Sheet 7

November 24, 2025

Please hand in a zip-archive, containing a pdf for exercise 1, 2 and 3, as well as the plots for exercises 2 and 3, which is named *<firstname>_<lastname>_sheet_<number>*. Also include the in- and output files for exercises 2 and 3.

The deadline is Monday, Dec. 1st, 12:00 (noon). Please hand in your solution via moodle.

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1 Hellmann-Feynman theorem and force calculations

Prove the Hellmann-Feynman theorem, i.e., that derivatives of the total energy can be written as derivatives of the Hamiltonian:

$$\frac{\partial E_\lambda}{\partial \lambda} = \langle \psi(\lambda) | \frac{\partial H_\lambda}{\partial \lambda} | \psi(\lambda) \rangle . \tag{1}$$

Starting from this, show that the forces on nucleus I can be written as

$$F_I(\vec{R}_I) = \int d^3r n(\vec{r}) \frac{Z_I e^2 (\vec{r} - \vec{R}_I)}{\left|\vec{r} - \vec{R}_I\right|^3} + \sum_{J \neq I} \frac{Z_I Z_J e^2 (\vec{R}_I - \vec{R}_J)}{\left|\vec{R}_I - \vec{R}_J\right|^3}, \tag{2}$$

where Z_I is the electric charge of nucleus I. *3 points*

2 Hydrogen: Optimizing molecular structure

1. Perform an *scf* calculation for a single "isolated" hydrogen atom. Therefore prepare an input file containing a large ($a = 20$ Bohr radii) cubic lattice and one H atom, e.g., at position 0. Moreover, you will have to include smearing (see listing 1 for parameters). And, you will have to provide a pseudopotential for H.

   Listing 1: Please add these parameters to the input file to include smearing.

   ```
   occupations='smearing'
   smearing='gaussian'
   degauss = 0.01
   ```

   - Why do you have to use a large lattice parameter?
   - Why will it be enough to have only one k-point at Γ?

2 points

2. Next, include a second H atom in your calculation. Vary the distance between the two H atoms, and plot the total energy E_{tot} as a function of distance d_{HH}.
   What do you observe? And what is the physical interpretation?

   1 point

3. Finally, do a "*relax*" calculation. Start with the second atom at a distance of 2 Bohr radii. What do you observe? What happens if you start with a lattice parameter of 40 Bohr radii, and the second atom at a distance of 15 Bohr radii?
   Hint: you will need to introduce the &ions *namelist. Check* `https://www.quantum-espresso.org/Doc/INPUT_PW.html` *for how to include it.*

   1 point

3 Optimizing crystal geometry of diamond

1. Do a "*relax*" calculation for diamond. Start with a geometry, where you place the second atom at $\vec{r}_2 = (0.24, 0.24, 0.24)$ instead of $\vec{r}_2 = (0.25, 0.25, 0.25)$. Do you end up with the structure you expect?

   1 point

2. Now, also relax the unit cell parameters. What kind of calculation do you need for this?

   1 point

   Hint: you will additionally need to introduce the &cell *namelist.*

3. **Pulay stress:** repeat task 3.2, but vary the energy cutoff between 60 Ry and 100 Ry. What do you observe for the lattice parameter?

   1 point