Chemistry related exam questions and answers.

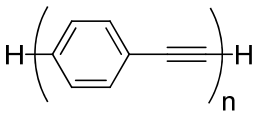
Questions

1. Draw a three dimensional structure of $Si(CH_3)_2Cl_2$ showing all valence electrons.

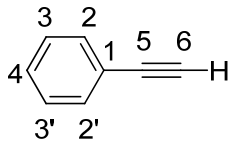
2. Draw a molecular orbital diagram for two interacting atomic orbitals (AOs) that belong to two different atoms. Outline how the covalent bond strength, i.e. the interaction energy, depends on the interaction between two atomic orbitals. What are the two most important parameters?

3. Describe briefly why strong hydrogen bonds A–H·····B are favored by A and B being highly electronegative atoms.

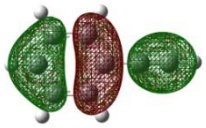
4. Conjugated organic molecules such as poly(1,4-phenyleneethynylene) are investigated as potential candidates to be used as molecular wires in molecular electronics and in nanotechnology. The repeating unit (building block) in the polymer is shown below. So are the highest occupied and lowest unoccupied molecular orbitals for the monomer ethynylbenzene.



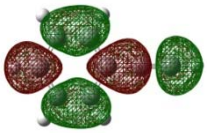
Poly(1,4-phenylene-ethynylene)



ethynylbenzene

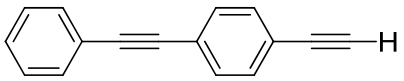


HOMO



LUMO

   a. To which class of molecular orbitals are HOMO and LUMO designated, σ or π, and what is the definition of such an orbital?
   b. Give a mathematical expression for the HOMO wave function in terms of suitable atomic orbitals φ_i, where *i* is the atom number shown in the structure of ethynylbenzene above. Numerical values for the constants used in your expression are not needed but the correct signs must be shown. What atomic orbital does φ_i correspond to?
   c. Will the HOMO-LUMO gap increase or decrease with increasing number of repeating units in the polymer? Rationalize your answer briefly.
   d. Draw the orbital shapes for the HOMO and the LUMO of the shortest possible polymer of ethynylbenzene, the dimer shown below.



   e. Compounds similar to the dimer shown above are also used as liquid crystals. What are the two most important intermolecular forces between molecules in assemblies of such compounds. Describe briefly the origin of each one of these two forces.

5. Lewis structures (the Lewis structure model) have a particular shortcoming that is resolved by the use of multiple Lewis structures, i.e. resonance structure. Give the reason for the shortcoming of the Lewis structure model and explain the concept resonance.

6. Explain the concept polarizability.

7. The following figure and figure caption are excerpts from the article **Self-assembly of long chain alkanes and their derivatives on graphite** published in Journal of Chemical Physics in 2008.

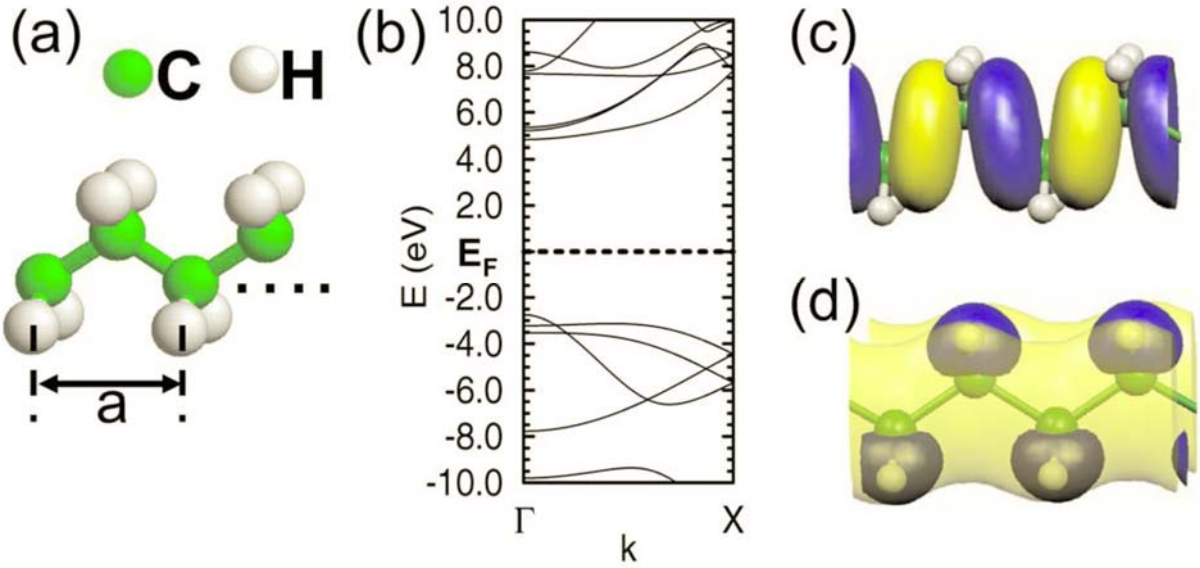


FIG. 1.(a) Equilibrium geometry and (b) electronic band structure of an infinitely long polyethylene chain. Wave functions of the states at k=Γ corresponding to (c) the top of the valence band and (d) the bottom of the conduction band are shown in the same perspective as used in (a). The wave function contours are presented for the amplitude $|\Psi|=0.04a_0^{-3/2}$ and superposed with the atomic positions. The wave function phase is distinguished by color.

   a. What hybridization should be attributed to the carbon atoms in the polyethylene chain?
   b. Give an orbital picture of the carbon-carbon bond using the valence bond theory.
   c. Rationalize the equilibrium geometry of the polyethylene chain shown in FIG. 1(a) in terms of proper forces.
   d. What are the relations between HOMO, LUMO, top of the valence band and the bottom of the conduction band?
   e. Using atomic orbitals as the basis give an approximate mathematical expression for the wave function corresponding to the top of the valence band.
   f. Does this wave function correspond to a bonding or an anti-bonding orbital? Rationalize your answer briefly.

8. What are the structural requirements for the formation of a strong hydrogen bond?

   A−H−B

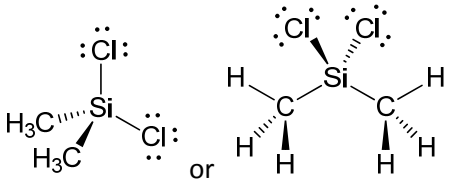
9. Define the concept “polarizability”.

10. Carbon monoxide has the molecular formula CO.
    a. Draw a correct Lewis structure for this compound. (1)

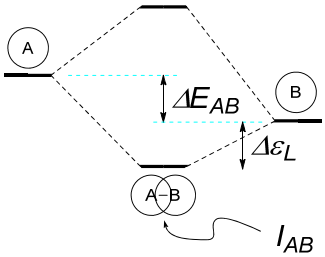
b. Below is shown the molecular orbital diagram for CO. The corresponding molecular orbitals (MOs) are shown to the right of the diagram. For each one of the four lowest energy levels, give a simple and approximate expression for the linear combination of two (2) atomic orbitals (AOs) that gives the best approximation of the corresponding molecular orbital (MO). Numerical values for the constants is not necessary, but for each expression indicate which one of the constants that is the largest. (2)
c. Use valence bond (VB) theory to describe the CO bond in carbon monoxide. Describe the bond both in text and using drawings. Compare the VB picture (your answer) and the MO picture (shown above). Relate your orbital pictures to the correct MOs shown above. (2)
d. The electrons not localized between the carbon and the oxygen, show where they are localized according to the VB theory. (1)

Answers

1. Draw a three dimensional structure of $Si(CH_3)_2Cl_2$ showing all valence electrons.
   Answer:

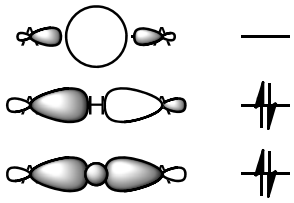


2. Draw a molecular orbital diagram for two interacting atomic orbitals (AOs) that belong to two different atoms. Outline how the covalent bond strength, i.e. the interaction energy, depends on the interaction between two atomic orbitals. What are the two most important parameters?
   Answer:



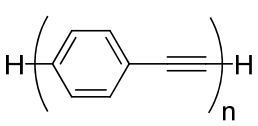
The two most important parameters are the orbital overlap integral $\boldsymbol{I_{AB}}$ *and the difference in energy* $\boldsymbol{\Delta E_{AB}}$ *for the two interacting orbitals. The larger the orbital overlap integral is and the smaller the energy difference is the larger the interaction energy will be, and thus the stronger the covalent bond will be.*

3. Describe briefly why strong hydrogen bonds A–H·····B are favored by A and B being highly electronegative atoms.
   Answer:
   The hydrogen bond is in the covalent limit a four-electron three-center bond:

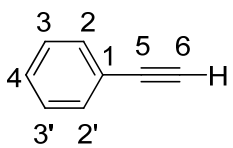


The four electrons will mainly be localized to the two atoms A and B. This is favored if these atoms are highly electronegative.

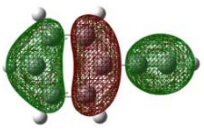
4. Conjugated organic molecules such as poly(1,4-phenyleneethynylene) are investigated as potential candidates to be used as molecular wires in molecular electronics and in nanotechnology. The repeating unit (building block) in the polymer is shown below. So are the highest occupied and lowest unoccupied molecular orbitals for the monomer ethynylbenzene.



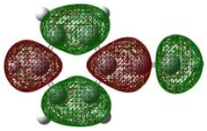
Poly(1,4-phenylene-ethynyl)



ethynylbenzene



HOMO



LUMO

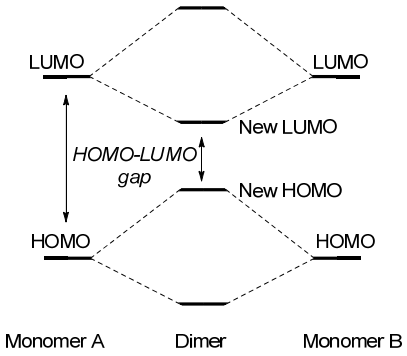
a. To which class of molecular orbitals are HOMO and LUMO designated, σ or π, and what is the definition of such an orbital?
Answer:
Both HOMO and LUMO are π-orbitals. A π-orbital has a nodal plane that coincides with the bond axis.

b. Give a mathematical expression for the HOMO wave function in terms of suitable atomic orbitals φ_i, where *i* is the atom number shown in the structure of ethynylbenzene above. Numerical values for the constants used in your expression are not needed but the correct signs must be shown. What atomic orbital does φ_i correspond to?
Answer:
The atomic orbitals φ_i to which the molecular orbital HOMO can be traced back to are the carbon-2p_z orbitals.

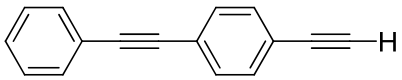
$$\psi_{HOMO} = C_4 2p_z(4) + C_{3,3'}[2p_z(3) + 2p_z(3')] - C_{2,2'}[2p_z(2) + 2p_z(2')] - C_1 2p_z(1) + C_5 2p_z(5) + C_6 2p_z(6)$$

Where all coefficients $C_i > 0$.

c. Will the HOMO-LUMO gap increase or decrease with increasing number of repeating units in the polymer? Rationalize your answer briefly.
Answer:
The HOMO-LUMO gap will decrease, see the interaction diagram for two units (monomers) forming one dimer.

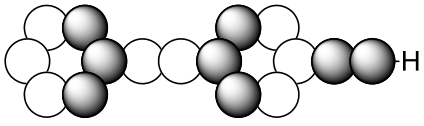


d. Draw the orbital shapes for the HOMO and the LUMO of the shortest possible polymer of ethynylbenzene, the dimer shown below.



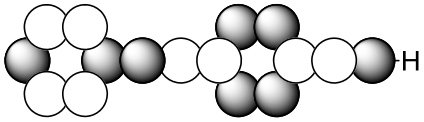
Answer:
The new HOMO(dimer) is constructed by linear combination of one HOMO orbital from each monomer in an antibonding fashion:

$$New\ HOMO = HOMO(Monomer\ A) - HOMO(Monomer\ B).$$

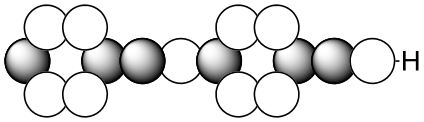


The new LUMO(dimer) is constructed by linear combination of one LUMO orbital from each monomer in a bonding fashion:

$$New\ LUMO = LUMO(Monomer\ A) - LUMO(Monomer\ B).$$



The other combination gives an additional node and is higher in energy (LUMO+1):



e. Compounds similar to the dimer shown above are also used as liquid crystals. What are the two most important intermolecular forces between molecules in assemblies of such compounds. Describe briefly the origin of each one of these two forces.
Answers:
The two most important intermolecular forces between molecules similar to the dimer shown above are π-interactions and van der Waals interactions.
The origin of the π-interactions is the interaction between the "electron deficient" σ-skelton and the "π-electron cloud".
van der Waals interactions can be divided into dispersion (London) interactions and exchange (Pauli)–repulsion. The London dispersion force is a weak intermolecular force arising from quantum induced instantaneous polarization multipoles in molecules.

5. Lewis structures (the Lewis structure model) have a particular shortcoming that is resolved by the use of multiple Lewis structures, i.e. resonance structure. Give the reason for the shortcoming of the Lewis structure model and explain the concept resonance.
Answer:
The Lewis model assumes that a chemical bond corresponds to an electron pair localized between two atoms. This is not true and this assumption often makes it impossible to represent the true structure (electron" distribution" as shown by the Lewis structure) with a single Lewis structure. The real structure is better represented as a linear combination of Lewis structures, e.g. conjugated and aromatic compounds.

6. Explain the concept polarizability.
Answer:
The relative tendency of the charge distribution, of an atom or a molecule, to be distorted from its normal shape by an external electric field (point charge).

7. The following figure and figure caption are excerpts from the article **Self-assembly of long chain alkanes and their derivatives on graphite** published in Journal of Chemical Physics in 2008.

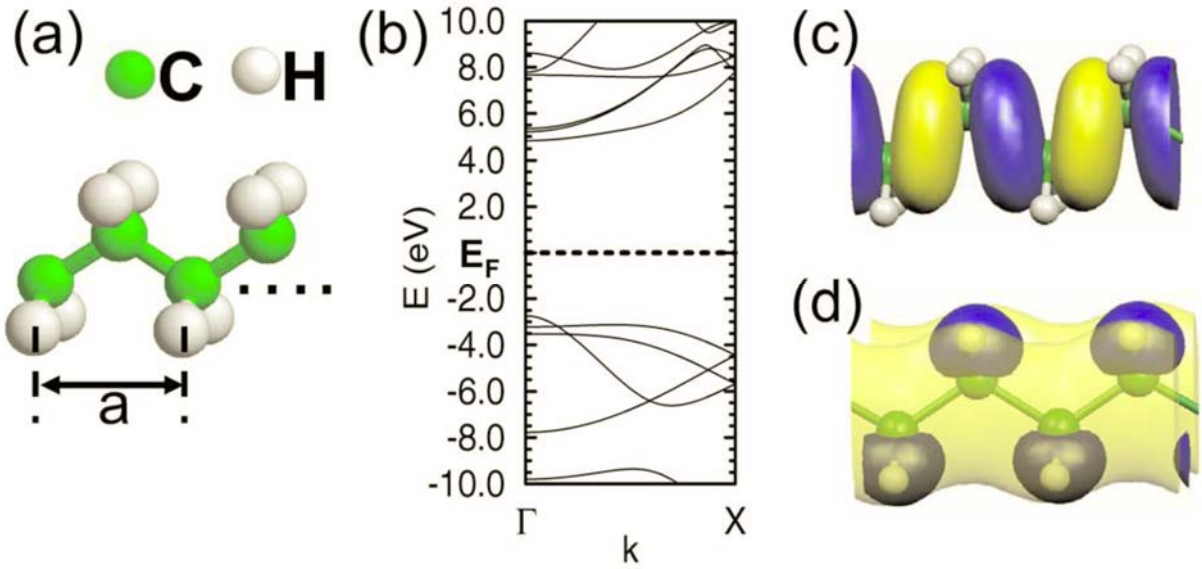
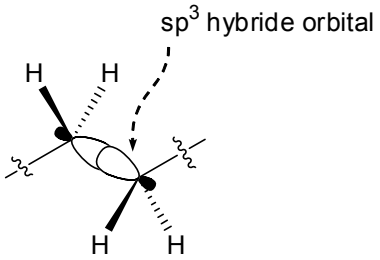
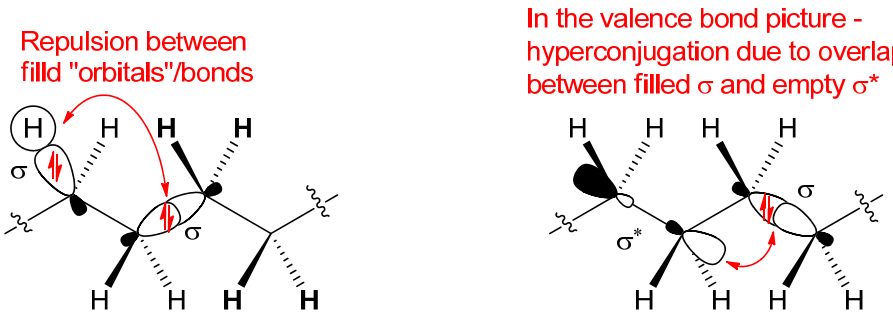


FIG. 1.(a) Equilibrium geometry and (b) electronic band structure of an infinitely long polyethylene chain. Wave functions of the states at k=Γ corresponding to (c) the top of the valence band and (d) the bottom of the conduction band are shown in the same perspective as used in (a). The wave function contours are presented for the amplitude $|\Psi|=0.04a_0^{-3/2}$ and superposed with the atomic positions. The wave function phase is distinguished by color.

a. What hybridization should be attributed to the carbon atoms in the polyethylene chain?
   Answer: *sp^3*
b. Give an orbital picture of the carbon-carbon bond using the valence bond theory.
   Answer:

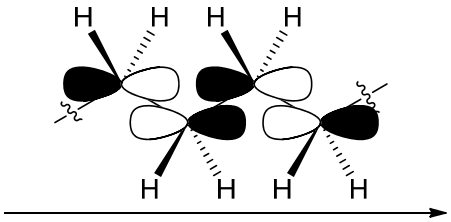


c. Rationalize the equilibrium geometry of the polyethylene chain shown in FIG. 1(a) in terms of proper forces.
   Answer:
   The geometry/conformation corresponding to the lowest possible potential energy is the one where the repulsion between the electrons/"bonds" is minimized (Pauli repulsion or steric repulsion). Hyperconjugation also plays an important role.



d. What are the relations between HOMO, LUMO, top of the valence band and the bottom of the conduction band?
Answer:
HOMO is the orbital with highest energy that is filled, which corresponds to the valance band. LUMO is the orbital of lowest energy that that does not holds any electrons (unoccupied), which corresponds to conduction band.

e. Using atomic orbitals as the basis give an approximate mathematical expression for the wave function corresponding to the top of the valence band.
Answer:



$HOMO = \sum_{i=1}^{n} c_i 2p_x$ where the constant c_i is positive when i is even and negative when i is odd, or vice vers.

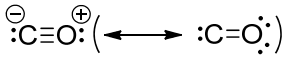
f. Does this wave function correspond to a bonding or an anti-bonding orbital? Rationalize your answer briefly.
Answer:
Bonding."Constructive overlap all the way"

8. What are the structural requirements for the formation of a strong hydrogen bond?
Answer:
Both atom A and B should be highly electronegative and, in absence of the proton, possess at least one lone pair each. The three atoms A, H and B should form a linear arrangement to achieve minimal electron repulsion and optimal orbital overlap.

A–H–B

9. Define the concept "polarizability".
Answer:
The relative ability of the electron distribution, of an atom or molecule, to be distorted from its normal shape by an external electric field.

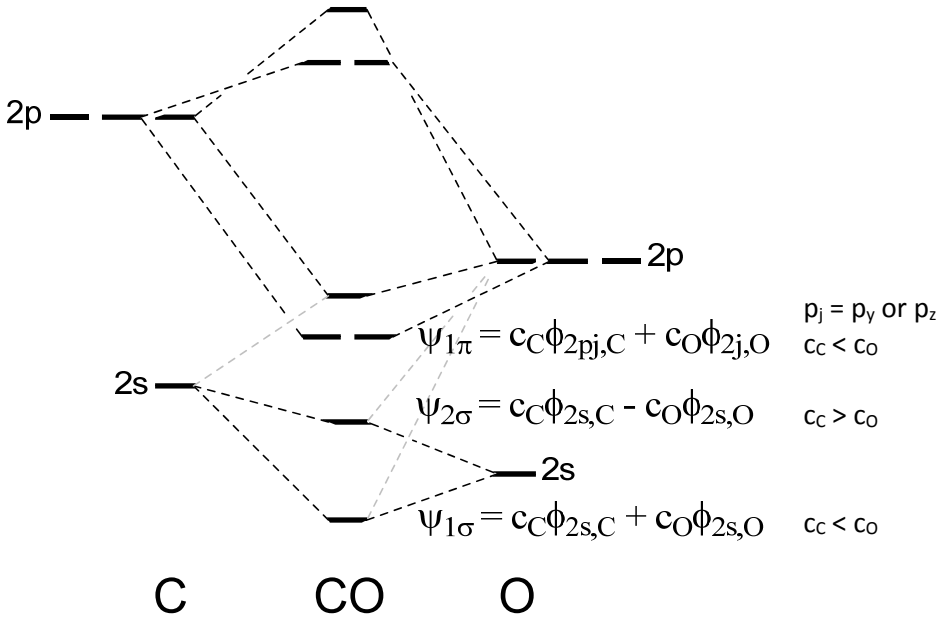
10. Carbon monoxide has the molecular formula CO.
    a. Draw a correct Lewis structure for this compound. (1)
    Answer:



Isoelectronic with N_2: :N≡N:

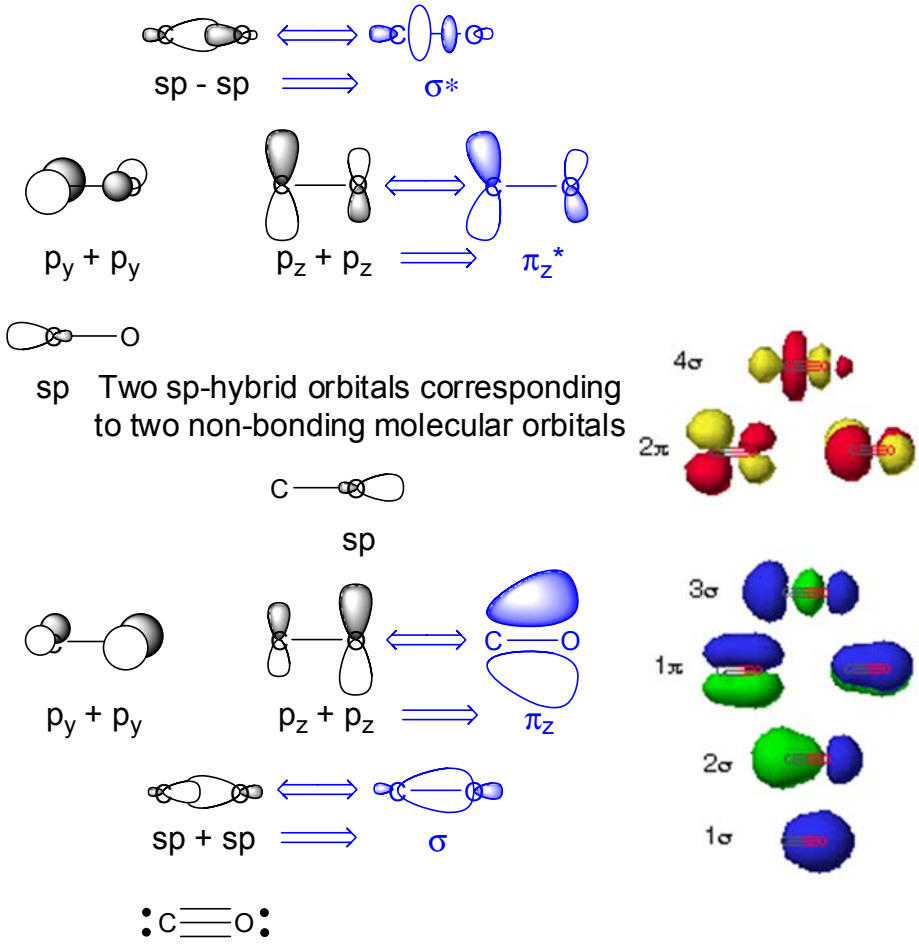
b. Below is shown the molecular orbital diagram for CO. The corresponding molecular orbitals (MOs) are shown to the right of the diagram. For each one of the four lowest energy levels, give a simple and approximate expression for the linear combination of two (2) atomic orbitals (AOs) that gives the best approximation of the corresponding molecular orbital (MO). Numerical values for the constants is not necessary, but for each expression indicate which one of the constants that is the largest. (2)

Answer:



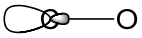
c. Use valence bond (VB) theory to describe the CO bond in carbon monoxide. Describe the bond both in text and using drawings. Compare the VB picture (your answer) and the MO picture (shown above). Relate your orbital pictures to the correct MOs shown above. (2)

Answer:



The two atoms in CO is according to the valence bond theory sp hybridized (Linear structure in accordance with the isoelectronic N_2). The valence bond molecular orbitals (VBMOs) obtained by a linear combination – either as the sum or as the difference – of a sp-hybride orbital from each atom corresponds to the bonding and anti-bonding σ–molecular orbitals 1σ and 4σ, respectively. For the bonding orbital, the linear combination sp + sp corresponds to the molecular orbital approximated above as $\Psi_{1\sigma} = c_C\Phi_{2s,C} + c_O\Phi_{2s,O}$. The VBMO obtained by a linear combination – either as the sum or as the difference – of a p-orbital from each atom corresponds to the bonding and anti-bonding π–molecular orbitals 1π and 2π, respectively. For the bonding orbital, the linear combination $p_j + p_j$ (j = y or z) corresponds to the molecular orbital approximated as $\Psi_{1\pi} = c_C\Phi_{2pj,C} + c_O\Phi_{2pj,O}$. The two sp hybrid orbitals pointing in the opposite direction compared to the CO-bond holds the two lone (free electron) pairs in CO. The orbitals appear at (correspond to) different energies because of the difference in electronegativity between the two atoms. These VBMOs do not show much resemblance to any of the two remaining MOs.

d. The electrons not localized between the carbon and the oxygen, show where they are localized according to the VB theory. (1)
Answer: *The probability amplitudes corresponding to the lone (free electron) pairs in the VB-picture are the two sp hybrid orbitals pointing in the opposite direction compared to the CO-bond:*



sp Two sp-hybrid orbitals corresponding to two non-bonding molecular orbitals