Molecular Modeling Problems

Part D. Electron and Spin Densities

1. CPK Models vs. Electron Density Surfaces for Hydrocarbons. Do the sizes and shapes of molecules depicted by simple space-filling (CPK) models reflect those based on electron density surfaces? Obtain electron density surfaces for methane, ethane, propane, *n*-butane, *n*-pentane and *n*-hexane that enclose 99% of the total number of electrons. Use the HF/6-31G* model. Plot the volumes of these surfaces against the volumes of the corresponding space-filling models. Is there a reasonable correlation?

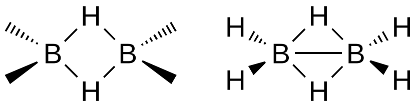
2. Sizes of Alkali Metal Cations. Compare electron density surfaces for lithium, sodium and potassium cations that enclose 99% of the total number of electrons. Use the HF/6-31G* model. Which is smallest and which is largest? Rationalize what you observe. How do the calculated radii compare with the usual van der Waals radii of the three elements? (The radii may be obtained from the calculated volumes.)

3. Sizes of Hydride and Halide Anions. Compare electron density surfaces for hydride, fluoride chloride and bromide anions that enclose 99% of the total number of electrons. Use the HF/6-31G* model. Which is smallest and which is largest? Rationalize what you observe. How do the calculated radii compare with the usual van der Waals radii of the three elements? (The radii may be obtained from the calculated volumes.)

4. Methyl Anion, Ammonia and Hydronium Cation. Methyl anion (CH_3^-), ammonia and hydronium cation (H_3O^+) are isoelectronic, in that all three have 8 valence electrons. Does this mean that they are the same size? To tell, compare electron density surfaces that enclose 99% of the total number of electrons. Base these on equilibrium geometries obtained from the HF/6-31G* model. If the three sizes are different, which is smallest and which is largest? What is the percentage change in volume from the smallest to largest? Rationalize what you observe.

Repeat your calculations and analysis for the corresponding second-row systems: silyl anion (SiH_3^-), phosphine (NH_3) and sulfonium cation (H_3S^+). Is the (percentage) change in volume noted here smaller, larger or about the same as noted for the first-row compounds?

5. Bonding in Diborane. Which Lewis structure, that lacking or including a boron-boron bond, provides the better description of diborane?

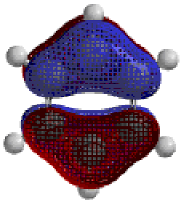


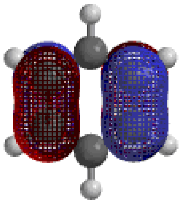
To decide, examine the electron density surface for diborane in between the two boron atoms. Is it convex (suggesting buildup of electron density) or concave (suggesting depletion of density)? Use the B3LYP/6-31G* model and choose a surface that encloses 40-50% of the total number of electrons.

6. Hydrocarbon Radicals. Loss of hydrogen atom from a hydrocarbon leads to a neutral radical. The common wisdom is that the more delocalized the unpaired electron, the less likely the radical is to react. This is the idea behind the clinical use of so-called antioxidants, molecules that can donate a hydrogen atom to a reactive (and potentially destructive) radical leading to a stable (and presumably less destructive) radical.

Use the B3LYP/6-31G* model to obtain equilibrium geometries for ethyl radical (from ethane), vinyl radical (from ethylene), ethynyl radical (from acetylene) and phenyl radical (from benzene), and compare spin density surfaces. For which, does the unpaired appear to be most localized? For which does it appear to be most delocalized? Obtain equilibrium geometries for ethane, ethylene, acetylene and benzene (as well as hydrogen atom) and calculate CH bond energies. Do the bond dissociation energies parallel the extent to which the spin is delocalized in the corresponding radicals?

7. Benzene Radical Cation. Ionization of benzene results in removal of an electron from the highest occupied molecular orbital which, in this case, is a pair of degenerate (equal energy) molecular orbitals.





This breaks the degeneracy and as a consequence necessarily leads to distortion away from six-fold symmetry. Use the B3LYP/6-31G* model to obtain the geometry of benzene radical cation. You need to start from a structure that has been distorted from six-fold symmetry. Does the resulting structure show delocalized bonds (as benzene) or is there significant bond alternation? Elaborate. Examine the spin density for benzene radical cation. What if anything does it tell you about where the electron was removed from?

8. Triplet Methylene: The ground state of methylene (CH_2) is known to be a triplet. If triplet methylene is linear, the 2p orbitals on carbon not involved in CH bonding ($2p_x$ and $2p_y$ were the molecule oriented on the z axis), would be equivalent and each could hold one of the unpaired electrons.

Use the B3LYP/6-31G* model to obtain the geometry for linear triplet methylene. Does the spin density reflect this simple picture? Distort and display the spin density.

Distort your structure away from a linear geometry and redetermine the geometry? Does it return to a linear structure? If not, compare the spin density for bent triplet methylene with that for the linear molecule. How has it changed?