Chemistry Departement

Third Winter School of Computational Chemistry

Computer Exercises

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1 Computer Exercise One

1.1 Illustrating ROHF vs. UHF (in relation to theoretical exercise 1)

The Li atom has been the topic of illustrating the details in a HF calculation in exercise-1. We will in this exercise perform calculations to quantify the theoretical considerations.

Perform calculations for a Li atom using UHF and ROHF wave functions (Method: Unrestricted or Restricted-Open) and the 3-21G basis set with the printing of all orbitals(AllPop keyword). View the results by opening the .out file with a text editor.

(a) Which of the two calculations gives the lowest total energy? Why must this necessarily be the case?
(b) Compare the orbital energies for the 1s- and 2s-orbitals for the ROHF and UHF cases, and the corresponding MO coefficients. How different are the α and β parts of the UHF orbitals compared to the ROHF ones in terms of MO-coefficients?
Perform a RHF/3-21G calculation of the Li^+ ion(set the correct charge and multiplicity in the input file).
(c) Calculate the energy difference between Li and Li^+, which is the ionization potential for Li. How does this compare with the UHF 2s-orbital energy?
The experimental value for the ionization potential is 5.39 eV.
(d) How does the value in c) compare with the experimental value? What could be the source of differences?

2 Computer Exercise Two

2.1 H_2 wave functions (in relation to theoretical exercise 3)

This reproduces the results you (hopefully) have obtained in the "theoretical exercise-3", run it after you have completed exercise-3.

Consider the H_2 molecule with an interatomic distance of 0.75 Å using the STO-3G basis set, which has only one s-type basis function on each nucleus.

Perform a RHF calculation with the STO-3G basis set and full printing of the orbitals:
Job Type: Energy, Method: RHF, Basis Set: STO-3G, Population Analysis: ALLPOP.
Create a new input by removing the RHF keyword and create a "%mdci" block. In this block set "citype" as "CISD" and "NatOrbs" as "true". Replace the "ALLPOP" keyword with "NOPOP" and redo the calculations. This produces a fullCI wave function for H_2.

The CISD wave function is calculated in intermediate normalization.

(a) Find the -0.11534 coefficient for the excited determinant and the total wave function normalization, and compare with the "theoretical exercise-3" calculated normalization constant.
(b) Find the occupancy numbers for the orbitals in the .out file and compare with those calculated in "theoretical exercise-3".
(c) Find the MP2 energy in the .out file and compare it with the value calculated in "theoretical exercise-3". Redo the HF and CI calculations with an interatomic distance of 2.00 and compare them with your "theoretical exercise-3" results. (Optional)

3 Computer Exercise Three

3.1 Getting the right wave function – spin multiplicity

The number of electrons is given implicitly by the charges of the nuclei in the system and the total charge on the system, but the user must specify how many electrons that should have α and β spin. This is normally done by specifying the spin multiplicity of the total wave function, where Spin = singlet has $N_\alpha = N_\beta$, Spin = doublet has $N_\alpha = N_\beta + 1$, Spin = triplet has $N_\alpha = N_\beta + 2$, Spin = quartet has $N_\alpha = N_\beta + 3$, etc. The Spin indicates the spin-degeneracy of the wave function, a doublet state has two energetically equivalent states (in the absence of a magnetic field) corresponding to the unpaired electron having either α or β spin, a triplet state has three energetically equivalent states corresponding to the unpaired electrons having either $\alpha\alpha$, $\alpha\beta$ or $\beta\beta$ spin, etc. The convention is to perform calculations on the sub-state with all unpaired electrons having α spin. We will in this exercise perform calculations with different spin multiplicity for the same system.

Consider a Mn^{2+}-ion, which has the electron configuration: [Ar]=$3\,d^5$.

(a) How many different spin multiplicities can the five electrons in the d-orbitals give rise to? What is the expected energetic ordering, i.e. which spin multiplicity is expected to be most/least stable?
(b) Perform UHF calculations with the cc-pVDZ basis set for the above different spin multiplicities with printing of all orbitals (determine the corresponding charge and multiplicity in the input file and use AllPop keyword). Does the calculated stability order agree with the expectations from (a)?
(c) Think carefully about HF wave functions corresponding to the above spin multiplicities, perhaps drawing orbital occupancy pictures with up and down arrows for representing electrons with α and β spin. If there are ambiguities for some of the spin multiplicities, try to analyze the log files from (b).

Return to point c) after you have done the next exercise, and perform calculations to check your analysis.

4 Computer Exercise Four

4.1 Getting the right wave function - orbitals

Besides specifying the spin multiplicity, it may also be necessary to consider/specify which orbitals should be occupied and which should be unoccupied (virtual). This will normally be assigned according to the aufbau principle, i.e. electrons are assigned to orbitals based on orbital energies, and given a set of orbital energies, and this can be done automatically without user involvement. However, orbitals for initiating the SCF procedure are obtained by simplified methods (like extended Hückel theory), which may produce an incorrect energetic ordering of the orbitals. This is especially problematic if there are orbitals of almost the same energy. A prime example is an open shell system involving a transition metal, fourth row transition metals for example have 4s and 3d orbitals with almost the same energy. The user should in such cases check that the desired wave function is obtained. We will in this exercise perform calculations of different electron configurations for the same system.

Consider a Cu-atom, which has atomic number 29. The isolated atom can have two different electron configurations: [Ar]=$4\,s^2\,3\,d^9$ and [Ar]=$4\,s^1\,3\,d^{10}$

(a) Which of these do you expect to be the lowest in energy? Perform an UHF calculation of a Cu atom (what is the spin multiplicity?) using the cc-pVDZ basis set and with printing of all orbitals.
(b) Which of the above two electron configurations does the converged wave function correspond to? You can look in the .out file for deciding which electron configuration you have obtained. Device a strategy for obtaining a wave function corresponding to the other electron configuration. This will need the

use of the additional Keyword rotate in the %scf block in your input (check the ORCA manual for more details) to switch occupied and virtual orbitals in the initial guess. Once you have obtained HF wave functions for both electron configurations, use the methodology for performing unrestricted MP2 calculations for both electron configurations.

(c) Which of the two-electron configurations is lowest in energy at the HF and at the MP2 level?
The [Ar]=$4\,s^2\,3\,d^9$ electron configuration is split into two states by spin-orbit coupling and these are experimentally found to be 1.39 and 1.64 eV [Ar]=$4\,s^1\,3\,d^{10}$ above the electron configuration. We can estimate the energy difference between the two electron configurations without the spin-orbit splitting to be 1.52 eV (average of the two energy values).

(d) How does the HF and MP2 values compare to the experimental value? Can you suggest a calculation that would give better agreement with the experimental result? Depending on your ambitions/curiosity, you can consider returning to exercise 2 point (c) and use your new insight to perform additional calculations (optional).

Exercises 3 and 4 illustrate that it sometimes is important to pay attention to the spin multiplicity and orbital occupancy. Organic molecules, however, are in general unproblematic as they, with almost no exceptions, have a spin multiplicity of 1 (spin multiplicity of 2 for radical, i.e. even-electron systems are singlets and odd-electron systems are doublets). The orbital energies are furthermore so well separated that the default guess for orbitals is in almost all cases sufficiently good for obtaining the right electron configuration.

5 Computer Exercise Five

5.1 Geometries, Vibrational Frequencies and Relative stabilities of 2-butene isomers

Many molecules can exist in (many) different structural forms with the same formal bonding. If they can be interconverted at normal temperatures, they are called conformations, if not, they are called isomers. We will in this exercise probe the sensitivity of the energy difference between two isomers of 2-butene to the solvent. The E-isomer is experimentally found to be 3.1 ± 1.6 kJ/mol more stable than the Z-isomer (https://webbook.nist.gov/chemistry/).

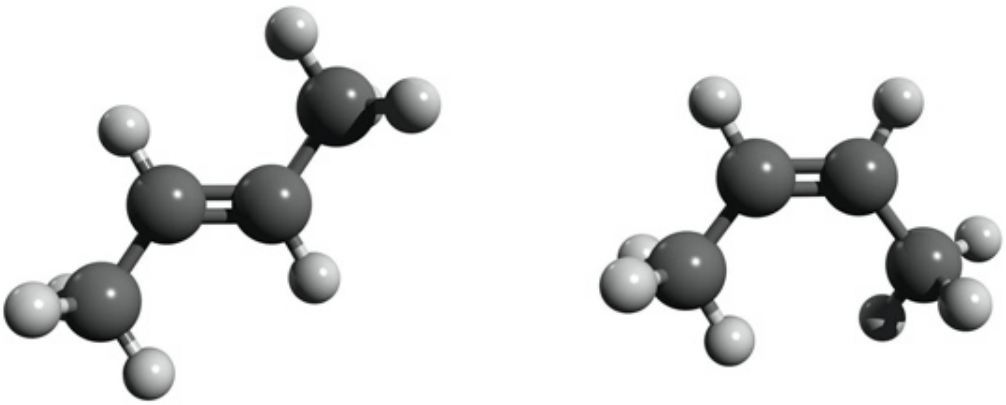

Figure 1: E and Z form of butene

(a) Calculate the optimized structures of the E and Z forms of 2-butene using Hartree-Fock and the DFT (functional WB97X-D3) with the 6-31G(d) basis set, and make sure to get the lowest energy confor-

mations (open the output with Avogadro/text editor and check there are no imaginary frequencies) in each case.

(b) For each level of calculations, compare the optimized geometries of Z form with the experimental values: $R_{C-C} = 1.506$ Å, $R_{C=C} = 1.346$ Å, $\Theta_{CC} = 125.4°$.

(c) Perform the energy calculations (a single point calculation, requires no method indication in command line of the input) in both the gas phase and in an implicit water solvent model (To use SMD the user must simply specify smd true in the %cpcm block and provide the name of the solvent, check ORCA manual for further details) and compare the relative energy.

(d) Which isomer is the most stable in the two environments? Does the prediction depend on whether you are using raw electronic energies or Gibbs free energies? How does the relative stability depend on the polarity of the environment? How does the calculated value compare to the experimental value?

(e) For E form of 2-butene, compare the calculated harmonic vibrational frequencies with the three main high-intensity of experimental anharmonic values by calculating the Mean Absolute Deviations (MAD). This may be easiest to do using a spreadsheet by listing the frequencies and calculating the average absolute differences. What are the trends regarding behavior with respect to the level of calculations?

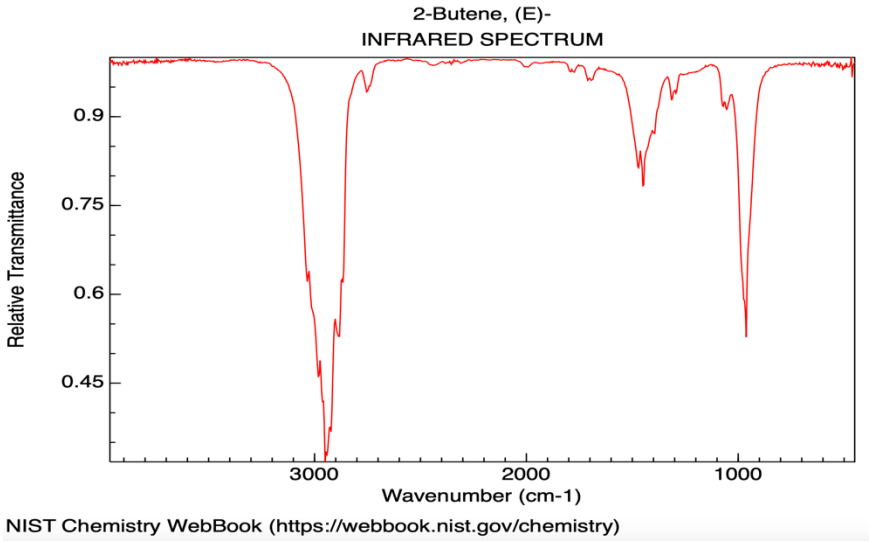

Figure 2: Experimental vibrational IR spectrum of E conformer of Butene

6 Computer Exercise Six

6.1 Transition structures

This exercise aims at calculating a transition structure in a chemical reaction. We will focus on calculating the TS for the keto-enol tautomerization of acetone, and we will investigate the difference between the uncatalyzed and water-catalyzed reactions. We will use the WB97X-D3/6-31G(d) method/basis set combination and an implicit water solvent model (SMD) for all the calculations.

(a) Build and Optimize the reactant (acetone) and check the stability of the optimized structure (make sure there are no imaginary modes obtained) (OPT FREQ keywords).
Use the optimized reactant structure to build the product structure. Optimize the product (enol)

and check the stability of the optimized structure (make sure there are no imaginary modes obtained) (OPT FREQ keywords).
Having both reactant and product optimized coordinates, build the TS structure as an intermediate between the reactant (acetone) and product (enol) coordinates, considering the bond formation between O and H in the product. Then use the built-up coordinates and run a TS optimization (using the OptTS keyword).

(b) When the TS optimization has converged, verify that it indeed is a TS by visualizing the normal coordinate associated with the imaginary frequency. This is the reaction coordinate at the TS, i.e. the atomic movements corresponding to lowering the energy.

(c) Perform an IRC calculation (block %irc, check the ORCA manual for more details) using the optimized TS geometry. Visualize the IRC Path (Avogadro→ Extensions→ Animation) and note how the geometry and energy changes. This verifies that the TS really connects the reactant and the product. (Optional)

(d) Calculate the reaction (Eproduct-Ereactant) and activation (ETS-Ereactant) energies for the above two model reactions, using both electronic and (Gibbs free energies (optional)). Is there a difference in the behavior of the reaction and activation energies between electronic and Gibbs free energies?

7 Computer Exercise Seven

7.1 Excited States

Excited states are often described by response theory, where the excitation energies and transition moments are calculated from the ground state wave function as the response to an external time-dependent electric (dipole) field. The nature of the excitation can be analyzed in terms of the canonical MOs, but a more compact representation can be obtained by Natural Transition Orbitals, which are eigenvectors associated with the (largest) eigenvalues in the transition density matrix. We will in this exercise analyze the two lowest excited singlet states in formaldehyde and probe the geometry of the lowest excited state.

(a) Optimize the geometry of the H_2CO molecule with the DFT WB97X-D3 functional and the aug-cc-pVDZ basis set (why aug-?).

(b) On the optimized geometry from section (a), perform a calculation of the three lowest excited states using the DFT WB97X-D3 functional and the aug-cc-pVDZ basis set (use the %tddft block in the input and specify the number of roots, inclusion of triplet states and calculation of natural transitions, check the ORCA manual for more details).
Visualize the UV-Vis spectrum and note the lowest energy excitation at 308 nm has a zero intensity. Visualize the two NTOs with eigenvalues close to 1 and put a label on this excitation. Can you rationalize why the intensity for this transition is zero?

(c) Optimize the geometry of the molecule in the first excited state (keywords: OPT and block %CIS NRoots 1 IRoot 1 end, check the manual for further details, you can remove the population options used in sections (b) and (c). Visualize the vibrational frequencies and make a decision based on these. (Optional)

(d) Compare the optimized ground and excited state geometries. Is the change in geometry upon excitation consistent with the nature of the excitation as analyzed in (b)? (Optional)