Introduction to the Theory of Lattice Vibrations and their Ab Initio Calculation

Lecture 5: Hands-on tutorial on the calculation of harmonic phonons with DFT

Ion Errea

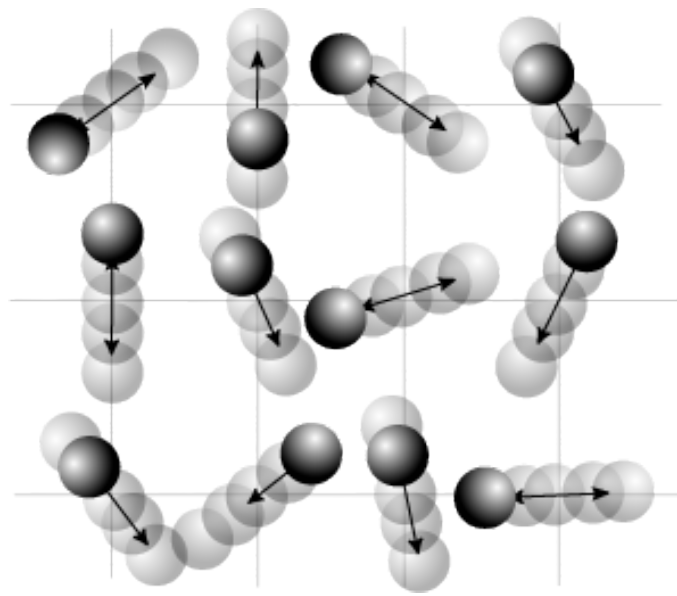
Dept. Applied Physics, University of the Basque Country (UPV/EHU), San Sebastian, Spain

Centro de Fśica de Materiales (CSIC-UPV/EHU), San Sebastian, Spain

Donostia International Physics Center, San Sebastian, Spain

University of Science and Technology Beijing

March and April 2022



eman ta zabal zazu

Universidad del País Vasco

Euskal Herriko Unibertsitatea

CFM Materials Physics Center

Centro de Física de Materiales

DIPC Donostia International Physics Center

REMARKS BEFORE STARTING:

This tutorial is based on different calculations performed with Quantum Espresso. All the input files are provided in
Lecture5_Phonon_Tutorial/TiSe2_DFPT/
Lecture5_Phonon_Tutorial/TiSe2_Frozen_Phonon/
Lecture5_Phonon_Tutorial/BaTiO3_DFPT/
Lecture5_Phonon_Tutorial/BaTiO3_Finite_Difference/

If you have Quantum Espresso installed you can run these examples yourself with the scripts called run.sh. If not you can install it yourself locally in your computer.

I will use matplotlib to plot the phonon spectra so you will need to have python and matplotlib installed in your computer.

In order to perform the last example you will need to install phonopy. If you have python you can install it through Conda as
conda install -c conda-forge phonopy

Outline

$TiSe_2$: Crystal structure

Example: $TiSe_2$ DFPT calcultion

- A transition metal dichalcogenide with a layered structure
- Crystal structure:
  - $P\bar{3}m1$ (164) space group, ($\bar{3}m$ point group)
  - Wyckoff positions

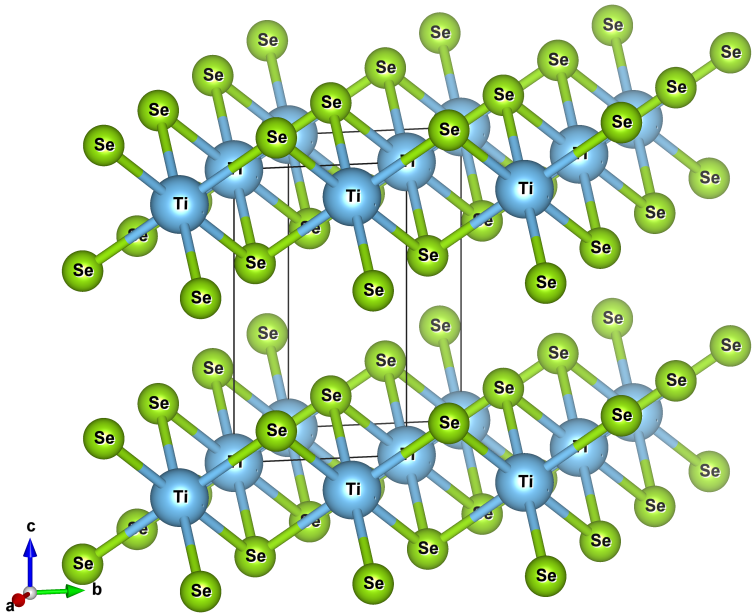
    Ti 1a $(0, 0, 0)$

    Se 2d $(1/3, 2/3, z)$
- Structural parameters taken for the example correspond to $\sim$ 10 GPa

  $a = b = 6.239a_0$ $\quad c = 10.353a_0$

  $\alpha = \beta = 90^\circ$ $\quad \gamma = 120^\circ$

  $z = 0.2832$



$TiSe_2$: Crystal structure

bilbao crystallographic server

Exercise 1

- Determine the number of symmetry operations with GENPOS
- Will forces on atoms vanish by symmetry?
  Use WYCKPOS to help you answer the question

$TiSe_2$: Crystal structure

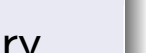
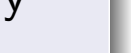
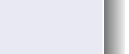
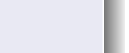
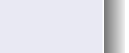
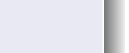
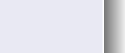
bilbao crystallographic server

Exercise 1

- Determine the number of symmetry operations with GENPOS
  There are 12 symmetry operations
- Will forces on atoms vanish by symmetry?
  Use WYCKPOS to help you answer the question

General Positions of the Group 164 (*P*-3*m*1)

Click here to get the general positions in text format

No.	(x,y,z) form	Matrix form	Symmetry operation	
			ITA	Seitz
1	x,y,z		1	{1 | 0}
2	-y,x-y,z		3^+ 0,0,z	$\{3^+_{001} \mid 0\}$
3	-x+y,-x,z		3^- 0,0,z	$\{3^-_{001} \mid 0\}$
4	y,x,-z		2 x,x,0	$\{2_{110} \mid 0\}$
5	x-y,-y,-z		2 x,0,0	$\{2_{100} \mid 0\}$
6	-x,-x+y,-z		2 0,y,0	$\{2_{010} \mid 0\}$
7	-x,-y,-z		-1 0,0,0	{-1 | 0}
8	y,-x+y,-z		-3^+ 0,0,z; 0,0,0	$\{-3^+_{001} \mid 0\}$
9	x-y,x,-z		-3^- 0,0,z; 0,0,0	$\{-3^-_{001} \mid 0\}$
10	-y,-x,z		m x,-x,z	$\{m_{110} \mid 0\}$
11	-x+y,y,z		m x,2x,z	$\{m_{100} \mid 0\}$
12	x,x-y,z		m 2x,x,z	$\{m_{010} \mid 0\}$

$TiSe_2$: Crystal structure

bilbao crystallographic server

Exercise 1

- Determine the number of symmetry operations with GENPOS
  There are 12 symmetry operations
- Will forces on atoms vanish by symmetry?
  Use WYCKPOS to help you answer the question
  The force on the Ti atoms in the $2d$ Wyckoff positions along the z direction will not vanish by symmetry. All the rest will be 0 by symmetry

Wyckoff Positions of Group 164 (*P*-3*m*1)

Multiplicity	Wyckoff letter	Site symmetry	Coordinates
12	j	1	(x,y,z) (-y,x-y,z) (-x+y,-x,z) (y,x,-z) (x-y,-y,-z) (-x,-x+y,-z) (-x,-y,-z) (y,-x+y,-z) (x-y,x,-z) (-y,-x,z) (-x+y,y,z) (x,x-y,z)
6	i	.m.	(x,-x,z) (x,2x,z) (-2x,-x,z) (-x,x,-z) (2x,x,-z) (-x,-2x,-z)
6	h	.2.	(x,0,1/2) (0,x,1/2) (-x,-x,1/2) (-x,0,1/2) (0,-x,1/2) (x,x,1/2)
6	g	.2.	(x,0,0) (0,x,0) (-x,-x,0) (-x,0,0) (0,-x,0) (x,x,0)
3	f	.2/m.	(1/2,0,1/2) (0,1/2,1/2) (1/2,1/2,1/2)
3	e	.2/m.	(1/2,0,0) (0,1/2,0) (1/2,1/2,0)
2	d	3m.	(1/3,2/3,z) (2/3,1/3,-z)
2	c	3m.	(0,0,z) (0,0,-z)
1	b	-3m.	(0,0,1/2)
1	a	-3m.	(0,0,0)

$TiSe_2$: DFT calculation

- The example can be found in

  `Lecture5_Phonon_Tutorial/TiSe2_DFPT`

- QE website:
  `https://www.quantum-espresso.org`
- We will use the Bilbao Crystallographic Server to perform the symmetry analysis and help us in the calculations:
  `https://www.cryst.ehu.es`

We will use QE to calculate

- TA simple DFT KS calculation to get the electronic density and KS potential
- DFPT calculation at Γ
- DFPT calculation at M
- DFPT calculation at A
- DFPT calculation on a regular grid
- Fourier transform to calculate force constants
- Fourier transform back to get the phonon spectrum in a path

$TiSe_2$: 1BZ and special points

Exercise 2

- Open the 1BZ corresponding to $TiSe_2$ crystal with KVEC
- Determine a path along high-symmetry lines with its coordinates (CDML coordinates)

bilbao crystallographic server

$TiSe_2$: 1BZ and special points

Exercise 2

- Open the 1BZ corresponding to $TiSe_2$ crystal with KVEC
- Determine a path along high-symmetry lines with its coordinates (CDML coordinates)

  A possible path along high-symmetry lines is $\Gamma MK\Gamma ALHA$

$$\mathbf{q}_\Gamma = (0,0,0) = 0$$

$$\mathbf{q}_M = (1/2,0,0) = \frac{\mathbf{b}_1}{2}$$

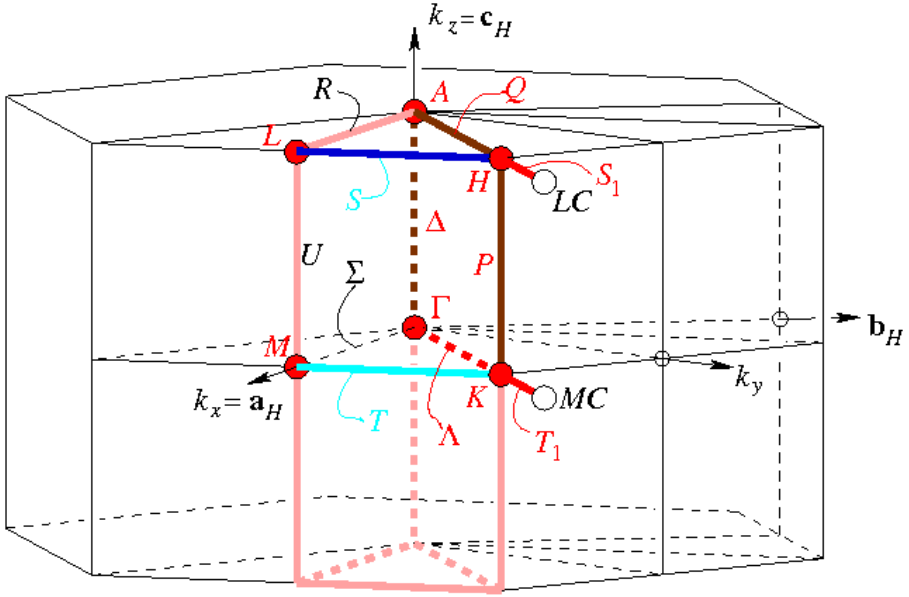
$$\mathbf{q}_K = (1/3,1/3,0) = \frac{\mathbf{b}_1}{3} + \frac{\mathbf{b}_2}{3}$$

$$\mathbf{q}_A = (0,0,1/2) = \frac{\mathbf{b}_3}{2}$$

$$\mathbf{q}_L = (1/2,0,1/2) = \frac{\mathbf{b}_1}{2} + \frac{\mathbf{b}_3}{2}$$

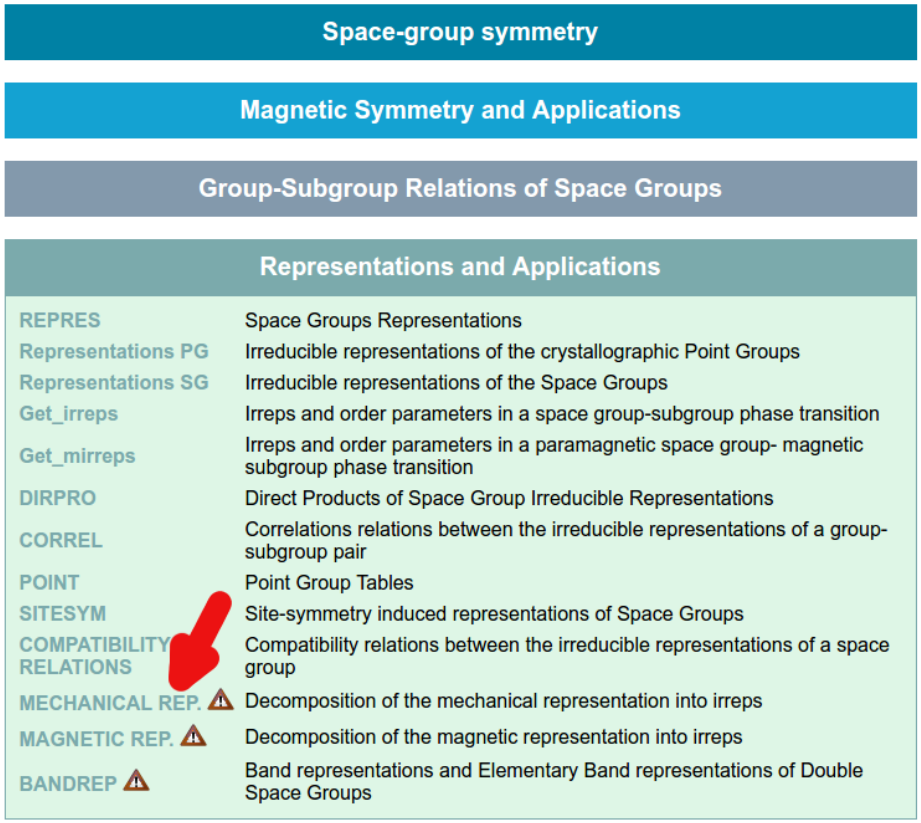
$$\mathbf{q}_H = (1/3,1/3,1/2) = \frac{\mathbf{b}_1}{3} + \frac{\mathbf{b}_2}{3} + \frac{\mathbf{b}_3}{2}$$

bilbao crystallographic server



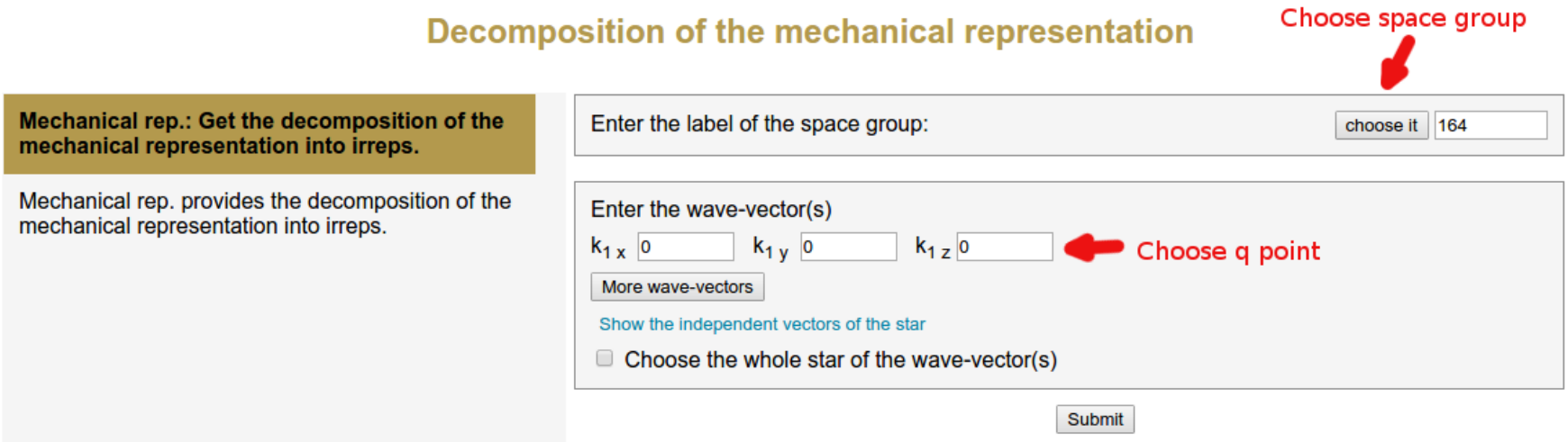
MECHANICAL REP.

- The number of phonon modes expected with different frequencies for a given **q** point is determined by symmetry
- It coincides with the number of irreps in the little co-group of **q** present in the crystal: **Mechanical representations**
- The BCS has the MECHANICAL REP. program to calculate the mechanical representations for a given **q** point



MECHANICAL REP.

- Choose the space group and the **q** point



- The mechanical representations decomposed into irreps for each Wyckoff position

Decomposition of the mechanical representation of the space group (N. 164)

Wave-vector: GM:(0,0,0)

Wyckoff position	Decomposition into irreps
12j:(x,y,z)	3 GM1+(1) ⊕ 3 GM2+(1) ⊕ 6 GM3+(2) ⊕ 3 GM1-(1) ⊕ 3 GM2-(1) ⊕ 6 GM3-(2)
6i:(x,-x,z)	2 GM1+(1) ⊕ GM2+(1) ⊕ 3 GM3+(2) ⊕ GM1-(1) ⊕ 2 GM2-(1) ⊕ 3 GM3-(2)
6h:(x,0,1/2)	GM1+(1) ⊕ 2 GM2+(1) ⊕ 3 GM3+(2) ⊕ GM1-(1) ⊕ 2 GM2-(1) ⊕ 3 GM3-(2)
6g:(x,0,0)	GM1+(1) ⊕ 2 GM2+(1) ⊕ 3 GM3+(2) ⊕ GM1-(1) ⊕ 2 GM2-(1) ⊕ 3 GM3-(2)
3f:(1/2,0,1/2)	GM1-(1) ⊕ 2 GM2-(1) ⊕ 3 GM3-(2)
3e:(1/2,0,0)	GM1-(1) ⊕ 2 GM2-(1) ⊕ 3 GM3-(2)
2d:(1/3,2/3,z)	GM1+(1) ⊕ GM3+(2) ⊕ GM2-(1) ⊕ GM3-(2)
2c:(0,0,z)	GM1+(1) ⊕ GM3+(2) ⊕ GM2-(1) ⊕ GM3-(2)
1b:(0,0,1/2)	GM2-(1) ⊕ GM3-(2)
1a:(0,0,0)	GM2-(1) ⊕ GM3-(2)

In parenthesis the dimension of the irreducible representation

- At Γ we expect 6 different irreps:
  - 3 non-degenerate modes
  - 3 doubly-degenerate modes

$TiSe_2$: modes at **q** points

bilbao crystallographic server

Exercise 3

Determine the number of non-degenerate modes and the expected degeneracies of $TiSe_2$ at M and A points

$TiSe_2$: modes at **q** points

bilbao crystallographic server

Exercise 3

Determine the number of non-degenerate modes and the expected degeneracies of $TiSe_2$ at *M* and *A* points

The dimension of the irreps are given for the full representation that contains all the **q** points in the star. Thus, the dimension for a given point should be divided by the number of **q** points in the star

- *M*
  We expect 9 modes, none of them degenerate
- *A*
  We expect 6 non-degenerate modes: 3 non-degenerate, 3 doubly-degenerate

Wave-vector: M:(1/2,0,0),(1/2,1/2,0),(0,1/2,0)

Wyckoff position	Decomposition into irreps
12j:(x,y,z)	9 M1+(3) ⊕ 9 M2+(3) ⊕ 9 M1-(3) ⊕ 9 M2-(3)
6i:(x,-x,z)	5 M1+(3) ⊕ 4 M2+(3) ⊕ 4 M1-(3) ⊕ 5 M2-(3)
6h:(x,0,1/2)	4 M1+(3) ⊕ 5 M2+(3) ⊕ 4 M1-(3) ⊕ 5 M2-(3)
6g:(x,0,0)	4 M1+(3) ⊕ 5 M2+(3) ⊕ 4 M1-(3) ⊕ 5 M2-(3)
3f:(1/2,0,1/2)	3 M1+(3) ⊕ 3 M2+(3) ⊕ M1-(3) ⊕ 2 M2-(3)
3e:(1/2,0,0)	3 M1+(3) ⊕ 3 M2+(3) ⊕ M1-(3) ⊕ 2 M2-(3)
2d:(1/3,2/3,z)	2 M1+(3) ⊕ M2+(3) ⊕ M1-(3) ⊕ 2 M2-(3)
2c:(0,0,z)	2 M1+(3) ⊕ M2+(3) ⊕ M1-(3) ⊕ 2 M2-(3)
1b:(0,0,1/2)	M1-(3) ⊕ 2 M2-(3)
1a:(0,0,0)	M1-(3) ⊕ 2 M2-(3)

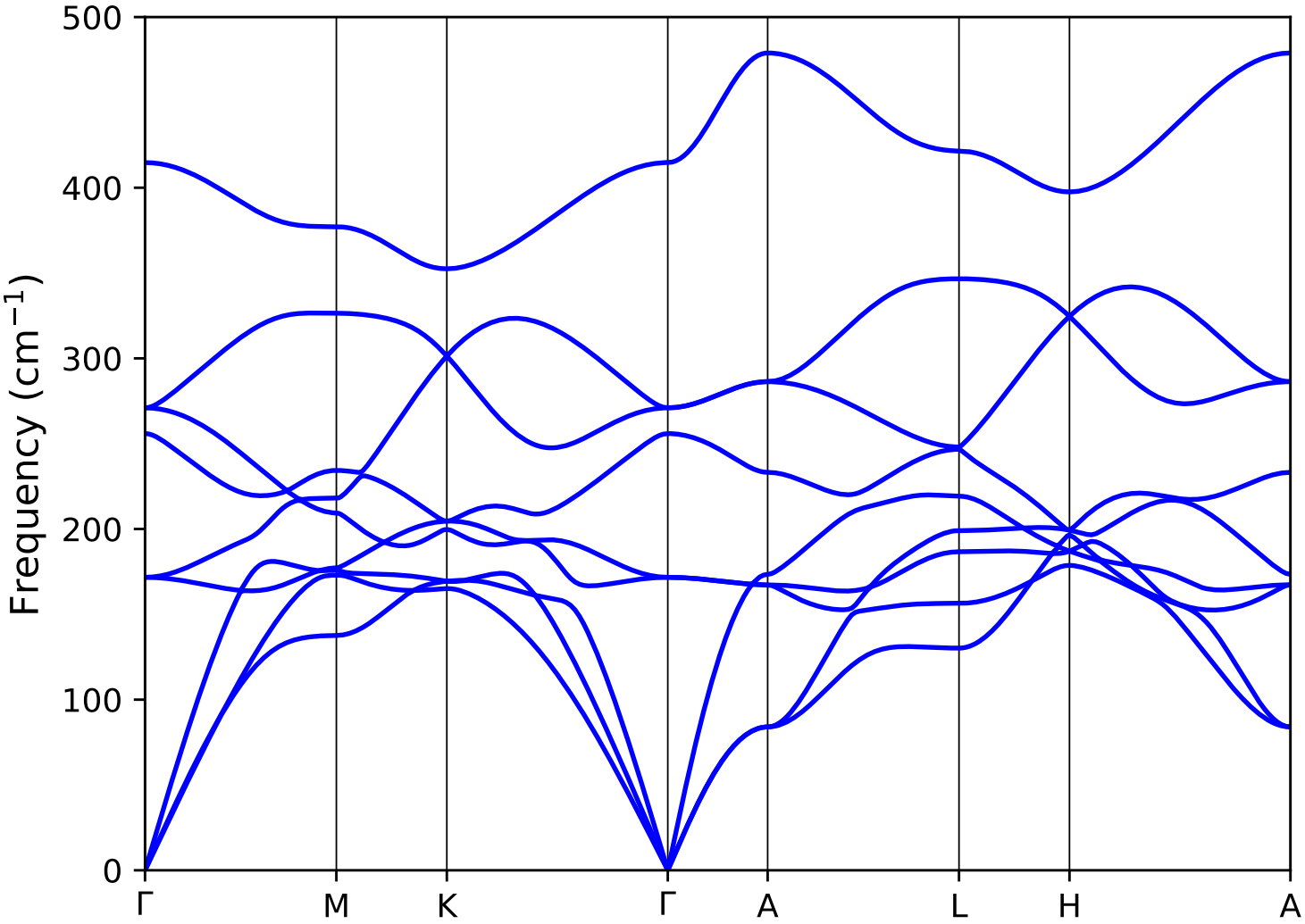
In parenthesis the dimension of the irreducible representation

Wave-vector: A:(0,0,1/2)

Wyckoff position	Decomposition into irreps
12j:(x,y,z)	3 A1+(1) ⊕ 3 A2+(1) ⊕ 6 A3+(2) ⊕ 3 A1-(1) ⊕ 3 A2-(1) ⊕ 6 A3-(2)
6i:(x,-x,z)	2 A1+(1) ⊕ A2+(1) ⊕ 3 A3+(2) ⊕ A1-(1) ⊕ 2 A2-(1) ⊕ 3 A3-(2)
6h:(x,0,1/2)	2 A1+(1) ⊕ A2+(1) ⊕ 3 A3+(2) ⊕ 2 A1-(1) ⊕ A2-(1) ⊕ 3 A3-(2)
6g:(x,0,0)	A1+(1) ⊕ 2 A2+(1) ⊕ 3 A3+(2) ⊕ A1-(1) ⊕ 2 A2-(1) ⊕ 3 A3-(2)
3f:(1/2,0,1/2)	2 A1+(1) ⊕ A2+(1) ⊕ 3 A3+(2)
3e:(1/2,0,0)	A1-(1) ⊕ 2 A2-(1) ⊕ 3 A3-(2)
2d:(1/3,2/3,z)	A1+(1) ⊕ A3+(2) ⊕ A2-(1) ⊕ A3-(2)
2c:(0,0,z)	A1+(1) ⊕ A3+(2) ⊕ A2-(1) ⊕ A3-(2)
1b:(0,0,1/2)	A1+(1) ⊕ A3+(2)
1a:(0,0,0)	A2-(1) ⊕ A3-(2)

In parenthesis the dimension of the irreducible representation

$TiSe_2$: DFPT calculation of phonon spectra



SAM: mode displacement

bilbao crystallographic server

In order to determine the displacements of the atoms of a mode at Γ we can use the SAM program

Modes Activity

This table is a summary of the activity of the different modes of the space group.

-	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_u	E_g
Infrared	·	·	·	x	x	·
Raman	x	·	·	·	·	x
Hyper-Raman	·	x	·	x	x	·

Note: x ≡ represents th modes which can be detected.

More information: show hide

SAM: mode displacement

- The program tells us for each irrep which are the Wyckoff positions that are moving

Mechanical Representation

The mechanical representation is defined as the direct product of the permutational r
the chosen Wyckoff positions is given in the following table.

WP	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_u	E_g	Modes
1a	·	·	·	1	1	·	Show
2d	1	·	·	1	1	1	Show

Note: Click in the *Show* option to obtain the symmetry adapted modes for a given orbit.

SAM: mode displacement

- Clicking in show it will tell us how each atom moves for each irrep

WP	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_u	E_g	Modes
1a	·	·	·	1	1	·	Show
2d	1	·	·	1	1	1	Show

Irrep: A_{2u}

M	1a	A_{2u}
X_1	(0,0,0)	·
Y_1		·
Z_1		1

Irrep: E_u

M	1a	E_u	
X_1	(0,0,0)	1	·
Y_1		·	1
Z_1		·	·

Irrep: A_{1g}

M	2d	A_{1g}
X_1	(1/3,2/3,z)	·
Y_1		·
Z_1		-1
X_2	(2/3,1/3,-z)	·
Y_2		·
Z_2		1

Irrep: A_{2u}

M	2d	A_{2u}
X_1	(1/3,2/3,z)	·
Y_1		·
Z_1		1
X_2	(2/3,1/3,-z)	·
Y_2		·
Z_2		1

Irrep: E_u

M	2d	E_u	
X_1	(1/3,2/3,z)	1	·
Y_1		·	1
Z_1		·	·
X_2	(2/3,1/3,-z)	1	·
Y_2		·	1
Z_2		·	·

Irrep: E_g

M	2d	E_g	
X_1	(1/3,2/3,z)	·	1
Y_1		-1	·
Z_1		·	·
X_2	(2/3,1/3,-z)	·	-1
Y_2		1	·
Z_2		·	·

SAM: mode displacement for frozen phonon

- If a given irrep only involves displcaments of one Wyckoff position the displacements given by the server correspond to (non-normalized) polarization vectors of the mode
- We can use this info to prepare a frozen phonon calculation of a phonon mode at Γ

$$u_a(Q_\mu) = \frac{e_\nu^a}{\sqrt{M_a}} Q_\mu$$

SAM: mode displacement for frozen phonon

Steps to follow to prepare the frozen phonon calculation

1. Get the polarization vectors by renormalizing the vectors given by the SAM program. For the A_{1g} mode

$$\boldsymbol{e}_{(1/3,2/3,z)}[A_{1g}\Gamma] = \frac{1}{\sqrt{2}}\begin{pmatrix}0\\0\\-1\end{pmatrix} \qquad \boldsymbol{e}_{(2/3,1/3,-z)}[A_{1g}\Gamma] = \frac{1}{\sqrt{2}}\begin{pmatrix}0\\0\\1\end{pmatrix}$$

Irrep: A_{1g}

M	2d	A_{1g}
X_1	(1/3,2/3,z)	·
Y_1		·
Z_1		-1
X_2	(2/3,1/3,-z)	·
Y_2		·
Z_2		1

2. Build the displacements as a funciton of A. For this mode

$$\boldsymbol{u}_{(1/3,2/3,z)}[A_{1g}\Gamma] = \frac{1}{\sqrt{2M_{Se}}}\begin{pmatrix}0\\0\\-1\end{pmatrix} Q$$

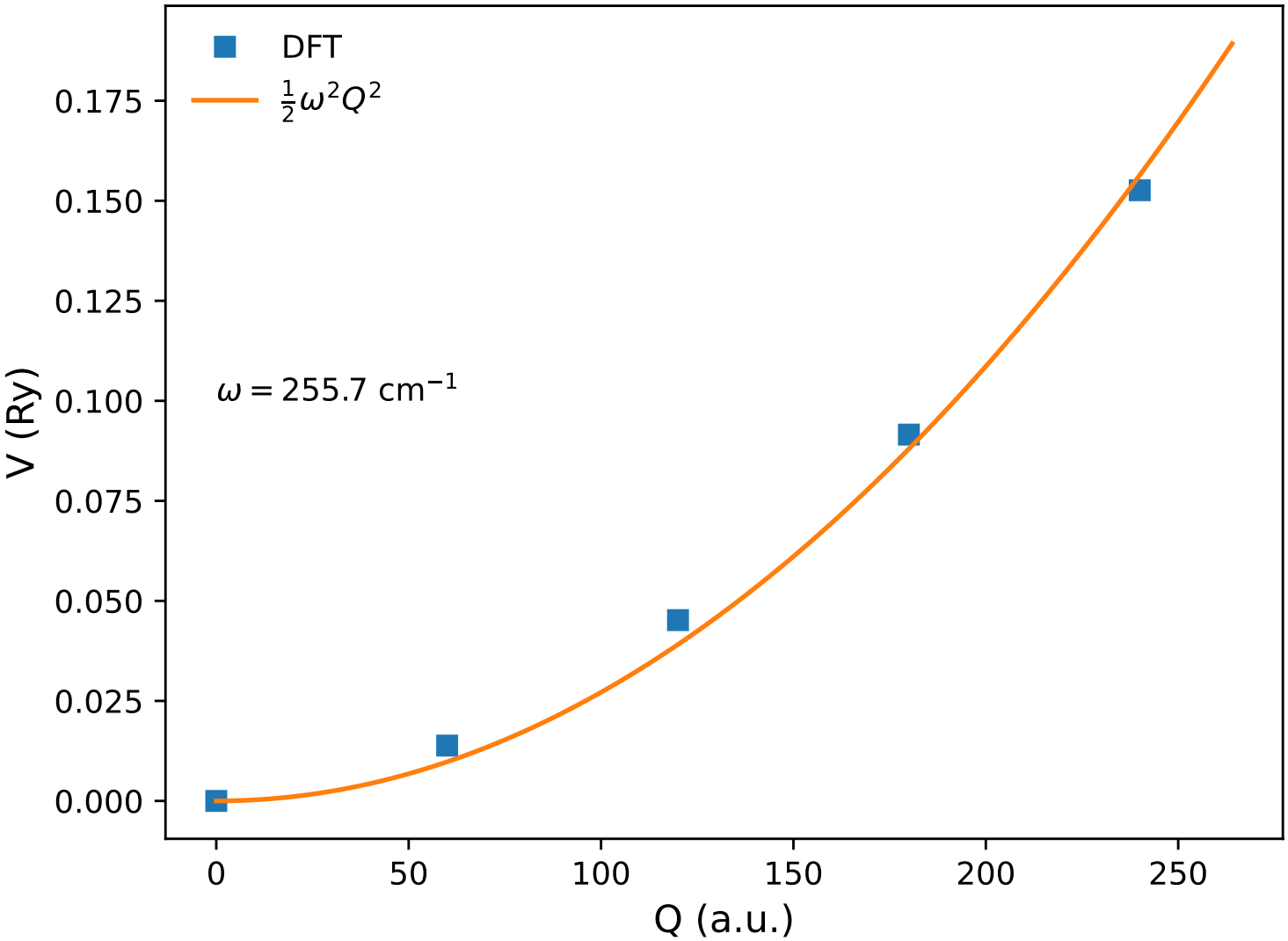
$$\boldsymbol{u}_{(2/3,1/3,-z)}[A_{1g}\Gamma] = \frac{1}{\sqrt{2M_{Se}}}\begin{pmatrix}0\\0\\1\end{pmatrix} Q$$

3. Calculate the DFT energy for the distorted structure as a function of Q, and calculate second derivative at $Q = 0$

$TiSe_2$: frozen phonon for the A_{1g} mode at Γ

The example can be found in

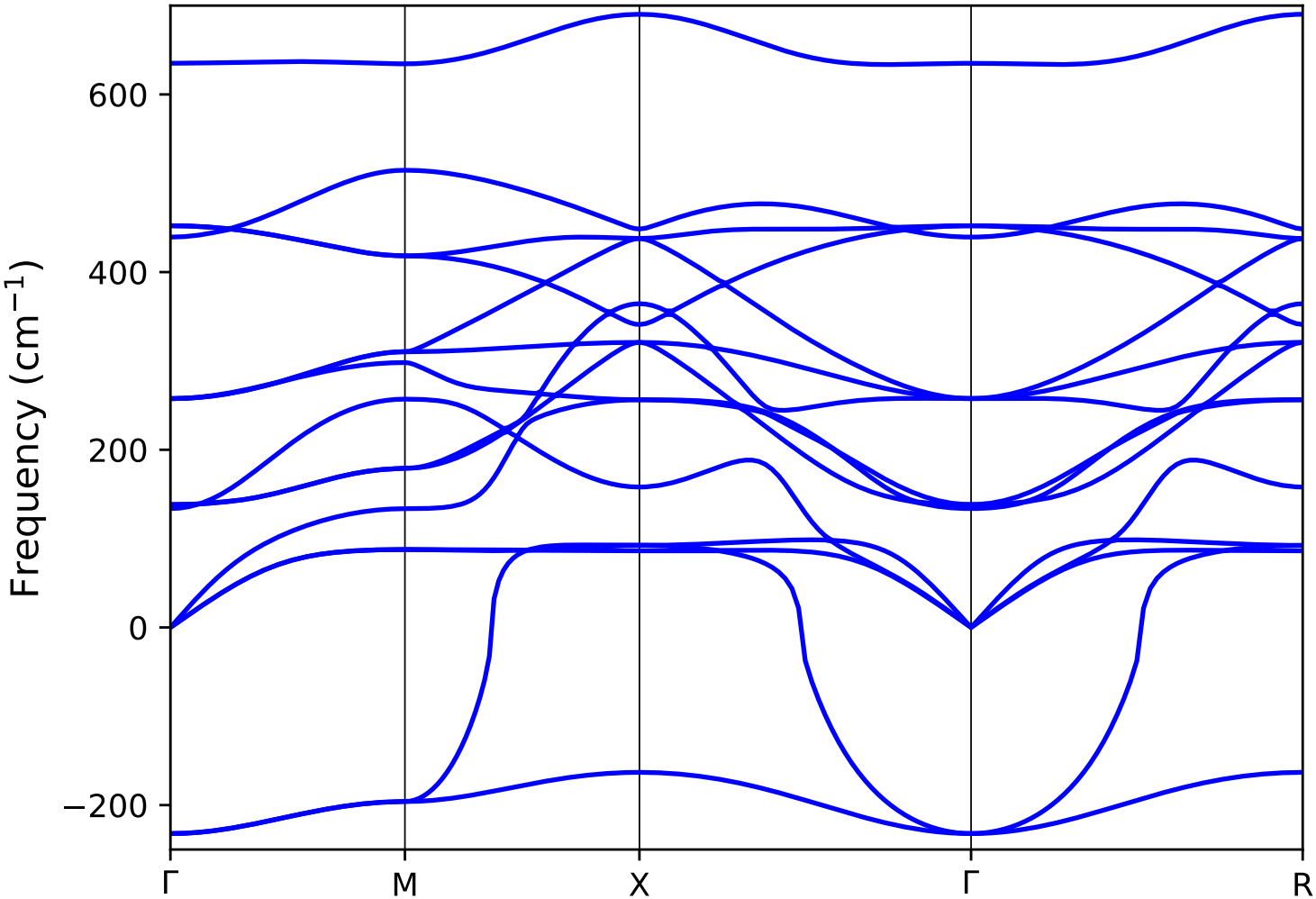
`Lecture5_Phonon_Frozen_Phonon/TiSe2_DFPT`



$BaTiO_3$: DFPT calculation of the phonon spectra in an insulator

The example can be found in

`Lecture5_Phonon_Frozen_Phonon/BaTiO3_DFPT`

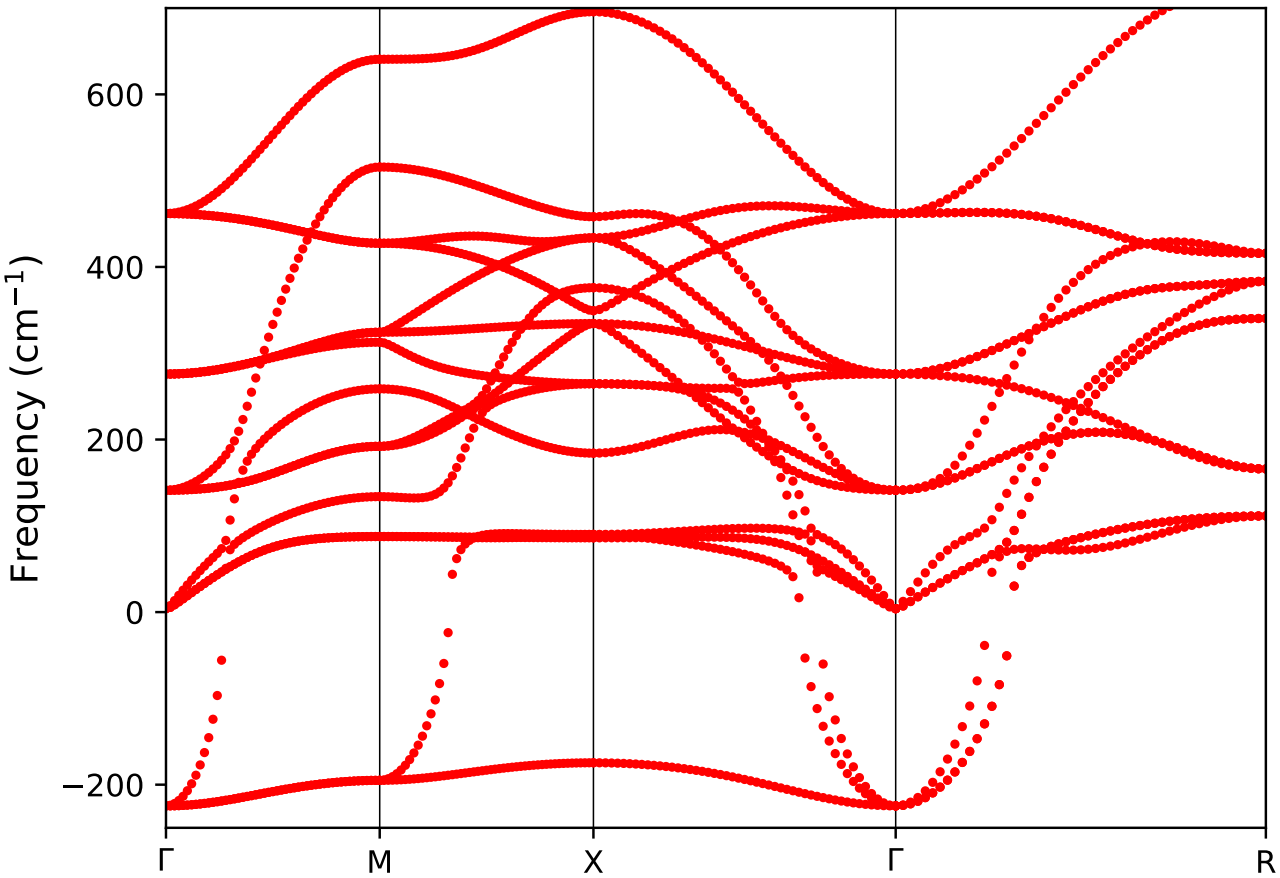


$BaTiO_3$: DFT finite displacements calculation of the phonon spectra in an insulator

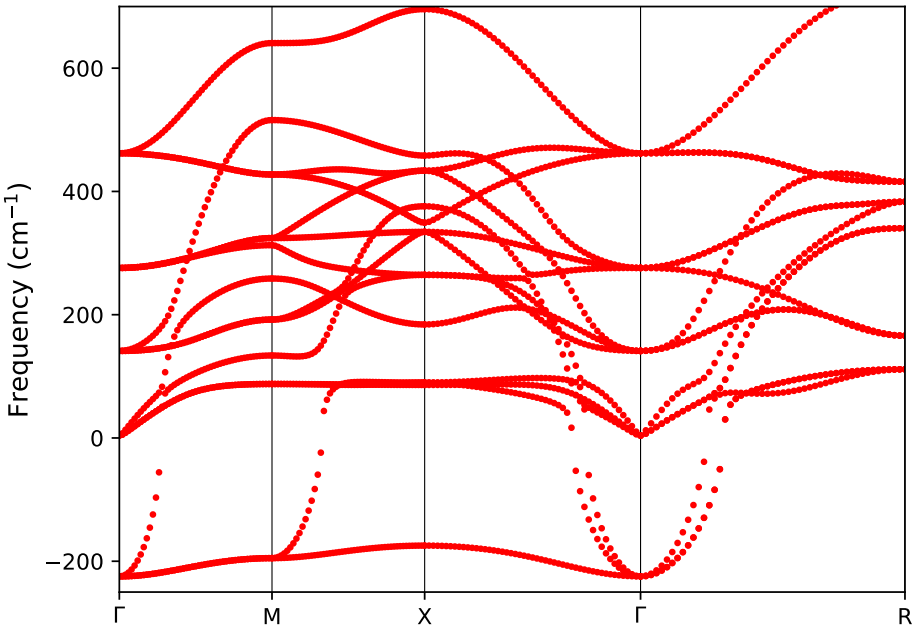
- The example can be found in

  `Lecture5_Phonon_Frozen_Phonon/BaTiO3_Finite_Difference`

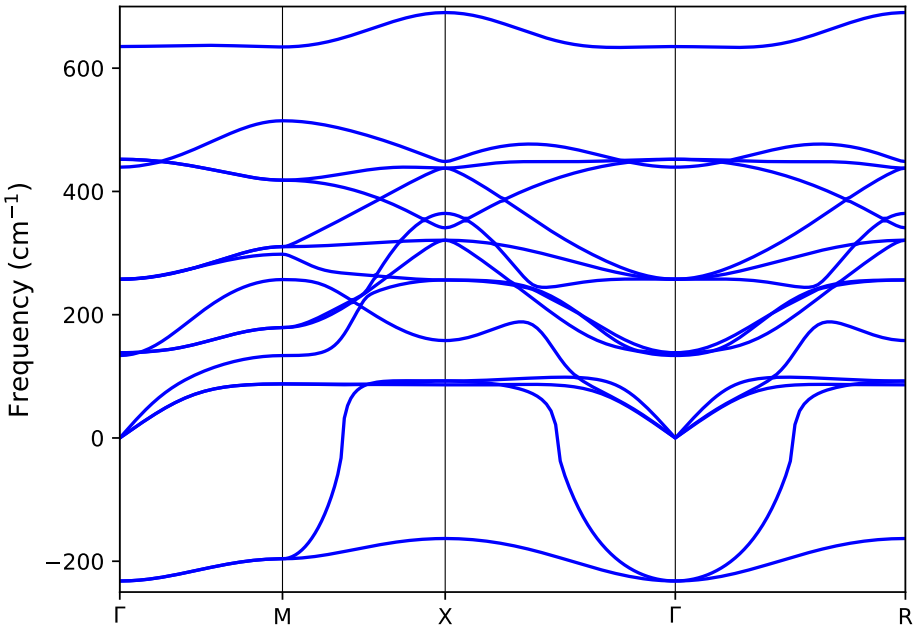
- The calculation is performed combining PHONOPY with QE



$BaTiO_3$: Comparison between DFPT and finite displacements methods



Finite Differences



DFPT