Molecular Modeling Problems

Part E. Atomic Charges and Electrostatic Potential Maps

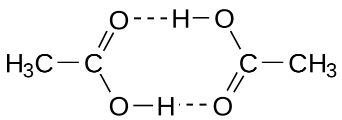
1. Atomic Charges and Atomic Electronegativities. Are charges anticipated by atomic electonegativities? Use the HF/6-31G* model to calculate equilibrium geometries and charges for first-row hydrides: LiH, BH_3, CH_4, NH_3, H_2O and HF, second-row hydrides: NaH, AlH_3, SiH_4, PH_3, H_2S and HCl as well as HBr. Plot the charge on hydrogen against the electronegativity of the atom to which it is bonded. (You can add H_2 to you plot without having to do any calculations.) Is there a simple relationship between the two quantities? Elaborate.

2. Dipole Moments for Ammonia and Trifluoroamine. Why is the dipole moment in ammonia (1.47 debyes) much larger than that in trifluoroamine (0.23 debyes)? Is it because the HNH bond angle in ammonia is smaller than the FNF bond angle in trifluoroamine? Is it because NH bonds are polarized with nitrogen at the negative end in the same direction as the nitrogen lone pair, whereas NF bonds are polarized with nitrogen at the positive end opposite to the direction of the lone pair? To help you decide, calculate equilibrium for ammonia and trifluoroamine using the B3LYP/6-31G* model. Is the HNH bond angle smaller than the FNF bond angle? Compare electrostatic potential maps for the two molecules. Is there a marked difference in polarity of the two molecules?

3. Ordering the Acidities of Ammonia, Water and Hydrogen Fluoride. In the gas phase, hydrogen fluoride is a stronger acid than water, which in turn is a stronger acid than ammonia. Is the trend in acidities reflected in the value of the electrostatic potential (at hydrogen) in the three molecules? To decide, obtain geometries and electrostatic potential maps for the three molecules using the HF/6-31G* model. Display the maps side-by-side on the same color scale with hydrogen clearly exposed.

4. Weak vs. Strong Acids. Ethanol is an example of a very weak acid, acetic acid of a moderately strong acid and sulfuric and nitric acids of very strong acids. Obtain geometries and electrostatic potential maps for these molecules using the HF/6-31G* model. Display the maps side-by-side on the same color scale with the acidic hydrogen clearly exposed. Do the maps reveal the known ordering of acid strengths in these compounds? Use electrostatic potential maps to try to identify compounds that are stronger acids than the nitric or sulfuric acid.

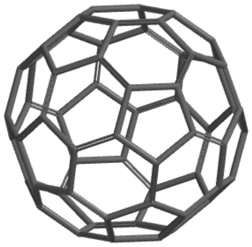
5. Acetic Acid Dimer. Acetic acid forms a symmetrical hydrogen-bonded dimer.



Obtain equilibrium geometries for acetic acid and its dimer using the HF/6-31G* model. Display electrostatic potential maps for the two side-by-side and on the same color scale.

Is there evidence for charge transfer away from the acidic hydrogen in acetic acid onto to oxygen to which it hydrogen bonded?

6. Inside Buckyball. Buckmeister fullerene, more commonly known as or buckyball or C_{60}, is a fascinating molecule on several grounds. For one, it is a form of elementary carbon, distinct from the other two known forms (graphite and diamond). It should be noted, however, that C_{60} is just one of several ball-shaped molecules that have come to light in the past two decades. There are perhaps many elementary forms of carbon!



Second, buckyball has been shown to be able to encapsulate a number of atoms and small molecules which are then unable to diffuse out. The obvious question is how the molecules get inside. The answer is that they don't "get in". Rather, buckyball needs to be formed from around them. The size of the cavity (and by inference the maximum size of a molecule that can be encapsulated) can be estimated using the known geometry of buckyball and the van der Waals radius of carbon. However, there is no way to assess the environment presented to a molecule held inside the cavity, and to know whether it will be more "hospitable" to neutral molecules or to cations or anions. An electrostatic potential map should provide insight.

A file containing the electrostatic potential map for C_{60} is available in ***buckyball electrostatic potential map***. The map has been sliced in half to allow the electrostatic potential for not only the outside but also the inside of buckyball to be seen. For comparison, the electrostatic potential map for benzene is provided alongside. The two maps are on the same scale (-100 to 100 kJ/mol).

Relative to benzene, does the map for the "outside" of C_{60} show more or less charge variation than the map for benzene? Would you expect it to be more or less soluble than benzene in non-polar solvents? In polar solvents? Elaborate. According to the electrostatic potential map, is the "inside" environment of C_{60} significantly different from the "outside" environment? Would cations, anions or neutral atoms and molecules be best accommodated inside of buckyball?

7. **S_N2 Reaction of Chloride and Methyl Bromide.** Electrostatic potential maps are not limited to stable molecules but can also be applied to transition states and more generally to the sequence of structures connecting reactants and products. Consider, for example, S_N2 reaction of chloride anion with methyl bromide leading to methyl chloride and bromide anion

$$Cl^- + CH_3Br \rightarrow CH_3Cl + Br^-$$

Use the HF/6-31G* model to obtain an energy profile. Start with chloride 3.5Å from the carbon in methyl bromide and move it in steps of 0.1Å to 1.7Å. Plot both the energy and the energy corrected for the effect of aqueous environment vs. the CCl distance (the "reaction coordinate"). Is the reaction *endothermic* or *exothermic* in the gas phase? How do the solvent corrections affect overall *endo* or e*xothermicity*? Does this preference maintain as the energies are corrected for the effect of aqueous solvent? Are your results consistent with the observation that bromide is a better leaving group than chloride? Elaborate.

Examine electrostatic potential maps for the structures along the reaction profile, with particular focus on the reactants and products and on the transition state. For which (reactant, product or transition state) is the charge most localized? For which is it most delocalized? What does this say about the relative abilities of Cl and Br to act as leaving groups? Does the energy along the reaction pathway appear to correlate with the extent to which charge is delocalized? Elaborate. Does the change in energy due to the solvent correction correlate with the extent to which charge is delocalized? Elaborate.

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