Introduction to Hartree-Fock calculations using ORCA and Chemcraft

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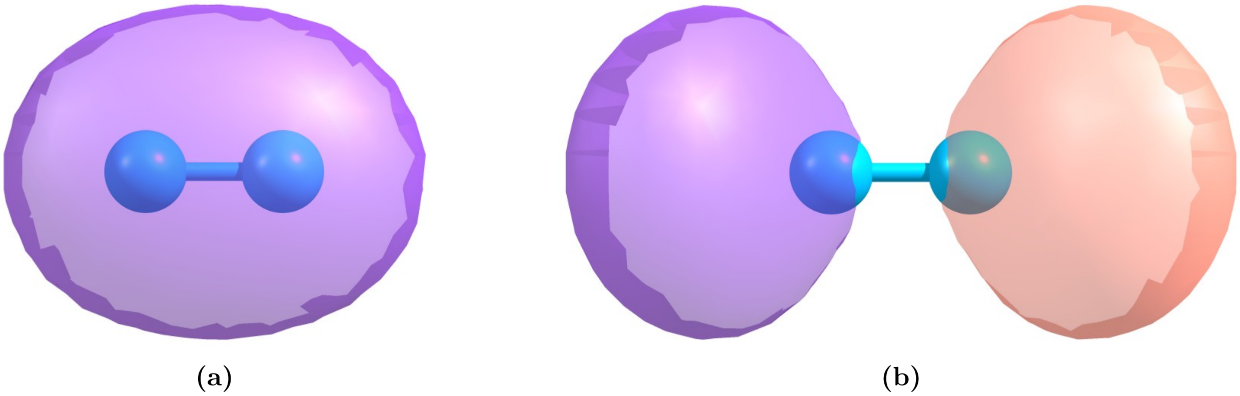
A. Molecular orbitals and electron density of H_2

Q1: Present the images of the *HOMO* and the *LUMO* in your report. Take care that the windows were all maximized and the camera settings were identical before you saved the images. Arrange the images of the *HOMO* and *LUMO* side by side. Write text underneath to label each molecular orbital as bonding or antibonding. Also, specify whether the molecular orbitals are σ or π orbitals.



(a) **(b)**

✓

Figure 1: *(a) The HOMO of the H_2 molecule is a bonding σ orbital. (b) The LUMO of the H_2 molecule is an antibonding σ^* orbital.*

Q2: What is the optimal bond length in a H_2 molecule predicted by the Hartree-Fock calculations in the 6-31G basis set? How many iterations did ORCA need to find the optimal bond length? Compare with the experimental value for the bond length, 0.74 Å.

The optimal bond length in a H_2 molecule was predicted to be 0.730 Å, by Hartree-Fock calculations in the 6-31G basis set. 9 geometric iterations were needed to find the optimal bond length. The experimental bond length is 0.74 Å, so the relative error of the calculations was only 1.35 %. ✓

> **Q3:** Record the energy of the H_2 molecule in your report. What is the zero of energy in this case? Using the exact value of the energy of an H-atom, what is the bond energy? (This is, actually, not a good procedure since the two numbers subtracted are not calculated at the same level of theory. Generally, one relies on cancellation of errors in calculations of bond energies and should, therefore, consistently use the same level of approximation for all numbers subtracted or added.)

The predicted energy of the H_2 molecule by Hartree-Fock calculations in the 6-31G basis set was -1.12683 Hartree or -30.6626 eV. The zero of energy refers to energy of two isolated hydrogen atoms at infinite distance. Since the calculated energy is negative, it indicates that the H_2 molecule is bound relative to two separate hydrogen atoms. The energy of an H-atom is -13.605693 eV. Thus the bond energy in H_2 is approximately ✓

$$E_{\mathtt{H_2\text{-}bond}} = 2\cdot E_{\mathtt{H}} - E_{\mathtt{H_2}} \approx 2\cdot(-13.59844)\mathtt{eV} - (-30.6626)\mathtt{eV} = 3.4657\mathtt{eV}. \tag{1}$$

> **Q4:** What is the predicted bond length and what is the energy of the molecule in this basis set? Is the energy higher or lower than for the 6-31G basis set? Is the bond length longer or shorter?

Hartree-Fock calculations predict a bond length of 0.733 Å for H_2 with the 6-31G** basis set, which is slightly longer than that predicted with the 6-31G. The corresponding energy was -1.13133 Hartree (-30.7852 eV), lower than that of the 6-31G, indicating a slightly more stable molecule. ✓

> **Q5:** Explain why the energy of the molecule is different and why it must necessarily change in the direction it does (lower or higher?). Recall, SCF calculations are variational calculations. Is there any such rule for how the bond length changes with the basis set?

The 6-31G** basis set includes polarization functions in addition to the functions used in the 6-31G basis set. As a result, the Hartree-Fock calculation can find a lower energy than with the smaller basis set, because it can better optimize the electron density. The calculated ground state energy is always an upper bound to the exact energy; thus, including additional basis functions can either lower the energy or have no effect on it, in accordance with the variational principle. ✓

In terms of bond lengths, there is no strict variational rule as there is for energy. The bond length can remain the same, increase, or decrease when more basis functions are added, depending on the specific system being analyzed. ✓

Q6: Does the bond energy necessarily also change in the same way as the energy of the molecule when the basis set is changed and both the molecule and the atoms are calculated at the same level of theory (why/why not)?

In variational SCF calculations, the energies of both the molecule and the atoms either decrease or remain constant when additional basis functions are added. However, there is no guarantee that energy differences — such as the calculated bond energy — will also decrease. This outcome depends on how the molecule and the individual atoms respond to the expanded basis set. For instance, the molecule may lower its energy while the energy of the individual atoms remains unchanged, which would lead to an increase in the calculated bond energy. ✓

B. Electron density of HF and LiH molecules

HF molecule

Q7: Does the electron density near the H atom increase or decrease when it binds to an F atom as compared to H_2? How does the size of the isosurface of the electron density near the H-atoms in the two molecules correlate with the electronegativity of the atoms?

The electron density around the hydrogen atom decreases when it binds to a fluorine atom compared to the hydrogen molecule (H_2). This decrease is due to the higher electronegativity of fluorine. As a result, the electron density isosurface surrounding the hydrogen atom in hydrogen fluoride (HF) is smaller than that in H_2. In contrast, the isosurface around the more electronegative fluorine atom is larger. This trend illustrates the shift of electron density toward the more electronegative atom, see figure 2. ✓

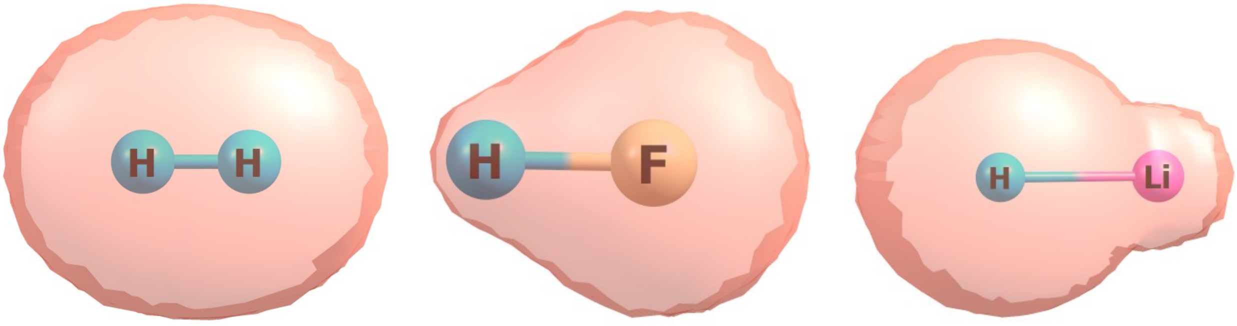
LiH molecule

Q8: Compare the results for LiH with those for the H_2 and HF molecules. Comment on how the electron density at the H-atom in LiH compares with that in H_2 and HF. Explain the trend.

The electron density around the hydrogen atom increases when it binds to a lithium atom compared to H_2, and especially compared to HF. This is because lithium has the lowest electronegativity of the three atoms, while fluorine has the highest. In a diatomic molecule, the electron density shifts toward the more electronegative atom, which explains why H in LiH has more electron density than in H_2 or HF.

✓

Q9: Include the images of the electron densities in your report. From the electron distribution, assign partial charges ($\delta-$, $\delta+$) to the atoms in the molecules.



(a) **(b)** **(c)**

Figure 2: *(a) In H_2, the total electron density is evenly distributed between the two H atoms. (b) In HF, the electron density is concentrated on the F atom, giving the H atom a partial positive charge (δ^+) and the F atom a partial negative charge (δ^-). (c) In LiH, the electron density is concentrated on the H atom, giving the Li atom a partial positive charge (δ^+) and the H atom a partial negative charge (δ^-).*

✓

Basis set errors

Q10: Which spin multiplicity should you select for the H-atom? Why? Why not select 'Equilibrium structure search' or 'OPT' in this case?

The H atom has one electron, giving a total spin of $S = \frac{1}{2}$. The corresponding spin multiplicity is $2S + 1 = 2$, so the correct choice is a doublet state. Since hydrogen is a single atom with no bonds, there is no geometry to optimize. An 'Equilibrium structure search' (OPT) is therefore unnecessary, as changing the absolute position of an isolated atom does not affect its energy.

✓

Q11: What is the absolute and relative deviation (in %) of the calculated energy of a hydrogen atom using the two basis sets compared with the exact value?

Using the 6-31G basis set, the energy of the hydrogen atom was calculated to be −0.49823 Hartree (−13.558 eV), which is 0.041 eV higher than the exact value of −13.59844 eV [1]. This corresponds to a relative deviation of 0.30%. Using the 6-31G** basis set, the calculated energy of the hydrogen atom is the same as with the 6-31G basis set. ✓

Q12: Does the larger basis set yield a stronger or weaker bond?

The bond energy of the hydrogen molecule was calculated using equation 1. It was found to be 3.5473 eV with the 6-31G basis set and 3.6699 eV with the 6-31G** basis set. Thus, the larger basis set yielded a stronger bond. ✓

Q13: How does the bond energy obtained here deviate from the values you obtained earlier (see questions Q3 and Q4)? (give absolute and relative deviation in %).

For the 6-31G basis set the bond energy was found to be 0.0817 eV lower using the exact value rather than using the calculated energy of the hydrogen atom, making the relative deviation 2.30 %. The calculated bond energy was also 0.0817 eV lower using the exact value rather than using the calculated energy for the 6-31G** basis set, however, in that case the relative deviation was 2.22 %. ✓

Q14: Do you agree with the following statement (if so, explain; if not, try to present a counter exam ple)? 'Adding basis functions to a basis set will always yield a lower or equal total energy in a variational calculation'.

I agree with the statement that 'adding basis functions to a basis set will always yield a lower or equal total energy in a variational calculation'. Additional basis functions increase the flexibility of the wavefunction, making it possible to reach a lower energy. If they do not contribute to lowering the energy, they will simply not affect the final result, since the SCF algorithm iteratively converges to the minimum energy. ✓

Q15: Do you agree with the following statement (if so, explain; if not, try to present a counter example)? 'A variational calculation using a basis set B which has a larger number of functions than basis set A, will always yield a lower or equal total energy as a calculation using A'.

I disagree with the statement that ‘a variational calculation using a basis set B with a larger number of functions than basis set A will always yield a lower or equal total energy’. According to the variational principle, if basis set B is a superset of basis set A (i.e., it contains all functions of A plus additional ones), the calculated energy with B cannot be higher than with A. However, if the larger basis set consists of functions that are poorly suited to the system (for example, 50 polynomials versus 10 Gaussians for a wavefunction that is best represented by Gaussians), then it is possible for the calculation using B to give a higher energy than by using A. Thus, the quality and type of basis functions, not just the number, determine whether the energy improves.

✓

References

[1] D. R. Lide, “Ionization potentials of atoms and atomic ions”, in *Handbook of chemistry and physics*, edited by D. R. Lide, 73rd (CRC Press, Boca Raton, FL, 1992), pp. 10–211.