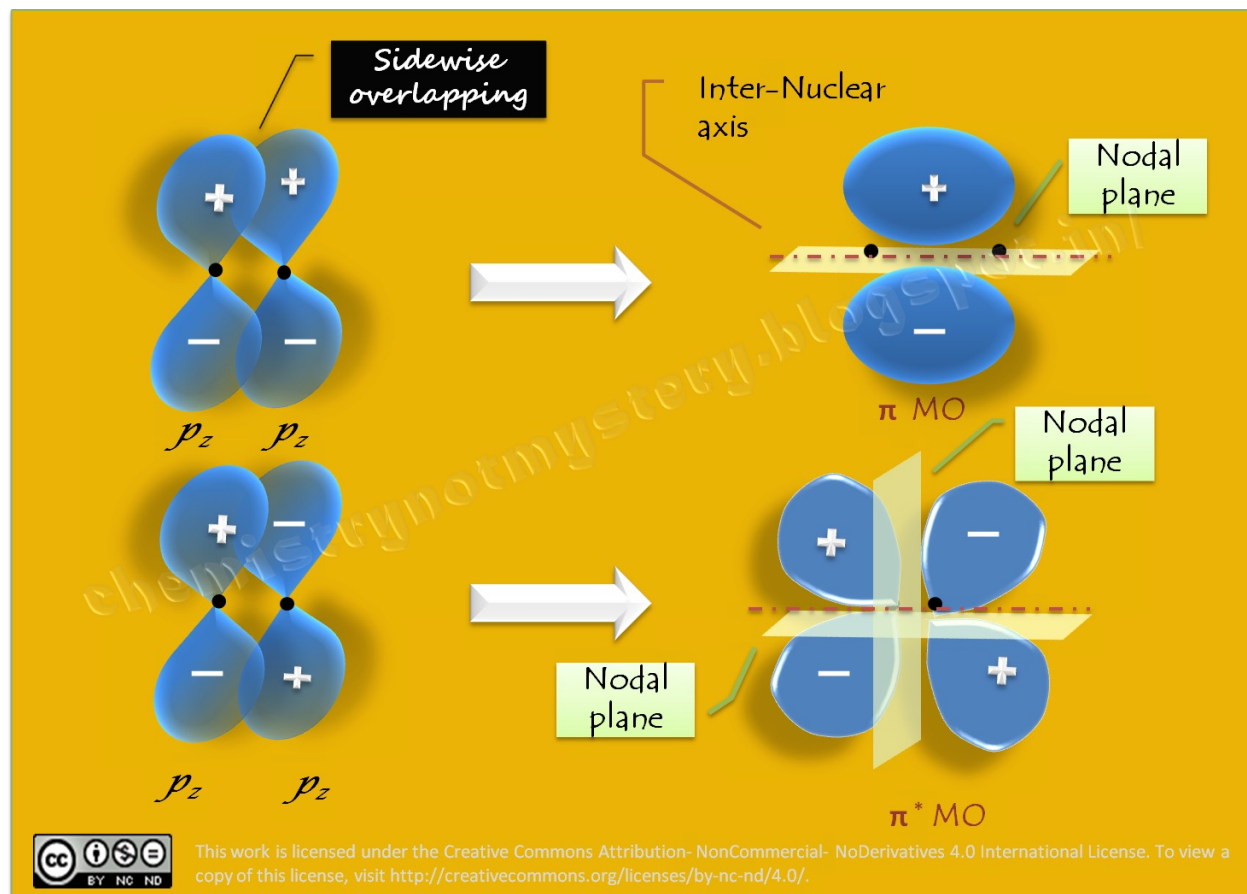
Electronic configuration of H_2

► Potential energy:

$$E_p = \frac{e^2}{4\pi\epsilon_0}\left(-\frac{1}{r_1} - \frac{1}{r_1'} - \frac{1}{r_2} - \frac{1}{r_2'} + \frac{1}{r_{12}} + \frac{1}{r}\right)$$
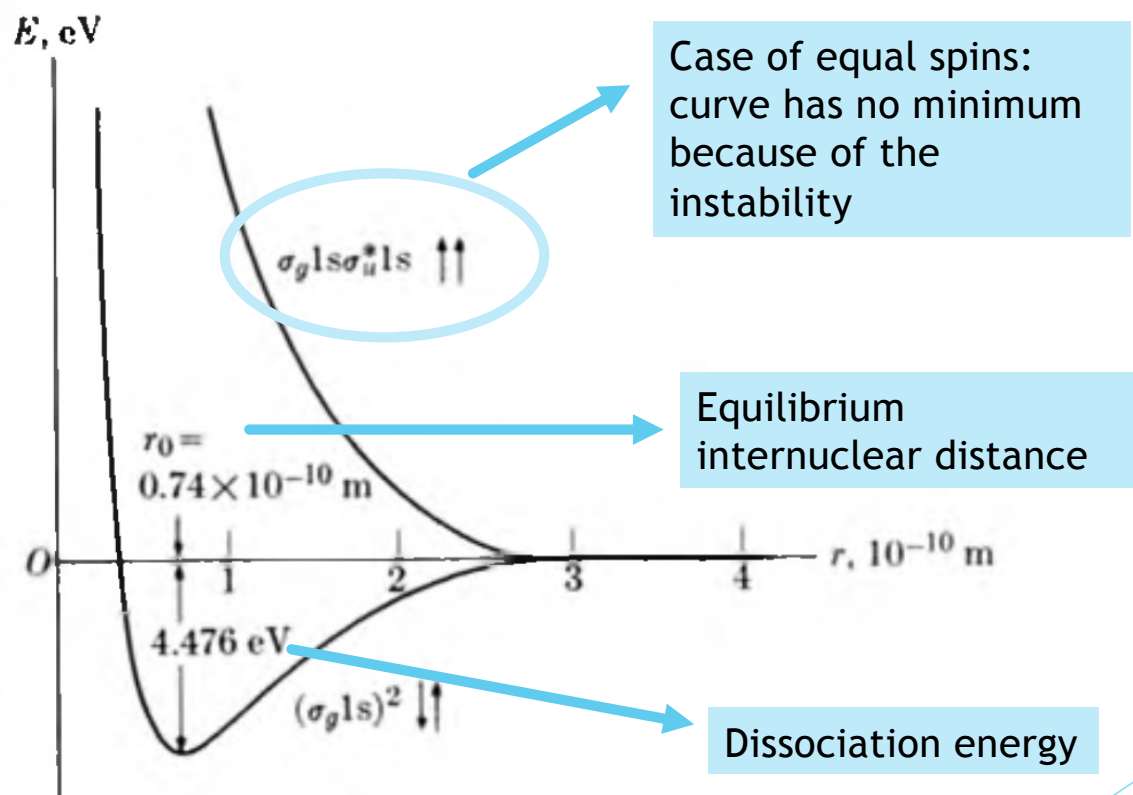
| Attractive potential energy between electrons and the protons | Repulsive potential energy between two electrons and two protons |

► We know from H_2^+ case that the bonding state $\sigma_g 1s$ can accomodate the two electrons. ⟹ FORMATION OF A STABLE MOLECULE

► Pauli exclusion principle: the two electrons have opposite spins.

► If we consider them having equal spin, then they should go each on a different orbital: one electron in the $\sigma_g 1s$ and the other one in the $\sigma_u 1s$. This leads to an UNSTABLE MOLECULE.

Molecular energy vs. internuclear distance (H$_2$)

E, eV

Case of equal spins: curve has no minimum because of the instability

$\sigma_g 1s \sigma_u^* 1s$ ↑↑

Equilibrium internuclear distance

$r_0 = 0.74 \times 10^{-10}$ m

r, 10^{-10} m

4.476 eV

$(\sigma_g 1s)^2$ ↓↑

Dissociation energy

MO diagram rules

- MO diagrams show the sequence of the different energy levels for a molecule

- # MOs = # AOs

- Pauli principle (each orbital can have max 2 e^-)

- Aufbau principle (lowest energy orbitals are filled first)

- Hund's rule (unpaired electrons have parallel spins)

- Bond order = ½ (# bonding e^- - # antibonding e^-)
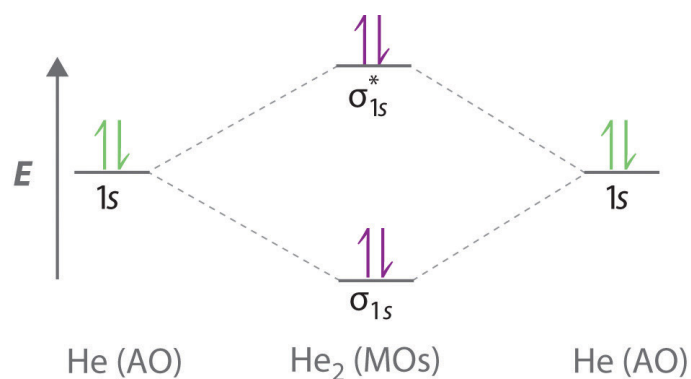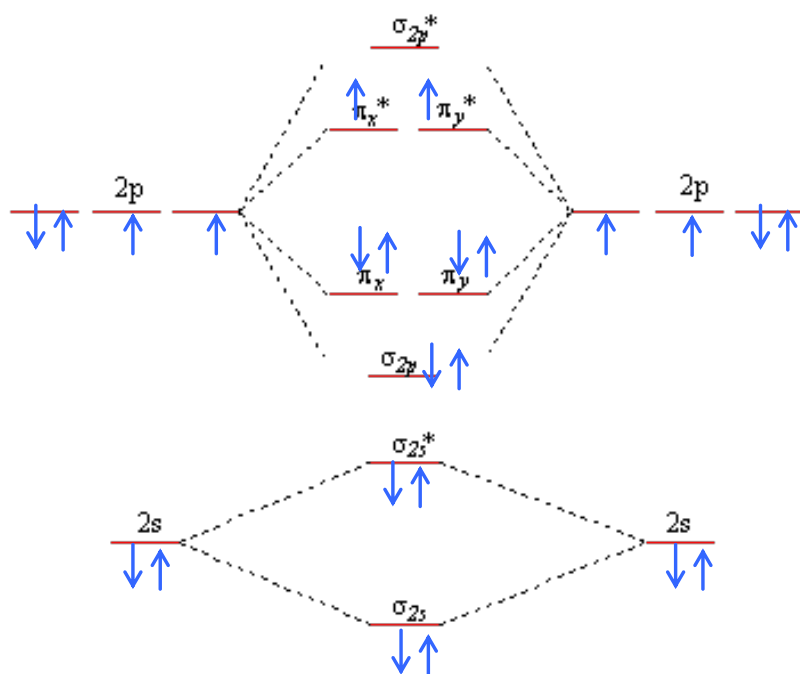
Why He$_2$ is unstable?

Bond order of He$_2$ = 0

This explains why helium is a monatomic gas. However, an excited He$_2$ molecule may be formed if one of the $\sigma_u 1s$ electrons is excited to the bonding state $\sigma_g 2s$.

O$_2$ MO diagram

- σ bonding orbital is lowest in energy due to greater overlap end-on-end

- Bond order = ½ (8-4) = 2

- The repulsion among the electrons favors the most antisymmetric space wave function. This requires the most symmetric spin wave function according to the exclusion principle, which means in this case that the two electrons have their spins parallel.

- Since the resultant spin of O$_2$ is one, the oxygen molecule has a permanent magnetic dipole moment, thereby explaining why oxygen is a paramagnetic gas, while most homonuclear diatomic gases are diamagnetic.

Electronic Configuration of Homonuclear Diatomic Molecules

- Binding energy and the bond length of the ground state of these molecules

- The stability of the molecule will depend on the relative number of bonding and antibonding pairs of electrons

- The stability of N_2, O_2, F_2, and Ne_2 (as measured by the dissociation energy) decreases because the difference between bonding and antibonding pairs for these molecules is 3, 2, 1, and 0, respectively.

| Molecule	Configuration							Dissociation energy, eV	Bond length, Å	Ground state
	$\sigma_g 1s$	$\sigma_u^* 1s$	$\sigma_g 2s$	$\sigma_u^* 2s$	$\pi_u 2p$	$\sigma_g 2p$	$\pi_g^* 2p$	$\sigma_u^* 2p$			
H_2^+	↑								2.65	1.06	$^2\Sigma_g$
H_2	↑↓								4.48	0.74	$^1\Sigma_g$
He_2^+	↑↓	↑							3.1	1.08	$^2\Sigma_u$
He_2	↑↓	↑↓							Not stable		$^1\Sigma_g$
Li_2	↑↓	↑↓	↑↓						1.03	2.67	$^1\Sigma_g$
Be_2	↑↓	↑↓	↑↓	↑↓					Not stable		$^1\Sigma_g$
B_2	↑↓	↑↓	↑↓	↑↓	↑↑				3.6	1.59	$^3\Sigma_g$
C_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓				3.6	1.31	$^1\Sigma_g$
N_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓			7.37	1.09	$^1\Sigma_g$
O_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓	↑↑		5.08	1.21	$^3\Sigma_g$
F_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓	↑↑↓↓		2.8	1.44	$^1\Sigma_g$
Ne_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓	↑↑↓↓	↑↓	Not stable		$^1\Sigma_g$

Heteronuclear molecules

▶ Molecules with nuclei of different chemical elements

▶ In these molecules the Coulomb interaction of each nucleus with the electrons is different, and the molecule no longer has a center of symmetry.

▶ Example: NaCl. 11 electrons from the sodium atom and the 17 electrons from the chlorine atom in the electric field produced by the nuclei of Na and Cl at their equilibrium separation

▶ To simplify we assume that, since the electrons in closed shells are tightly bound to their respective nuclei, they are not affected by the presence of a second nucleus.

▶ The electrons which are in unfilled shells and which have their spins coupled are not expected to participate strongly in the binding of the molecule.

▶ This leaves us with only two unpaired electrons, the 3s-electron in Na and one 3p-electron in Cl.

NaCl molecule

▶ A stable structure is produced when the two electrons are concentrated in the space between the two atoms BUT in the case of the NaCl molecule the electronic distribution is not symmetric: the electronic charge is displaced toward the Cl nucleus, since the Cl nucleus produces a stronger attractive field.

▶ This results in a molecule which has an uneven charge distribution and which is therefore polarized. The electric dipole moment of NaCl in the gaseous phase is about 3.0 x I0-29 m C.

▶ 75% of the electronic distribution of the valence electron in Na is displaced toward the Cl atom and we may consider the molecule as being composed of two ions held together by their Coulomb attraction.

▶ Na$^+$Cl$^-$ **ionic bond**

Potential energy of the NaCl system
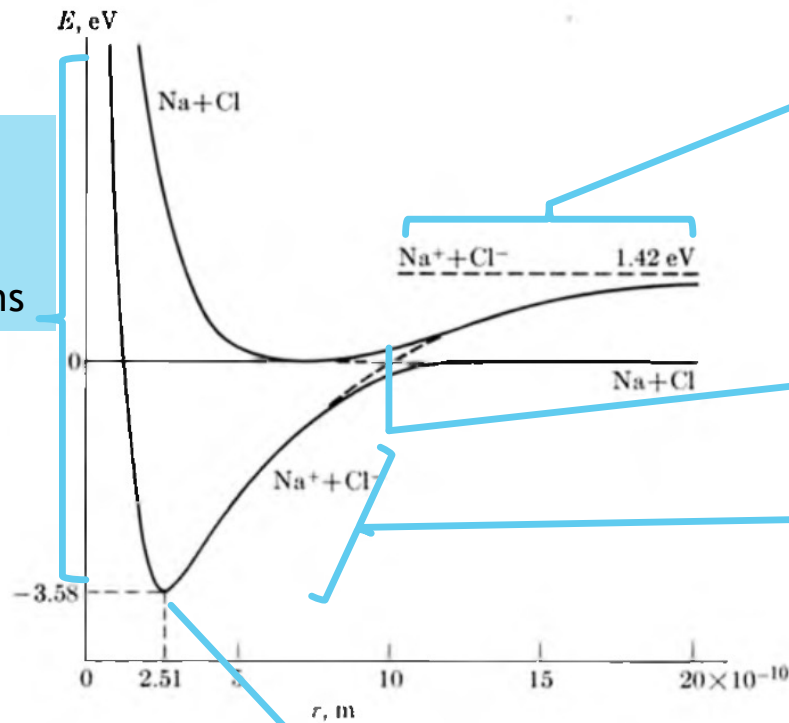
The repulsion between the nuclei and the closed shells of the two ions

At great distances, the two interacting systems are the Na and Cl atoms and their interaction is very small, so that, the potential energy is practically constant

Here the charge transfer from Na to Cl begins to enter into effect.

Attractive coulomb potential between the ions Na^+ and Cl^-

Minimum of the potential energy or equilibrium position

Molecular orbital of heteronuclear molecules

▶ The molecular orbital or wave function of a heteronuclear diatomic molecule cannot be symmetric, hence we write

$$\psi = \psi_A + \lambda\psi_B$$

▶ where ψ_A and ψ_B are the atomic wave functions of the electron in relation to each nucleus.

▶ The parameter λ is chosen so that the calculated energy agrees with the experimental value.

▶ Depending on the value o f λ, the electronic distribution is enhanced in the region between the two nuclei or towards one of them. In the first case the bond is predominantly covalent and in the second case it is mostly ionic.

CO MO diagram

Why is CO a poison?

Empty orbitals are also large on C

LUMO

HOMO

Significant electron density on C

Carbon atom

Oxygen atom
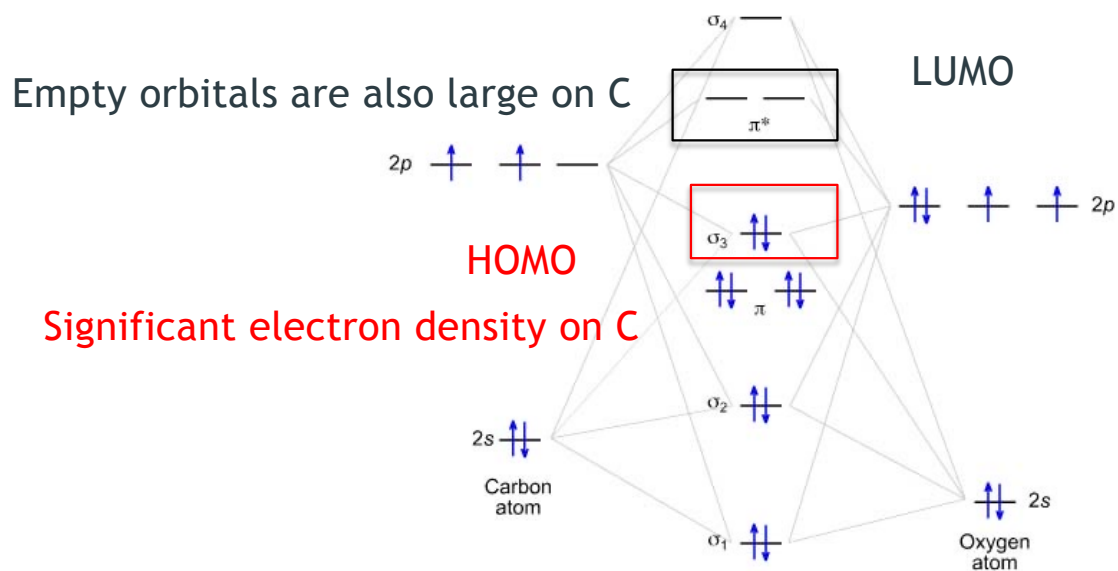
- Bond order = ½ (8- 2) = 3
- In heteronuclear bonds the MO diagram is asymmetric
- Generally, bonding MOs are closer to most electronegative atom
- Antibonding MOs are closer to the less electronegative atom (C)
- *CO can work as σ donor and π acceptor. Metals (e.g. Fe) have matching symmetry so they back bond with CO.*

Dissociation Energies D, Bond Lengths r_o, and Electric Dipole Moments p of Some Diatomic Molecules

	Covalent				Ionic		
Molecule	D, eV	r_0, Å	p, D	Molecule	D, eV	r_0, Å	p, D
H_2	4.48	0.74	0	NaCl	3.58	2.51	8.5
Li_2	1.03	2.67	0	HCl	4.43	1.27	1.07
O_2	5.08	1.21	0	LiH	2.5	1.60	5.88
N_2	7.37	1.09	0	KBr	3.96	2.94	1.29
Cl_2	2.47	1.99	0	KF	5.9	2.55	8.60
HI	3.06	1.61	0.38	CsCl	3.76	3.06	9.97
CO	11.11	1.13	0.12	KCl	4.92	2.79	8.0
NO	5.3	1.15	0.15	KI	3.0	3.23	9.24

➤ For most heteronuclear diatomic molecules, the situation is intermediate between the pure covalent bond and the pure ionic bond.
➤ The more ionic the bond is, the larger the electric dipole moment of the molecule.

Morse potential

▶ The potential energy of a bound state of a diatomic molecule for a given electronic configuration can be empirically expressed by the Morse potential:

$$E_p(r) = D[1 - e^{-a(r-r_0)}]^2$$

▶ where the constants D, a, and r_0 are adjustable parameters characteristic of each molecule

▶ The minimum of E_p is obtained by finding dE_p/dr and equating it to zero:

$$-2Dae^{-a(r-r_0)}[1 - e^{-a(r-r_0)}] = 0$$

▶ The solutions are either $e^{-a(r-r_0)} = 1$ or $r = r_0$ (eq position)

▶ For very large r the exponential is negligible and E_p tends to the constant value D. Thus we could say that D is the energy required to separate or dissociate the molecule
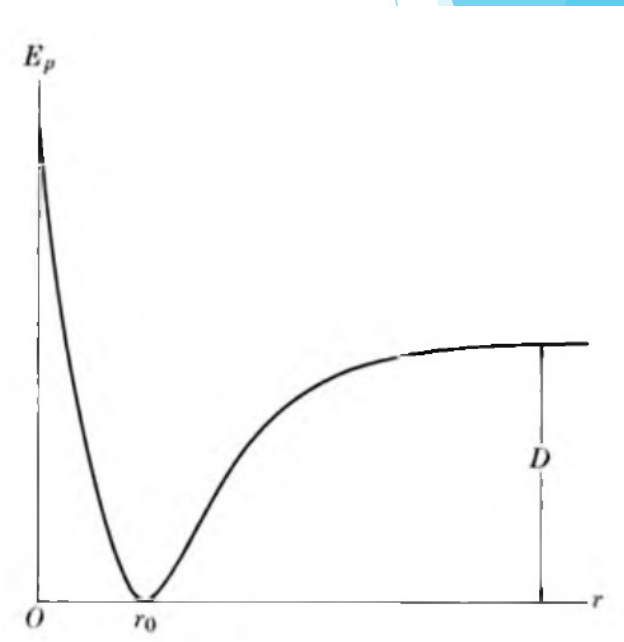
Potential energy of a diatomic molecule for ionic binding.

▶ An empirical expression which gives a fairly accurate description of the potential energy for ionic binding is

$$E_p(r) = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{b}{r^9}$$

> Coulomb attraction between ions

> Repulsion of nuclei and closed shells. Since depends on r^{-9}, it falls off rapidly with the nuclear separation.

▶ The equilibrium separation r is obtained by finding the minimum of E_p:

$$\left(\frac{dE_p}{dr}\right)_{r=r_0} = \frac{e^2}{4\pi\epsilon_0 r_0^2} - \frac{9b}{r_0^{10}}$$

▶ $r_0 = 2.51 \times 10^{-10}$ m, and the dissociation energy is 5.12 eV. In the case of NaCl, this is the energy required to separate the molecule into the ions Na^+ and Cl^-.

Polyatomic Molecules

▶ For molecules with more than two atoms, an important new element enters into the analysis o f electronic motion: the geometrical arrangement of the electrons and the nuclei (or in other words, the molecular symmetry).

▶ The **principle of maximum overlap** is very helpful when we wish to determine the shape or geometry of a molecule:

▶ *A bond between two atoms occurs in the direction in which the respective atomic wave functions making up the molecular orbital are concentrated or overlap; the strength of the bond depends on the degree of overlapping of the atomic wave functions.*

Case of water molecule

▶ 10 electrons and three nuclei

▶ In the oxygen atom we may forget (in a first approximation) all electrons except the two unpaired p-electrons in the L-shell. These two electrons, which have parallel spins must differ in their orbital motion.

▶ We may assume that one electron is concentrated along the x-axis and the other electron along the y-axis; that is, the unpaired 2p-electrons occupy states p_x and p_y.

▶ The two H atoms, each with one 1s electron, are located so that their respective electrons gives maximum overlapping of their wave functions with the two unpaired electrons in O. Therefore the two H atoms must be located on the x- and y-axes, respectively, at equal distances from the O atom.
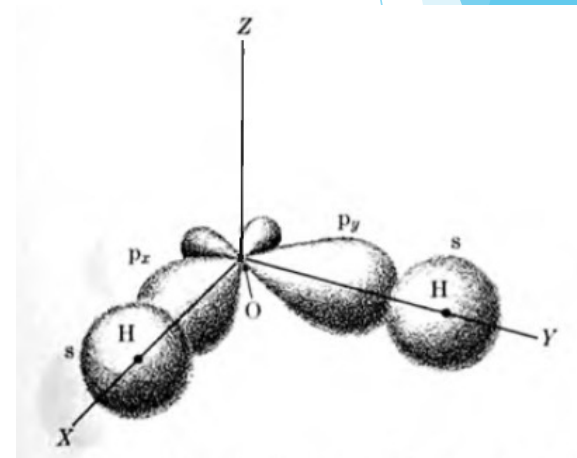
Case of ammonia NH_3

▶ The three unpaired 2p electrons in the N atom concentrated along the x-, y-, and z-axes, occupying p_x, p_y, and p_z states, so that the NH_3 molecule has a pyramidal structure, with the N atom at one vertex and the H atoms at the other vertexes forming the base

▶ The angles at the N vertex of the pyramid are 107.3° instead of 90° because of the repulsion between the H atoms.

▶ The pyramidal structure gives rise to an electric dipole moment of 5.0 X 10^{-30} m C directed along the axis of the pyramid. The dipole moment would be zero if the molecule were planar.
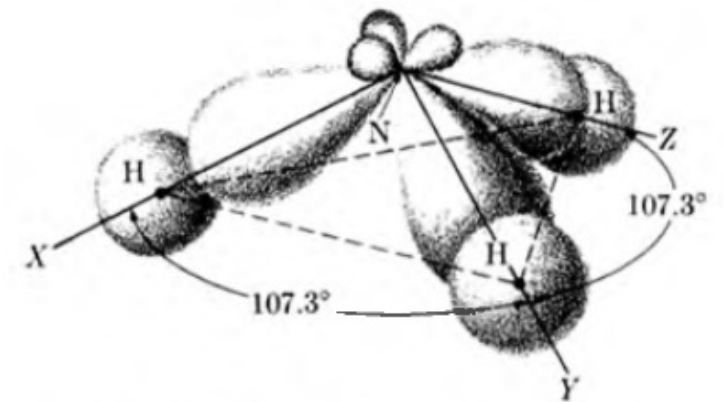
The Carbon atom, sp³ hybridization

- In its ground state it has only two unpaired 2p-electrons, and this cannot explain many compounds of carbon.

- **Hybridization of wave functions:** to produce new atomic wave functions oriented in the desired directions. The one 2s and the three 2p wave functions of carbon do not have exactly the same energy, but the difference in their energy is very small.

- By making proper linear combinations of the four functions, we may obtain new or hybrid wave functions, all corresponding to the same energy and having a pronounced maximum in any desired direction.

- Four new hybrid wave functions with maxima which point toward the vertexes of a tetrahedron

- The directions along which the new wave functions have their maxima form angles of 109,28°.
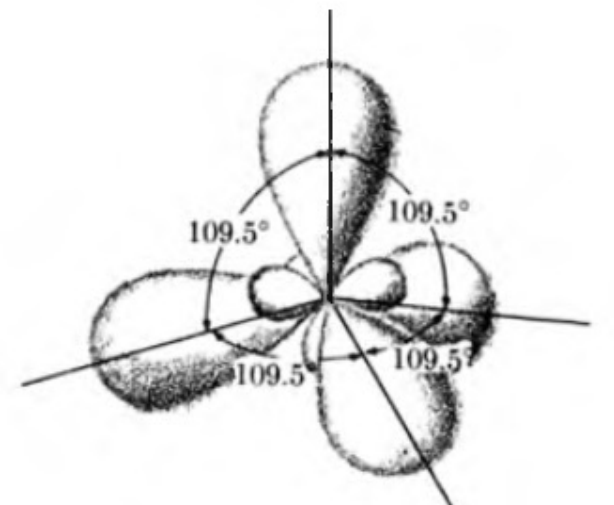
$$\psi_1 = \frac{1}{2}(s + p_x + p_y + p_z)$$

$$\psi_2 = \frac{1}{2}(s + p_x - p_y - p_z)$$

$$\psi_3 = \frac{1}{2}(s - p_x + p_y - p_z)$$

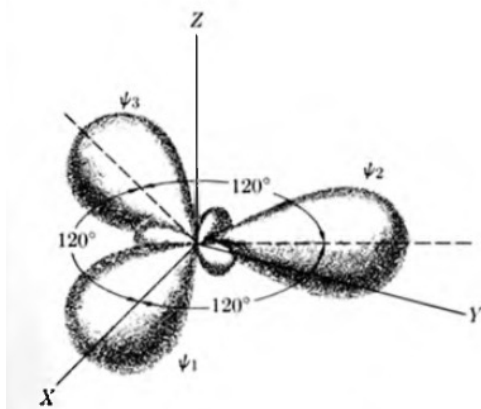$$\psi_4 = \frac{1}{2}(s - p_x - p_y + p_z)$$

The methane CH_4 and ethane C_2H_6 molecules

▶ The maximum strength of the bonds is obtained when the 1s-electrons of each hydrogen atom achieve maximum overlapping with each of the four sp^3 hybrid wave functions of carbon

▶ CH_4 is a tetrahedral molecule

▶ In the C_2H_6 molecule, the two carbon atoms are held together by the overlapping of two hybrid sp^3 wave functions. This is called a σ -bond, due to its similarity to the situation o f σ -orbitals in diatomic molecules.
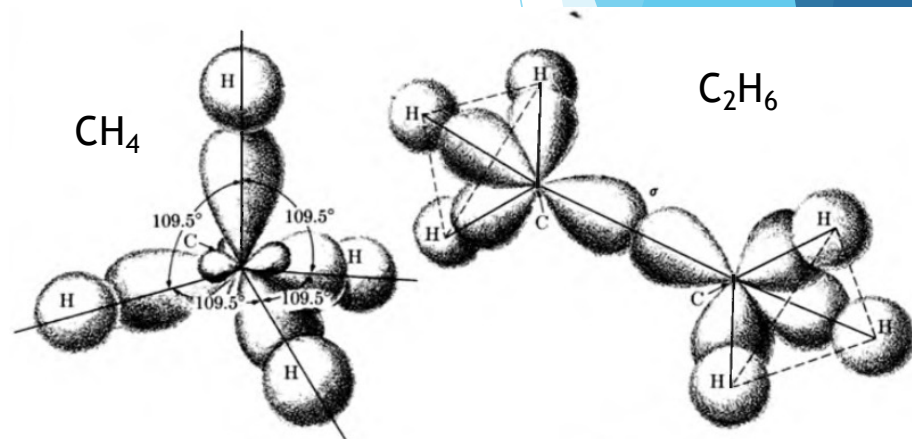
The Carbon atom, the sp² hybridization

σ-bond

▶ s, p_x, and p_y wave functions combine to produce three wave functions in the XY-plane, with their maxima pointing in directions making angles of 120°

▶ This is the type of hybridization required to explain molecules such as ethylene $H_2C = CH_2$

$$\psi_1 = \frac{1}{\sqrt{3}}(s + \sqrt{2}\, p_z),$$

$$\psi_2 = \frac{1}{\sqrt{3}}\left(s - \frac{1}{\sqrt{2}}\, p_z + \sqrt{\tfrac{3}{2}}\, p_y\right),$$

$$\psi_3 = \frac{1}{\sqrt{3}}\left(s - \frac{1}{\sqrt{2}}\, p_z - \sqrt{\tfrac{3}{2}}\, p_y\right).$$

π-bond
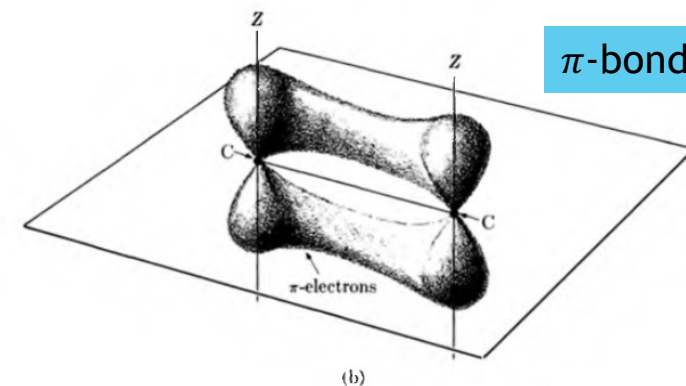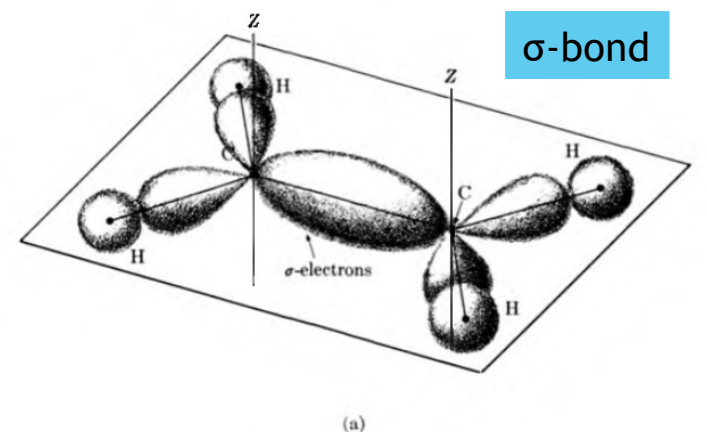
The Carbon atom, sp hybridization

▶ Corresponds to wave functions s ± p_z which have pronounced maxima in the ±z direction.

▶ Hybrid sp wave functions are required to explain molecules such as acetylene, HC≡CH

▶ The triple bond between the two carbon atoms results from the overlapping of one sp hybrid wave function from each carbon atom (σ -bond) and the overlapping of p_x and p_y wave functions, resulting in two π -bonds. The hydrogen atoms are attached to the remaining sp wave functions. As a result, acetylene is a linear molecule.
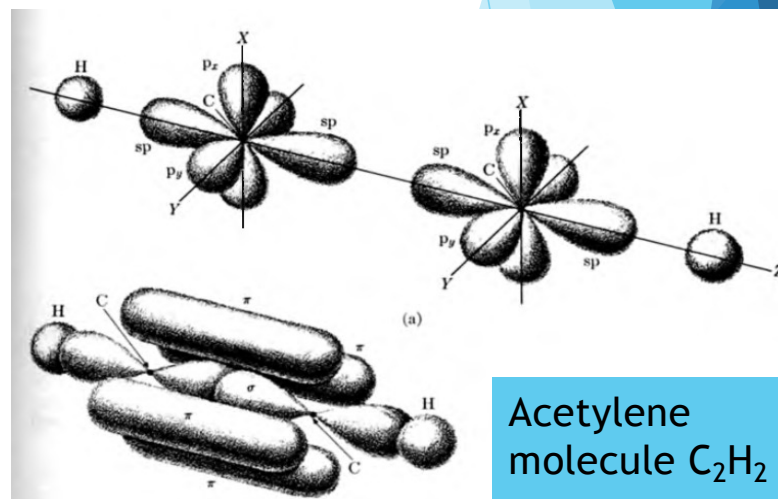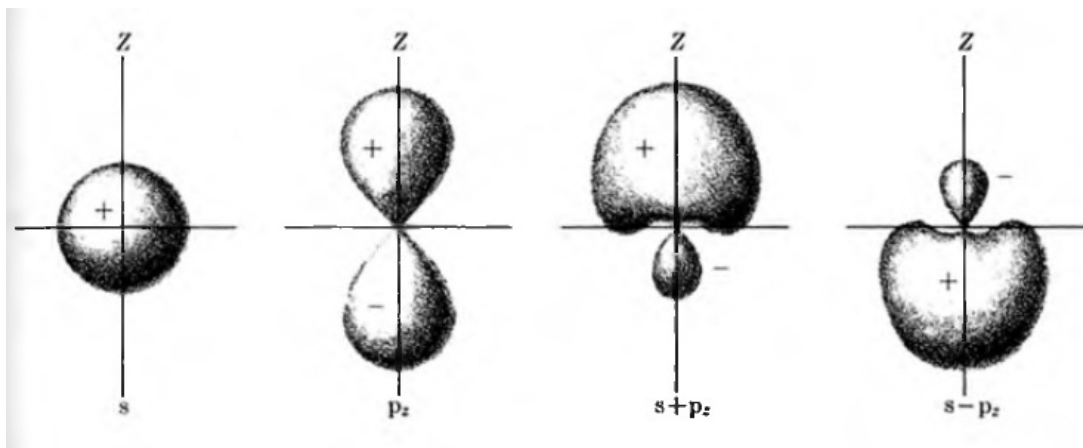

Acetylene molecule C_2H_2

Conjugated molecules

▶ An example is butadiene C_4H_6 (in Figure a **σ**-bonds and b **π**-bonds)

▶ The carbon atoms along the chain are bonded by σ – bonds using sp2 hybrid wave functions.

▶ The hydrogen atoms are attached to the carbon atoms using the remaining sp2 wave functions.

▶ In addition there are four p_z electrons forming **π**-bonds along the carbon atom chain. (the Z-axis is taken perpendicular to the plane of the molecule)
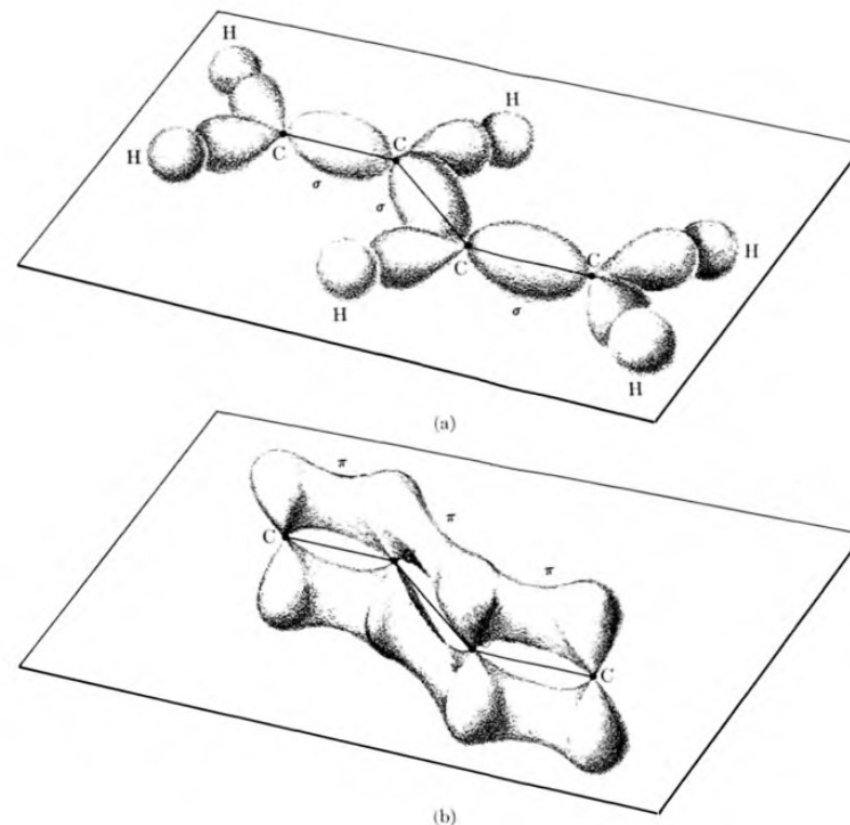
Π Wave functions

- In conjugated molecules, the π-bonding electrons instead of being localized in particular regions of the molecule are more or less free to move along the molecule

- The four possible molecular wave functions of the π-electrons are designated by ψ_1, ψ_2, ψ_3 and ψ_4 obtained by making proper linear combinations of the individual or atomic wave functions.

- Each corresponds to a different energy, which increases with the number of nodes of the wave function.
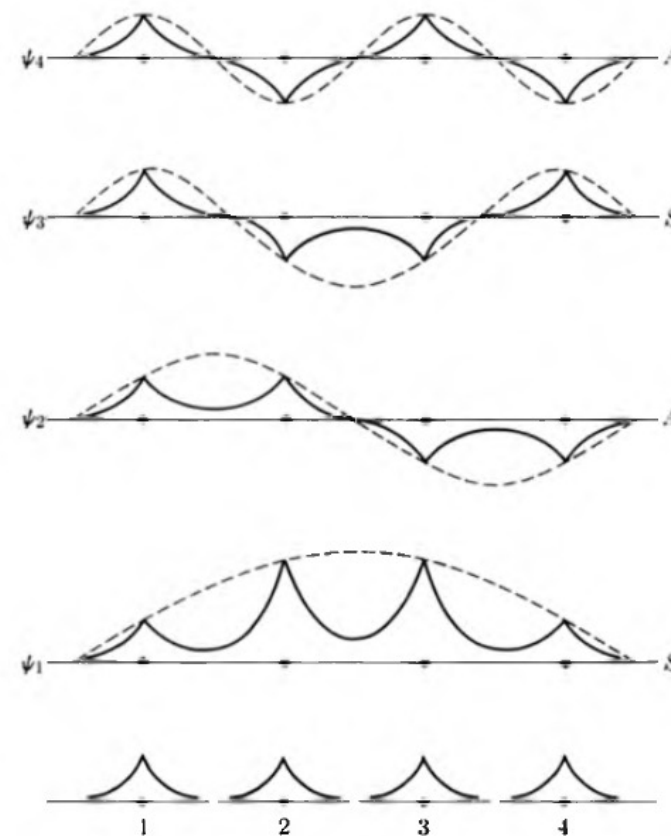
Wave functions or molecular orbitals of the four π-electrons

Electronic potential energy of π-electrons

▶ The energy of the system splits into four closely spaced levels

▶ Each energy level can accept two electrons with opposite spins. Thus, in the ground state of butadiene, the four π - electrons occupy the states corresponding to ψ_1 and ψ_2.

▶ The next two nearby states, corresponding to ψ_3 and ψ_4 are empty.

▶ Molecular orbital ψ_1 is of the bonding type for each pair of carbon atoms, while ψ_2 is bonding for the pairs 1-2 and 3-4 of carbon atoms and antibonding for the pair 2-3.

▶ For this reason the total probability distribution shows a dip at the center of the molecule. This means that the strength of the bond between the pair 2-3 of carbon atoms must be less than for the pairs 1-2 and 3-4.

▶ Experimentally the length of the bond 2-3 is $1.46*10^{-10}$ m, while bonds 1-2 and 3-4 have a length of $1.35*10^{-10}$ m.

Electronic potential energy of ir-electrons in butadiene as a function of internuclear separation.
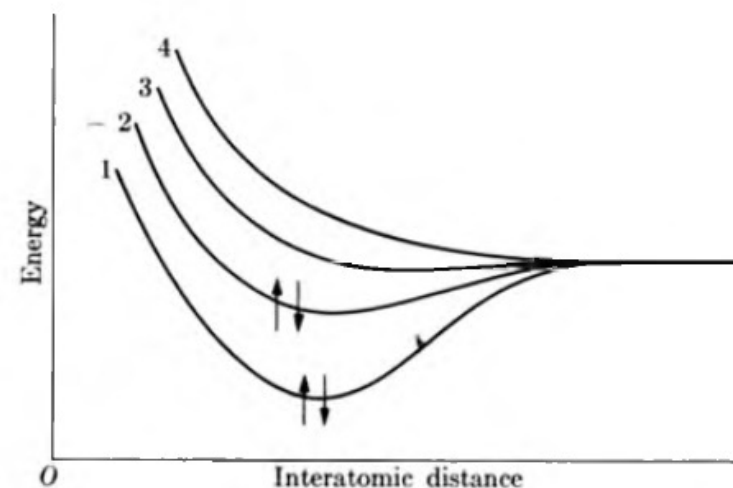
Total probability distribution of π - electrons in butadiene
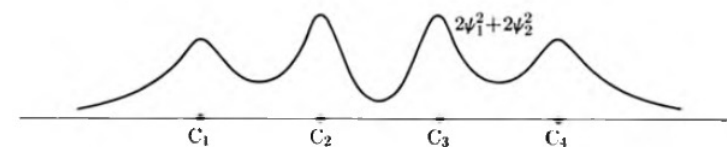
Conjugated 2n Carbon chain

▶ Conjugate compound consisting of a carbon chain of 2n atoms contains 2n π-electrons spread along the molecule

▶ There are then 2n closely spaced energy levels available, with capacity for 4n electrons, to be filled by the 2n π-electrons.

▶ Hence, when these molecules are in the ground state only the lower half of the energy levels are occupied. Electronic motion in these molecules can be excited by a relatively small amount of energy because of the nearby empty levels.

▶ For this reason, many of these conjugate molecules absorb photons in the visible region and therefore have characteristic colors.
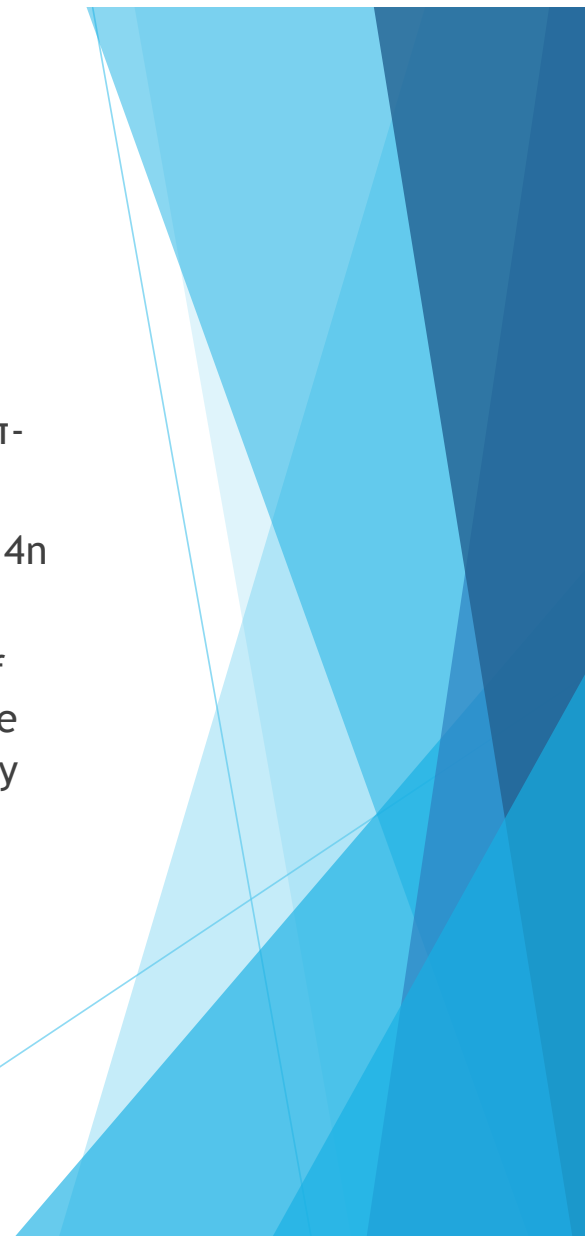
Benzene C_6H_6

▶ It's a cyclic conjugate molecule

▶ The carbon atoms are located at the vertexes of a regular hexagon and joined by σ -bonds using sp2 hybrid wave functions along each C— C line

▶ The hydrogen atoms are attached at the remaining sp2 orbital of each carbon atom.

▶ There are also six π-electrons, one from each carbon atom in p_z, orbitals (the Z-axis is taken perpendicular to the plane of the molecule). These π-electrons are free to move along the hexagon, constituting a sort of closed current
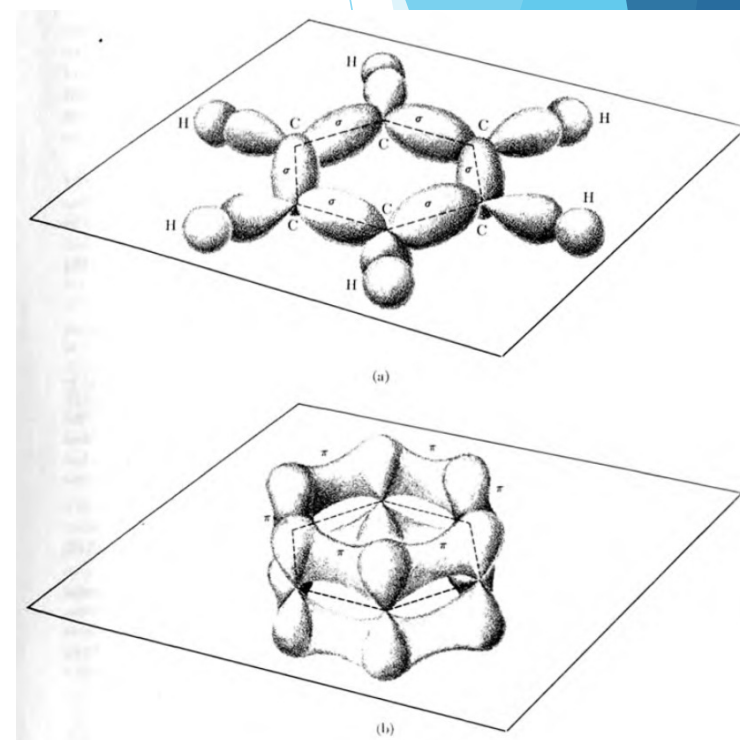
# Exercise 3: *Estimate the first excitation energy of a π-electron in a conjugate molecule.*

▶ One can estimate the excitation energy of a π-electron by considering that π-electrons move independently of each other and that their motion within the molecule resembles motion in a potential box whose dimension is of the order of the length of the carbon chain.

▶ The energy difference between the nth and $(n+1)^{th}$ levels is the first excitation energy:

$$\Delta E = \frac{\pi^2 \hbar^2 (n+1)^2}{2ma^2} - \frac{\pi^2 \hbar^2 n^2}{2ma^2} = \frac{\pi^2 \hbar^2}{2ma^2}(2n+1)$$

▶ where a is the length of the region in which the π-electrons move

▶ For example, in the case of butadiene, with a about $5.6*10^{-10}$ m and n = 2, we get A E = 5.86 eV, which corresponds to photons of wavelength $2.12*10^{-7}$ m.

▶ It has been observed that butadiene has strong absorption for radiation of wavelength $2.17*10^{-7}$ m, therefore our approximation is valid

Molecular rotation of diatomic molecules

▶ The simplest nuclear motion is that of rotation of the molecule around its center of mass as if the molecule were a rigid body

▶ The principal axes of inertia of a diatomic molecule are

   ▶ the line joining the two nuclei, N_1 and N_2, or the Z_0 axis,

   ▶ and any line perpendicular to it through the center of mass.

▶ Because their mass is so small, we can neglect the moment of inertia due to the electrons, and therefore the moment of inertia of the molecule relative to the Z_0 axis is zero.

▶ Thus the angular momentum of the molecule, for rotation around the Z_0 axis, is also zero and the total angular momentum L of the molecule is perpendicular to the molecular axis.
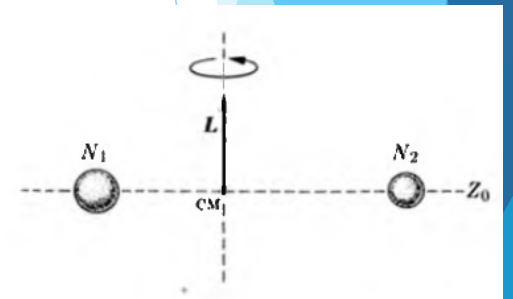
Molecular rotation of diatomic molecules

▶ Given that r_0 is the equilibrium separation of the nuclei and μ the reduced mass of the molecule, the moment of inertia about an axis perpendicular to Z_0 and passing through the center of mass of the molecule is $I = \mu\, r_0^2$.

▶ The kinetic energy of rotation of the molecule is $E = \dfrac{L^2}{2I}$ where L is the angular momentum.

▶ L is quantized: $L^2 = \hbar^2 l(l+1)$

▶ Therefore the kinetic energy of rotation of the molecule becomes:
$$E = \frac{\hbar^2}{2I} l(l+1) = B\hbar c\, l(l+1)$$

▶ Successive energy levels are $\Delta E = 2B\hbar c(l+1)$

Rotational energy states of a diatomic molecule

▶ By giving successive values to l, we can obtain the rotational energy levels of the molecule

▶ Because of the small value of $\frac{\hbar^2}{2I}$ (~ 10^{-4} eV) when compared with the translational kinetic energy (which is of the order of kT = $2.5*10^{-2}$ eV at room temperature), many molecules are found in excited rotational states at room temperature.

▶ The parity of each level is $(-1)^l$, and thus successive energy levels have opposite parity, since they are similar to the s-, p-, d-, . . . atomic orbitals.
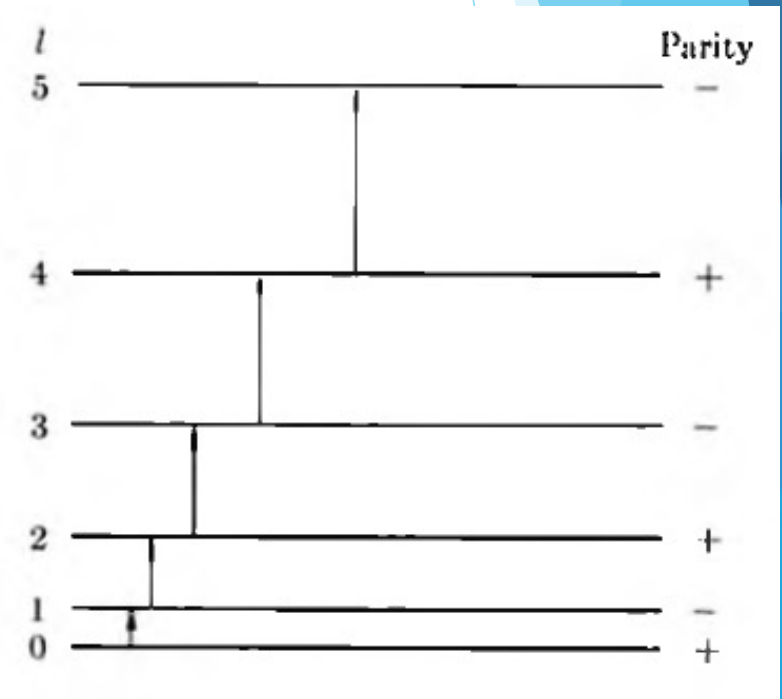
Transition selection rule

▶ For electric dipole radiation, the allowed transitions are those for which $\Delta l = \pm 1$

▶ Thus the only transitions possible are those between successive levels.

▶ The frequency of the radiation emitted or absorbed in a rotational transition is

$$\upsilon = \frac{\Delta E}{h} = 2Bc(l+1) \text{ or } \tilde{\upsilon} = 2B(l+1)$$

▶ where $\tilde{\upsilon}$ is the wave number expressed in cm^{-1}.

▶ Thus the rotational spectrum of diatomic molecules consists o f a series of lines equally spaced an amount $\Delta\tilde{\upsilon} = 2B$ cm^{-1}

▶ By measuring $\Delta\tilde{\upsilon}$, we can compute B and thus the moment of inertia, and from it estimate the nuclear separation r_0

Rotational spectrum

▶ Pure rotational spectra fall in the microwave or far-infrared regions of the spectrum.

▶ In addition, for a molecule to exhibit a pure rotational spectrum, it must possess a permanent electric dipole moment.

▶ In the process of absorption of radiation, the permanent electric dipole moment interacts with the electric field of the incoming wave. In the process of emission of radiation, the rotation of the dipole is responsible for the radiation.

▶ Homonuclear diatomic molecules (which do not have a permanent electric dipole) do not show pure rotation spectra
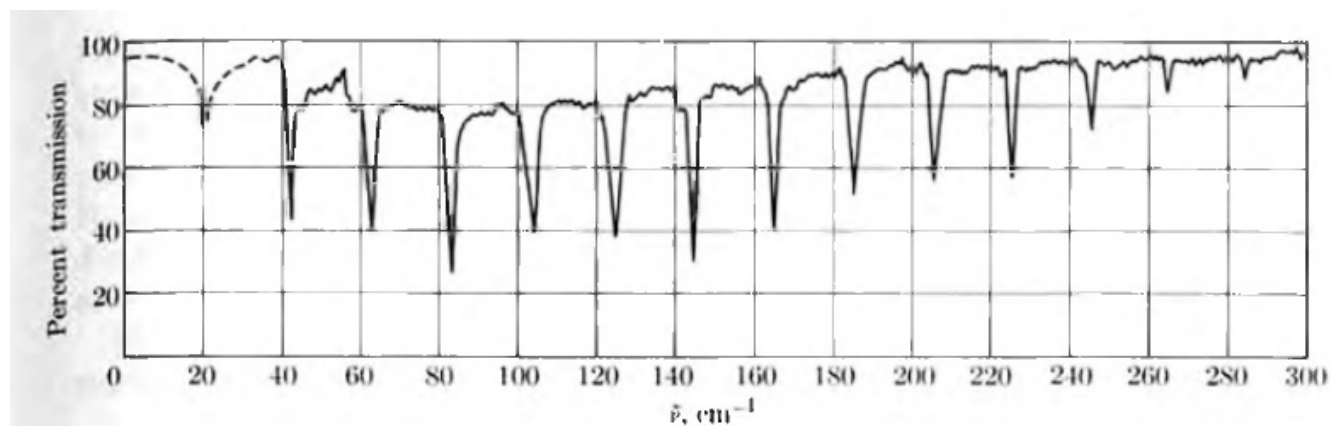
Rotational absorption spectrum of HCl in the gaseous phase

Molecular vibration

▶ Let us consider a diatomic molecule which has a potential energy as shown in the figure, which we approximate with a simple harmonic oscillator, represented by the parabola $\frac{1}{2}k(r - r_0)^2$

▶ The angular frequency of the oscillations is $\omega_0 = \sqrt{\dfrac{k}{\mu}}$

where μ is the reduced mass of the molecule

▶ The energy of the oscillatory motion is quantized, therefore:

$$E = \left(v + \frac{1}{2}\right)h\omega_0$$

▶ where v is a positive integer

Fig. 5–32. Electronic potential energy in a diatomic molecule.

$v = 0$ (vibrational ground state)
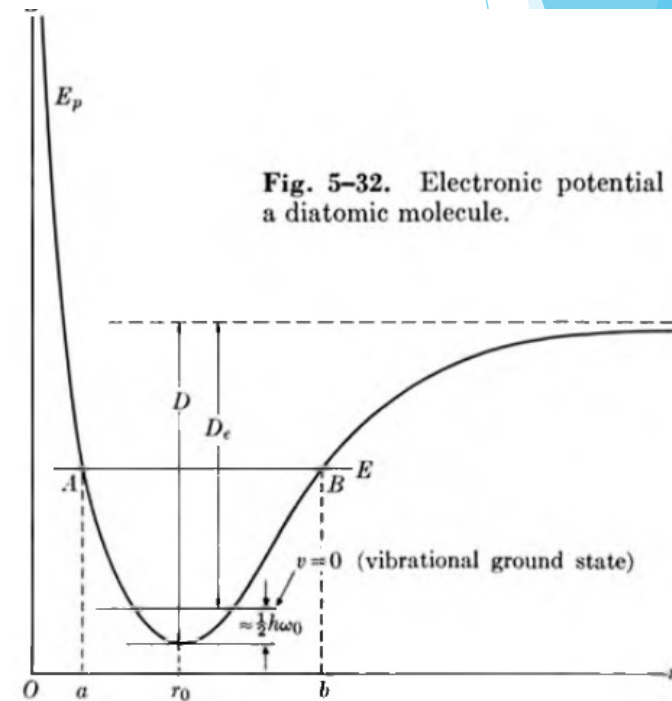
$\approx \frac{1}{2}h\omega_0$

Molecular vibration

► Therefore the vibrational energy levels of the molecule are equally spaced an amount $h\omega_0$ and the molecule has a zero point vibrational energy equal to $\frac{1}{2}h\omega_0$.

► Because of the zero-point energy, the dissociation energy of a diatomic molecule is $D_e = D - \frac{1}{2}h\omega_0$,

► The selection rule for electric dipole transitions among vibrational levels is $\Delta v = \pm 1$

► The vibrational frequencies of most diatomic molecules fall in the infrared region of the spectrum.

► For a vibrational transition to occur, either in emission or absorption, the diatomic molecule must have a permanent electric dipole moment.

► Homonuclear molecules do not show pure vibrational transitions

Vibrational and rotational energy levels

▶ The molecular energy due to both rotation and vibration can be expressed by

$$E = E_r + E_v = \left(v + \frac{1}{2}\right)h\omega_0 + \frac{\hbar^2}{2I}l(l+1)$$

▶ The quantity $\frac{\hbar^2}{2I}$ is much smaller (~10^{-4} eV) than $h\omega_0$ (~10^{-1} eV), hence, to each vibrational level, there correspond several rotational levels

Vibrational levels

$$E_v = (v + \tfrac{1}{2})h\omega_0$$

Rotational levels

$$E_r = \frac{\hbar^2}{2I}l(l+1)$$
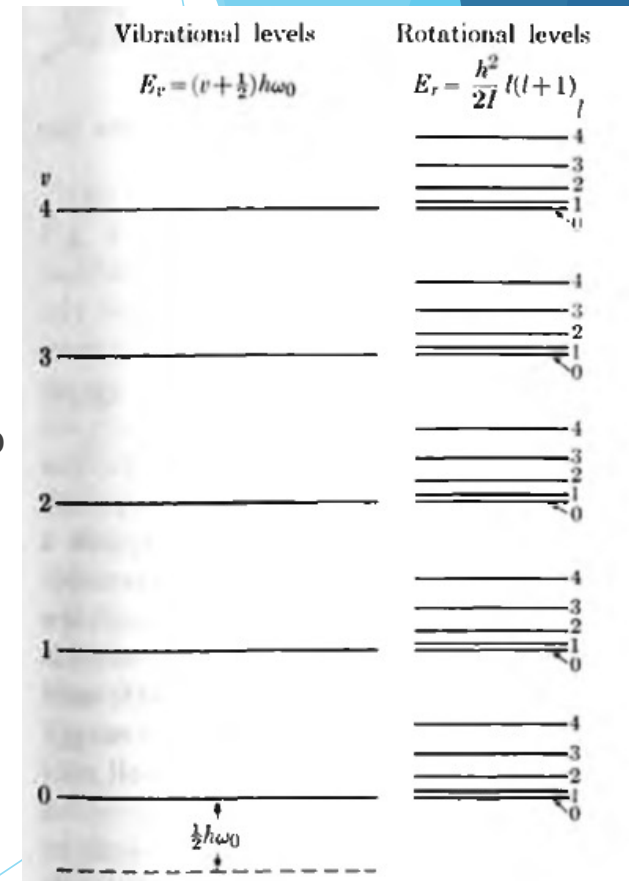
Roto-vibrational spectrum

▶ The transition between two rotational levels belonging to two adjacent vibrational levels has frequency of
$$v_{v,r} = v_0 \pm 2Bc(l+1)$$

▶ The frequencies are equally spaced an amount 2Bc on both sides of the central frequency v_0.

▶ The line of frequency v_0 is missing from the spectrum because it requires a transition with $\Delta l = 0$, which is forbidden

▶ The lines with $\Delta l = +1$ are called the R-branch of the spectrum; the name P-branch is used to designate those lines with $\Delta l = -1$.
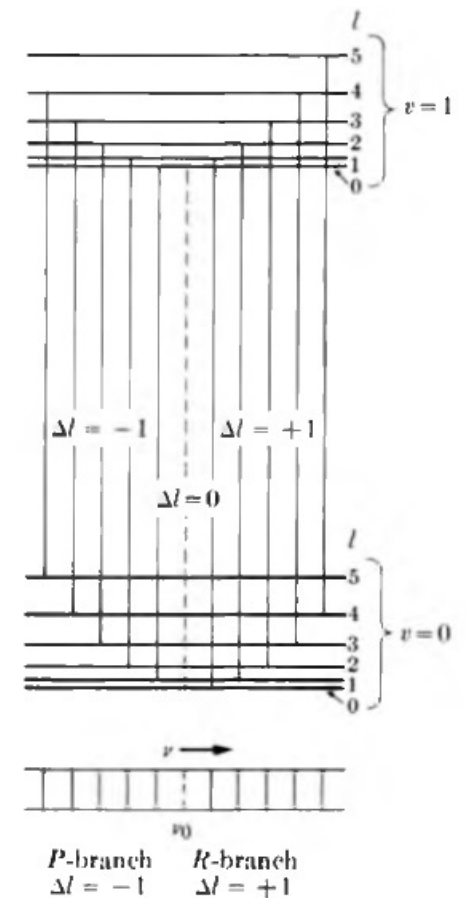
Vibration-rotation absorption spectrum of HCl
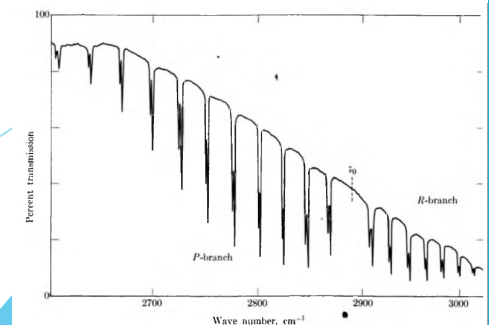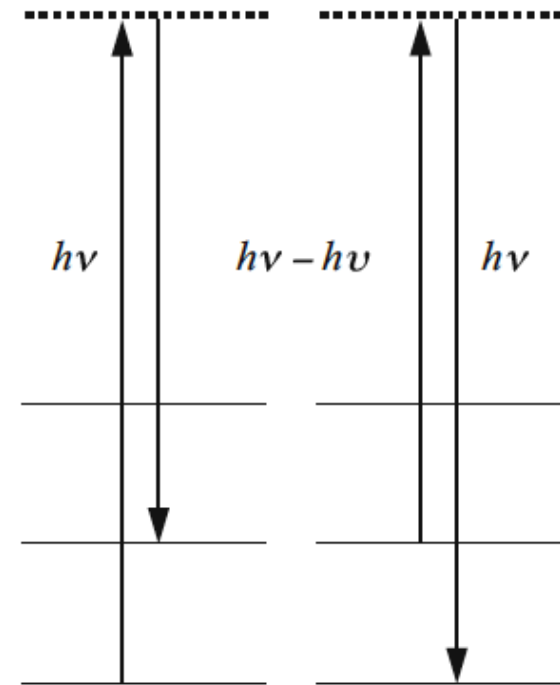
Normal modes of triatomic molecules

► A vibration mode indicate a vibration in which all nuclei vibrate with constant phase relations

► To each normal mode there corresponds, in general, a different frequency of vibration.

► The bending and symmetric stretching modes maintain reflection symmetry, whereas the asymmetric stretching mode destroys this symmetry.

► For a frequency to be active in the vibrational or infrared spectrum, the corresponding normal vibration must induce an oscillating electric dipole in the molecule.

Symmetrical stretching   Asymmetrical stretching   Bending
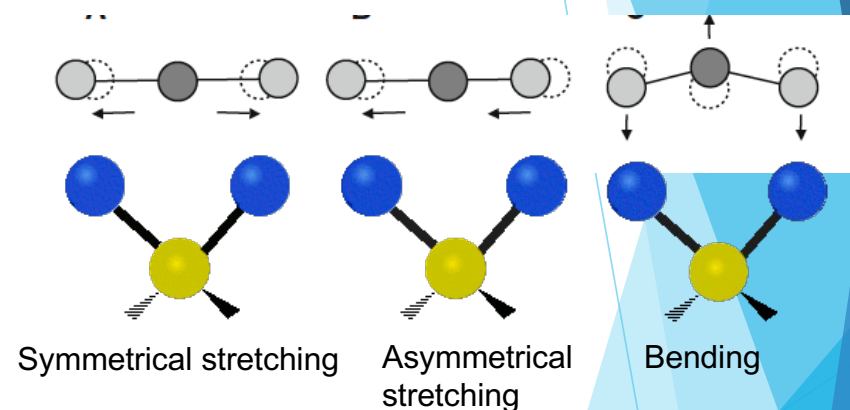
Raman scattering

▶ Raman scattering: vibrational or rotational transitions that occur when a molecule scatters light of higher frequencies.

▶ Raman scattering is an inelastic process in which the incident and departing photons differ in energy and the molecule is either promoted to a higher vibrational or rotational level (Stokes) of the ground electronic state, or demoted to a lower level (anti-Stokes). The strength of anti-Stokes scattering increases with temperature, and the ratio of anti-Stokes to Stokes scattering provides a way to measure the effective temperature of a molecule.
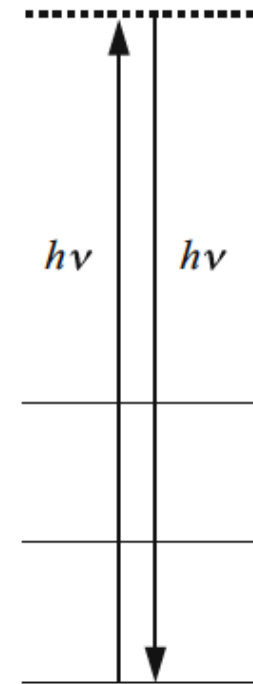
Rayleigh (elastic) scattering

▶ Rayleigh scattering is an elastic process, in which there is no net transfer of energy between the molecule and the radiation field: the incident and emitted photons have the same energy.

$h\nu$ $h\nu$

Electronic transitions in molecules

▶ A given molecule may have several electronic configurations or stationary states

▶ Let us consider, for simplicity, a diatomic molecule; to each electronic state there corresponds a potential energy curve as in the Fig.

▶ The two nuclei in the excited electronic states have, in general, equilibrium distances which are different from the one for the ground state.

▶ The separation of these energy curves is of the order of 1 to 10 eV. Thus when a molecule experiences an electronic transition, jumping from one electronic configuration to another, the radiation involved falls in the visible or the ultraviolet regions of the spectrum.
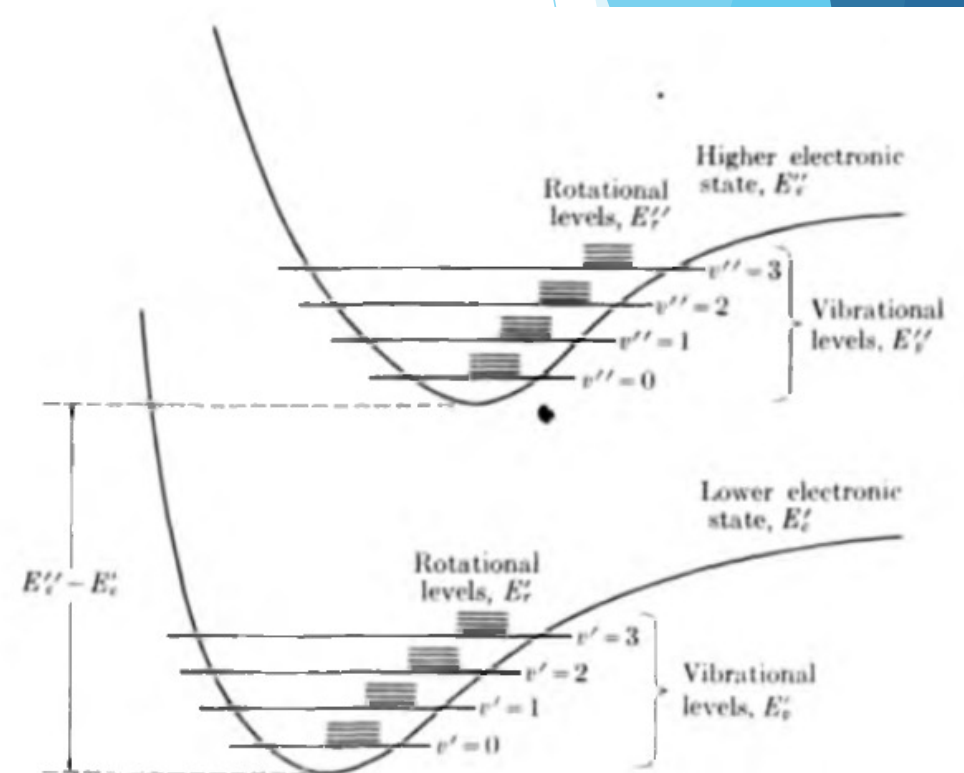
Electronic transitions in molecules

▶ A given electronic state there correspond many vibrational states and to each vibrational state there correspond several rotational states.

▶ As a first approximation, we may write the energy of the molecule in the form

$$E = E_e + E_r + E_v = E_e + \left(v + \frac{1}{2}\right)h\omega_0 + \frac{\hbar^2}{2I}l(l+1)$$

▶ In an electronic transition all three energies may change.

▶ For a given electronic transition the spectra consist of a scries of bands; each band corresponds to a vibrational and several rotational transitions.

▶ Only vertical transitions are allowed

Franck-Condon principle

▶ Suppose that a molecule initially in the vibrational state v' = 5 of electronic state C' suffers an absorption transition up to electronic state C "

▶ The most probable final vibrational states are obtained by drawing vertical lines a and b at the ends of the classical oscillation and extending them up to intersect curve C ".

▶ Line a falls near v "= I, resulting in a transition v' = 5 → v " = 1. Line b falls above the dissociation energy and would result in the dissociation o f the molecule.

▶ When the transition involves the lowest vibrational state (v' or v" = 0), the vertical line should be drawn through the center of the oscillations, as in c and d.

▶ The reason for this is that the maximum of the wave function for the ground state of an oscillator occurs at the center
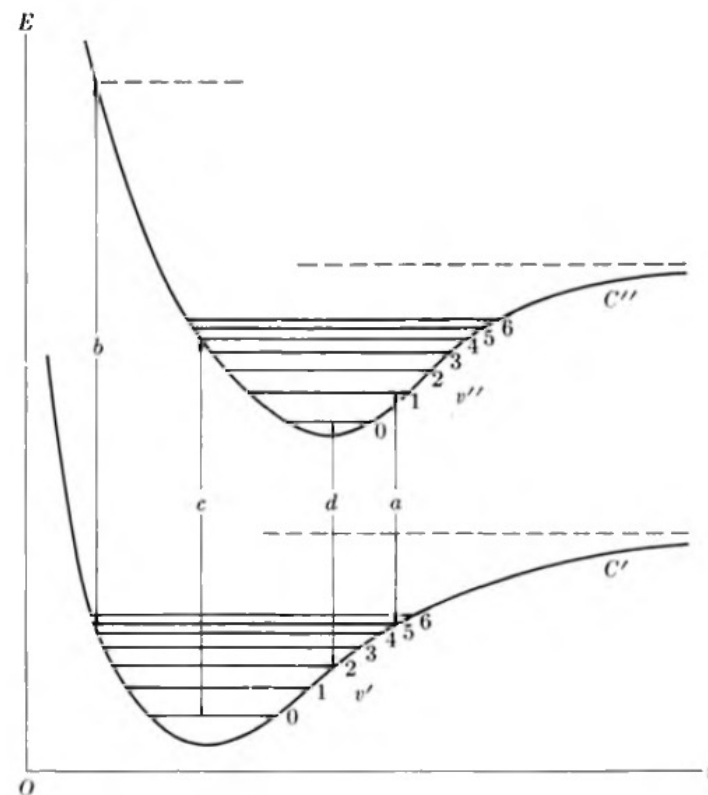
Questions

- What says the theory of molecular orbitals?

- How can we calculate the MO orbitals of simple diatomic molecules?

- Which info can be derived from the MO diagrams?

- Why in heteronuclear bonds the MO diagram is asymmetric?

- What is the principle of max overlap?

- How are the π-electrons arranged in a conjugated molecule?

- What is the rotational (vibrational) energy of a diatomic molecule?

- When are rotational (vibrational) transitions allowed?

- How does the roto-vibrational spectrum of a diatomic molecule look like?

- Describe the electronic transitions and the Frank-Condon principle

Reference

- Chapter 5 from Alonso-Finn "Fundamental University Physics. III Quantum and Statistical Physics"

Problem 1

Dissociation and ionization energies are frequently expressed in kcal mole^{-1}.

▶ Show that one kcal mole^{-1} is equal to $4.338*10^{-2}$ eV.

▶ Express the dissociation energy of H_2 in kcal mole^{-1}.

Problem 2

- Explain why the bond length of H_2^+ is 1.06 Å, while H_2 has a shorter bond length equal to 0.74 Å. Also explain why the dissociation energy of H_2^+ (103.2 kcal mole^{-1}) is less than twice the dissociation energy of H_2^+ (61.06 kcal mole^{-1}).

Problem 3

► Explain why the ion H_2^- is less stable than the ion He_2^+ if both have the same electronic configuration. Which ion should have the larger internclear separation?

Problem 4

- Given the molecule NO, discuss its electronic configuration and bond structure. Compare with the N_2 molecule and state. Decide which molecule is more stable.

Problem 5

- Show that the four sp^3 hybrid wave functions are orthogonal. Repeat for the sp^2 wave functions.
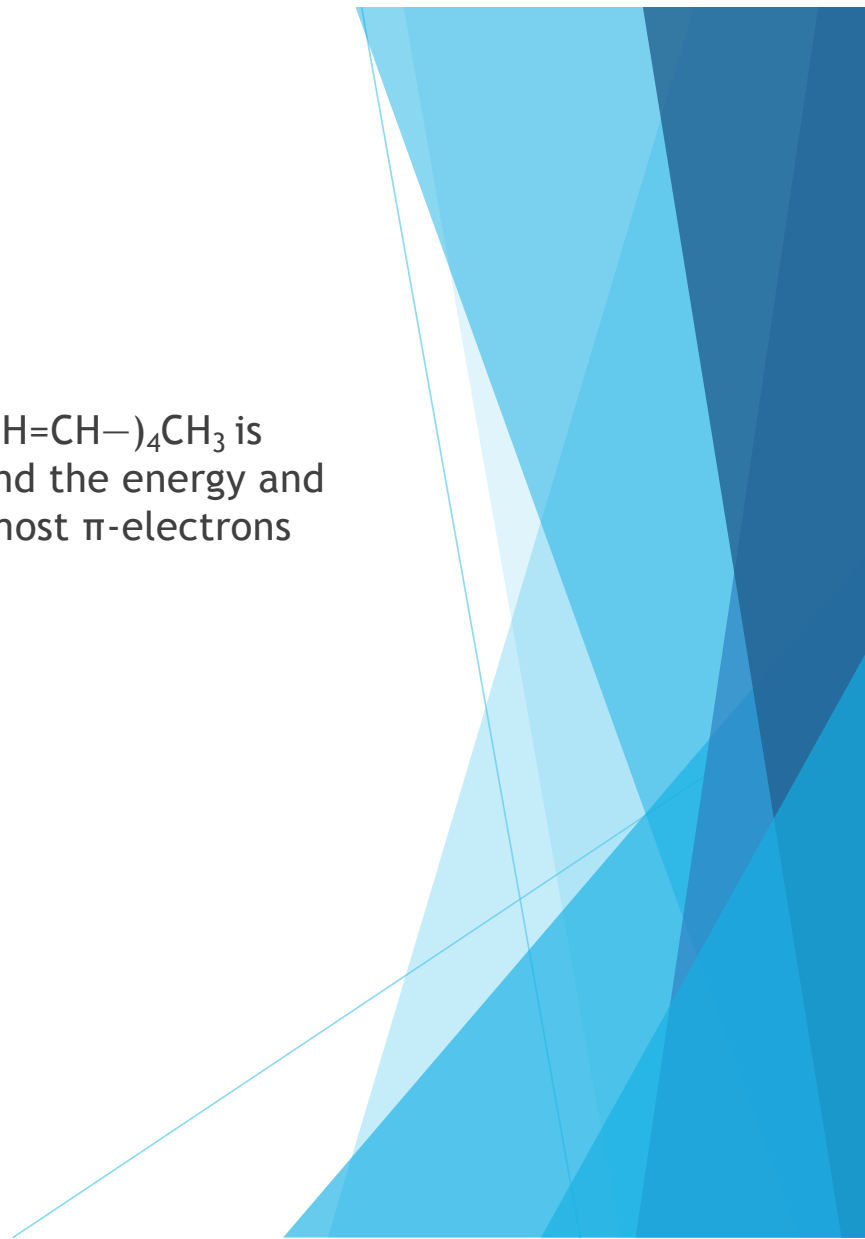
Problem 6

- The electric dipole moment of H_2O is 6.2×10^{-30} m C. Find the dipole moment corresponding to each O— H bond. Given that the bond length of O— H is 0.958 Å, what fraction of the hydrogen electron has been transferred to the oxygen atom?
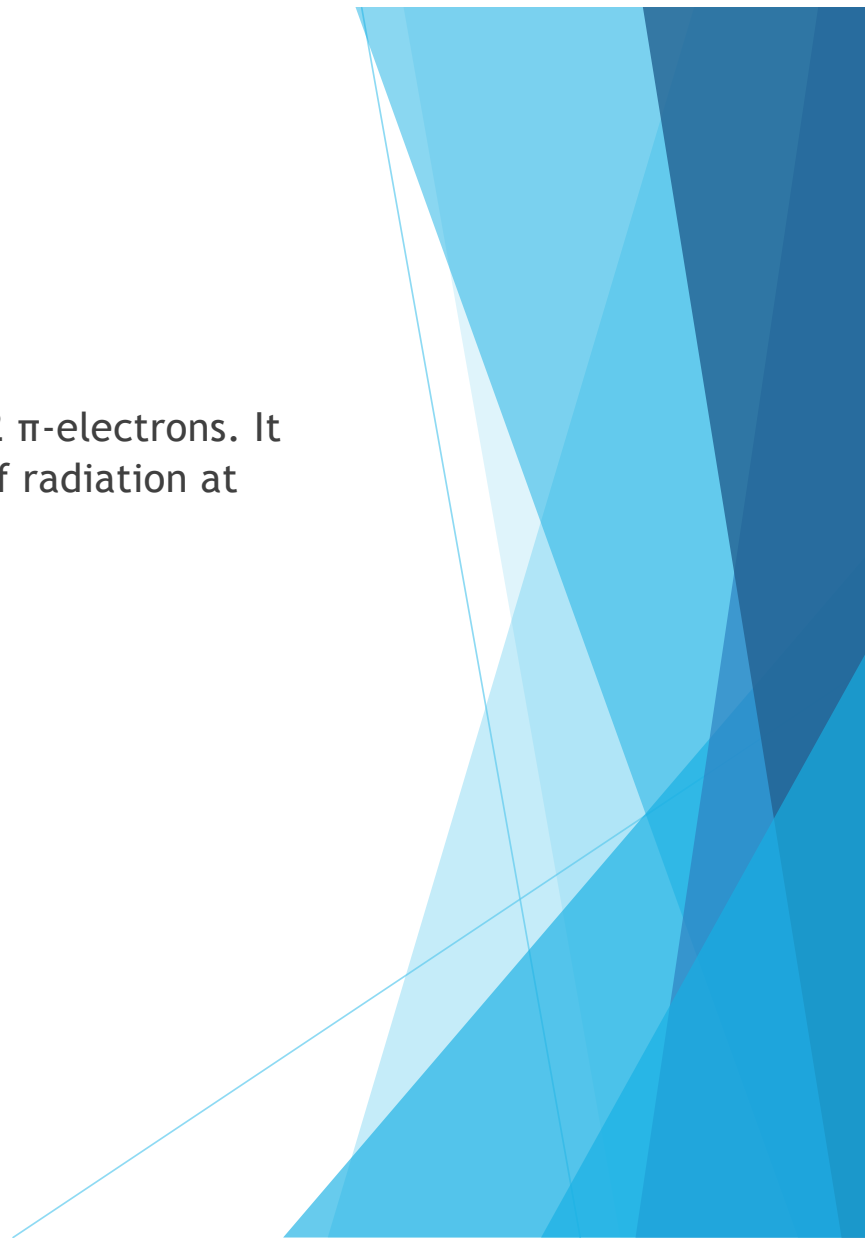
Problem 7

▶ The effective total length of the conjugate molecule $CH_3-(CH=CH-)_4CH_3$ is 9.8 Å. Plot the energy levels occupied by the π-electrons. Find the energy and wavelength of the photons absorbed when one of the uppermost π-electrons is excited.

Problem 8

▶ The **β**-carotene molecule is a conjugated molecule having 22 π-electrons. It has been found that this molecule shows strong absorption of radiation at 4510 Å. Estimate the total length of the molecule.

Problem 9

▶ The adjacent lines in the pure rotational spectrum of $^{35}\text{Cl}^{19}\text{F}$ are separated by a frequency of $1.12*10^{10}$ Hz. What is the interatomic distance of this molecule?

Problem 10

The rotational energy levels of a molecule having two equal principal moments of inertia are given by

$$E_{rot} = \frac{1}{2I_1} L^2 + \frac{1}{2}\left(\frac{1}{I_2} - \frac{1}{I_1}\right) L_z^2$$

where I_1 corresponds to axes X and Y and I_2 corresponds to the Z-axis, and

$L^2 = l(l+1)\hbar^2$ and $L_z = m\hbar$

Using this equation, estimate the relative position of the rotational energy levels of a molecule having (a) $I_2 = 0.8\ I_1$, (b) $I_2 = 1.2\ I_1$. Plot the levels as multiples of

$\hbar^2 / 2I_1$.

Problem 11

- Two bodies of masses m_1 and m_2, respectively, are joined by a spring with an elastic constant k. Show that if the spring is stretched and released the masses will oscillate with a frequency $v = \frac{1}{2}\pi\sqrt{k/\mu}$, where μ is the reduced mass of the system.

Problem 12

- Calculate the energy of the three lowest vibrational levels in HF, given that the force constant is $9.7*10^2$ N m^{-1}. Find the wave number of the radiation absorbed in the transition v = 0 → v = I.

Problem 13

► The infrared spectrum of CO, at low resolution, shows an absorption band centered at 2170 cm^{-1}. Find the force constant in CO. Plot, to scale, the potential energy curve.

Problem 14

▶ The molecule CO has an electronic transition that produces several bands in the visible region (around 6000 Å). Estimate the separation among adjacent rotational lines in each band. Do you expect the band to appear continuous in a low-resolution spectroscope?