CHEM 1422 - Homework # 9-10
Gaussian & GaussView
Due Thursday, April 30 (by 4:00 PM)

Please download Gaussian 03 and GaussView 4 from Tigerware (located under Scientific Software, Chemistry software) and install on your Windows computer. Up to 3 people can work together on this assignment. Macintosh users should pair up with those with PC/Windows computers. Submit one copy of your report and don’t forget to put all the names of those working together on the report. All reports should be typed, formatted nicely, and include color images (when possible).

Prof. Stanley is available to answer questions about Gaussian & GaussView. Separate instructions for using GaussView and Gaussian have been posted by Prof. Stanley.

The last part of this assignment is the same as that given to the 1431 Honors Chemistry Lab students. This double assignment will count for 60 pts.

1. **(40 pts)** Do DFT molecular orbital calculations on perchloric, sulfuric, and phosphoric acids (optimize, DFT, B3LYP, 6-311G(d) basis set). Make sure you select a single d function on your basis set.

   ![Molecules](image1.png)

   **Questions:**

   a) Capture and display the optimized molecules with their Mulliken charges.

   b) Show the electrostatic surface potential plots using a density value of 0.04. Adjust the color scale for perchloric acid to best represent the atomic charges, then use the same numerical ranges for displaying the other two molecules.

   c) Do the charges tell you anything about the acidity of the molecule? Note that the calculation is done in “vacuum” with no solvent molecules around – a proton will not dissociate without water molecules to interact with. Discuss any correlation of the charges calculated with the acidity of the molecules.

   d) List and compare the bond distances for the 3 molecules in table format and discuss how they compare to the “localized” structures drawn above. Do the bond distances fit any periodic trends?

   e) Show the highest occupied molecular orbital (HOMO) for each molecule along with its energy in eV. Discuss and explain the trend (if any) in the energies of the HOMO’s (lower is more stable) for these three molecules with periodic properties and what we discussed in class for oxyacids. Discuss what kind of bonding, non-bonding (lone pair), or antibonding interactions are occurring within the HOMO for each molecule. Although one might expect hybrid orbitals (e.g., sp^3) for some of these, MO calculations often tend to display orbitals as more or less pure s, p, etc. For example, an oxygen lone pair is more likely to show up as a p orbital.
2. (20 pts) Shirakura & Suginome published a paper in the *Journal of the American Chemical Society* (2008, 130, 5410-5411) on nickel catalyzed coupling of silylacetylenes with dienes:

![Catalysis Reaction](image)

The first step in the catalysis is the oxidative addition (breaking) of the alkyne C-H bond to the nickel atom to make a nickel-hydride-alkynyl complex:

\[
\text{Me}_3\text{Si} \equiv \text{C} \equiv \text{C} - \text{H} + \text{Ni} \rightarrow \text{Ni} \equiv \text{C} \equiv \text{C} - \text{SiMe}_3
\]

In order for a C-H bond to do an oxidative addition to a Ni metal center the orbital associated with the C-H bond must be reactive enough to want to participate in this reaction. The higher the energy of the orbital the more reactive it will be (usually).

This reaction apparently does not work for regular alkynes that do not have silyl groups attached.

Use Gaussian (optimization, DFT, B3LYP method, 6-311G basis set) to perform calculations on the following alkyne molecules:

- \[\text{H} \equiv \text{C} \equiv \text{C} - \text{H}\]
- \[\text{H}_2\text{C} \equiv \text{C} \equiv \text{C} - \text{H}\]
- \[\text{H}_3\text{Si} \equiv \text{C} \equiv \text{C} - \text{H}\]

**Questions:**

a) Identify the highest energy (C≡)C-H bonding orbital (# from calculation), list the energy of each in eV, and show a picture of this molecular orbital for each alkyne.

b) How does the energy of the orbital from question # 2 affect the C-H bond strength? How does the group attached to the other side of the alkyne affect this energy?

c) List and compare the energies (in eV) of the alkyne \(\pi\)-bonding orbitals for each system and show a picture of one of these molecular orbitals for each alkyne. Although these aren’t directly involved in the C-H bond breaking step discussed above, what factor seems to be affecting the energy of these orbitals?