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

## Computational Nanoscience: Exercise Sheet No. 6

### Exercise 6.1: General questions on DFT

- (a) Why did we introduce Kohn-Sham DFT? Is Kohn-Sham DFT formally exact? Is Kohn-Sham DFT also exact in practice when doing a calculation on a big molecule or a solid? [3]
- (b) Does full-CI in the complete-basis-set limit yield the same electron density as Kohn-Sham DFT with the exact exchange-correlation functional in the complete-basis-set limit? [2]
- (c) Does the Slater determinant  $\Psi_{\text{KS}}$  built of Kohn-Sham orbitals (computed from Kohn-Sham DFT with the exact exchange-correlation functional) yield the exact electron density from the equation

$$n(\mathbf{r}) = \langle \Psi_{\text{KS}} | \hat{n}(\mathbf{r}) | \Psi_{\text{KS}} \rangle ? \quad (1)$$

[2]

- (d) Is the Kohn-Sham Slater determinant  $\Psi_{\text{KS}}$  equal to the many-electron ground state wavefunction? [2]
- (e) Employ Levy's search scheme to write Hartree-Fock as a density functional theory. [2]

### Exercise 6.2: Density Functional Theory Numerical Performance

- (a) In CP2K, the exchange-correlation energy is evaluated on the real-space grid onto which the Gaussian orbitals are projected, while the Hartree energy is evaluated on a reciprocal space grid, where the Hartree operator is diagonal. The transformation between the grids is done by efficient fast Fourier transform algorithms.

In this exercise, we will compare the performance of DFT to that of HF and determine the calculation bottlenecks. We will use the same  $\text{H}_2$  chains that were used in Exercise Sheet 4. The following table serves as a guide through this exercise, using timings from a machine with 12 threads - your previous timings may be different.

Number of $\text{H}_2$ molecules, $N_{\text{H}_2}$	HF time (s)	DFT time (s)	DFT time - single thread (s)
1	1.083		
2	1.903		
4	23.541		
6	92.218		
8	269.496		

First, calculate the total energy of the chains in DFT, using PBE functional and def2-QZVPP basis set. Note the timings of `qs_ks_update_qs_env`. [4]

**Hint:** Set `OMP_NUM_THREADS` environment variable to the number of threads available on your machine. You can use the following input file

```

&GLOBAL
  RUN_TYPE ENERGY
  PROJECT_NAME H2_8
&END GLOBAL
&FORCE_EVAL
  METHOD QS
  &DFT
    BASIS_SET_FILE_NAME def2-qzvpp.1.cp2k
    POTENTIAL_FILE_NAME POTENTIAL
  &QS
    METHOD GAPW
  &END QS
  &XC
    &XC_FUNCTIONAL PBE
  &END XC_FUNCTIONAL
  &END XC
  &POISSON
    PERIODIC NONE
    POISSON_SOLVER ANALYTIC
  &END POISSON
&END DFT
&SUBSYS
  &CELL
    ABC 25.0 10.0 10.0
    PERIODIC NONE
  &END CELL
  &TOPOLOGY
    &CENTER_COORDINATES
  &END CENTER_COORDINATES
    COORD_FILE_FORMAT XYZ
    COORD_FILE_NAME H2_8.xyz
  &END TOPOLOGY
  &KIND H
    BASIS_SET def2-QZVPP
    POTENTIAL ALL
  &END KIND
&END SUBSYS
&END FORCE_EVAL

```

- (b) Now, repeat the calculations, but force the number of threads to just one thread. Compare the timings of DFT calculations and of HF calculations. [3]
- (c) Repeat the calculations for chain of 2 H<sub>2</sub> molecules, again with more threads, but with different cell size in the x direction - 20, 30 and 40 Å. Compare the timings with different cell size. Is the calculation time dominated by real-space grid operations or by atomic basis operations? [2]