School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

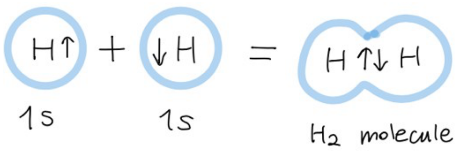
Organic Electronic Materials 2025 Exercise 2 Solutions

Solutions

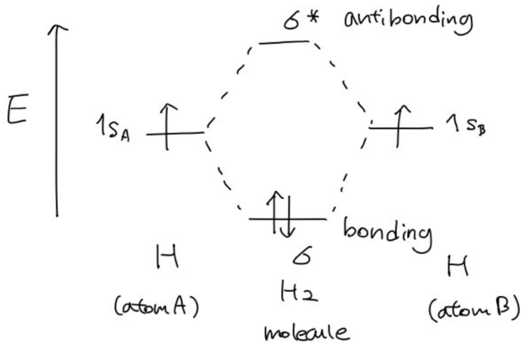
1. **Homework** – In the paper “Week 2 Slater 1965 Molecular Orbitals”, Slater compares both the valence bond and molecular orbital theory. What is the difference between both models in terms of interactions involved in them? Try and illustrate your answer with a diatomic molecule with 2 electrons?

   Valence bond theory assumes that the electrons in a molecule occupy atomic orbitals for the individual atom. In valence bond theory, overlapping atomic orbitals form a chemical bond (covalent bond) through electron pairing.

   Molecular orbital theory assumes electrons are delocalized throughout molecules, so the orbitals belong to the whole molecule. In molecular orbital theory, each atom tends to combine and form molecular orbitals.

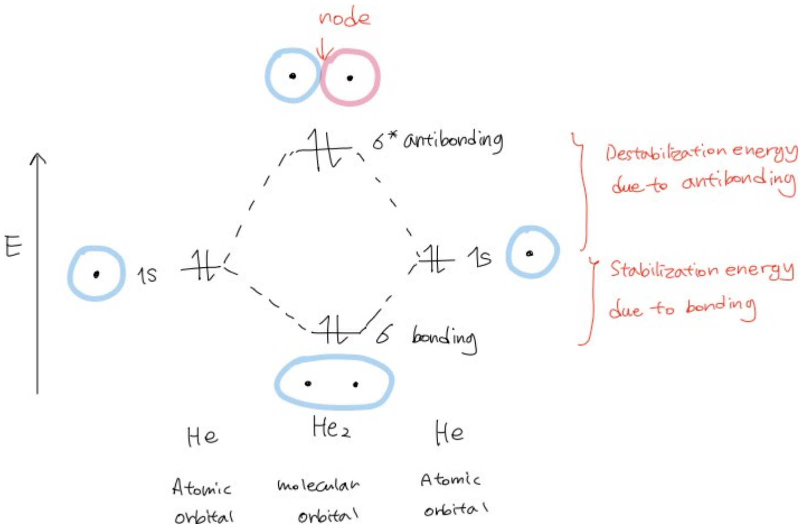


Valence bond theory



Molecular orbital theory

2. Draw a schematic MO energy level diagram as well as pictorial representations of the resulting MO for the interaction of two helium atoms. Name the AO and MO and add the electrons. Explain the terms “bonding” and “antibonding” MO. Explain why He_2 is not stable and give a qualitative expression for the destabilization energy of He_2 compared to two He atoms.



Because orbitals are wave functions, waves can combine either constructively (in-phase) or destructively (out-of-phase).

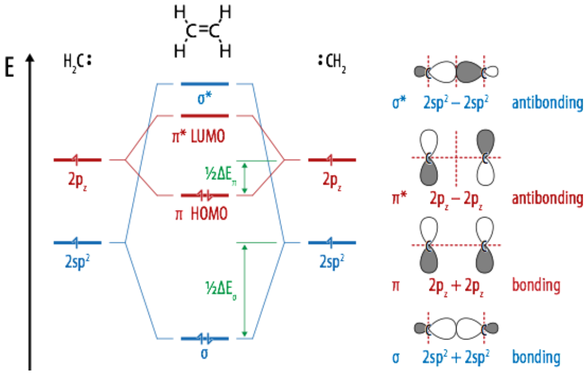
"Bonding MO" indicates a MO showing a lower energy than the energy of the atomic orbitals with constructive interference between wavefunctions. "Antibonding MO" indicates MO having higher energy than the energy of atomic orbitals with a destructive interference between wavefunctions.

He2 molecule would have a both a bonding and antibonding MO full. However, since destabilizing energy of an antibonding MO is higher than the stabilizing energy of the associated bonding MO:

$4 \times E(1s) < 2 \times E(\sigma^*) + 2 \times E(\sigma)$ *so no bond forms between two He atoms and* He_2 *does not exist.*

3. Draw the MO energy level diagram of the C=C double bond in ethene. Start by briefly explaining which atomic orbitals or hybridized orbitals are involved in the double bond and why the chosen hybridization is required. Briefly explain the difference between σ-bonds and π-bonds, and draw graphical representation of the molecular orbitals.

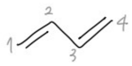
   In ethene, both carbons do 3 bonds. The sp2 hybridized orbitals are therefore the best choice to describe the C=C double bond, as revealed by the following scheme:



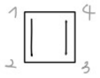
σ-bonds are directional bonds formed by head-on overlapping of orbitals and concentrated mostly along the bond axis between the atoms involved. π-bonds are formed by side-to-side overlapping of orbitals around the bonding axis.

4. Give the Hückel matrices for a linear and a cyclic π-system with four carbon atoms. Why are they different? Draw the MO energy level diagram of both systems and explain the difference in stability. What is aromaticity?

Linear 1.3 butadien



1.3 cyclobutabiene



$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} \qquad \begin{vmatrix} \alpha-E & \beta & 0 & \beta \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ \beta & 0 & \beta & \alpha-E \end{vmatrix}$$

reason why two matrices are different:

Interaction between "first" (C_1) and "Last" (C_4) Carbons of the cycle result in additional off-diagonal elements

stable

very unstable

partially filled MOs, open shell

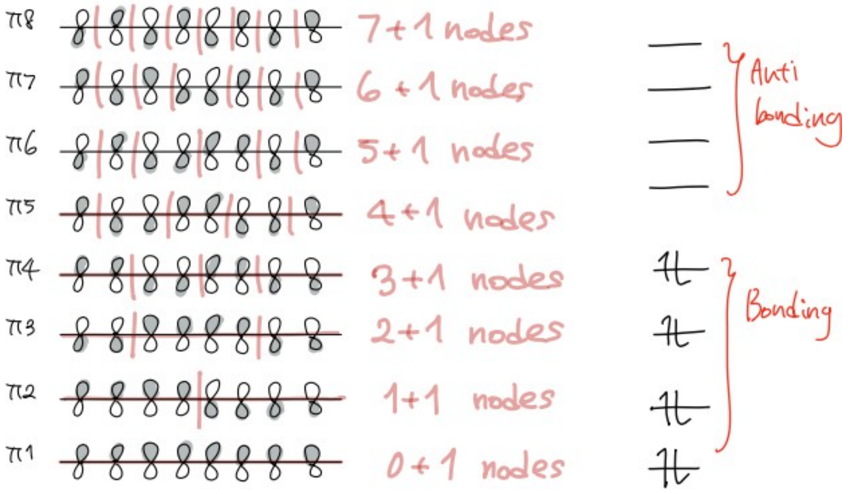
not aromatic

(no 4π+2 electrons)

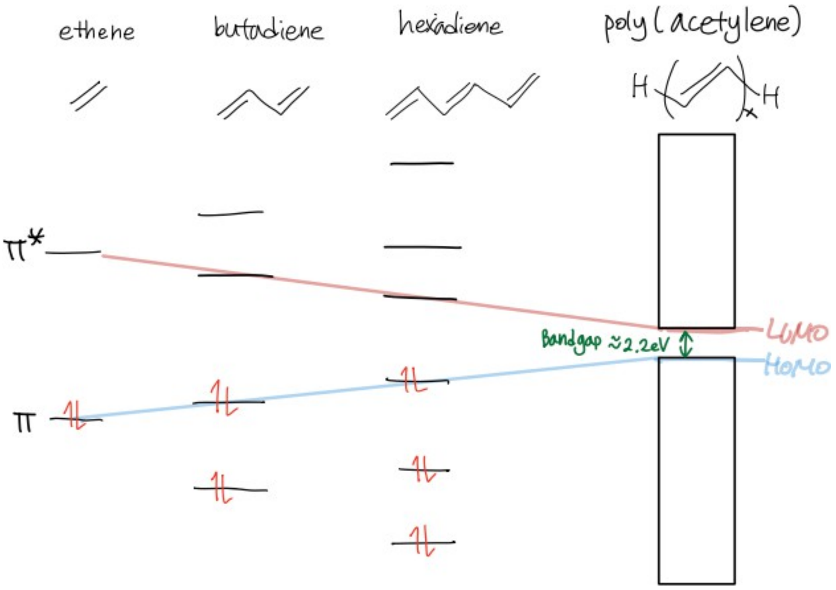
5. Give the formula for the energy values of linear π-conjugated systems according to the Hückel theory. Draw the MO energy diagram of the π-system of 1,3,5, 7-octaatetraene as an example. Give

the energy values of the different MO levels. Include simplified graphical representations of all MO (hint: consider the node planes).

$$E_n = \alpha + 2\beta \cdot \cos\left(\frac{n \cdot \pi}{N+1}\right)$$



6. Draw a simple MO energy level diagram (just the MO, not the constituting AO) comprising the π–systems of ethene, butadiene, hexatriene, and the “realistic” limiting case of poly(acetylene). Why does poly(acetylene) not strictly follow the Hückel theory?



Poly(acetylene) not strictly follow the Hückel theory due to Peierl's distortion, which associates the geometry distortions with the formation of a band gap because a one-dimensional equally spaced chain with one pi electron per carbon atom is unstable.

Further Reading:

Clayden, Greeves & Warren, *Organic Chemistry*, **2012**; *"Chapter 7 – Delocalization and Conjugation"*.

Nordholm et al., *"The Mechanism of Covalent Bonding"*, *J. Chem. Ed.* **2007**, *84*, 1201.

Fox et al., *"Electronic Structure in π-Systems"*, *J. Chem. Ed.* **1985**, *62*, 367 (just the first two pages).