

Terminal exercise: DFT via Quantum ESPRESSO

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Summary

- 1 Information on Quantum ESPRESSO
- 2 Exercise: Graphene
- 3 Exercise: Graphite
- 4 Exercise: Silicene

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- 1 Information on Quantum ESPRESSO
- 2 Exercise: Graphene
 - Cut-off energy
 - Lattice constant
 - Band structure
 - Phonon (vibrational) modes at Γ point
 - Small comments
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Graphene

Change to the directory graphene

Cut-off energy

- Change value of input variable `ecutwfn` from 20 Ry upwards in steps of 5 Ry until the total energy changes less than 10 meV per atom between subsequent calculations
- Execute `pw.x` for the input file `relax.in`
(`mpirun -np 2 pw.x -in relax.in > relax.out &`)
- You can find the energy (in Ry!! $1 \text{ Ry} \approx 13.6056915 \text{ eV}$) with
`grep '! relax.out | tail -n 1`; remember to note down the value (or write into a different file)
- Question: Why does the calculation terminate immediately, without doing further optimisation steps of the ionic structure? Hint: Symmetry

Lattice constant

- Change the lattice constant (input variable a) in steps of $\pm 0.01 \text{ \AA}$ until you have found the lattice constant of lowest energy
- Use the value in the sub-sequent calculations

Band structure

- After the latest calculation with your chosen value of `ecutwfn` and `a`, run once again `pw.x`
- Then modify into the file `bs.in` your values
- Execute `pw.x` for the input file `bs.in`
- Execute `bands.x` for the input file `bands.in`
(`mpirun -np 2 pw.x -in bands.x -in bands.in`); you can directly plot the file `bands.out.gnu`, or you can execute the following steps
- Execute `plotband.x`; try how the input variables modify the resulting plot
- Use `gnuplot` or `xmgrace` to plot the output files generated in the latest step (with the filename prefix that you used)

Phonon (vibrational) modes at Γ point

- Execute `pw.x` for the input file `relax.in`
- Execute `ph.x` for the input file `ph.in`
- Study the output file
- Execute `dynmat.x` for the input file `dynmat.in`
- Study the phonon displacement modes with `xcrysden --axsf dynmat.axsf`; press `f` to view the displacement pattern drawn as arrows, pressing `F` you can modify the length scaling of the vectors (Length Factor). Which modes are lateral (along atomic plane), which ones vertical? What are the other modes?
- Study the symmetries of the modes; which modes are degenerate?

Small comments

- The value for the convergence in total energy is “arbitrary”. Actually one better use the target quantity (for example geometry, frequencies, ...) as the observable to choose reasonable cut-off energy
- Also the number of k points should be optimised (more points, better accuracy, but slower computations). This was not done here due to limitations in duration of the course
- One would actually fit the total energy as a function of time instead of only looking at the minimum of the energy (due to *eg* incomplete convergence of basis set *etc*)

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Graphite

Change to the directory `graphite`

Structure

- Investigate the geometry
- How do you obtain graphene from the structure of graphite?
- How many different kind of atoms (different coordination/number of neighbours) are there in graphite? What about graphene?

Band structure

- With your chosen values of `ecutwfn` and `a` for graphene, run `pw.x` on `relax.in`
- Then modify into the file `bs.in` your values
- Execute `pw.x` for the input file `bs.in`
- Execute `bands.x` for the input file `bands.in`
- Execute `plotband.x`; try how the input variables modify the resulting plot
- Use `gnuplot` or `xmgrace` to plot the output files generated in the latest step (with the filename prefix that you used)
- Compare the band structures of graphene and graphite. Question: Why the additional bands in the latter are flat? Hint: Strength of interaction

Small comments

- The example is again quite over-simplified: Actually the cell has two degrees of freedom, as also the length of the cell perpendicular to the planes, c , should be optimised. This is, however, a more complicated issue, as the GGAs are not able to capture the weak interaction between the layers (Question: Why?); thus a more appropriate treatment would be necessary, which we cannot go here in detail

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Silicene

Change to the directory `silicene`

Band structure

- Run `pw.x` for the file `relax.in`
- Execute `pw.x` for the input file `bs.in`
- Execute `bands.x` for the input file `bands.in`
- Execute `plotband.x`; try how the input variables modify the resulting plot
- Use `gnuplot` or `xmgrace` to plot the output files generated in the latest step (with the filename prefix that you used)
- Compare the structures and band structures of graphene and silicene

Phonon (vibrational) modes at Γ point

- Execute `pw.x` for the input file `relax.in`
- Execute `ph.x` for the input file `ph.in`
- Study the output file
- Execute `ph.x` for the input file `ph.in`
- Visualise the phonon modes
- What is striking in the resulting results? What does this mean? Hint: Look at the corresponding phonon displacement mode with `xcrysden`
- If you have time, what can one try to do to fix the “problem”? What is the result? Calculate the electronic band structure; is it qualitatively different from the first calculation? Why? Hint: Symmetry

Small comments

- As hint for the last point, try moving one of the two atoms out of plane in positive direction in z , the other one with the same amount in negative direction (this is the kind of distortion of lattice suggested by the normal mode having an imaginary, or “negative” frequency), and perform again the relaxation. Afterwards, run the rest of the calculation in the optimised geometry. You can also optimise the lateral lattice constant (a) before running the other calculations, if you have time