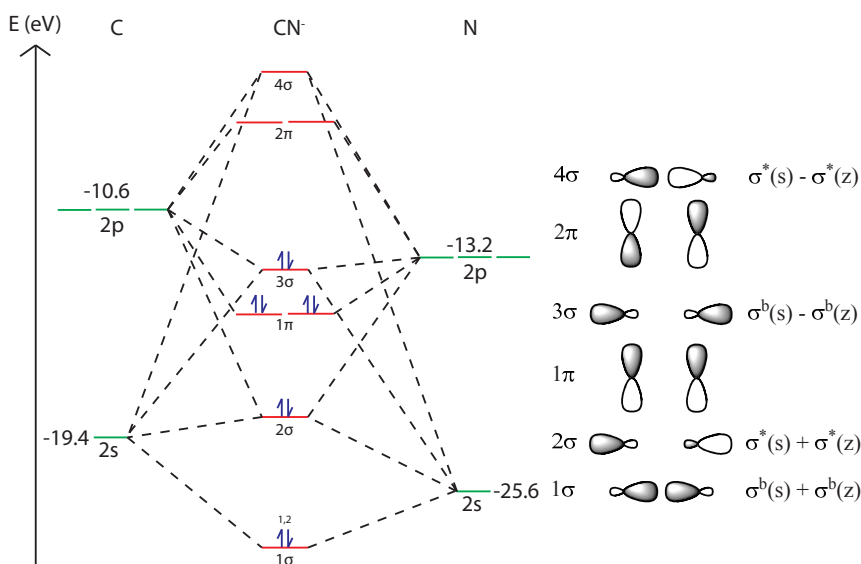


Problem Set 5 Solutions

Chemistry 104a

Problem 1

- (a) Prepare a molecular orbital energy level diagram for the cyanide ion. Use sketches to show clearly how the atomic orbitals interact to form MOs.



- (b) What is the bond order, and how many unpaired electrons does cyanide have?

We can say that the bond order is approximately 3 because the 1σ and the two 1π orbitals are filled; 2σ and 3σ are considered non-bonding. $\frac{1}{2}(6 - 0) = B.O.$

Looking at the molecular orbital diagram, you can see that there are no unpaired electrons.

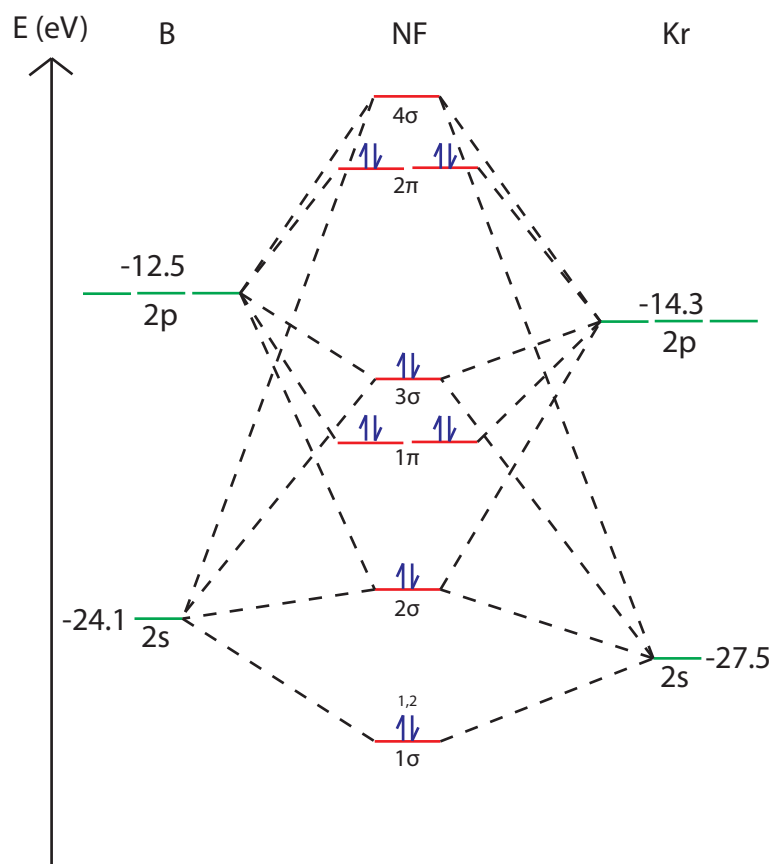
- (c) Which molecular orbital of CN^- would you predict to interact most strongly with a hydrogen $1s$ orbital to form an H-C bond in the reaction $\text{CN}^- + \text{H}^+ \rightarrow \text{HCN}$? Explain.

The 3σ (HOMO) of CN^- would interact most with the LUMO of H^+ $1s$ orbital, which has an energy of -13.6 eV, because they match in symmetry and in energy.

Problem 2

Although KrF^+ and XeF^+ have been studied, KrBr^+ has not yet been prepared. For KrBr^+ :

- (a) Propose a molecular orbital diagram, showing the interactions of the valence shell s and p orbitals to form molecular orbitals.



- (b) Toward which atom would the HOMO be polarized? Why?

The HOMO = 2π . The HOMO is more polarized toward the Br $4p_x$ and $4p_y$. These Br $4p_x$ and $4p_y$ orbitals are closer in energy to the 2π MO than the Kr $4p_x$ and $4p_y$.

(c) Predict the bond order.

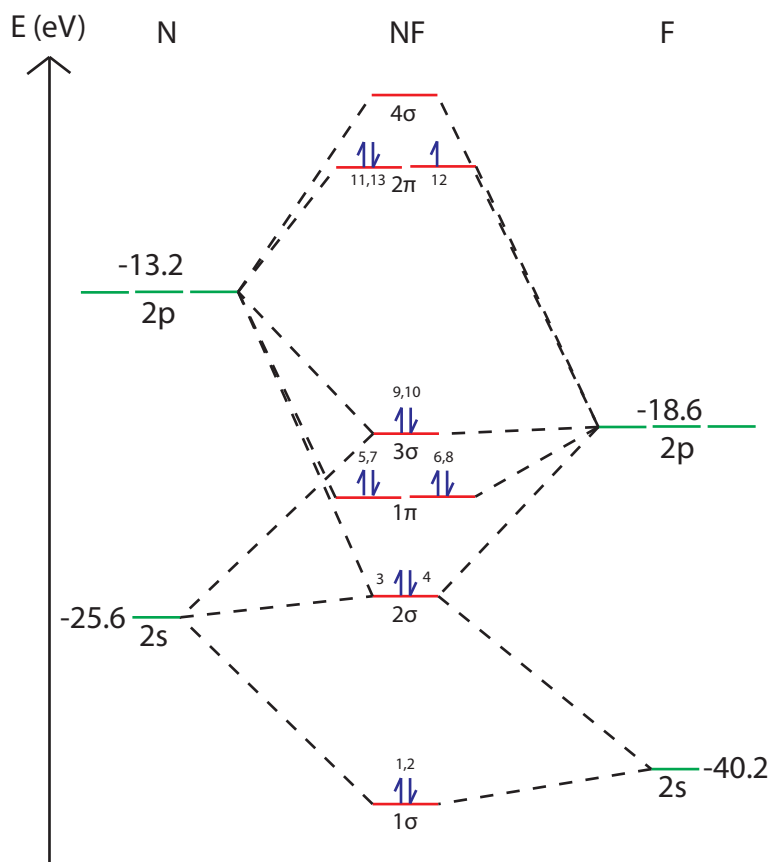
Bond order is approximately 1 since the effects of the 2σ and 3σ cancel each other out just like the 1π and the 2π .

(d) Which is more electronegative, Kr or Br? Explain your reasoning.

Kr is more electronegative because its atomic orbitals are lower in energy than the corresponding Br atomic orbitals. As a result, you can see more filled orbitals have Kr character than Br character.

Problem 3

Consider the molecule NF and the ions NF^+ and NF^- . Write the Lewis structure and the molecular orbital description of the ground state for each species. Determine which of the three species would be paramagnetic, and tell how many unpaired electrons there would be in each paramagnetic molecule. Predict the bond orders for all three species.



NF⁺

11 electrons

8 electrons are bonding and 3 electrons are antibonding. The bond order is $5/2$, and the molecule is paramagnetic due to one unpaired electron.

NF

12 electrons

8 electrons are bonding and 4 electrons are antibonding. The bond order is 2, and the molecule is paramagnetic due to 2 unpaired electrons.

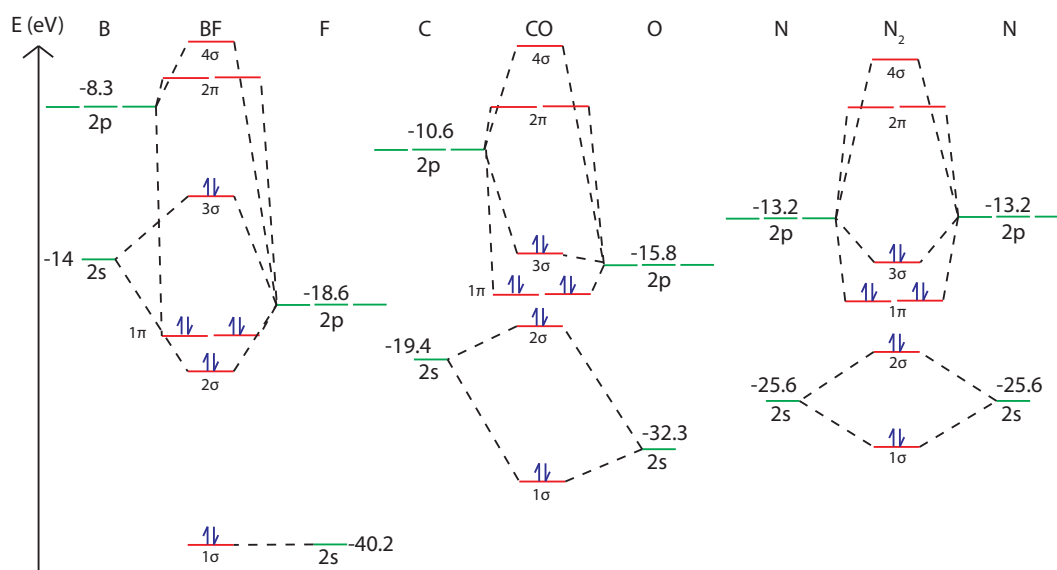
NF⁻

13 electrons

8 electrons are bonding and 5 electrons are antibonding. The bond order is $3/2$, and the molecule is paramagnetic due to one unpaired electron.

Problem 4

The first ionization energies of BF, CO, and N₂ are 11.06 eV, 14.01 eV, and 15.57 eV, respectively. Explain the increase in ionization energy for this isoelectronic series on the basis of atomic-orbital composition of the highest occupied molecular orbital.



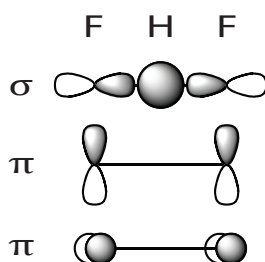
Note: Not showing s-p mixing for all 3 molecules.

We can answer this question simply by inspecting the HOMO levels of each molecule because the HOMO level is a minimum value for ionization energy (IE). The HOMO level of BF is the highest since it is higher than -14.0 eV. The HOMO level of CO is slightly higher than the O 2p orbital (-15.8 eV) from s-p mixing; therefore, its HOMO level is lower than the HOMO level of BF, so its IE is larger. The HOMO level of N₂ is the lowest because its 3σ bond is strongly bonding despite weak s-p mixing. Therefore, diatomic nitrogen has the largest IE.

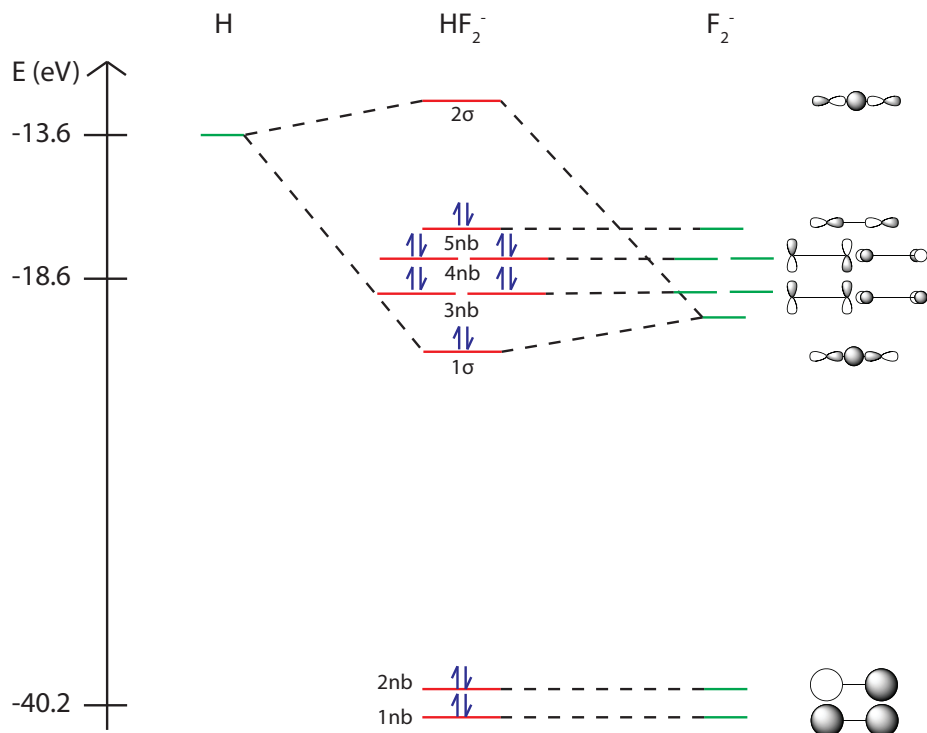
Problem 5

The species of HF_2^- is linear and symmetrical, F-H-F^- , and has one of the strongest known systems of “hydrogen bonding”.

- (a) Draw atomic overlap representations for each of the σ and π orbitals of HF_2^- .



- (b) Draw a molecular-orbital energy-level scheme for HF_2^- . Place the H atom $1s$ orbital on the left, the fluorine $2s$ and $2p$ atomic orbitals (or the appropriate SALCs) on the right, and the orbitals of HF_2^- in the center.



- (c) Given the energy-level scheme derived in part (b), would you expect HF_2^- to be diamagnetic or paramagnetic?

diamagnetic (all electrons are paired up)

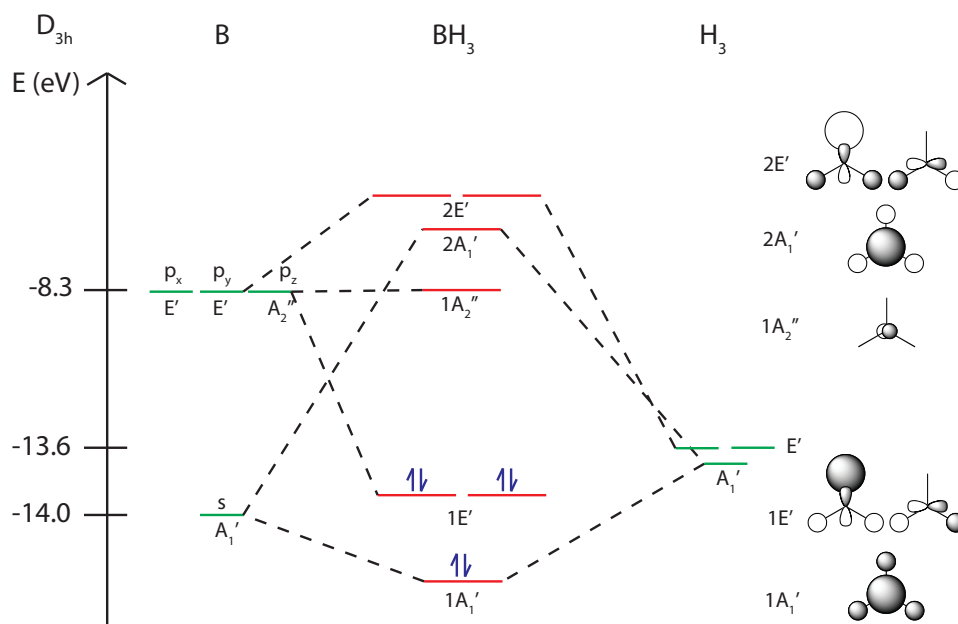
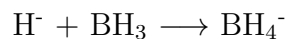
- (d) What is the H-F bond order in HF_2^- ?

The total bond order $= \frac{1}{2}(2 - 0) = 1$, which represents the bond order over two H-F bonds.

A single $\text{BO}_{\text{H-F}}$ would then be $1/2$

Problem 6

Consider the borohydride anion, BH_4^- , to be formed in the reaction

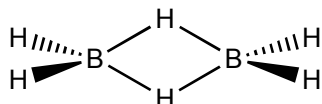


Which orbital will the H^- nucleophile attack on the BH_3 molecule?

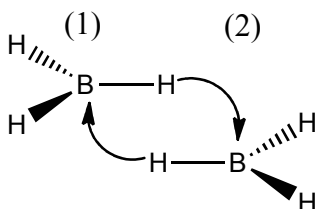
Following the symmetry rules for chemical reactions laid out in pg. 324 - 328 of DG, we can argue that H^- will act as a nucleophile and attack the LUMO on BH_3 . The LUMO is a non bonding a_2'' orbital, which corresponds to the $2p_z$ orbital of boron.

Problem 7

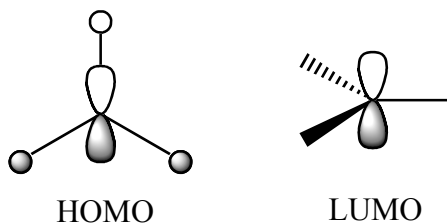
Diborane, B_2H_6 , has the structure shown. Using molecular orbitals (and showing appropriate orbitals on B and H from which the MOs are formed), explain how hydrogen can form “bridges” between two B atoms. (This type of bonding is discussed in Chapter 8 of MT)



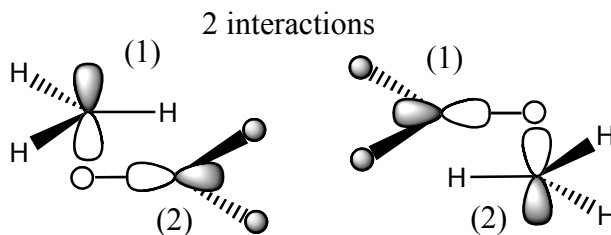
You can look at this problem as 2 molecules of BH_3 , labeled (1) and (2), reacting with each other to make B_2H_6 .



Problem #6 shows us that the HOMO and LUMO of each BH_3 molecule will look like:

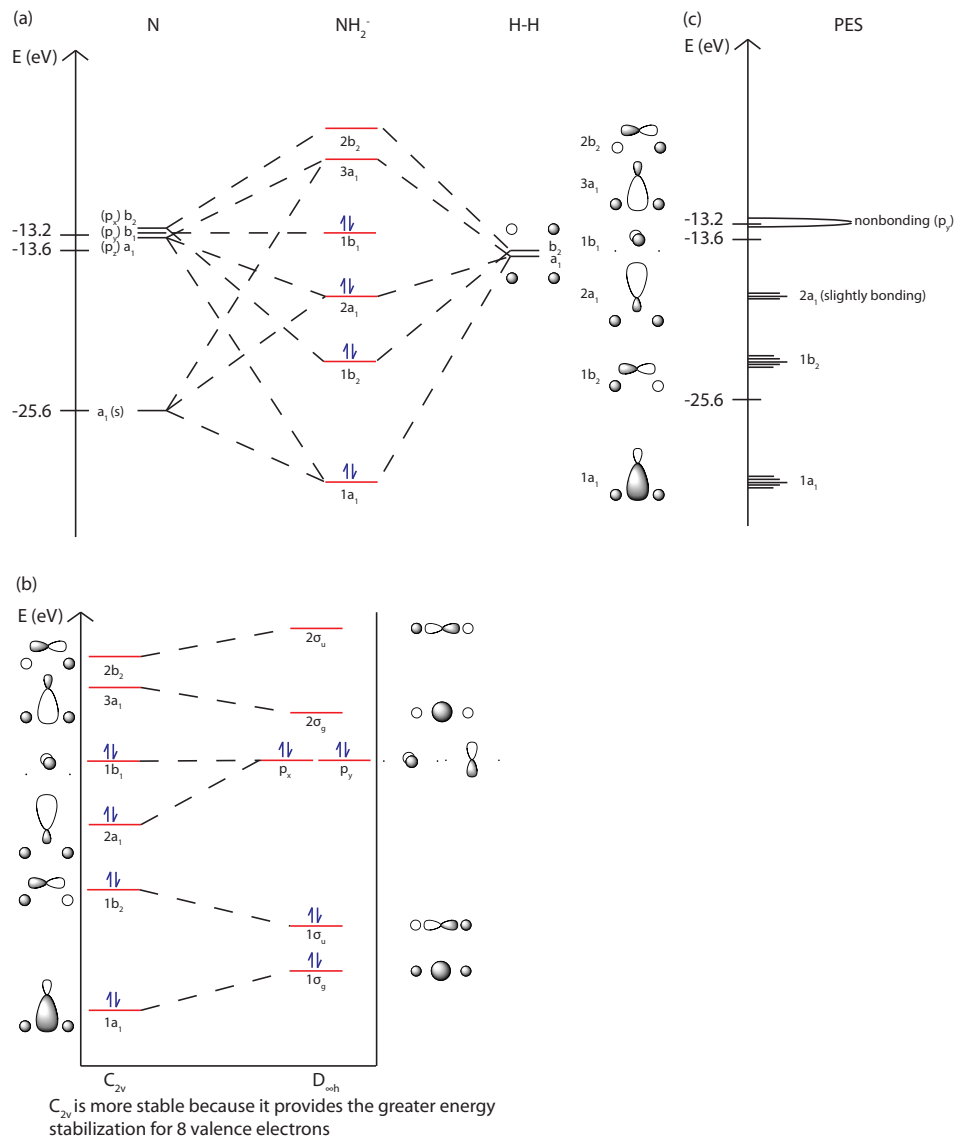


The goal now is to orient the HOMO on (1) with the LUMO on (2) to create one interaction. To create another interaction, we can orient the HOMO on (2) with the LUMO on (1) to create another interaction while the molecules are still in the same relative position. This can create a “bridged” molecule.



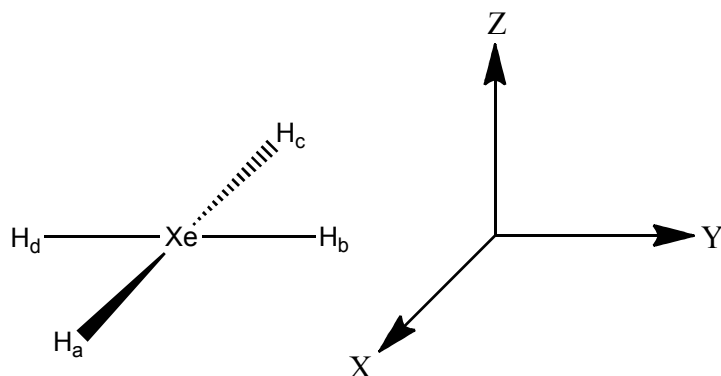
Problem 8

In the bent geometry, we should consider s-p mixing. The Walsh diagram is made with s-p mixing. Please note that the position of $2a_1$ is system dependent.



Problem 9

Consider the hypothetical square-planar molecule XeH_4 in the following coordinate system:



- (a) Write appropriate SALCs of the hydrogen $1s$ atomic orbitals which will overlap with each of the following xenon orbitals that can form molecular orbitals: $5s$, $5p_x$, $5p_y$, and $5d_{x^2-y^2}$.

D_{4h}	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{red}	4	0	0	2	0	0	0	4	2	0

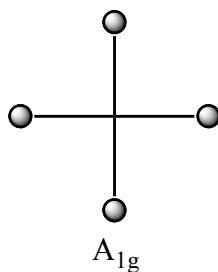
Applying the reduction formula:

$$\Gamma_{red} = A_{1g} + B_{1g} + E_u$$

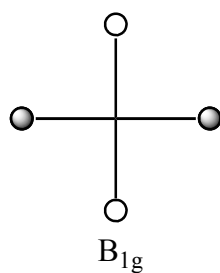
We can now apply the Projection operator to generate LGOs.

Don't pay too much attention to the shading. The sign is arbitrary. Just know when the sign flips on a symmetry.

$$\hat{P}^{A_{1g}}(H_a) = 4(H_a + H_b + H_c + H_d)$$



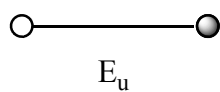
$$\hat{P}^{B_{1g}}(H_a) = 4(H_a - H_b + H_c - H_d)$$



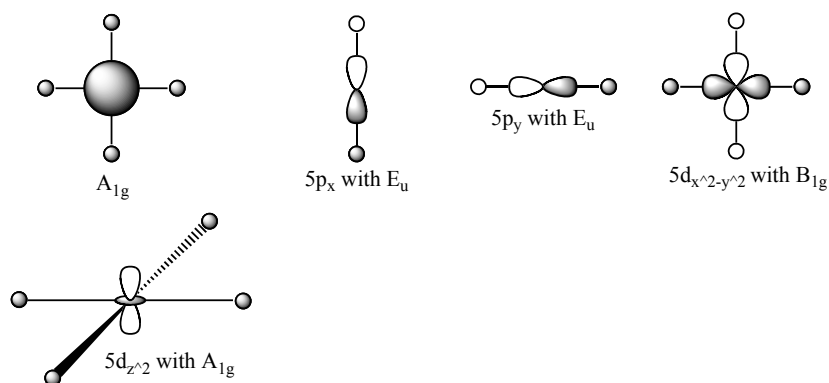
$$\hat{P}^{E_u}(H_a) = 4(H_a - H_c)$$



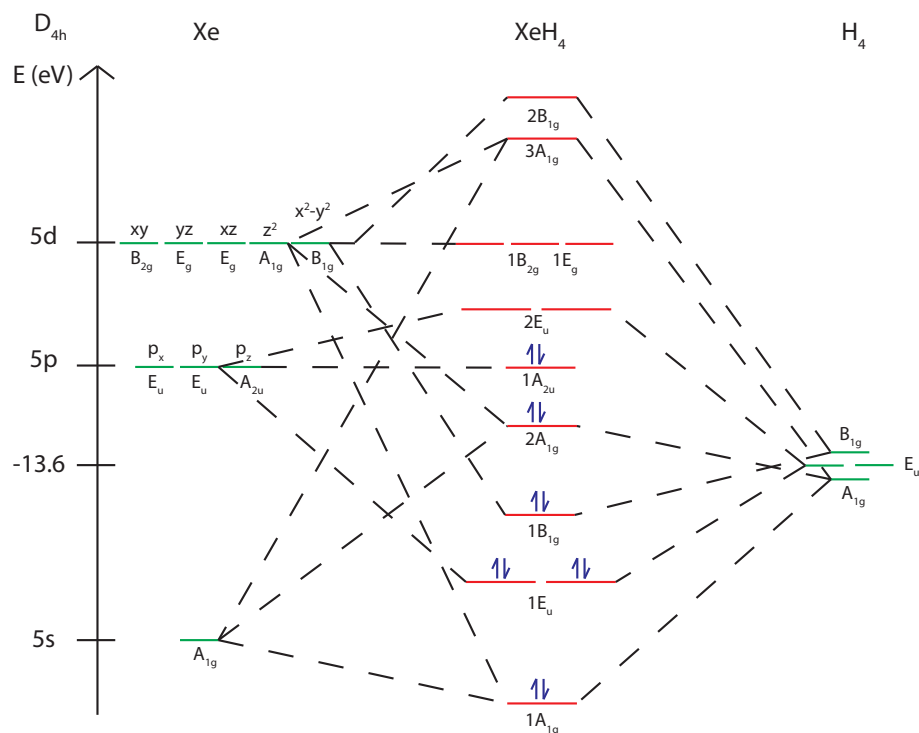
$$\hat{P}^{E_u}(H_b) = 4(H_b - H_d)$$



- (b) Draw atomic-orbital overlaps with the appropriate Xe orbital for each of these SALCs.



- (c) Sketch a molecular-orbital energy-level diagram for XeH_4 , showing the Xe atomic orbitals on the left, the H 1s orbitals on the right, and the XeH_4 orbitals in the center.



- (d) Indicate which molecular orbitals are occupied, and calculate the net Xe-H bond order, based on the molecular-orbital model.

a_{1g}^b , e_u^b , b_{1g}^b and a_{1g}^* are occupied.

$$\text{Bond Order} = \frac{1}{4} \cdot \frac{1}{2}(8 - 2) = 3/4$$

Problem 10

Consider the molecule SiCl₄:

- (a) Draw the MO diagram for the molecule in a planar configuration.

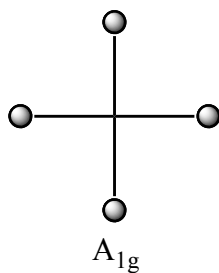
Use isolobal analogy so that we can use only *s*-orbitals for our LGO's. This will make life easier. These orbitals will be take on the energy of the chlorine 3*p* (13.7 eV) orbitals.

D_{4h}	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{red}	4	0	0	2	0	0	0	4	2	0

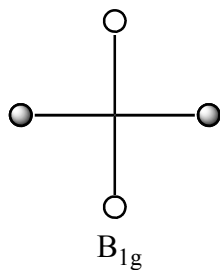
$$\Gamma_{red} = A_{1g} + B_{1g} + E_u$$

Don't pay too much attention to the shading. The sign is arbitrary.
Just know when the sign flips on a symmetry.

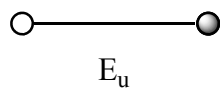
$$\hat{P}^{A_{1g}}(\sigma_1) = 4(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$$



$$\hat{P}^{B_{1g}}(H_1) = 4(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$$

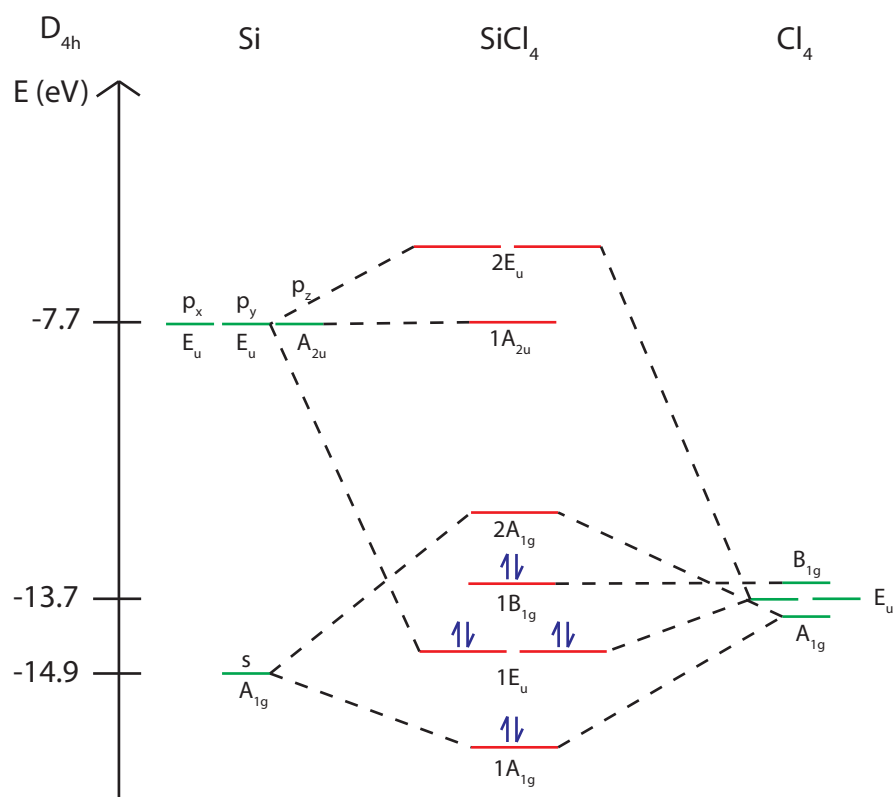


$$\hat{P}^{E_u}(H_1) = 4(\sigma_1 - \sigma_3)$$



$$\hat{P}^{E_u}(H_2) = 4(\sigma_2 - \sigma_4)$$





(b) It will be tetrahedral.

