Computational Nanoscience: Exercise Sheet No. 3

Exercise 3.1: Derivation of the Rothaan-Hall equations

Derive the Rothaan-Hall equations,

$$\mathbf{FC} = \mathbf{SC}\varepsilon \qquad \Leftrightarrow \qquad \sum_{\nu=1}^{N_b} F_{\mu\nu} C_{n\nu} = \sum_{\nu=1}^{N_b} S_{\mu\nu} C_{n\nu}\, \varepsilon_n$$

with

$$F_{\mu\nu} = \int d^3\mathbf{r}\, d^3\mathbf{r}'\, \phi_\mu(\mathbf{r})\, F(\mathbf{r},\mathbf{r}')\, \phi_\nu(\mathbf{r}')\,, \qquad S_{\mu\nu} = \int d^3\mathbf{r}\, \phi_\mu(\mathbf{r})\, \phi_\nu(\mathbf{r})$$

starting from the closed-shell Hartree-Fock equations and the basis expansion,

$$\int F(\mathbf{r},\mathbf{r}')\, \psi_n(\mathbf{r}')\, d\mathbf{r}' = \varepsilon_n\, \psi_n(\mathbf{r})\,, \qquad \psi_n(\mathbf{r}) = \sum_{\nu=1}^{N_b} C_{n\nu}\, \phi_\nu(\mathbf{r})\,.$$

Exercise 3.2: Hartree-Fock energy from eigenvalues

Use the equations for closed-shell Hartree-Fock from Figure 5.2 in the lecture notes to derive

$$E_{\mathrm{HF}} = 2 \sum_{n=1}^{N/2} \varepsilon_n - (E_\mathrm{H} + E_\mathrm{x}) + E_{\mathrm{NN}}\,. \tag{1}$$

You may use the fact that $\mathbf{C}^\mathrm{T}\mathbf{SC} = \mathrm{Id}$ since

$$\sum_{\mu\nu} C_{n\mu} S_{\mu\nu} C_{m\nu} = \int d^3\mathbf{r} \sum_\mu C_{n\mu}\phi_\mu(\mathbf{r}) \sum_\nu C_{m\nu}\phi_\nu(\mathbf{r}) = \int d^3\mathbf{r}\, \psi_n(\mathbf{r})\psi_m(\mathbf{r}) = \delta_{nm}\,.$$

Interpret the result (1):

(a) Give a physical reason, why a factor 2 is appearing in front of the eigenvalue sum.

(b) Give a physical reason, why it is necessary to subtract the Hartree energy and the exchange energy from the occupied eigenvalue sum to obtain the total energy.

(c) Compare Eq. (1) to the result from MO theory on Sheet 1 and explain the difference.

(d) How many eigenvalues ε_n are calculated in a Hartree-Fock calculation? Is there a reason why not all eigenvalues are summed up in Eq. (1)?

Exercise 3.3: Reaction energy of the H_2O forming reaction

In this exercise, we compute the reaction energy Δ of the reaction

$$H_2 + \tfrac{1}{2} O_2 \ \rightarrow \ H_2O$$
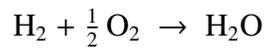
with Hartree-Fock. The goal of this exercise is to fill the following table, see a) - d) and to discuss in e). The values for H_2O are provided as a check.

Geometry	Basis set	E_{HF} of H_2 (H)	E_{HF} of O_2 (H)	E_{HF} of H_2O (H)	Δ (H)	Δ (kJ/mol)
Force field	def2-QZVPP			-76.06243772492		
Hartree-Fock	def2-QZVPP			-76.06747231486		
Hartree-Fock	def2-TZVPP			-76.06317801681		

(a) Retrieve the geometries of H_2, O_2 and H_2O you have created by a force-field geometry optimization in avogadro. Make sure that you have relaxed the O_2 molecule with double bonds in avogadro. Carry out Hartree-Fock calculations on all three molecules and fill the Hartree-Fock energy ('HF energy') in Hartree (H) in upper table (Hartree is the standard unit that is displayed in Turbomole since Hartree is the atomic unit for energy).

(b) Perform a geometry optimization with Hartree-Fock in the def2-QZVPP basis. You can efficiently do this by copying your Hartree-Fock calculations from a) to new directories and entering `jobex`. Collect the total energy of the relaxed geometry that should be present in the file `job.last` inside the new directories.

(c) Use the geometry that you have relaxed in b) to compute the Hartree-Fock energy with the def2-TZVPP basis set. You can do this efficiently by copying the files from your calculation in b), changing inside `control` the basis set from def2-QZVPP to def2-TZVPP and going through define again where you only have to press enter and *.

(d) Complete upper table by computing the reaction energy Δ in Hartree and in kJ/mol and judge, which number is accurate with respect to numerical convergence and which number is accurate with respect to the accuracy of the employed method.

(e) Have a look at reference data for the formation enthalpy of the water molecule, e.g. on

<center>https://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Mask=1</center>

and compare to your results from the table. What are the main sources for the differences?