# Structure and Singlet-Triplet Splitting of Methylene

In this exercise, you will carry out Hartree-Fock calculations of the methylene molecule, $CH_2$. Recall, that the Hartree-Fock calculations use a single Slater determinant as trial function and are, therefore, highly approximate. The results you obtain here are not in close agreement with best experimental or theoretical estimates (which now do agree quite well). Later, you will use higher level methods to get more accurate estimates, in particular post-Hartree-Fock calculations based on perturbation theory or configuration inter- action calculations involving variational optimization of a linear combination of several Slater determinants. You will check how large the set of basis functions needs to be to reach full flexibility in the orbitals, i.e. the Hartree-Fock limit for a single Slater determinant calculation. Read the lecture notes on basis sets (see 'Ie. More about basis sets' on the course web page). But, the basic rule is: More is better.

The story of the experimental and theoretical studies of the $CH_2$ molecule is often cited as one of the early triumphs of electron wavefunction calculations (see the review article by H. F. Schaefer III in Science, **231**, 1100 (1986)). In the late 1960's both experimental and theoretical (i.e., analytical theory 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 (or even impossibility) of constructing a numerical solution of the Schrödinger equation for electrons in molecules (so called *ab initio* calculations, i.e., calculations where no experimental information about chemical bonds is used as input) with sufficient accuracy. Subsequent numerical calculations of higher and higher accuracy, however, confirmed the prediction of a bent geometry. Eventually, the experiments were reinterpreted and found to be consistent with bent geometry. Ironically, the VSEPR model, which is now taught in first year chemistry courses (but is not that old) can be used to get quite good estimates of the geometry of the molecule, in both the triplet ground state and the first excited state which is a singlet.

The energy difference between the triplet ground state and the lowest energy singlet state (the first excited state of the molecule) also became a matter of controversy between experimentalists and computational chemists. Such 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. Read the review article by Schaefer to learn about the best estimates of the ground state geometry and singlet/triplet splitting. The bond angle in the singlet state was, furthermore, a matter of controversy. The best current estimate for the singlet state bond angle is 102°.

## A. The bond angle of methylene in the ground state

In this first part, you carry out Hartree-Fock calculations of the ground, triplet state of the methylene molecule and record the energy and geometry obtained with several basis sets.

It is possible to display coordinates, distances, angles and dihedral angles in ChemCraft by selecting one, two, three and four atoms, respectively. The geometric properties are displayed in the geometry editor. Alternatively, you can display structural information alongside the molecule by going to **View→Structural Parameters**. You can also read the bond angle from the output file of a calculation. The Z matrix of the final geometry can be found below the last occurrence of **INTERNAL COORDINATES (ANGSTROEM)**.

Construct a methylene $CH_2$ molecule and do an equilibrium structure search with the minimal basis set, STO-3G. Create a new ORCA input file. Select triplet, i.e., a spin multiplicity of **3**. Run the calculation. When it has finished, record the angle and the total energy.

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 does not change. Then convergence is reached with respect

to the basis set and Hartree-Fock results are obtained (while we should really refer to calculations with incomplete basis set as SCF calculations). In this part and later calculations in this exercise, increase the basis set until convergence is reached. In particular, carry out the calculations using the following basis sets: **3-21G**, **6-31G**, **6-311G**, **6-311G\***, **6-311G\*\***, **6-311++G\*\***, **6-311++G(2d,2p)**, **6-311++G(2df,2pd)**, **6-311++G(3df,3pd)**.

To run a calculation using a larger basis set, you can simply copy the input file (and job-script) to a new directory and substitute the basis set keyword in the input file. It is good practice to use a geometry obtained from a smaller basis set as an initial guess for a calculation using a larger basis set, to save computational effort. When you have finished the 6-31G calculation, use the final structure obtained with this basis set as the initial structure for the next larger set, etc.

> **Q1:** *Present a table in your report, showing the calculated energy and angle of the triplet state $CH_2$ using the various basis sets.*

> **Q2:** *Explain the difference 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 the discrepancy between calculated and experimentally measured values?*

> **Q4:** *Consider starting with a linear geometry of the $CH_2$ molecule and then carrying out geometry optimization. Would this lead to different results for the bond angle? Explain.*

The Hartree-Fock calculations use only a single Slater determinant trial function. Each electron is subject to only the average interaction with the other electrons. So, no matter how large a basis set is used, a crude approximation is being made in the functional form of the wave function. The difference in energy obtained with the best single determinant wave function (the Hartree-Fock limit) and the true, non-relativistic wave function is called *correlation* energy. The reason for this name is that the missing feature in the Hartree-Fock approximation is the fact that the probability of finding an electron in any particular part of space should be correlated with the instantaneous (not averaged) position of the other electrons. Electron correlation can be included in electronic structure calculations in various ways and you will do that in later exercises using so-called 'post-Hartree-Fock' methods. In this exercise, you only do Hartree-Fock calculations.

# B. Bond angle in first excited state and singlet/triplet splitting

Carry out Hartree-Fock calculations of the excited, singlet state using the same basis sets as in part A. Note, that this excited state is a 'ground state' within the subspace of singlet states, so it can be obtained by carrying out a 'ground state calculation' with the constraint that the spin state is a singlet (analogous to doing a variational calculation for a harmonic oscillator using only odd trial functions).

Repeat the calculations of part A for the singlet state. Record the energy and angle of the optimized geometry for each basis set. Calculate the 'singlet-triplet splitting', i.e., the energy difference between the two states.

> **Q5:** *Present a table in your report showing the calculated energy and angle of the singlet state $CH_2$ as well as the singlet-triplet splitting using the various basis sets.*

> **Q6:** *How does the predicted singlet-triplet splitting using the Hartree-Fock approximation compare with the best estimate (see the article by Schaeffer)? What could be the reason for the discrepancy? (Recall the discussion of exchange-correlation and the Fermi hole).*

> **Q7:** *How does the predicted bond angle using the Hartree-Fock approximation compare with the current best estimate?*

**Q8:** *It is an important rule to add or subtract only numbers obtained at the same level of theory, in particular with the same basis set. Why is that? (make sure you follow that rule in the calculations of the singlet-triplet splitting).*

# C. Discussion

**Q9:** *Why is the ground state of $CH_2$ a triplet state? (recall the expression for the contribution of each pair of electrons to the total energy in restricted Hartree-Fock calculations and make use of that in your argument).*

**Q10:** *Predict the hybridization of the carbon in the singlet state and in the triplet state of $CH_2$. Use this to rationalize the bond angle in the singlet and triplet states of the molecule. How would the VSEPR rules predict qualitatively the bond angle in the singlet and triplet states?*