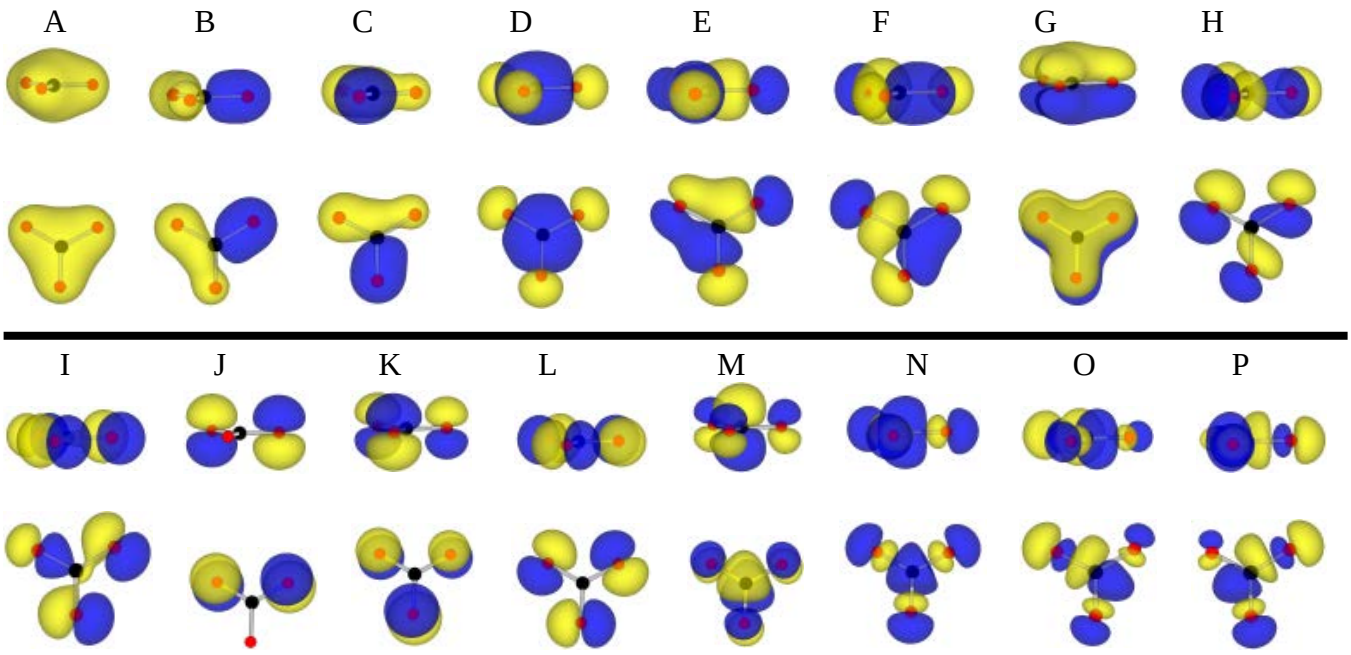
Practice Test Questions 4
Molecular Orbital Theory: Polyatomic Molecules

1. The images below show the valence molecular orbitals obtained for the carbonate ion via a semi-empirical calculation. *Both side views and top views are provided, and each MO has been assigned an identifying letter.*



(a) In a semi-empirical calculation, the core molecular orbitals are not calculated. Instead, a "core potential" is used to approximate the nucleus plus core electrons. How many core MOs are there in a carbonate ion, and why is it reasonable to approximate them as part of a core potential?

(b) Which of the MOs shown above are σ-MOs?

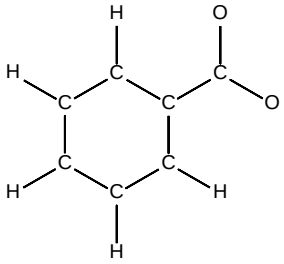
(c) Which of the MOs shown above are π-MOs?

(d) Which two π-MOs form a degenerate pair?

(e) Which of the π-MOs are bonding? Which are nonbonding? Which are antibonding?

(f) Use the pictured MOs to help you construct an MO energy level diagram for the <u>valence π orbitals only</u> of the carbonate ion. Remember to include the valence π electrons on your MO diagram.

2. Consider the benzoate ion ($C_6H_5CO_2^-$). The diagram below shows the connectivity for this ion.



(a) Draw all valid resonance structures for the benzoate ion. *Include all non-zero formal charges.*

(b) If you were to construct a valence molecular orbital energy level diagram for the benzoate ion:

i. How many MOs would it have? _____

ii. How many π MOs would it have? _____

iii. How many σ MOs would it have? _____

iv. How many electrons would be in σ MOs? _____

v. How many electrons would be in π MOs? _____

Note that you are <u>NOT</u> being asked to actually construct the diagram!

3. Consider the nitrite ion (NO_2^-).

(a) Draw both valid resonance structures of the nitrite ion.

(b) If you were to construct a valence molecular orbital energy level diagram for the nitrite ion:

i. How many MOs would it have? _____

ii. How many π MOs would it have? _____

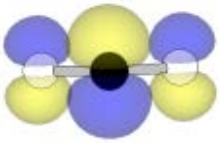
iii. How many σ MOs would it have? _____

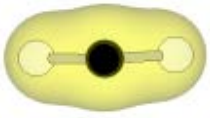
iv. How many electrons would be in σ MOs? _____

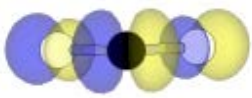
v. How many electrons would be in π MOs? _____

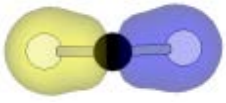
Note that you are <u>NOT</u> being asked to actually construct the diagram!

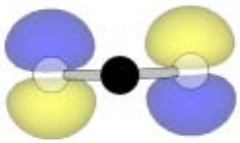
(c) The following pictures show some valence molecular orbitals of the nitrite anion (side view; black atom = N; white atoms = O). Indicate whether each orbital is sigma- or pi-symmetric ***<u>and</u>*** whether it is bonding, nonbonding or antibonding.

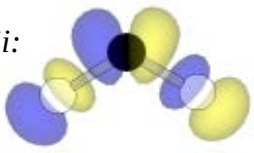
i. 

ii. 

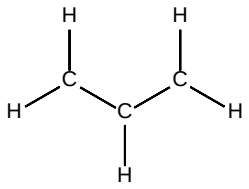
iii. 

iv. 

v. 

top view of iii: 

4. The connectivity of the allyl cation ($C_3H_5^+$) is shown:



(a) Draw both resonance structures for the allyl cation.

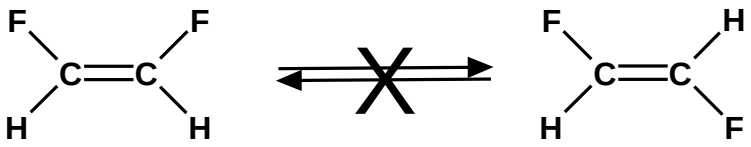
(b) Draw a valence pi molecular orbital energy level diagram of the allyl cation.

Be sure to: (i) show the relative energies of the molecular orbitals,
(ii) draw a picture of each molecular orbital,
(iii) label each molecular orbital as bonding, nonbonding or antibonding,
(iv) include electrons on your diagram.

(c) Calculate the average C–C bond order based on your MO diagram.

(d) Based on your MO diagram, would adding two more π electrons change the average C–C bond order? Why or why not?

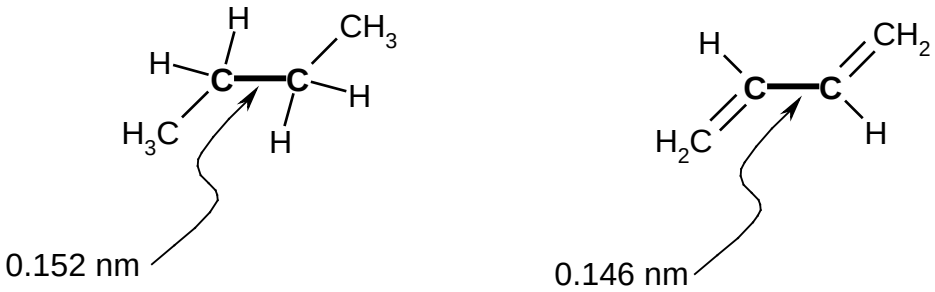
5. Use diagram(s) to explain why it is not possible to rotate about the double bond in molecule A to make molecule B:



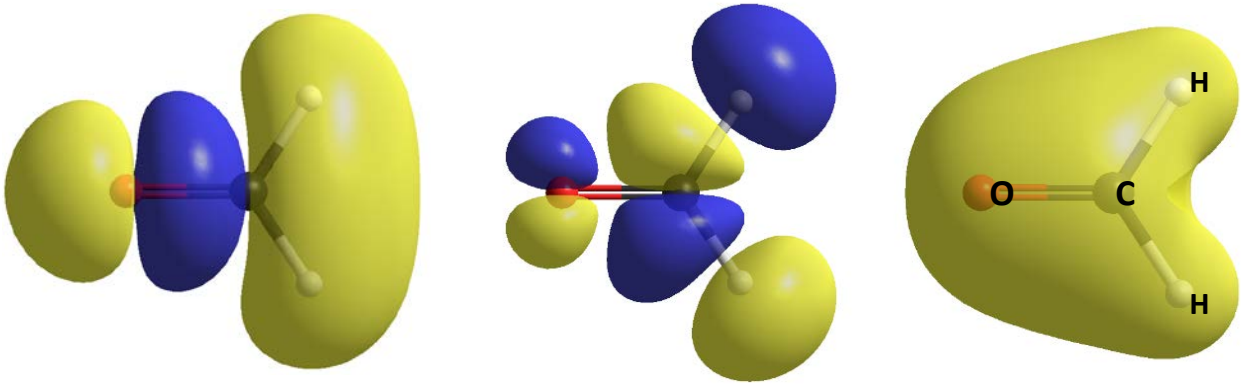
molecule A **molecule B**

6. The central C–C bond in butane ($CH_3CH_2CH_2CH_3$) is longer than the central C–C bond in butadiene ($CH_2CHCHCH_2$). Use molecular orbital theory to explain why this is the case.

butane **butadiene**



7. Formaldehyde (CH_2O) is a naturally occurring *planar* molecule that is primarily used in the production of industrial resins. Three of the sigma (σ) MOs of formaldehyde are shown below (the plane of the molecule is flat with this paper and they are all facing the same direction):



(a) Indicate whether each of the MOs shown above is <u>overall</u> bonding or antibonding.

(b) Rank the three MOs from lowest in energy to highest in energy.

(c) Sketch <u>one</u> of the π-molecular orbitals of the formaldehyde molecule. You may change the orientation of the molecule, but be sure to label all atoms and include phases in your diagram.

8. Consider SO_2 (a triatomic molecule with sulfur in the middle).

(a) i. Draw all resonance structures for SO_2 in which S obeys the octet rule.

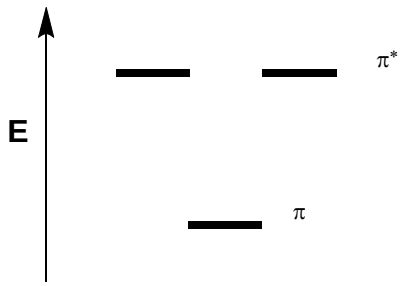
ii. What is the average bond order for each S-O bond in the SO_2 according to your resonance structures?

(b) i. Draw a valence pi molecular orbital energy level diagram for SO_2. Show **energy levels** and **clear sketches** of each molecular orbital. *(A "top view" of the π-MO's is acceptable, but show the AO's in perspective view.)*

ii. Complete your diagram by adding the appropriate number of π electrons for SO_2

iii. What is the average bond order for each S-O bond in SO_2 according to MO theory?

9. The valence π molecular orbital energy level diagram shown below can be used to describe the π bonding in C_3H_3, $C_3H_3^+$ or $C_3H_3^-$. Each of these compounds consists of a triangle of carbon atoms with one hydrogen attached to each carbon.



(a) i. Draw all valid resonance structures for the $C_3H_3^+$ cation.

ii. What is the average bond order for each C-C bond in the $C_3H_3^+$ cation according to your resonance structures?

(b) i. Fill the π MOs in the diagram above with the appropriate number of π electrons for the $C_3H_3^+$ cation.

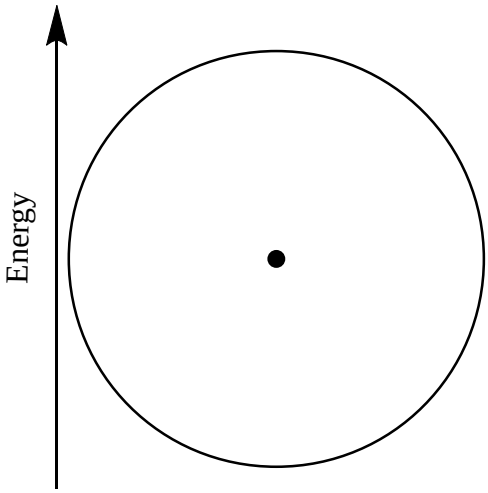
ii. What is the average π bond order for each C-C bond in the $C_3H_3^+$ cation according to the MO diagram?

iii. What is the average bond order for each C-C bond in the $C_3H_3^+$ cation according to MO theory?

(c) On the π MO energy level diagram above, draw a picture of the lowest energy π MO.

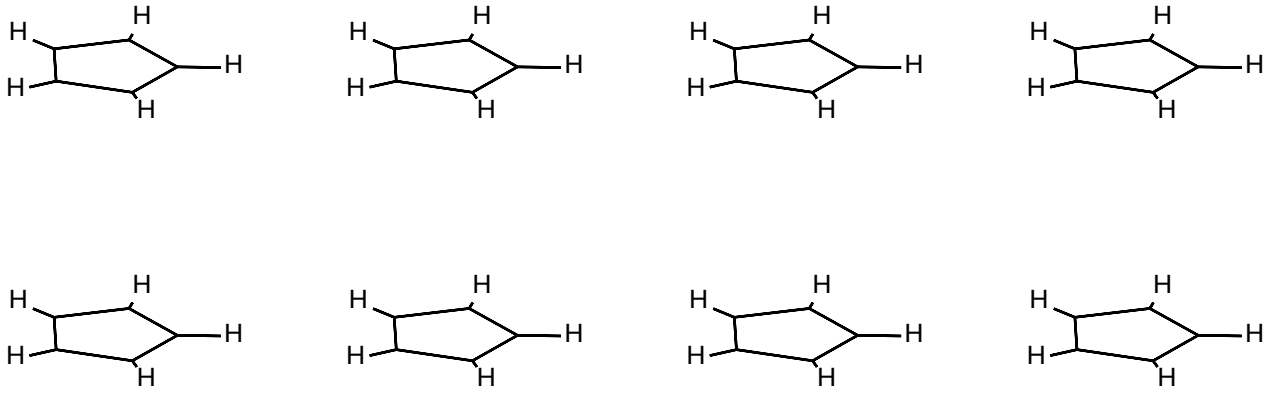
10.

(a) Use the "Frost circle" approach to generate an approximate valence π-MO energy level diagram (energy levels only!) for cyclic hydrocarbon species of the form $[C_5H_5]^x$. Be sure to label each molecular energy level on your diagram with the correct label. Indicate the *dominant* bonding character with the usual symbols. Pay attention to multiplicity of levels!



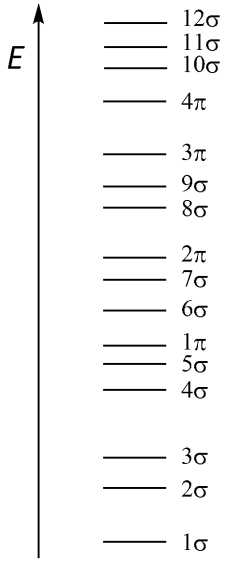
(b) Sketch approximate orbital shapes for each of the π MOs in your MO diagram. *Fill in as many of the rings as required to complete this project; you may not need to use them all.* Clearly label each MO you decide to draw. Show the resultant ⊥ nodes.

It is sometimes easier just to draw the atomic p_z *orbitals with the correct relative shading (phase).*



(c) Which value of "*x*" (i.e. which charge of $[C_5H_5]^x$) will provide the *optimal π-bonding* in this type of hydrocarbon? Show your work or explain your reasoning.

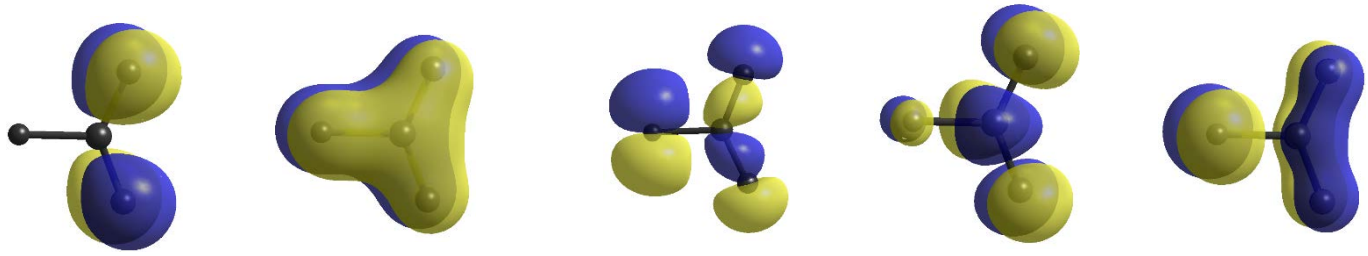
11. The valence molecular orbital energy level diagram for planar nitryl fluoride (NO_2F with nitrogen as the central atom) is shown below. Note that the σ or π character of each MO is indicated, but NOT the nature of the overall interaction (i.e. whether it has bonding, antibonding, or non-bonding character).



(a) Draw both resonance structures for NO_2F.

(b) What is the $N - O$ bond order in NO_2F according to your Lewis diagrams?

(c) Five orbital pictures for NO_2F are provided below. In each case, the atom at the left is fluorine. Identify each MO as either a π MO or a σ MO. The π MOs should be labeled as 1π, 2π, 3π, etc. while the σ MO can just be labeled as σ (i.e. not assigned to a specific energy level).

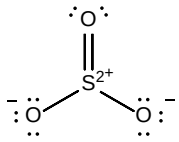


(d) Identify each π MO as bonding, antibonding or nonbonding. Justify your answers.

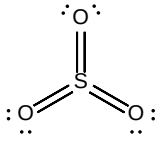
(e) Fill in the valence electrons on the energy level diagram above. How many electrons are in σ MOs and how many are in π MOs?

(f) Label the HOMO and LUMO on the MO energy level diagram above.

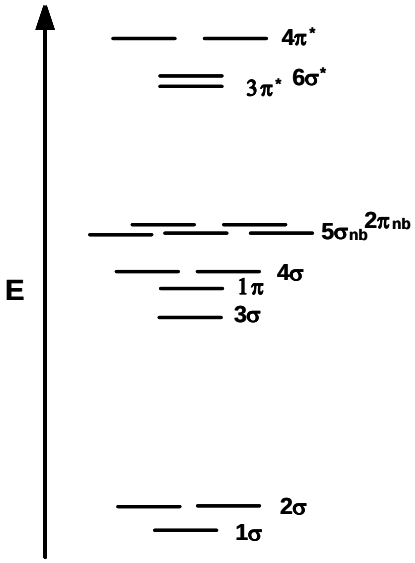
12. Consider sulfur trioxide (SO_3). You may recall that, in CHEM 1000, you were introduced to a debate as to whether the Lewis diagram should look more like the one on the left (plus resonance structures) or the one on the right.



vs.

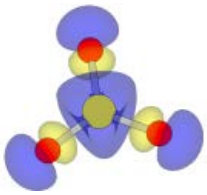


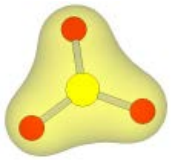
Consider what molecular orbital theory tells us about these alternatives. The valence molecular orbital energy level diagram for SO_3 is shown below.

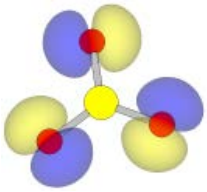


(a) Fill in the electrons on the diagram above.

(b) Of the pictures below, one is 1σ, one is a $5\sigma_{nb}$ and one is $6\sigma^*$. Identify each picture and **briefly** explain your reasoning.

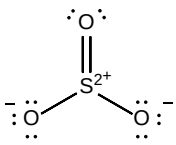




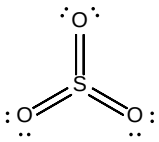


(c) Use information from the MO energy level diagram to argue in favour of **each** of the two options.

Hint: You may want to sketch a π MO diagram as well as looking at the overall MO diagram. No credit will be given for answers not involving the MOs or MO diagram.

i. 

is a better Lewis diagram because…

ii. 

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