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 interaction 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 section 7.2 (starting on page 97) in the book by Koch and Holthausen to learn about the various basis sets. 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 (so called ab initio calculations, i.e., 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 VSPER 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 also 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 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).

Create a methylene CH$_2$ molecule and do a 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. In this 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 the calculations using the larger basis sets, you can simply substitute the basis in the input file of the first calculation and save it under a different file name. But, since the geometry may change significantly when increasing the basis set, you should use a 'better' initial guess for the larger basis sets, to save time during the calculation. 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.

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: Would you get different results if the initial geometry of the molecule is linear? Why?

The Hartree-Fock calculations use only a single Slater determinant wave 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 introduced in the wave function by taking a linear combination of the ground state Slater determinant and the excited Slater determinants corresponding to higher energy electron configurations. This is referred to as ‘configuration interaction’. Another approach is to add correlation with perturbation theory. A second order perturbation calculation is referred to as MP2. ORCA is first and foremost a wavefunction theory code and offers a plethora of high-level wavefunction methods. These ‘post-Hartree-Fock’ methods will be introduced later in the course. In this exercise, you just do the 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 the singlet state is a ground state within the subspace of singlet states, so this excited state of the system 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 CH₂ a triplet state (recall the restricted Hartree-Fock expression for the total energy, can you make use of that in your argument?).

Q10: Predict the hybridization of the carbon in the singlet state and in the triplet state of CH₂. Can you use this to rationalize the bond angle in the singlet and triplet states of the molecule? What estimates of the bond angle do the VSEPR rules give for the singlet and triplet states of CH₂?