

Spring Semester 2006

*Christopher J. Cramer*Lecture 33, April 17, 2006**Solved Homework**

The assignment was to compare and contrast HF/STO-3G calculations on H₂O and H₂S.

One issue is that S is the chalcogen below O in the periodic table. Thus, it has eight more electrons: its valence electrons are 3s and 3p and it has a filled 2s and 2p core. There will thus be 4 additional occupied orbitals.

To accommodate the larger S atom, we will need 4 more basis functions (one 3s, three 3p).

So, for each of 9 total occupied MOs, we will have 11 coefficients for 11 basis functions, compared to water, which was 5 occupied MOs formed from 7 basis functions.

Note, though, that the two systems are what is called "valence isoelectronic". That is, except for core orbitals (where S adds 4 more), the MOs should be very similar. So, we expect the four highest energy molecular orbitals in hydrogen sulfide to be very similar to those for water. There should be an all bonding σ orbital lowest, a one-node σ orbital next, an in-plane lone pair next, and an out-of-plane lone pair last.

Total energy? Much more negative for hydrogen sulfide, since it has core electrons bound to a nucleus of total charge 16.

Bond lengths? Sulfur bonds through valence orbitals that are 3s and 3p instead of 2s and 2p. With higher quantum numbers, orbitals decay more slowly with distance from the nucleus and are more "spread out". So, bonding overlap between hydrogen 1s orbitals and sulfur 3s and 3p orbitals occurs further from the sulfur nucleus than from the oxygen nucleus with its 2s and 2p orbitals. Typical H–S bond distances are about 1.35 Å, compared to H–O distances of just under 1 Å.

Bond angle? A somewhat tricky question, to be honest. The answer is that, with increasing principle quantum number, the energy separation between s and p orbitals increases, so that bond orbitals tend to involve more p character and less s character. Because p orbitals have angles between them of 90 deg, this tends to reduce bond angles. Hydrogen sulfide thus has a narrower bond angle than water. By the time one gets to hydrogen selenide, the bond angle is already quite close to 90 deg exactly.

Dipole moment? In this case, we don't need to know much about quantum mechanics, necessarily. It's enough to know that sulfur is less electronegative than oxygen (the rule is that elements that are up and/or to the right in the periodic table are more electronegative than atoms that are down and/or to the left). As such, there will be less polarization in each S–H bond than in the O–H bonds, so the dipole moment will decrease. Similarly, we expect the Mulliken charges to be smaller (much smaller, actually, since the bond distance lengthening will otherwise tend to contribute to an *increase* in dipole moment).

Review and Catch-up

I'll try to give a recapitulation of key points to be covered by Exam IV, but I am particularly eager to field questions from the class. Please be prepared to ask about any issues that you have found confusing or unclear!

Homework (n/a, study for Exam IV)

Sample Exam Problems

1. In a restricted Hartree-Fock calculation on ethane (C_2H_6), how many occupied MOs will be used to construct the HF wave function?

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|-------|-------|
| (a) 3 | (e) 9 |
| (b) 2 | (f) 6 |
| (c) 5 | (g) 7 |
| (d) 8 | (h) 4 |

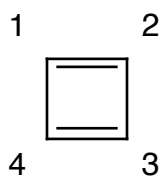
2. What is the name for *any* kind of surface defined by $\left\langle \Psi \left| \frac{q}{r} \right| \Psi \right\rangle = C$ where C is a constant and q is a test charge on the surface?

- | | |
|---------------------------|---------------------------|
| (a) isodensity surface | (e) Lennard-Jones surface |
| (b) isopotential surface | (f) isoenergy surface |
| (c) van der Waals surface | (g) isotired surface |
| (d) isometric surface | (h) reentrant surface |

3. Which of the below statements about the overlap matrix \mathbf{S} in Hartree-Fock calculations is/are *not* true?

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|---|--|
| (a) The matrix is $N \times N$ where N is the number of basis functions | (e) If \mathbf{S} is unchanged after a self-consistent-field step, the HF calculation is converged |
| (b) The matrix elements depend on the molecular geometry | (f) (c) and (e) |
| (c) For all m, n , $S_{mn} = S_{nm}$ | (g) (a), (d), and (e) |
| (d) $-1 \leq S_{mn} \leq 1$ for all matrix elements of \mathbf{S} | (h) All of the above |

4. Which of the following statements is/are *not true* about a Hückel theory calculation for 1,3-cyclobutadiene (shown with atom numbering below)?



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|--|-----------------------|
| (a) There are four occupied MOs in the final wave function | (e) $H_{11} = S_{11}$ |
| (b) $H_{23} = H_{14}$ | (f) (a) and (c) |
| (c) $H_{13} = S_{13}$ | (g) (a) and (e) |
| (d) The terms in the secular determinant have dimension 4×4 | (h) (b) and (e) |