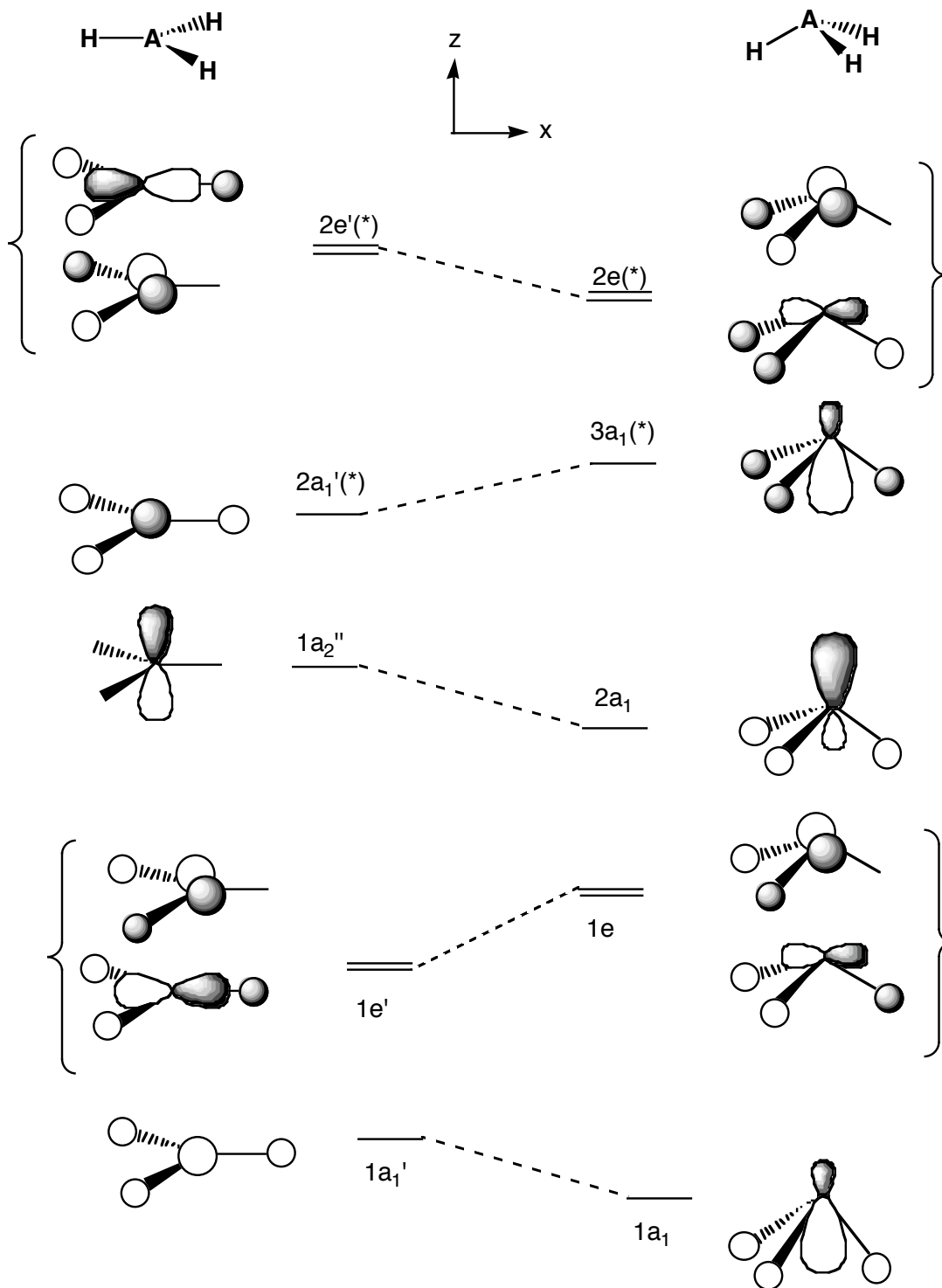


Chem 64 PS3 Solutions

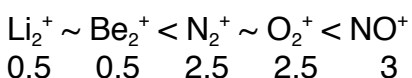
Problem 4.5. Walsh diagram (cut and pasted from the lecture handouts):
 Constructing a Walsh diagram from scratch is difficult, without detailed computation of MO energy levels.

AH₃ Planar/Pyramidal Correlation Diagram

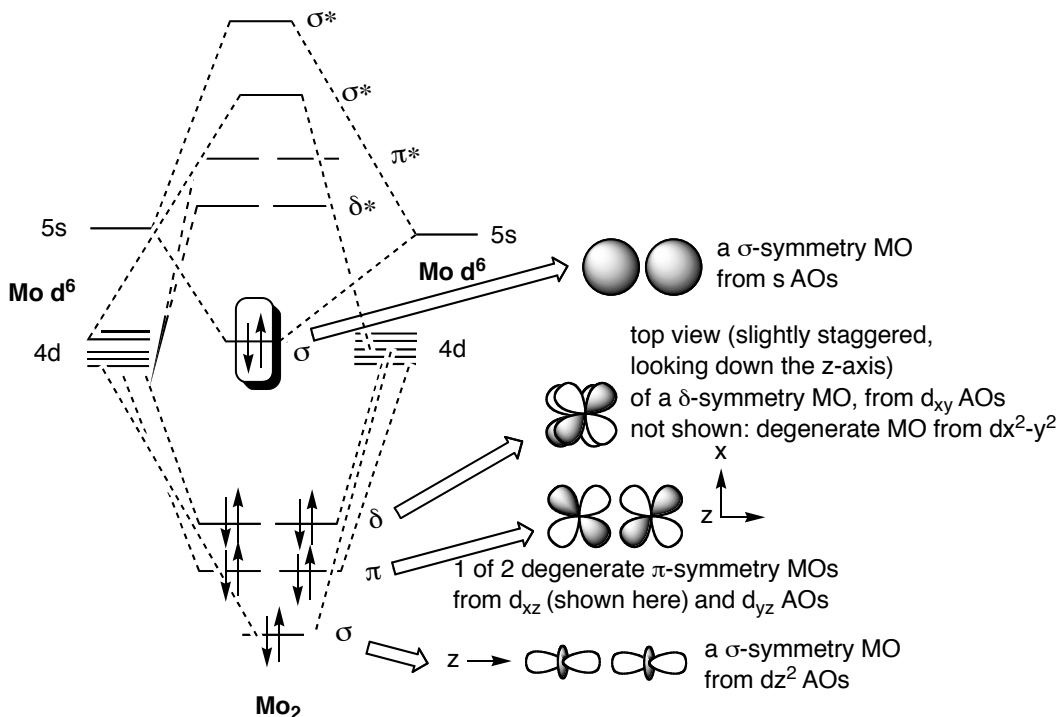


However, given such a diagram, you should be able to explain qualitatively why, for example, the $1a_1'$ energy goes down on pyramidalization (it becomes more bonding), or why the $1a_2''$ also decreases (starts off nonbonding, but becomes a bonding MO). Likewise, the $1e'$ pair becomes less bonding and goes up in energy. You can continue to play this game with all the MO's; the general approach is to see how an MO energy is expected to change as the structure is perturbed (for example, it could become more bonding (or less), or more antibonding (or less), etc).

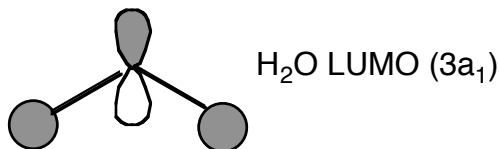
2. In each of these diatomics, a higher bond order is associated with a stronger bond and thus a higher bond dissociation energy (BDE). In order of increasing BDE (bond orders are given beneath the molecules):



3. Mo_2 . Only the 4d and 5s AOs are shown (assuming the 5p are too high in energy). Bonding MOs having σ , π , and δ symmetry are also sketched. The energy level ordering of the d-orbital derived MOs ($\sigma < \pi < \delta$) is the standard one. However, you can't tell the relative energies of the bonding σ (5s) MO [in the box] and the antibonding δ^* (4d) MO. Here I have shown $\sigma < \delta^*$, which gives an overall Mo-Mo bond order of $1/2 [2 + 4 + 4 + 2] = 6$, consistent with computational results. However, if these were reversed, two electrons would be in the antibonding d^* MO instead of the bonding s (5s) MO, and the bond order would be $1/2 [2 + 4 + 4 - 2] = 4$



4. (a) The MO diagram for water (bent) is found in a class handout. The HOMO is $1b_1$, a purely O-based $3p_x$ orbital.



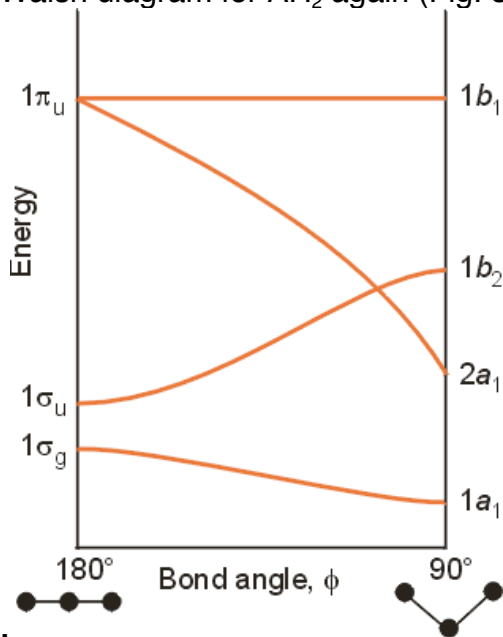
The first excited state of H_2O is formed by an electronic transition from the HOMO to the LUMO ($3a_1$). So we must consider the effects on the geometry of 2 things:

(a) Removing 1 electron from $1b_1$ -- since $1b_1$ is non-bonding, its population does not influence the geometry, so there will be no change.

(b) Adding 1 electron to $3a_1$. This MO is antibonding (see picture), and its energy would be lowered (i.e. it would be less antibonding) if the bond angle was increased.

So....the first excited state should be more linear (less bent).

(b) Now for BH_2 . The general Walsh diagram for XH_2 is shown below. Walsh diagram for AH_2 again (Fig. 3.38, p. 102)

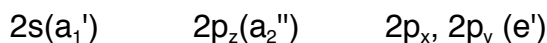


BH_2 has 5 electrons. As usual, start with the linear geometry. The HOMO is π_u , which will clearly be stabilized on bending. So the ground state of BH_2 should be bent.

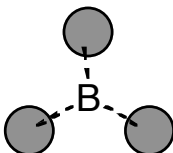
Now consider the first excited state. The answer (linear vs bent) will depend on the degree of bending, i.e. the energy crossover between $1b_2$ and $2a_1$. For convenience, just consider the middle of the diagram, where $2a_1$ is higher in

energy than $1b_2$. [This should be OK qualitatively since the strong geometric preference of $2a_1$ typically controls the geometry in these AH_2 molecules.] Then, excite an electron from the bent ground state $(1a_1)^2(1b_2)^2(2a_1)^1$ to the first excited state $(1a_1)^2(1b_2)^2(1b_1)^1$. The HOMO of this excited state is thus the nonbonding $1b_1$, which has no geometric preference. So look at the NHOMO. Now $2a_1$ is empty, so the next highest occupied MO (NHOMO) is $1b_2$. Its geometric preference is linear, so we predict that the 1st excited state of BH_2 is linear. [This is in fact found to be so by experiment].

5. This is a (much) more complicated problem than for BH_3 , solely because the basis set for the F ligands is more extensive than that for H ligands. The problem can be approached in exactly the same systematic way. First, the symmetries of the B valence AOs in BF_3 (D_{3h} symmetry) can be found in the D_{3h} character table:



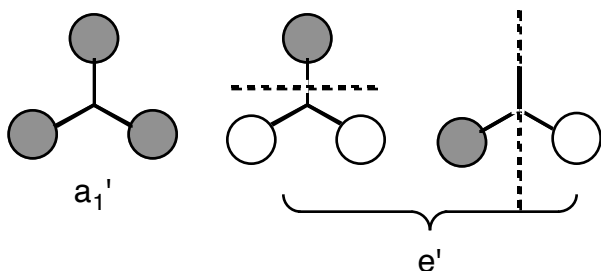
Now we have to obtain the SALCs for the F basis set. First, look at sigma bonding. Consider the 2s orbitals on the F atoms as a symmetry related set of 3 (see figure). Run it through all operations of the group, and reduce the resultant reducible representation to arrive at the symmetries of the SALCs.



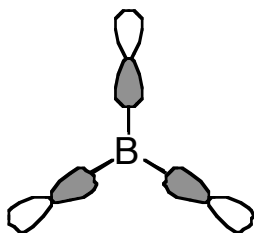
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_σ	3	0	1	3	0	1

$\Gamma_\sigma = a_1' + e'$. Look in appendix 4 (page 723 ff.) to find what these combinations of s orbitals look like:

note mutually perpendicular nodal planes



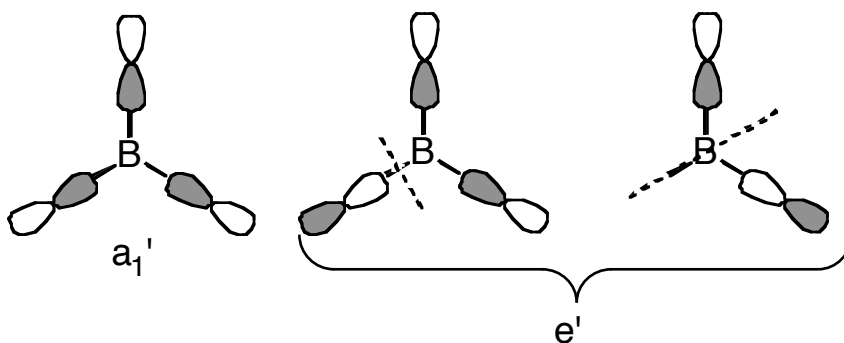
Next, repeat for the F 2p orbitals. Choose the x-direction for each F to point along the B-F bond. Then the basis will look like this for the $2p_x$ orbitals:



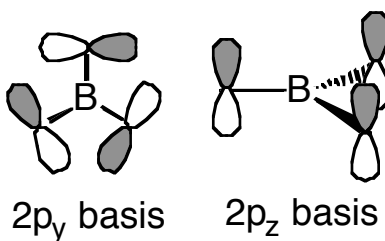
Run this through the group operations to obtain

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{2pz}	3	0	1	3	0	1

Note that this is the same symmetry ($a_1' + e'$) as that for the s-orbitals. The resultant combinations look like this:



Repeat for $2p_y$ and $2p_z$. The appropriate bases, reducible representations, and combinations are shown below.

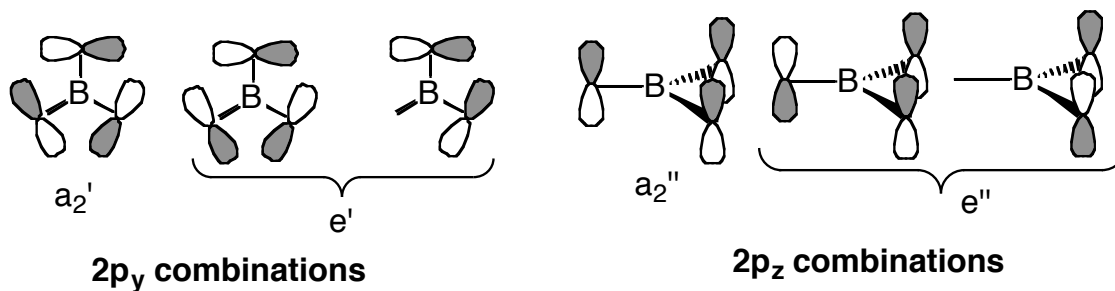


D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{2py}	3	0	-1	3	0	-1

$$\Gamma_{2py} = a_2' + e'$$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{2pz}	3	0	-1	-3	0	1

$$\Gamma_{2pz} = a_2'' + e'$$

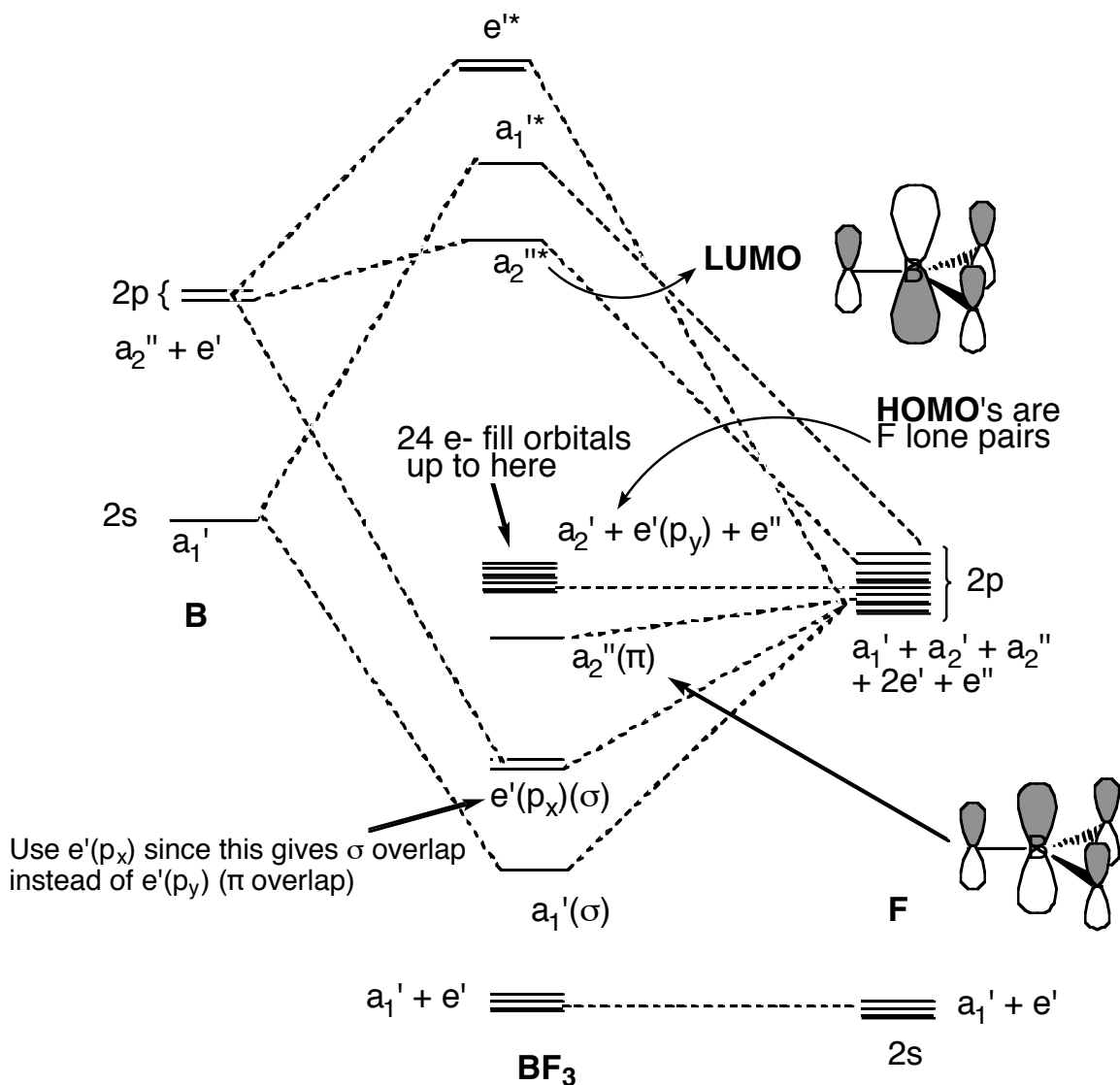


NET: Symmetry adapted linear combinations (SALCs)

$$2a_1' + 3e' + a_2' + a_2'' + e'' = 12 \text{ orbitals}$$

(recall that E orbitals are doubly degenerate)

Taking all of this you can get a qualitative MO diagram for BF₃ (first-order):



Note: we neglect overlap of B orbitals with the F_{2s} SALCS because of the large energy difference. So these orbitals ($a_1' + e'$) do not mix and are left at the bottom of the energy diagram.

Also note: since we already have B-F σ -bonding involving the F p_x AOs (e' symmetry), we neglect B-F π -bonding involving the p_y AOs of the same e' symmetry, assuming that σ -bonding is more important than π -bonding. We will see a similar approximation later for MOs of octahedral metal complexes.

An important qualitative conclusion: the B p_z orbital (LUMO of BH_3 , nonbonding) is stabilized by π -bonding to the F p-orbitals. This is relevant in describing the Lewis acidity of BF_3 .

No, you won't have to do something this complicated on the exam.