Chem 30324, Spring 2025, Homework 8

Due April 4, 2025

1. The overlap between two 1s orbitals on A and B can be shown to be:

$$S = \left\{ 1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2 \right\} e^{-R/a_0}$$

Plot out the overlap as a function of the internuclear distance R. Qualitatively explain why it has the shape it has.

2. The overlap functions for other pairs of orbitals are more complicated, but the general features are easily inferred. Neatly sketch the orbital overlap between a 1s orbital on A and $2p_z$ orbital on B as a function R. Carefully indicate the limiting values as $R \to 0$ and $R \to \infty$.

3. Choose some other pair of atomic orbitals on A and B and sketch out their overlap as a function of R. Carefully indicate the limiting values as $R \to 0$ and $R \to \infty$.

4. What property besides overlap determines whether two atomic orbitals will form a bond?

5. For each pair, draw a Lewis dot structure. Indicate which bond is stronger in the pair, and give a very brief rationalization:

(a) H_2 vs LiH

(b) N_2 vs H_2

(c) N_2 vs CO

(d) H_2 vs He_2

Computational chemistry.

Today properties of a molecule are more often than not calculated rather than inferred. Quantitative molecular quantum mechanical calculations require specialized numerical solvers like Orca. Following are instructions for using Orca with the Webmo graphical interface.

Now, let's set up your calculation (you may do this with a partner or partners if you choose):

1. Log into the Webmo server https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi using "guest" as your username and password.
2. Select New Job-Creat New Job.
3. Use the available tools to sketch a molecule.
4. Use the right arrow at the bottom to proceed to the Computational Engines.
5. Select Orca
6. Select "Molecular Energy," "B3LYP" functional and the default def2-SVP basis set.
7. Select the right arrow to run the calculation.
8. From the job manager window choose the completed calculation to view the results.

The molecule you are to study depends on your last name. Choose according to the list:

- A-G: **CO**
- H-R: **BN**
- S-Z: **BeO**

For your convenience, here are the total energies (in Hartree, 27.212 eV/Hartree) of the constituent atoms, calculated using the B3LYP DFT treatment of v_{ee} and the def2–SVP basis set:

Atom	Energy	Atom	Energy
B	−24.61703	N	-54.51279
Be	-14.64102	O	-74.98784
C	-37.79271	F	-99.60655

6. Construct a potential energy surface for your molecule. Using covalent radii, guess an approximate equilbrium bond length, and use the Webmo editor to draw the molecule with that length. Specify the "Molecular Energy" option to Orka and the def2–SVP basis set. Calculate and plot out total molecular energy vs. bond distance in increments of 0.05 Å about your guessed minimum, including enough points to encompass the actual minimum. (You will find it convenient to subtract off the individual atom energies from the molecular total energy and to convert to more convenient units, like eV or kJ/mol.) By fitting the few points nearest the minimum, determine the equilibrium bond length. How does your result compare to literature?

7. Use the quadratic fit from Question 6 to determine the harmonic vibrational frequency of your molecule, in cm^{-1}. Recall that the force constant is the second derivative of the energy at the minimum, and that the frequency (in wavenumbers) is related to the force constant according to

$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

8. Use your results to determine the zero-point-corrected bond energy of your molecule. How does this model compare with the experimental value?

Computational chemistry, part deux

Diatomics are a little mundane. These same methods can be used to compute the properties of much more complicated things. As example, the OQMD database http://oqmd.org/ contains results for many solids. We don't have time to get this complicated in class, but at least you can compute properties of some molecules.

9. Working with some of your classmates, compute the equilibrium structures of C_2H_6, C_2H_4, and C_2H_2. Compare their equilibrium C-C bond lengths. Do they vary in the way you expect?

1. Log into the Webmo server https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi using "guest" as your username and password.
2. Select New Job–Creat New Job.
3. Use the available tools to sketch a molecule. Make sure the bond distances and angles are in a plausible range.
4. Use the right arrow at the bottom to proceed to the Computational Engines.
5. Select Orca
6. Select "Geometry optimization," "B3LYP" functional and the default def2–SVP basis set.
7. Select the right arrow to run the calculation.
8. From the job manager window choose the completed calculation to view the results.

10. Compute the corresponding vibrational spectra. Could you distinguish these molecules by their spectra?

1. Log into the Webmo server https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi using "guest" as your username and password.
2. Select the job with the optimized geometry and open it.
3. Use the right arrow at the bottom to proceed to the Computational Engines.
4. Select Orca
5. Select "Vibrational frequency," "B3LYP" functional and the default def2–SVP basis set.
6. Select the right arrow to run the calculation.

7. From the job manager window choose the completed calculation to view the results.

11. Compute the structure and energy of H$_2$. Use it to compare the energies to hydrogenate acetylene to ethylene and ethylene to ethane. Which is easier to hydrogenate? Can you see why selective hydrogenation of acetylene to ethylene is difficult to do?

The two-state system.

Consider a closed system containing N objects, each of which can be in one of two energy states, of energy either 0 or ε. The total internal energy U of the box is the sum of the energies of the individual objects.

Boltzmann

12. Write down all the possible microstates for a box in which $N = 4$ and the internal energy $U = 2\varepsilon$.

13. What does the postulate of *equal a priori probabilities* say about the relative likelihood of occurance of any one of these microstates?

14. What is the entropy of the box? (Thank you, Ludwig Boltzmann.)

15. Suppose two identical such boxes are brought into thermal contact and allowed to come to equilibrium. Calculate the change in internal energy ΔU and in entropy ΔS associated with this process.