Electron Wavefunctions:
Calculations of Methylene using HF, MP2 and DFT

Introduction

In this exercise you will carry out various types of calculations of the methylene molecule. At the lowest level, you will do Hartree-Fock calculations where the wave function is a single Slater determinant. Then, a more accurate, post-HF, calculation will be carried out using a perturbation theory estimate of the correlation energy, so-called MP2 calculations. Finally, you will use a density functional theory (DFT) approach and carry out such calculations with two different functionals, a gradient dependent functional, BLYP, and then with a hybrid functional, B3LYP (which involves a linear combination of DFT and HF calculations).

The methylene molecule

The story of the experimental and theoretical efforts towards an understanding the basic properties of the CH_2 molecule is often cited as one of the early triumphs of large scale electron wavefunction calculations (see the article by H. F. Schaefer III in Science, **231**, 1100 (1986)). In the late 1960's both experimental and theoretical (i.e. analytical rather than 'computational') studies had concluded the molecule in its triplet ground state (with two unpaired electrons) is linear. Earlier pioneering computations by Foster and Boys (1960) had, however, indicated a bent geometry. This was sometimes cited as a clear indication of the difficulty of carrying out numerical calculations with sufficient accuracy. Subsequent *ab initio* calculations of higher and higher accuracy confirmed the prediction of a bent geometry. High level calculations of Schaefer and coworkers in 1972 predicted the angle to be $134 \pm 2°$. Later, various experimental measurements also indicated bent geometry. Re-evaluation of the early spectroscopic studies also confirmed the consistency with bent geometry. This established some credibility for *ab initio* calculations.

The energy difference between the triplet ground state and the lowest energy excited singlet state also became a matter of controversy between experimentalists and computational chemists. This energy difference is often referred to as the singlet/triplet splitting. Various experiments gave different results, ranging from 2 $kcal/mol$ to 20 $kcal/mol$. Early *ab initio* calculations gave 11.5 $kcal/mol$ but were not taken seriously by many scientists. The bond angle in the singlet state is much smaller than in the triplet state.

A. The bond angle of methylene, CH_2, in the triplet state:

Set up a calculation of the CH_2 molecule in Spartan. Select **File**, **New** and the **Inorganic** mode (the default is 'Organic' mode). Select a C atom forming two bonds. Select **Save** under the **File** menu and then exit the molecule builder (by clicking on **V** in the menu bar). The CH_2 molecule should be displayed on the screen.

Carry out HF calculations of the ground, triplet state of the molecule. Remember to set the multiplicity to 3. Record the energy and bond angle of the molecule using the various basis sets available in Spartan. The energy can be found from the **Display** and **Output** menu. The calculated bond angle can be found by selecting **Angle** under the **Geometry** menu, and then clicking on the atoms in the molecule, one after the other, using the left mouse button.

The calculations become more accurate as the basis set is extended. Typically, one should increase the basis set until the quantity that is being computed converges, that is, does not change upon further improvement of the basis set. In this and later calculations in this exercise, increase the basis set until convergence is obtained. Keep track of how the numbers converge as more Gaussians are added to the basis set and present in a table.

Q1: Make a table of the calculated energy and angle for the triplet state of CH_2 using the various basis sets in HF calculations.

Q2: Explain what the difference is between the various basis sets and identify the simplest basis set that gives 'converged' results.

Q3: How well does the calculated bond angle agree with experiment (the experimental estimates can be found in the article of Schaeffer)? What could be the reason for discrepancy between the calculated and experimentally measured value?

The Hartree-Fock calculations use only a single Slater determinant wavefunction. Each electron only sees the average effect of the other electrons. So, no matter how large a basis set is used, an approximation is being made in the functional form of the wave function. The difference between the best calculation with a single determinant wavefunction (the Hartree-Fock limit) and the true, non-relativistic wavefunction is called *correlation* energy. The reason for this name is that what is missing in the HF approximation is the fact that the probability of finding a given electron in any particular part of space should be correlated with the simultaneous (not just averaged) position of the other electrons. Electron correlation can be introduced in the wave function by taking a linear combination of the ground state HF Slater deteriminant and the excited Slater determinants corresponding to excited electron configurations. This is referred to as 'configuration interaction'. Another approach is to add correlation with perturbation theory. The second order perturbation calculation is referred to as MP2. Spartan offers the possibility of doing MP2 calculations.

Q4: Explain what the MP2 method involves.

Carry out MP2 calculations and record the energy and angle predicted by the calculations. Then, repeat the calculations above using density functional theory (DFT) calculations. In particular, use the BLYP functional which is a commonly used gradient dependent functional (belongs to the family of functionals that collectively get referred to as 'generalized gradient approximation', GGA). Also, do calculations using the B3LYP hybrid functional. In each case check how large a basis set is needed to reach convergence.

Q5: How large is the correlation energy in the triplet state of CH_2 according to the MP2, BLYP and B3LYP approximations?

B. Bond angle of CH_2 in the excited, singlet state and singlet/triplet splitting:

Carry out HF, MP2, BLYP and B3LYP calculations of the excited, singlet state using large enough basis sets. Record and make a table of the energy of the singlet state, the singlet/triplet splitting and bond angle in singlet state. In each case note which basis set was used.

Q6: How well does the predicted bond angle compare with experiment? Which level of theory gives the best prediction?

Q7: It is an important rule never to subtract two numbers obtained with different basis sets. Why is that? (make sure you calculate the singlet-triplet splitting by subtracting two numbers obtained with the same level of theory, including the exact same basis set)

Q8: How well do the calculations compare with experimental estimate of the singlet/triplet splitting? What could be the reason for the large discrepancy between the HF prediction and experimental estimates? (Recall the discussion of HF and the different contribution of electron pairs with parallel spins and those that are spin paired)?

Q9: How important is correlation energy for determining the singlet/triplet splitting (give a numerical estimate)? Is it likely that adding more correlation to the wavefunction beyond MP2 (i.e. to go to higher order perturbation corrections) would further affect the singlet/triplet splitting?

Q10: Which one of the methods used in this exercise gives the best agreement with experimental data?

D. Further discussion

Q11: Why is the ground state of CH_2 a triplet state (make a reference to the Hartree-Fock expression for the total energy).

Q12: Predict the hybridization of the carbon in the singlet state and in the triplet state of CH_2. Can you use this to rationalize the bond angle in singlet and triplet CH_2? What range in bond angle do the VSEPR rules predict for the singlet and triplet CH_2?