Homework 5

1. When one electron is added to an oxygen molecule, a superoxide ion (O_2^-) is formed. The addition of two electrons gives a peroxide ion (O_2^{2-}) . Removal of an electron from leads to O_2^+.
(a) Construct the correlation diagram for O_2^-.
(b) Give the valence electron configuration for each of the following species: O_2^+ , O_2 , O_2^- , O_2^{2-}
(c) Give the bond order of each species.
(d) Predict which species are paramagnetic.
(e) Predict the order of increasing bond dissociation energy among the species.

2. Describe the hybrid orbitals on the chlorine atom in the ClO_4^- and ClO_3^- molecular ions. Sketch the expected geometries of these ions.

3. Formulate the MO structure of (NO_2^+) for localized π bonds and de-localized π bonds. Is it linear or nonlinear? Do you expect it to be paramagnetic? Repeat the analysis for NO_2 and for NO_2^-.

4. Discuss the nature of the bonding in the nitrate ion (NO_3^-) . Draw the possible Lewis resonance diagrams for this ion. Use the VSEPR theory to determine the steric number, the hybridization of the central N atom, and the geometry of the ion. Show how the use of resonance structures can be avoided by introducing a de-localized π MO. What bond order is predicted by the MO model for the N-O bonds in the nitrate ion?

5. (a) Sketch the occupied MOs of the valence shell for the N_2 molecule. Label the orbitals as σ or π orbitals, and specify which are bonding and which are antibonding.
(b) If one electron is removed from the highest occupied orbital of N_2, will the equilibrium N-N distance become longer or shorter? Explain briefly.

6. According to recent spectroscopic results, nitramide is a nonplanar molecule. It was previously thought to be planar.
(a) Predict the bond order of the N-N bond in the nonplanar structure.
(b) If the molecule really were planar after all, what would be the bond order of the N-N bond?