

Sheet 8

November 27, 2025

Please hand in a zip-archive, containing a pdf for exercise 2, as well as the plots and input files for exercise 1, which is named `<firstname>_<lastname>_sheet_<number>`.

The deadline is Monday, Dec. 8th, 12:00 (noon). Please hand in your solution via moodle.

1 DFT: Phonons in diamond

In order to calculate phonons, second derivatives of the total energy have to be calculated. This can either be done by using finite displacements or, as implemented in Quantum Espresso, by using *Density Functional Perturbation Theory (DFPT)*. Follow the below steps to calculate phonon properties of diamond:

1. Perform an *scf* calculation.
2. Perform many “single phonon” calculations, i.e., phonon calculations on specific reciprocal points \vec{q} , starting from the below input and using *ph.x*. You can check the list of input variables here https://www.quantum-espresso.org/Doc/INPUT_PH.html.

Hint: you can provide ph.x a uniform grid of q-points.

This calculation might take on the order of 25 minutes on the virtual machine!

Listing 1: Example input file for *ph.x*.

```
&INPUTPH
  outdir = '...'
  prefix = '...'
  ldisp = .true.
  amass(1)      = 12.0107
  nq1 = 4
  nq2 = 4
  nq3 = 4
  fildyn = '...'
/
```

3. Use the below input and *q2r.x* to transform the dynamical matrix to real space.

Listing 2: Example input file for *q2r.x*.

```
&INPUT
  fildyn = '...' !Needs to be the same as above
```

```

zasr='no'
flfrc = 'force_constant_matrix.fc'
/

```

4. Perform a phonon dispersion calculation using *matdyn.x*. And plot the phonon dispersion. What path in reciprocal space has been provided? What does *asr* stand for? What changes if you use different parameters, e.g., *asr* = '*crystal*' and *asr* = '*no*'?

Listing 3: Example input file for *matdyn.x*.

```

&INPUT
asr              =  '... ',
amass(1)        =  12.0107,
flfrc           =  '... ',
q_in_band_form  =  .true.
/
2
0.0000000      0.0000000      0.0000000  20
0.0000000      1.0000000      0.0000000  20

```

5. Repeat task 1.4 with the path used for electronic bands on sheet 6, i.e., $\Gamma - X - K - \Gamma$. (You can use the coordinates for the points used in that sheet, one option to generate k-paths is e.g. <https://www.materialscloud.org/work/tools/seekpath>.)
6. Adapt the input for *matdyn.x* such that the *phonon density of states* is calculated instead of the dispersion. And plot the result.

5 points

2 Born-Oppenheimer and adiabatic approximations

In order to solve a many-body Schrödinger equation which describes electrons and ions which are interacting with each other, it makes sense to expand the wave-function in terms of the electronic eigenstates

$$\Psi_{e,n}(\{\vec{r}\}, \{\vec{R}\}) = \sum_i c_{n,i}(\{\vec{R}\}) \Psi_{e,i}(\{\vec{r}\} | \{\vec{R}\}). \quad (1)$$

In the lecture you derived the non-adiabatic coupling operator

$$\Lambda_{ij} = \int d^3r \Psi_{e,j}^* \left(-\sum_I \frac{\hbar^2 \nabla_{\vec{R}_I}^2}{2M_I} \right) \Psi_{e,i} + \sum_I \frac{1}{M_I} \int d^3r \Psi_{e,j}^* (-i\hbar \nabla_{\vec{R}_I}) \Psi_{e,i} (-i\hbar \nabla_{\vec{R}_I}). \quad (2)$$

Here the index I labels the ions, and i and j label electronic states. Together with the electronic eigenenergies $E_i(\{\vec{R}\})$ and the ionic potential $V_n(\{\vec{R}\})$ the non-adiabatic

coupling operator acts on the nuclear wave functions $c_{n,i}(\{\vec{R}\})$ associated with the i -th electronic state, resulting in the Schrödinger equation

$$\sum_j \left(\Lambda_{ij} + \delta_{ij} E_j(\{\vec{R}\}) \right) c_{n,j}(\{\vec{R}\}) + \left(V_n(\{\vec{R}\}) + \hat{T}_n \right) c_{n,i}(\{\vec{R}\}) = E_n c_{n,i}(\{\vec{R}\}). \quad (3)$$

We can see that this equation would be far simpler if $\Lambda_{ij} \propto \delta_{ij}$, since then there would be no coupling between the different electronic eigenstates. Making the assumption that this is the case is called the *adiabatic approximation*.

1. Look up the *adiabatic theorem*, and explain why the adiabatic approximation has that name, and what the physical intuition behind it is.

1 point

2. Show that the diagonal elements of Λ_{ij} can be written as

$$\Lambda_{ii} = - \sum_I \frac{\hbar^2}{2M_I} \int d^3r \Psi_{e,i}^* \nabla_{\vec{R}_I}^2 \Psi_{e,i}, \quad (4)$$

if the electronic wave-functions $\Psi_{e,i}$ can be chosen to be real. (Point out why this condition is necessary.)

Hint: The electronic wave functions are normalised, and $\frac{\partial}{\partial x} 1 = 0$.

2 points

3. Show that the adiabatic approximation is solved by a product Ansatz of a single electronic and a single nuclear state $\Psi_{e,n}(\{\vec{r}\}, \{\vec{R}\}) = c_{n,i}(\{\vec{R}\}) \Psi_{e,i}(\{\vec{r}\} | \{\vec{R}\})$.

1 point

4. For the Born-Oppenheimer approximation we also assume $\Lambda_{ii} = 0$. Does this imply whether the ions should be treated classically or quantum mechanically? Justify your answer.

1 point