

Chem 30324, Spring 2017, Homework 9

Due April 19, 2017

Multi-electron atoms and the self-consistent field.

Modern calculations on atom and molecules take advantage of the variational principle and are made with sophisticated computer programs that solve the many-electron Schrödinger equation. *Density functional theory* (DFT) is the most common set of approximations for the electron-electron interactions used today. In this problem you'll do a DFT calculation using the *Gaussian* program (<http://www.gaussian.com> (<http://www.gaussian.com>)).

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

1. Log into the Webmo server <https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi> (<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 draw an argon (Ar) atom on the screen.
4. Use the right arrow at the bottom to proceed to the Computational Engines.
5. Choose Gaussian
6. Select "Molecular Orbitals" for the Calculation type, "B3LYP" for theory, "Minimal" for the basis set, "0" for the charge, and "Singlet" for the multiplicity.
7. Select the right arrow to run the calculation.
8. From the job manager window choose the completed calculation to view the results.

1. Write down the energies of the occupied molecular orbitals and identify them by their shell ($n = 1, 2, \dots$) and subshell (s, p, d, ...). For fun, click on the Magnifying Glass icons to see the molecular orbitals in 3-D. You may have to play around with the Display Settings and Preferences to get good views.

You are welcome to play around with other atoms. For anything other than the noble gases, be sure to set the Multiplicity to a sensible value.

Molecular Orbitals.

The orbitals in molecules can be constructed from linear combinations of atomic orbitals on the constituent atoms (in this context, the atomic orbitals are called “basis functions”). One of the factors that determines whether two atomic orbitals can form a molecular orbital is their ability to overlap. Consider two atoms, A and B, aligned on the z axis and separated by a distance R .

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 $R \rightarrow 0$ and $R \rightarrow \infty$.

3. Ditto for 1s orbital on A and $2p_x$ orbital on B.

4. Ditto for $2p_z$ orbital on A and $2p_z$ orbital on B.

5. Ditto for $2p_z$ orbital on A and $3d_z^2$ orbital on B.

6. What property besides overlap determines whether two atomic orbitals will form a molecular orbital?

The Hückel model and π orbitals

One of the first successes of molecular orbital theory was application to the π systems of conjugated hydrocarbons. (See Roberts, Notes on Molecular Orbital Theory (<http://resolver.caltech.edu/CaltechBOOK:1961.001>).) In the Hückel model, one constructs a π -only secular matrix and uses simple rules for the matrix elements. $S_{ii} = 1$ for a basis function with itself and $S_{ij} = 0$ otherwise. $F_{ii} = \alpha$ for a basis function with itself, $F_{ij} = \beta$ between adjacent atoms, and $F_{ij} = 0$ otherwise.

1. Construct and solve the secular matrix for cyclopentane, C_5H_5 . Make an energy level diagram for the π system.

2. Use back-substitution to determine the coefficients for each molecular orbital.

3. Predict the spin-multiplicities of $C_5H_5^+$, C_5H_5 , and $C_5H_5^-$. In which one do you expect all the C-C distances to be the same?

Make sure you understand how to do these procedures. The math can get tedious, however, so here is a snippet of python code appropriate to butadiene. You would have to customize to cyclopentene.

```
In [1]: from sympy import *
```

```
In [2]: init_printing(use_unicode=True)
```

```
In [3]: alpha,beta = symbols('alpha beta')
```

```
In [4]: M=Matrix([[alpha, beta, 0 , 0],[beta, alpha, beta, 0],
[0,beta,alpha,beta],[0,0,beta,alpha]])
```

```
In [5]: M
```

```
Out[5]:
```

$$\begin{bmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{bmatrix}$$

In [6]: `M.eigenvects()`

$$\text{Out[6]: } \left[\left(\alpha - \frac{\beta}{2} + \frac{\sqrt{5}\beta}{2}, 1, \begin{bmatrix} \frac{4}{(1+\sqrt{5})(-\sqrt{5}+1)} \\ -\frac{2}{1+\sqrt{5}} \\ \frac{2}{1+\sqrt{5}} \\ 1 \end{bmatrix} \right), \left(\alpha + \frac{\beta}{2} + \frac{\sqrt{5}\beta}{2}, 1, \begin{bmatrix} -\frac{4}{(1+\sqrt{5})(-\sqrt{5}+1)} \\ -\frac{2}{-\sqrt{5}-1} \\ -\frac{2}{-\sqrt{5}-1} \\ 1 \end{bmatrix} \right), \right. \\ \left. \left(\alpha - \frac{\sqrt{5}\beta}{2} - \frac{\beta}{2}, 1, \begin{bmatrix} -\frac{4}{(-1+\sqrt{5})(1+\sqrt{5})} \\ \frac{2}{-1+\sqrt{5}} \\ -\frac{2}{-1+\sqrt{5}} \\ 1 \end{bmatrix} \right), \left(\alpha - \frac{\sqrt{5}\beta}{2} + \frac{\beta}{2}, 1, \begin{bmatrix} \frac{4}{(-1+\sqrt{5})(1+\sqrt{5})} \\ -\frac{2}{1+\sqrt{5}} \\ -\frac{2}{1+\sqrt{5}} \\ 1 \end{bmatrix} \right) \right]$$

In []: