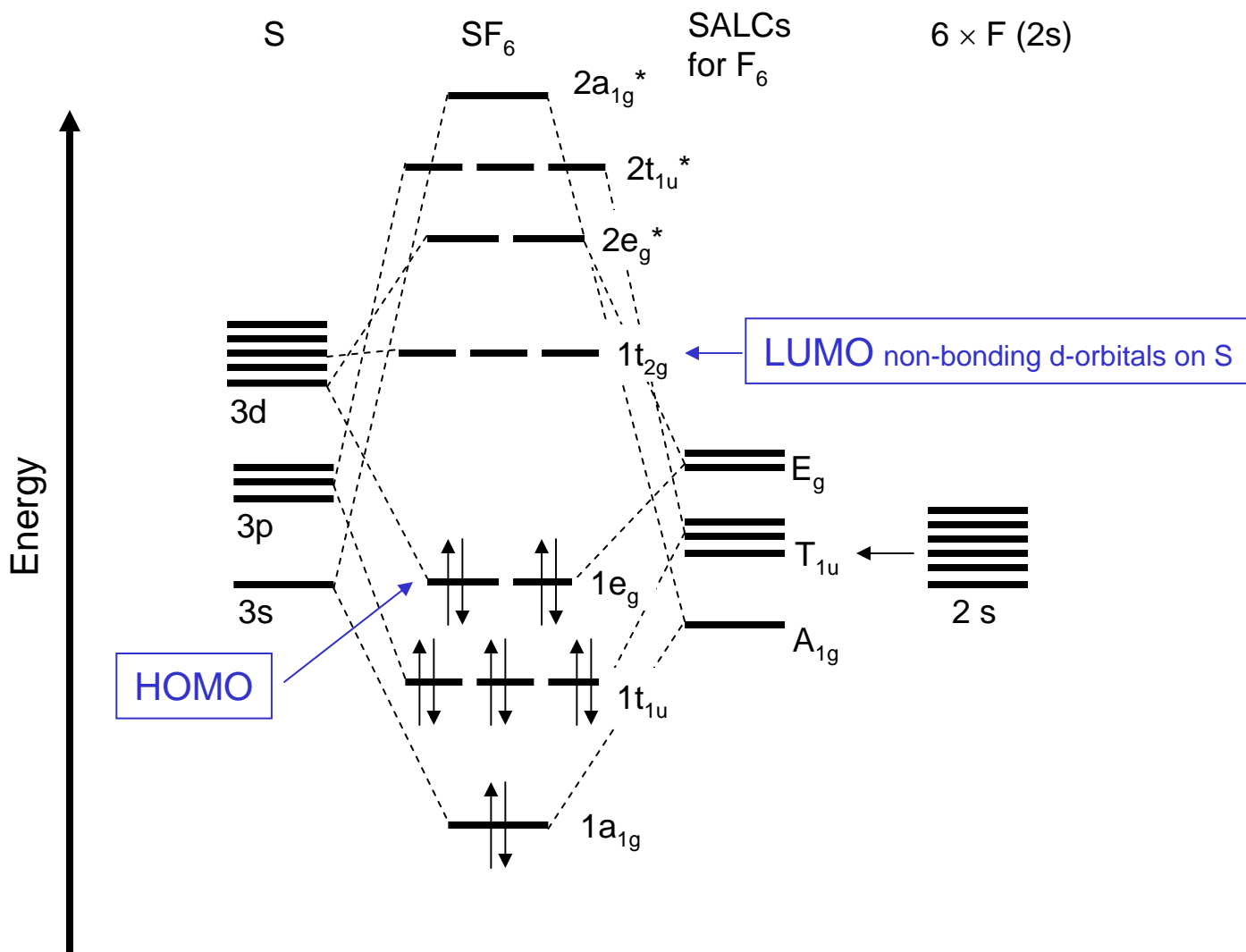


Question #1

Molecular Orbital Diagrams

Construct a valence MO diagram for the octahedral molecule SF₆; to simplify the problem, you should only use the 2s orbitals on the F atoms. Write an acceptable normalized LCAO for ONE of the MO's that you have produced.



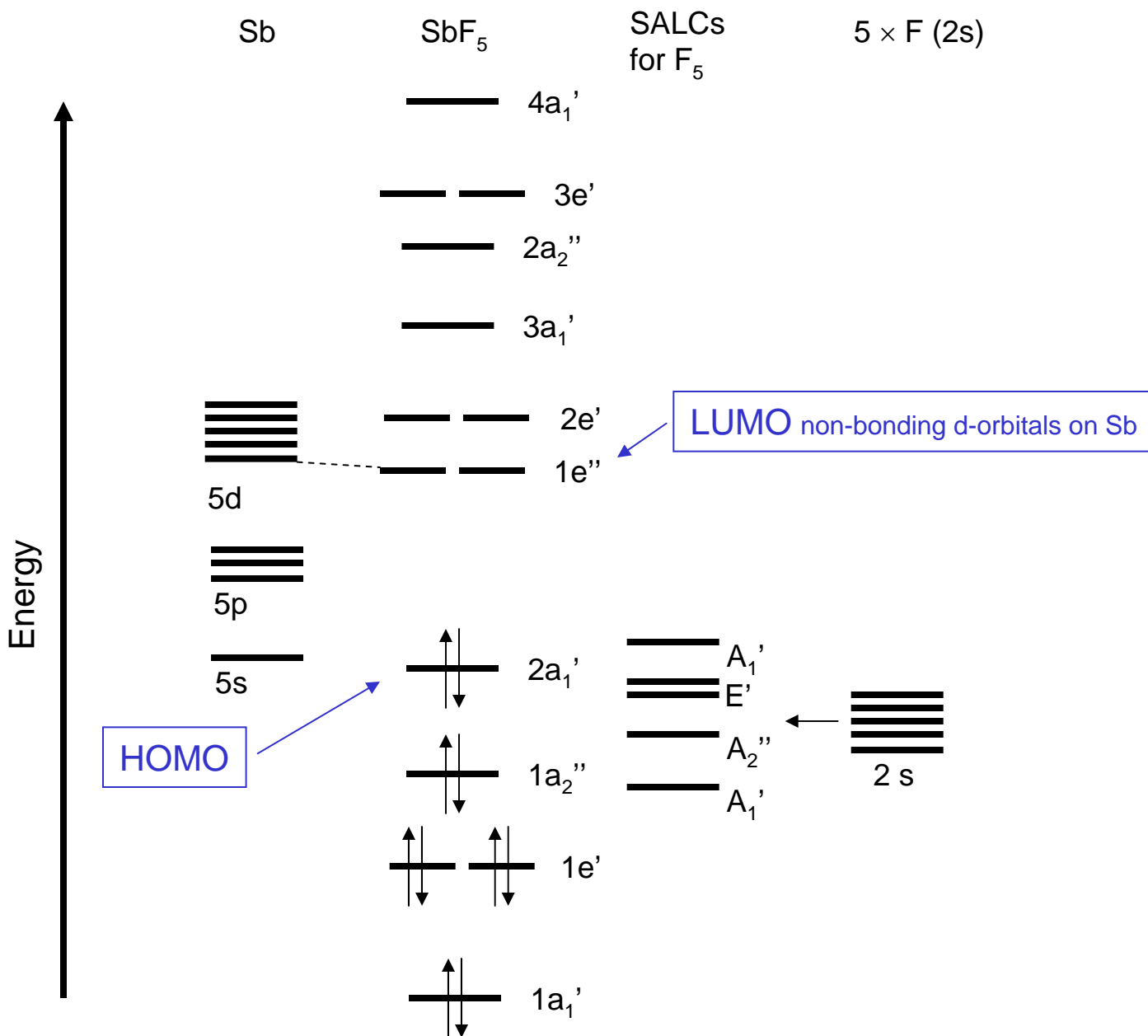
A reasonable LCAO for the most bonding MO is:

$$1a_{1g} = \sqrt{0.1} 3s_S + \sqrt{0.15} 2s_{Fa} + \sqrt{0.15} 2s_{Fb} + \sqrt{0.15} 2s_{Fc} + \sqrt{0.15} 2s_{Fd} + \sqrt{0.15} 2s_{Fe} + \sqrt{0.15} 2s_{Ff}$$

Question #2

Molecular Orbital Diagrams

Construct a valence MO diagram for the octahedral molecule SbF_5 ; to simplify the problem, you should only use the 2s orbitals on the F atoms. Write an acceptable normalized LCAO for ONE of the MO's that you have produced.



A reasonable LCAO for the most bonding MO (using the all in-phase A_1' combination from the F atoms) is:

$$1a_1' = \sqrt{0.3} 5s_{\text{Sb}} + \sqrt{0.14} 2s_{\text{Fa}} + \sqrt{0.14} 2s_{\text{Fb}} + \sqrt{0.14} 2s_{\text{Fc}} + \sqrt{0.14} 2s_{\text{Fd}} + \sqrt{0.14} 2s_{\text{Fe}}$$

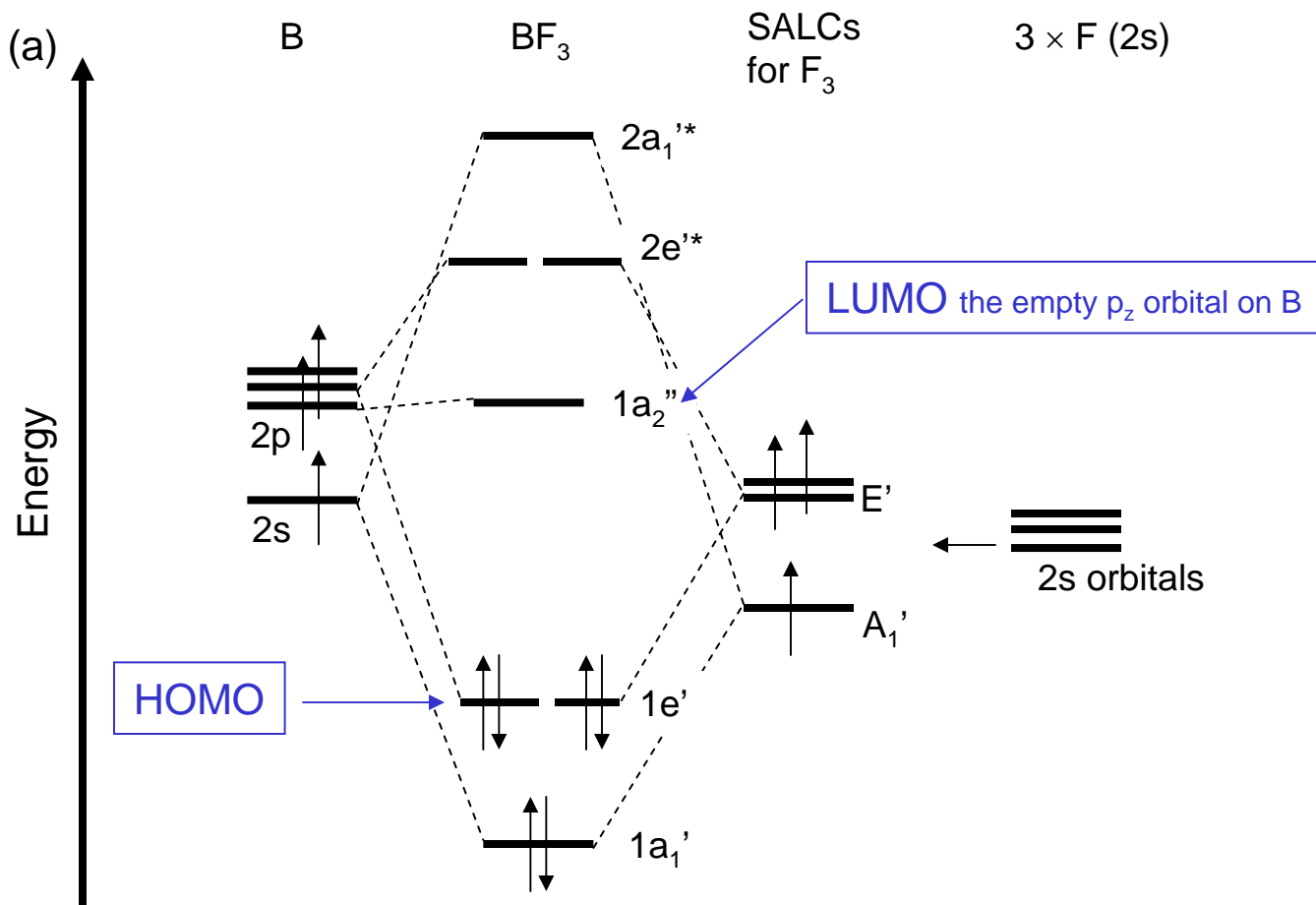
Question #3

Molecular Orbital Diagrams

(a) Construct a valence MO diagram for the σ bonding in the trigonal planar molecule BF_3 ; to simplify the problem, you should only use the $2s$ orbitals on the F atoms.

(b) Write an acceptable pair of normalized LCAO's for the most stable of the doubly-degenerate pairs of SALC's that you have produced for the F atoms and draw a reasonable picture of this pair of SALC's. Indicate which AO on B can interact with each of the SALC's that you drew.

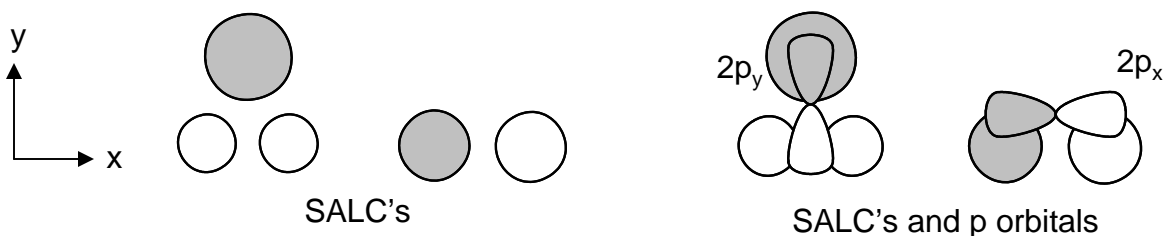
(c) Construct a valence MO diagram for the π bonding in the trigonal planar molecule BF_3 ; to simplify the problem, you should only use the $2p_z$ orbitals on the F atoms.



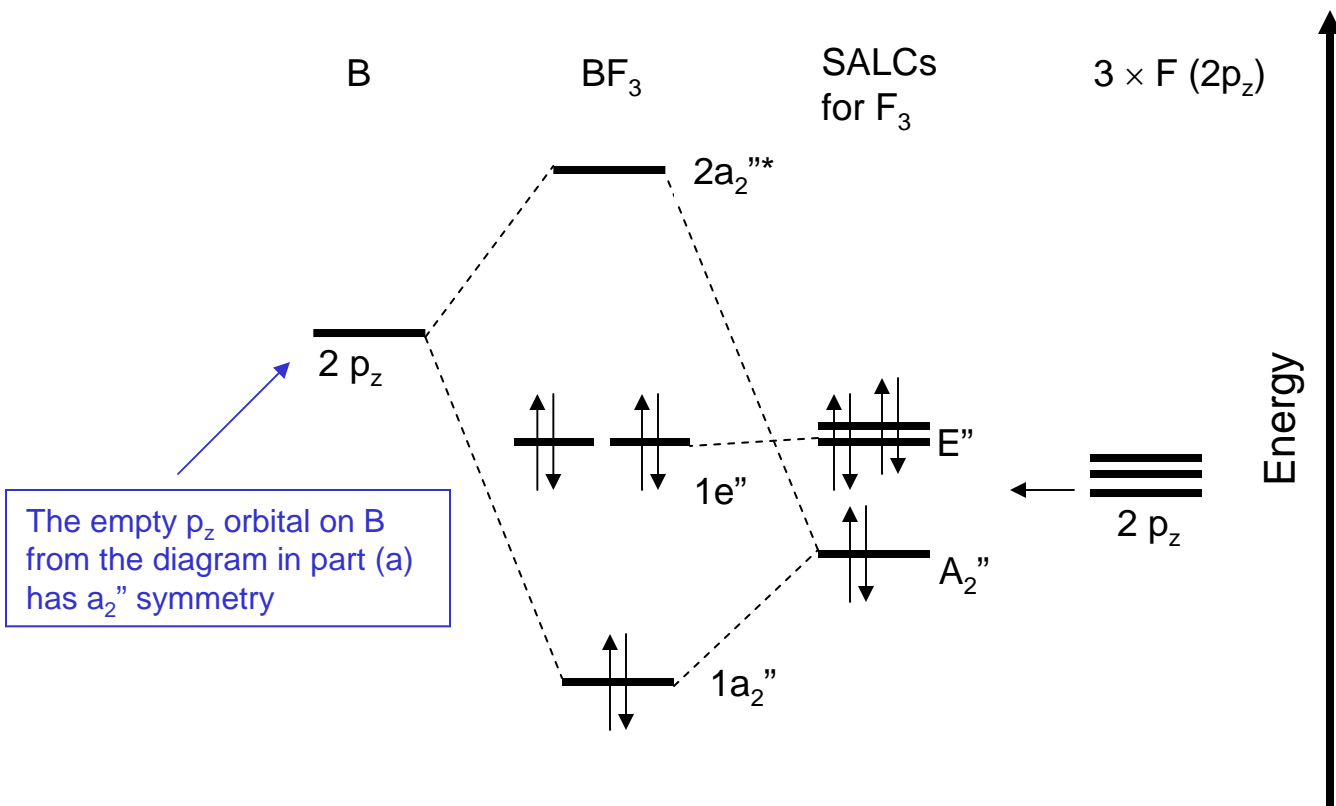
The 6 electrons come from the 3 valence electrons on B and one electron from each of the Cl atoms (as you would expect for a covalent bond).

$$(b) \quad e' = (1/\sqrt{2} 2s_B - 1/\sqrt{2} 2s_C) \quad e' = (2/\sqrt{6} 2s_A - 1/\sqrt{6} 2s_B - 1/\sqrt{6} 2s_C)$$

The pictures just must show that the SALC's are of the correct symmetry to interact with the $2p_x$ and $2p_y$ orbital on B (the choice of x and y axes in this example is arbitrary).



(c)



This diagram is essentially identical to the one in your notes for CO_3^{2-} and the SALCs and MO's will look the same. The only difference is that all 6 electrons come from the orbitals on F.

A complete MO diagram for BF_3 would include both the σ and π bonding together and would also have to include all the MO's derived from the other p orbitals on the F atoms (the ones that contain the lone pairs that are not involved in the π bonding). This makes for a messy and confusing diagram, which is why I asked you to draw separate diagrams.

Question #4

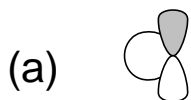
Use drawings and equations to estimate the values of the overlap integrals in the molecule F_2 for the combination of the following orbitals:

(a) $2s$ and $2p_x$

(b) $2s$ and $2p_z$

(c) $2p_x$ and $2p_x$

(d) $2p_y$ and $2p_x$



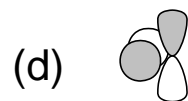
Not appropriate symmetry so $\int(\psi_{2sFa}) (\psi_{2pxFb})\delta\tau = 0$



σ symmetry so $\int(\psi_{2sFa}) (\psi_{2pzFb})\delta\tau \approx 0.3$



π symmetry so $\int(\psi_{2pxFa}) (\psi_{2pxFb})\delta\tau \approx 0.1$

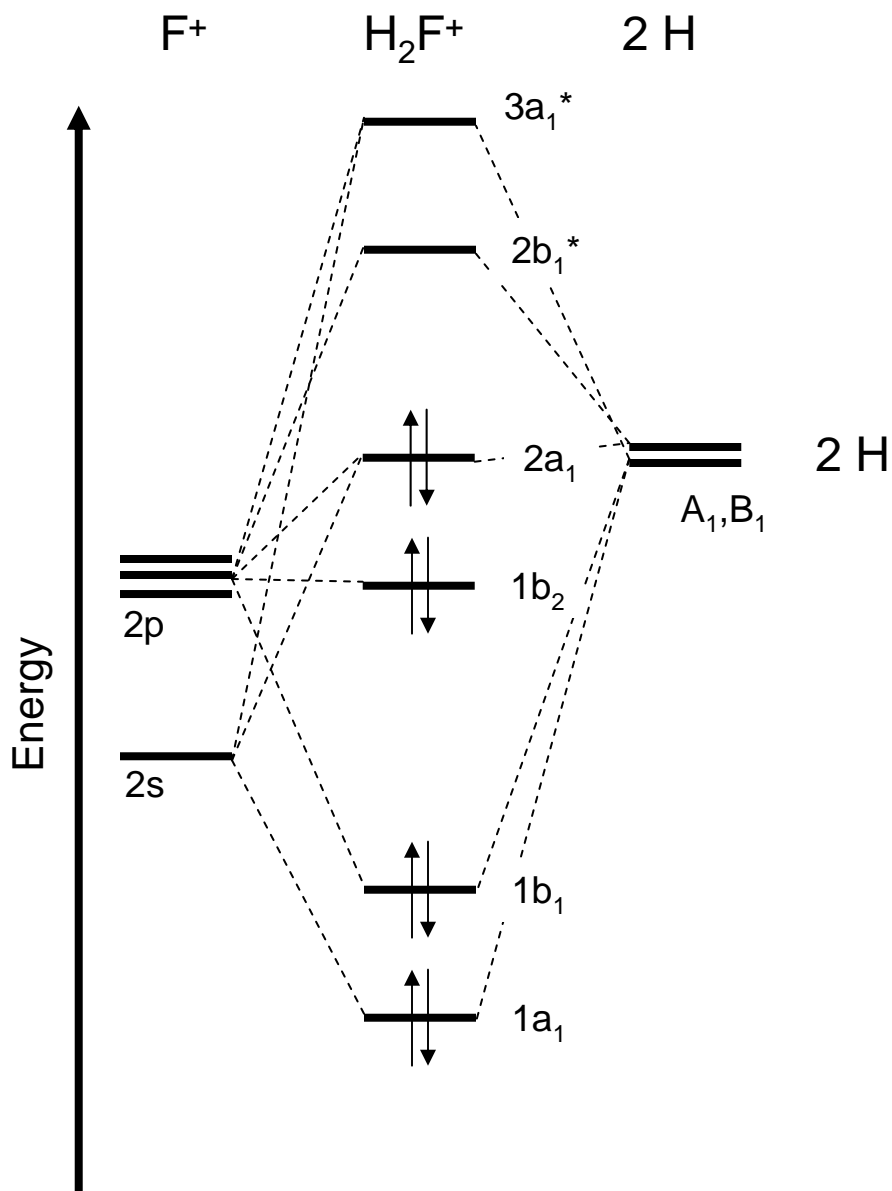


Not appropriate symmetry so $\int(\psi_{2pyFa}) (\psi_{2pxFb})\delta\tau = 0$

If you have drawn the orbitals reasonably consistently in each case (i.e. same nuclear separation and same size) you will see that there is significantly greater overlap in the sigma symmetry arrangement. This is why sigma bonds are usually stronger than pi bonds.

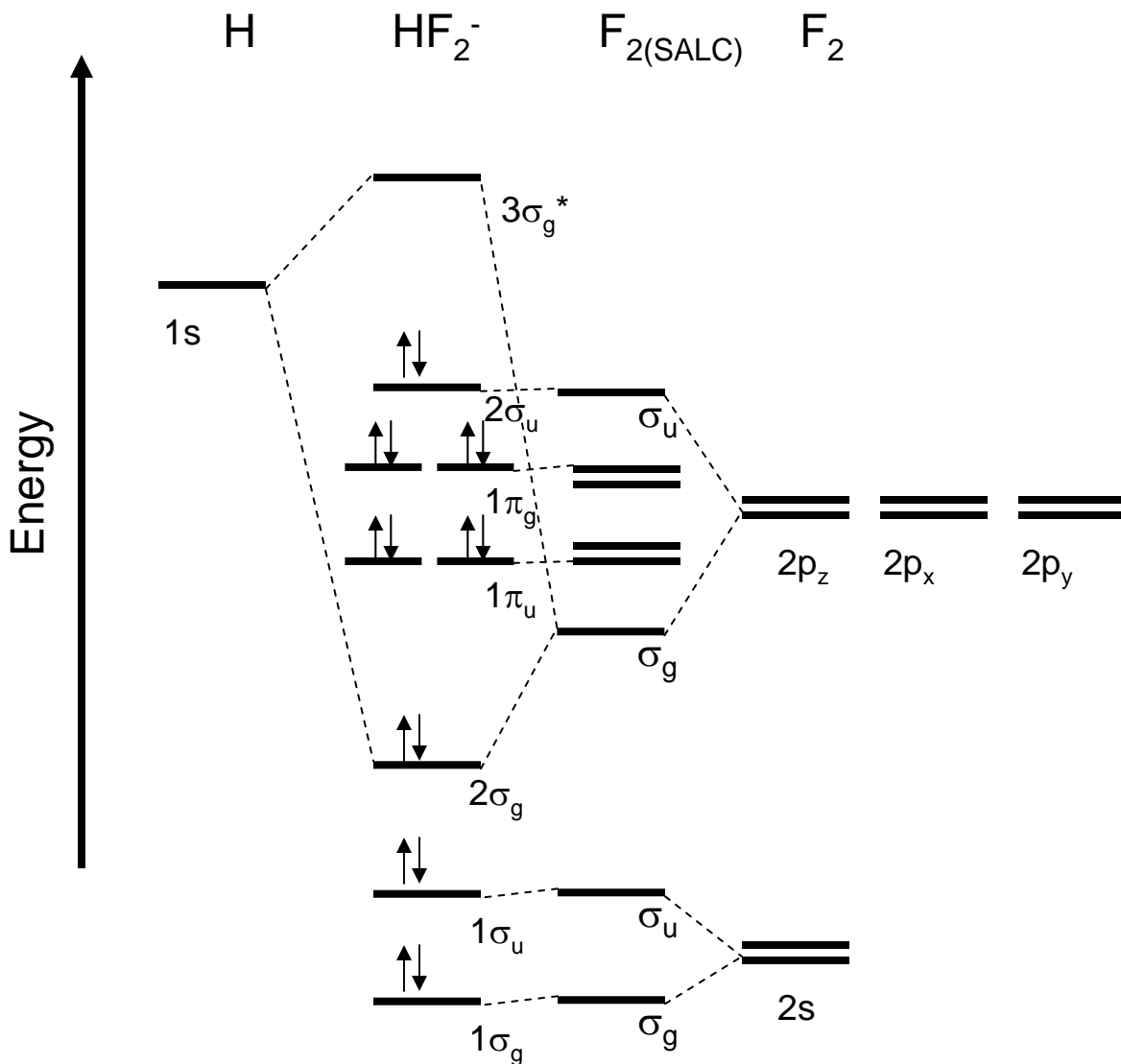
Question #5

Construct MO diagrams for (a) the cation $[\text{HFH}]^{+1}$ and (b) the anion $[\text{FHF}]^{-1}$. Use all the available valence orbitals and be sure to indicate and justify your choice of point group for each ion.



The labels in the diagram come from the point group C_{2v} (and the b_1 's and b_2 's can be interchanged, if you put the molecular plane in the y-axis instead of the x-axis). Please remember that the $1b_2$ and the $2a_1$ orbitals are "non-bonding"; the $1b_2$ orbital can not interact with either of the SALCs and the $2a_1$ MO is the one derived from the combination of 3 orbitals (and has essentially the same energy as when it started). The 8 electrons come from 6 on F^+ and 1 from each of the terminal H atoms.

FYI, the bond order is $(4-0)/2 = 2$, which means a BO of 1 for each H-F bond. This was not needed but is useful for comparison.



The labels in the diagram come from the point group $D_{\infty h}$, because there are only 2 objects around the central H atom ($AX_2 = \text{linear}$). I have assumed that the σ_g and σ_u orbitals derived from the 2s orbitals on the F atoms are too low in energy to participate in bonding with the 1s on the H atom and are thus non-bonding. Thus the bonding and anti-bonding orbitals come only from the interaction of the 1s orbital with the σ_g SALC from the 2p_z orbitals on the F atoms. The σ_u SALC from the 2p_z orbitals and the pairs of degenerate 1π_u and 1π_g orbitals are “non-bonding” and are based solely on the F atoms. The 16 electrons come from 7 on each F atom and 2 for the H⁺ ion.

The bond order in this ion is thus $(2-0)/2 = 1$, which means a BO of 0.5 for each H-F bond. Such an analysis can not be accomplished using only the Lewis structures.