2.13: Problems

1. The ionization energy of a hydrogen atom is 1312 kJ/mol and the bond dissociation energy of the H_2^+ molecular ion is 256 kJ/mol. The overlap integral S for the H_2^+molecular ion is given by the expression $S = (1 + R/a_0 + R^2/3a_0^2)\exp(-R/a_0)$, where R is the bond distance (1.06 Å) and a_0 is the Bohr radius, 0.529 Å. What are the values of α and β (in units of kJ/mol) for H_2^+?

2. Compare the bond order in H_2^+ and H_2 using the molecular orbital energy diagram for H_2. The bond dissociation energy of the H_2 molecule is 436 kJ/mol. Explain why this energy is less than twice that of H_2^+.

3. What is the bond order in HHe? Why has this compound never been isolated?

4. Would you expect the Be_2 molecule to be stable in the gas phase? What is the total bond order, and how many net σ and π bonds are there?

5. Give a plausible explanation for the following periodic trend in F-M-F bond angles for gas-phase alkali difluoride (MF_2) molecules. (Hint - it has something to do with a trend in s- and p-orbital energies; see Chapter 1, section 1.2)

Compound	F-M-F angle (degrees)
BeF_2	180
MgF_2	158
CaF_2	140
SrF_2	108
BaF_2	100

6. The most stable allotrope of nitrogen is N_2, but the analogous phosphorus molecule (P_2) is unknown. Explain.

7. Using molecular orbital theory, show why the H_3^+ ion has a triangular rather than linear shape.

8. Use MO theory to determine the bond order and number of unpaired electrons in (a) O_2^-, (b) O_2^+, (c) gas phase BN, and (d) NO^-. Estimate the bond lengths in $O_2^-$and O_2^+ using the Pauling formula, and the bond length in the O_2 molecule (1.21 Å).

10. Compare the results of MO theory and valence bond theory for describing the bonding in (a) CN^- and (b) neutral CN. Is it possible to have a bond order greater than 3 in a second-row diatomic molecule?

11. The C_2 molecule, which is a stable molecule only in the gas phase, is the precursor to fullerenes and carbon nanotubes. Its luminescence is also responsible for the green glow of comet tails. Draw the molecular orbital energy diagram for this molecule. Determine the bond order and the number of unpaired electrons.

12. Use the Pauling formula to estimate the bond order in C_2 from the bond distance, 1.31 Å. The C-C single bond distance in ethane is 1.54 Å. Does your calculation agree with your answer to problem 11? What bond order would valence bond theory predict for C_2?

13. Draw the MO diagram for the linear $[FHF]^-$ ion. The only orbitals you need to worry about are the frontier orbitals, i.e., the H 1s and the two F sp_z hybrid orbitals that lie along the bonding (z) axis. What is the order of the HF bonds? What are the formal charges on the atoms?

14. The cyclooctatetraene (cot) molecule (picture a stop sign with four double bonds) has a puckered ring structure. However in $U(cot)_2$, where the oxidation state of uranium is 4+ and the cot ligand has a formal charge of 2-, the 8-membered rings are planar. Why is cot^{2-} planar?