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<https://www.ur.de/physics/wilhelm/teaching/sose24-computational-nanoscience>

Computational Nanoscience: Exercise Sheet No. 3

Exercise 3.1: Derivation of the Rothaan-Hall equations

Derive the Rothaan-Hall equations,

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \quad \Leftrightarrow \quad \sum_{v=1}^{N_b} F_{\mu v} C_{nv} = \sum_{v=1}^{N_b} S_{\mu v} C_{nv} \varepsilon_n$$

with

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

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

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

[5]

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

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

[4]

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

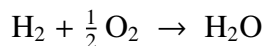
$$\sum_{\mu\nu} C_{n\mu} S_{\mu\nu} C_{m\nu} = \int d^3\mathbf{r} \sum_{\mu} C_{n\mu} \phi_\mu(\mathbf{r}) \sum_{\nu} C_{m\nu} \phi_\nu(\mathbf{r}) = \int d^3\mathbf{r} \psi_n(\mathbf{r}) \psi_m(\mathbf{r}) = \delta_{nm}.$$

Interpret the result (1):

- Give a physical reason, why a factor 2 is appearing in front of the eigenvalue sum. [1]
- 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. [1]
- Compare Eq. (1) to the result from MO theory on Sheet 1 and explain the difference. [1]
- 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)? [1]

Exercise 3.3: Reaction energy of the H₂O forming reaction

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



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 H₂O are provided as a check.

| Geometry | Basis set | E_{HF} of H ₂ (H) | E_{HF} of O ₂ (H) | E_{HF} of H ₂ O (H) | Δ (H) | Δ (kJ/mol) |
|--------------|------------|---------------------------------------|---------------------------------------|---|--------------|-------------------|
| Force field | def2-QZVPP | | | -76.06243772492 | | |
| Hartree-Fock | def2-QZVPP | | | -76.06747231486 | | |
| Hartree-Fock | def2-TZVPP | | | -76.06317801681 | | |

Retrieve the geometries of H₂, O₂ and H₂O you have created by a force-field geometry optimization in Avogadro. Make sure that you have relaxed the O₂ molecule with double bonds in Avogadro. Carry out Hartree-Fock calculations in CP2K on all three molecules and fill the total energy in Hartree (H) in upper table (Hartree is the standard unit that is displayed in CP2K since Hartree is the atomic unit for energy). Following input file can be used for Hartree-Fock calculation in CP2K (complete input documentation can be found at https://manual.cp2k.org/trunk/CP2K_INPUT.html).

```
&GLOBAL
```

```
  RUN_TYPE ENERGY
```

```
  PROJECT_NAME HF
```

```
&END GLOBAL
```

```
&FORCE_EVAL
```

```
  METHOD QS
```

```
  &DFT
```

```
    &XC
```

```
      &HF
```

```
        FRACTION 1.0
```

```
      &END HF
```

```
    &XC_FUNCTIONAL NONE
```

```
  &END XC_FUNCTIONAL
```

```
&END XC
```

```
&QS
```

```
  METHOD GAPW
```

```
&END QS
```

```
&POISSON
```

```
  PERIODIC NONE
```

```
  POISSON_SOLVER WAVELET
```

```
&END POISSON
```

```
BASIS_SET_FILE_NAME def2-qzvpp.1.cp2k
```

```
POTENTIAL_FILE_NAME POTENTIAL
```

```
! Do spin polarized calculation
```

```
! For H2 and H2O, comment the following two lines out
```

```
MULTIPLICITY 3
```

```
UKS
```

```
&END DFT
```

```
&SUBSYS
```

```

&CELL
  ABC 10.0 10.0 10.0
  PERIODIC NONE
&END CELL
&TOPOLOGY
  &CENTER_COORDINATES
  &END CENTER_COORDINATES
  COORD_FILE_FORMAT XYZ
  ! Here you can change the molecule that is being investigated
  COORD_FILE_NAME O2.xyz
&END TOPOLOGY
&KIND H
  BASIS_SET def2-QZVPP
  POTENTIAL ALL
&END KIND
&KIND O
  BASIS_SET def2-QZVPP
  POTENTIAL ALL
&END KIND
&END SUBSYS
&END FORCE_EVAL

```

You will need to download the basis def2-QZVPP from

<https://www.basissetexchange.org/>

and place it in the same directory as the input file and coordinate files.

- (a) Perform a geometry optimization with Hartree-Fock in the def2-QZVPP basis. This can be achieved by changing the RUN_TYPE parameter to GEO_OPT and running the calculation again. Collect the total energy of the relaxed geometry. [2]
- (b) Download the def2-TZVPP basis from Basis Set Exchange and run the geometrical optimisation again with this basis choice. [2]
- (c) 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. [1]
- (d) Have a look at reference data for the formation enthalpy of the water molecule, e.g. on

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

and compare to your results from the table. What are the main sources for the differences? [2]