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Computational Nanoscience: Solution to Exercise Sheet No. 6

Exercise 6.1: General questions on DFT

(a) 1. We introduced Kohn-Sham DFT to accurately compute the kinetic energy, since the kinetic energy is difficult to accurately compute from density functionals, as e.g. from the Thomas-Fermi approximation.

2. Yes, the exchange-correlation functional for KS-DFT is redefined such that one computes the exact ground state energy in KS-DFT when having the exact exchange-correlation functional.

3. No, because we don't have the exact exchange-correlation functional in practical calculations for large molecules or solids. For very small systems, the exact exchange-correlation functional may be reconstructed e.g. by Levy's search, but this is computationally extremely costly and is not applicable to large molecules or solids.

(b) Full CI in the complete basis set limit yields the exact ground state many-electron wavefunction Ψ and hence, full CI yields the exact ground state electron density from

$$n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle \ . \tag{1}$$

KS-DFT in the complete basis set limit yields the exact ground state density (2. Hohenberg-Kohn theorem). Therefore, full CI and KS-DFT yield the same ground state electron density.

(c) Yes, the electron density in KS-DFT is given by

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$$

where $\psi_i(\mathbf{r})$ are the MOs from the Slater determinant such that the expression from the exercise sheet is true, see exercise sheet 2, Eq. (2) and (3).

(d) No, in general, a ground state many-electron wavefunction is a superposition of many Slater determinants, as in full CI, see Eq. (6.1) in the lecture notes (full CI in the complete-basis-set limit yields the exact ground state wavefunction). Since the KS Slater determinant is only a single Slater determinant, the KS Slater determinant is in general not equal to the ground state many-electron wavefunction. (But, as discussed in (b), the KS-Slater determinant and the exact ground state many-electron wavefunction give the same electron density. This is not a contradiction since different many-electron wavefunctions can yield the same electron density.)

(e) In analogy to Eq. (8.9) in the lecture notes, we have for the Hartree-Fock energy density functional:

$$E_{\mathrm{HF}}[n] = \min_{\substack{\text{Slater determinant } \Psi_{\mathrm{SD}} \\ \text{that gives } n(\mathbf{r})}} \langle \Psi_{\mathrm{SD}} | \hat{H} | \Psi_{\mathrm{SD}} \rangle \tag{2}$$

where $\hat{H}$ is the many-electron operator, see Eqs. (5.20), (2.13) in the lecture notes. We minimize $\langle \Psi_{SD} | \hat{H} | \Psi_{SD} \rangle$ among all Slater determinants Ψ_{SD} (that is the constraint for Hartree-Fock, if we minimize among all many-electron wavefunctions, we will get the exact total energy density functional). By minimizing the functional $E_{HF}[n]$ with respect to the electron density, we can find the Hartree-Fock energy E_{HF}:

$$E_{HF} = \min_{n(\mathbf{r})} E_{HF}[n]. \tag{3}$$

In this way, we have written Hartree-Fock as a density functional theory.

Exercise 6.2: Density Functional Theory Numerical Performance

(a) I obtained the following data

Number of H_2 molecules, N_{H_2}	HF time (s)	DFT time (s)	DFT time - single thread (s)
1	1.083	17.946	19.861
2	1.903	13.329	15.082
4	23.541	13.849	16.308
6	92.218	16.189	19.740
8	269.496	18.687	23.517

(b) For DFT, the smaller calculations are more susceptible to random fluctuations of the system then to the number of atoms. In both the case of threaded and single thread calculation runs, the DFT calculation is significantly faster than the HF calculation.

The calculation time does not change significantly with larger number of CPU threads, signifying that the number of atoms is not the main bottleneck of the calculation.

(c) I obtained the following data

Cell size x	DFT Time (s)
20	10.199
25	13.329
30	15.604
40	18.521
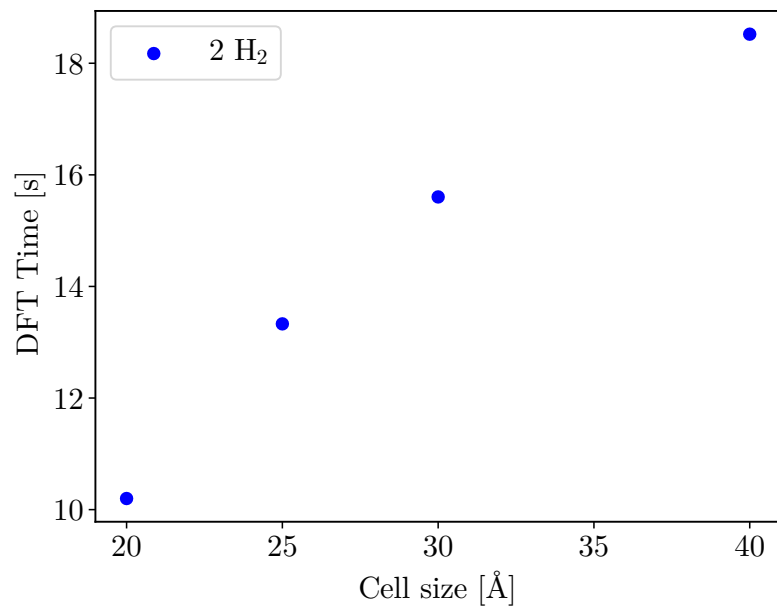
We can observe a dependence on the cell size that is stronger than the basis set size dependence. We conclude that the calculation time is dominated by real-space grid operations, which are dependent on the cell size (ffts and xc-energy evaluation).