EXAM assignment

Lecture: Atomistic Computer Modeling of Materials (ÚFV/APMM/19)

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Date: April 20, 2021

Submission Deadline: June 30, 2021 via email: *martin.gmitra@upjs.sk*

Assignment:

1. Calculate using density functional theory as implemented in Quantum Espresso code suite equilibrium lattice constant for sodium chloride (NaCl) crystal (space group #225, FCC) for LDA and PBESOL exchange-correlation functionals. Provide data of the total energy as a function of lattice constant in a column form or plot the dependencies. Discuss results.

2. Calculate cohesive energy of Na atom in equilibrium structures obtained for LDA and PBESOL functionals. Discuss results.

Evaluation:

- 10% construction of the input files
- 60% relaxation of the structure, finding equilibrium structures for LDA and PBESOL
- 30% calculation of the cohesive energy
- +20% bonus, online oral exam covering theory topics given on lectures, please submit the requested files 2 days before oral exam.

Submit:

- input files, output files for equilibrium structures only
- a short text report (pdf/odt/doc) with results figure/table with obtained results

Exam conditions:
Scale: A: 100% - 90% B: 89% - 75% C: 74% - 60% D: 59% - 40% E: 39% - 20% FX: 19% - 0

Note**:** For pseudopotentials use the ultra-soft pseudopotentials:

https://www.quantum-espresso.org/upf_files/Na.pz-spn-rrkjus_psl.0.2.UPF
https://www.quantum-espresso.org/upf_files/Cl.pz-n-rrkjus_psl.0.1.UPF
https://www.quantum-espresso.org/upf_files/Na.pbesol-spn-rrkjus_psl.0.2.UPF
https://www.quantum-espresso.org/upf_files/Cl.pbesol-n-rrkjus_psl.1.0.0.UPF

For energy cutoffs use the largest values as can be found in headers of the pseudopotentials files. For k-point sampling use 8 8 8 mesh.

ACMM 2021 Assignment

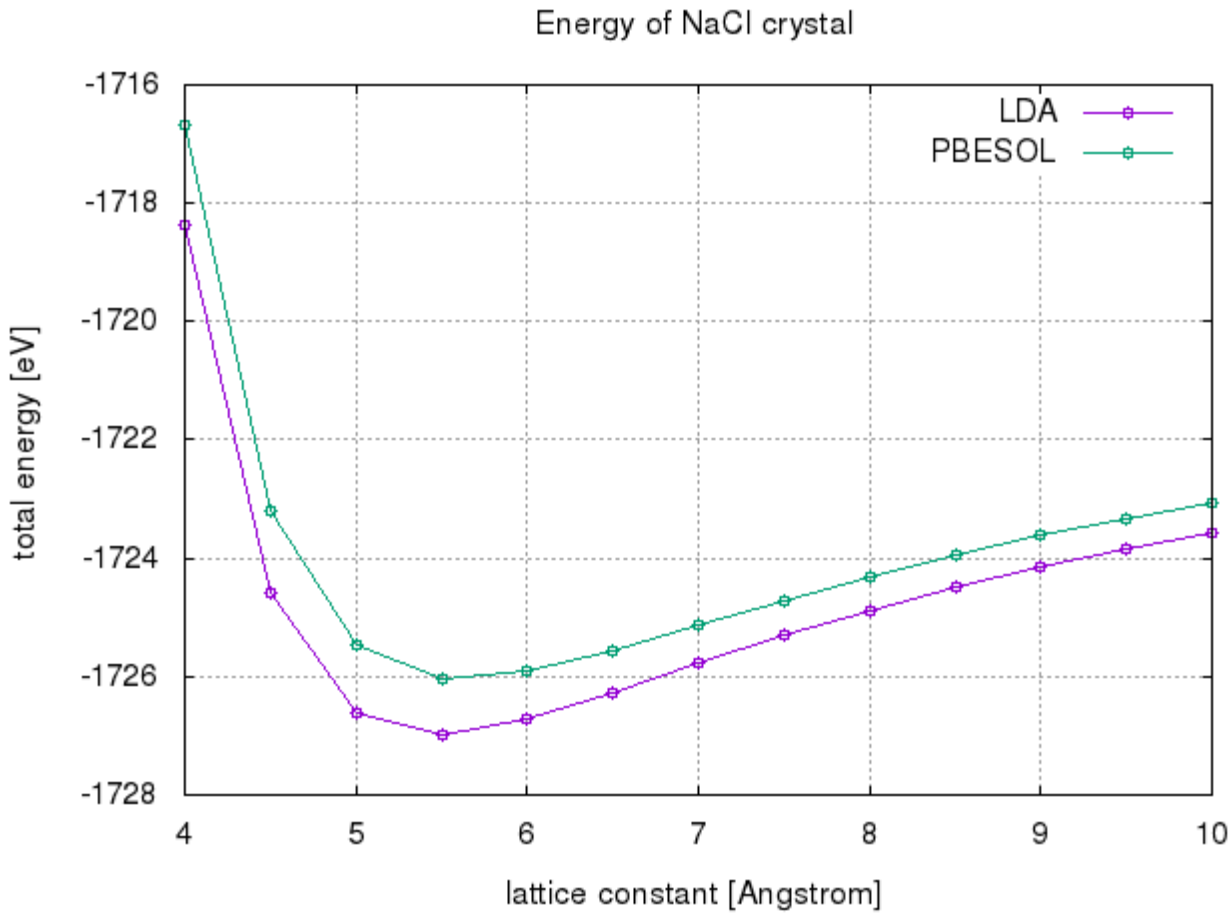
Dávid Lorko

1.

> Calculate using density functional theory as implemented in Quantum Espresso code suite equilibrium lattice constant for sodium chloride (NaCl) crystal (space group #225, FCC) for LDA and PBESOL exchange-correlation functionals. Provide data of the total energy as a function of lattice constant in a column form or plot the dependencies. Discuss results.

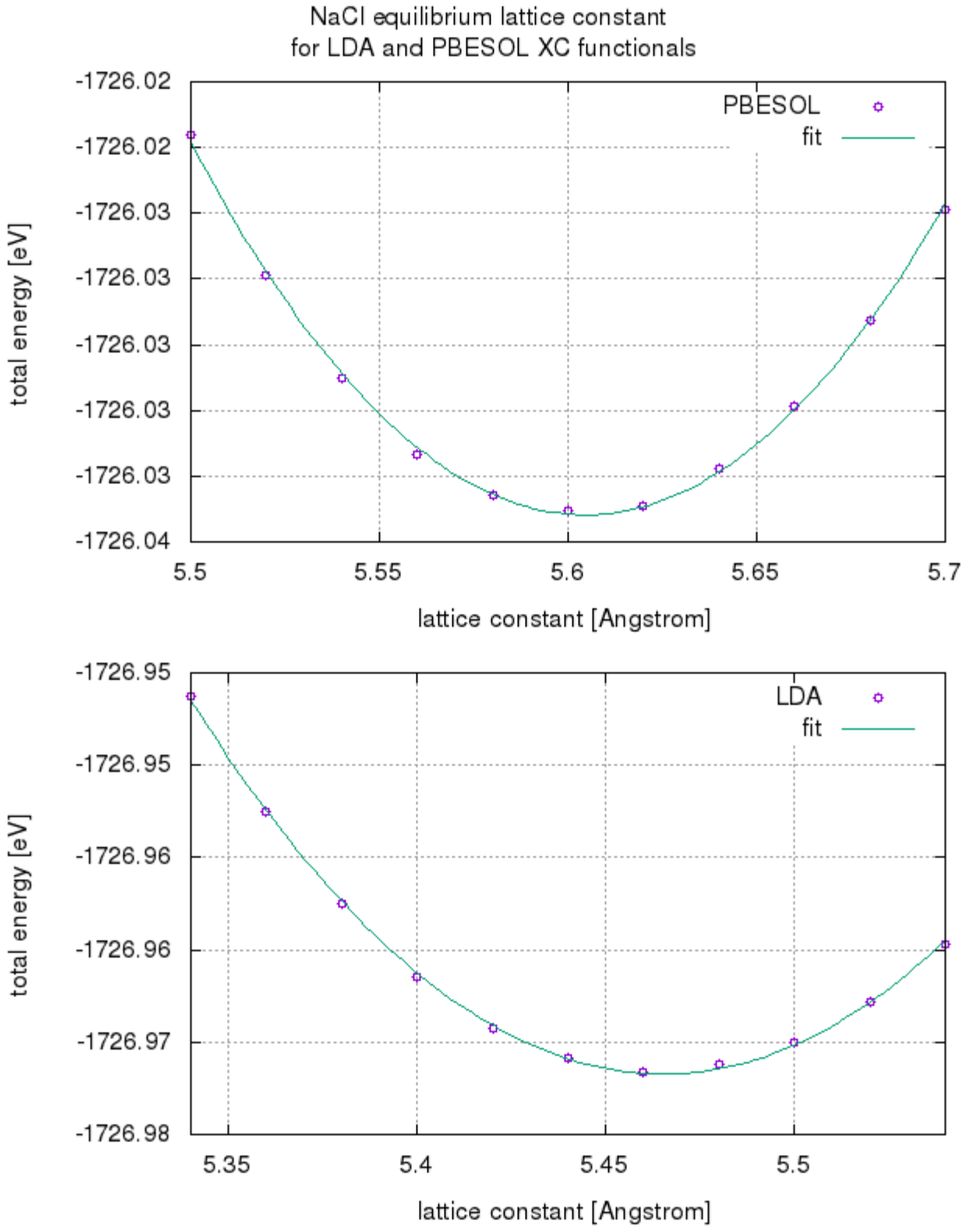
We've used the scripting package **PWTK 2.0** for all the Quantum Espresso calculations. First we've set up the basic input file `pw_NaCl_scf.pwtk` and then we've written a script `scan_lat_const.pwtk` which calculated total energies for different lattice constant values (ranging from *4 Å* to *10 Å* with *0.5 Å* step) for both LDA and PBESOL pseudopotentials.

In equilibrium, the crystal will have lattice constant that minimizes total energy. Using **Gnuplot** script `lat_const.plot`, the results of this search are:



We see that for both exchange-correlation functionals, the minimum appears to be somewhere around *5.5 Å*. Since every smooth function can be approximated by a parabola near its extremum, we've run another PWTK script `scan_lat_const_min`, now calculating total energies just close enough to the

anticipated minimum. Then we've used **Gnuplot** script `lat_const_min.plot` to visualize and fit the data with quadratic polynomial $f(x) = ax^2 + bx + c$. We can recover the minimum of this parabola as $x_{min} = \frac{-b}{2a}$. This dependence is:



and the calculated lattice constants:

Pseudopotential	Equilibrium lattice constant [Å]	Relative error
LDA	5.4652	3.08 %
PBESOL	5.6045	0.61 %

The lattice constant of NaCl is well-known and is equal to *5.639 Å* (http://lampx.tugraz.at/~hadley/ss1/crystalstructure/structures/nacl/nacl.php). Hence, the PBESOL pseudopotentials gave us by one order more precise answer than the LDA ones. Because LDA approximation is a very "rough" approximation, the bigger error is expected. On the other hand the result obtained using more refined PBESOL pseudopotential is in very good accordance with the tabulated value. Accuracy could be increased by using bigger energy cut-off and finer K-points mesh.

2.

> Calculate cohesive energy of Na atom in equilibrium structures obtained for LDA and PBESOL functionals. Discuss results.

Cohesive energy is defined as the difference between potential energy experienced by an atom in a given structure and energy of a free atom:

$$E_{coh}(a) = \frac{U(a)}{M} - E_{Na}$$

For this we first need to know the energy of a free sodium atom, which is calculated using scripts `pw_Na_atom_scf.pwtk` (setting of input) and `scan_free_Na_atom.pwtk` (actual calculation). Then we've found potential energies per atom (i.e. "total energy" in `pw.x` output files) for our calculated values of equilibrium lattice constants using `scan_eq_NaCl.pwtk` . Using `grep` on output files, we've found:

Pseudopotential	Free Na atom [Ry]	NaCl energy [Ry]	cohesive energy [Ry]
LDA	-91.9782	-126.9300	-34.9518
PBESOL	-92.0174	-126.8612	-34.8438

The calculated cohesive energies are close to each other, however we couldn't find any reference value (the only one being cohesive energy of NaCl crystalas a whole, where we need to additionaly subtract energy of a free Cl atom as well). Possible inaccuracies come from approximating energy of a free Na atom by energy of Na atoms in a cubic lattice with large lattice constant (*12 Å*). Furthermore, free Na atom has one unpaired valence electron, $3s^1$, which indicates a need to account for spin-polarization in calculations, which we haven't accounted for.