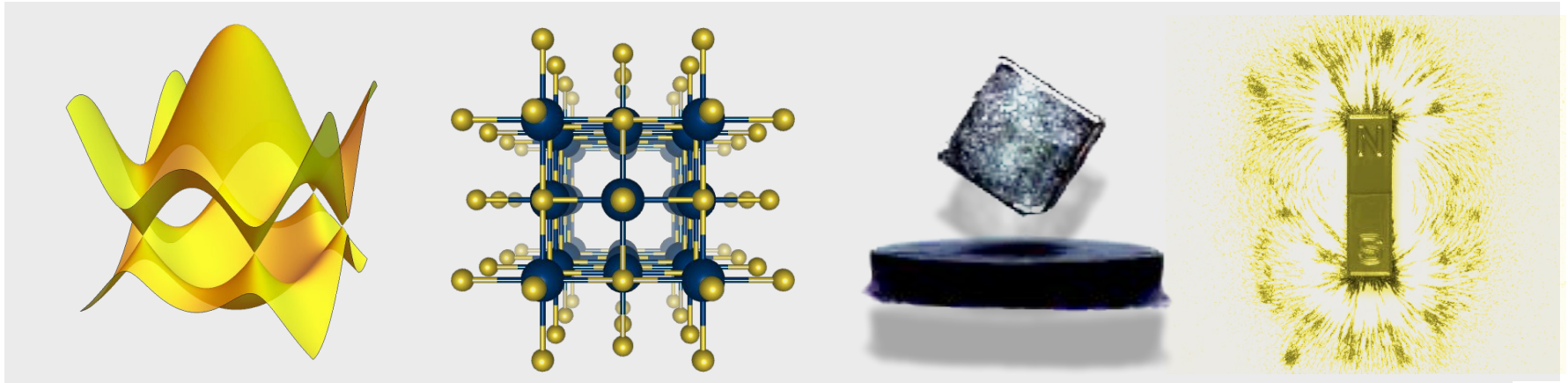


# ESCOLA SÉRGIO MASCARENHAS DE FÍSICA DA MATÉRIA CONDENSADA

Hands-On 3 - Computational

Phonons



## → Connecting to the VPN (Virtual Private Network)

```
>> sudo vpnc-connect /etc/vpnc/sdumont.conf --enable-weak-encryption
>> Enter password for login@146.134.0.14:
>> VPNC started in background (pid: ###)...
```

## → Log in to SDummont:

```
>> ssh your\_username@login.sdumont.lncc.br
>> password:
```

## → Go to your scratch area:

```
>> cd /scratch/efmc24/your\_username
```

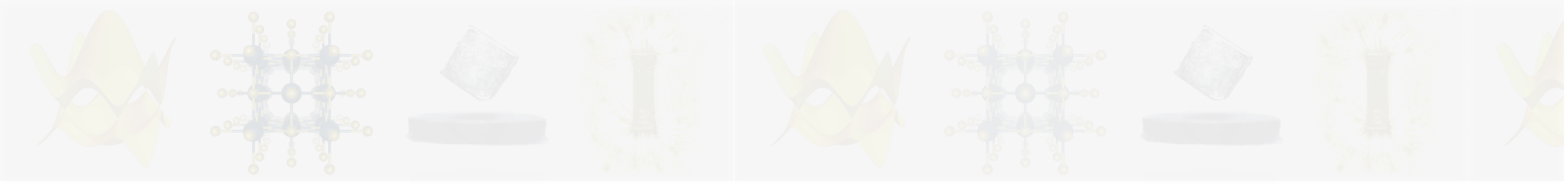
## → Copy files to you user area:

```
>> cp -r /scratch/efmc24/HandsOn_Material/day3 .
>> cd day3
>> ls
```



## Plan for today

1. Basic idea of *phonon*.
2. How do we compute phonon spectra.
3.  $\text{YIn}_3$  phonon spectrum calculation.

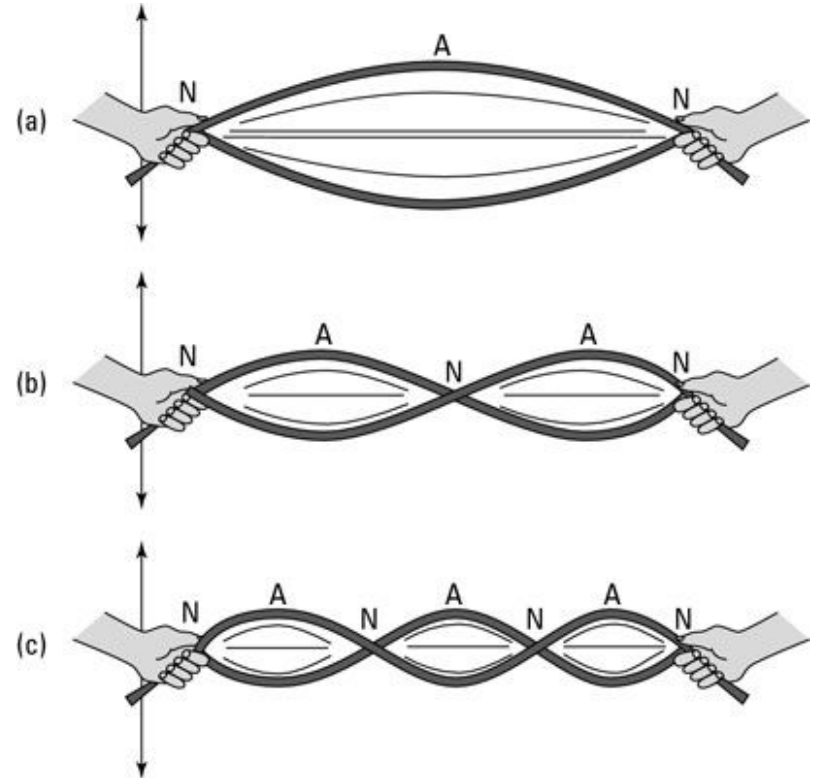
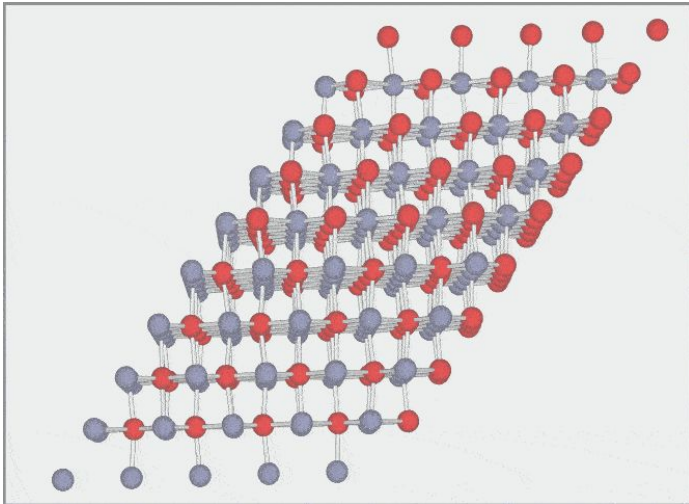


# Concept of phonon

# Concept of phonon

What is a phonon?

It is the quantum mechanical analogue of a normal mode of vibration of the crystal lattice.



# Concept of phonon

Take  $H_2$  as a toy model system.

Atoms will move much more slowly than electrons.

↓

Molecule stays in the ground state  $E_0(R)$ .

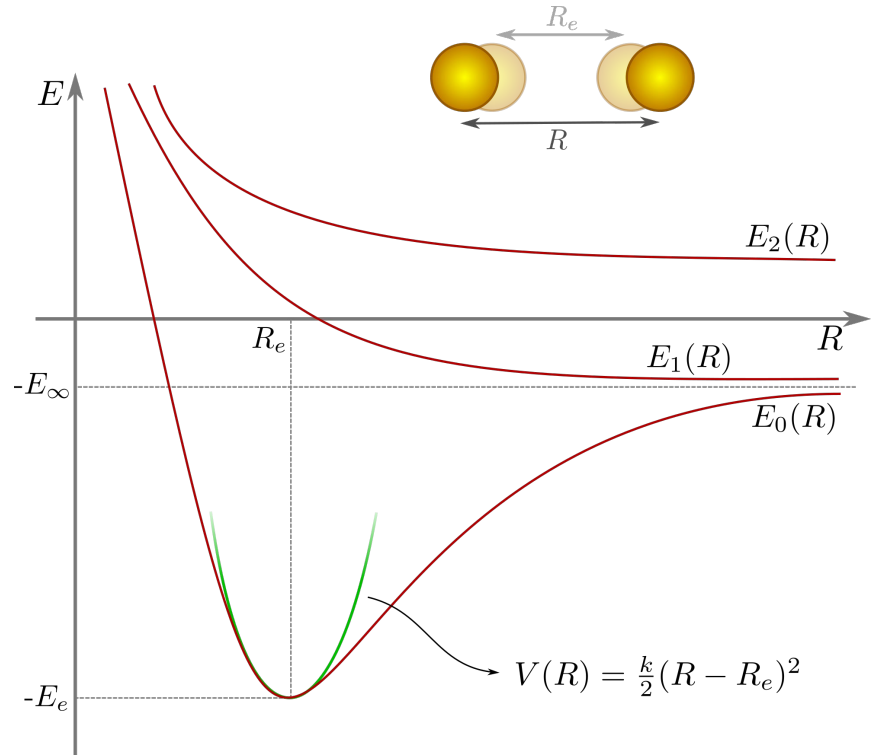
↓

Sufficiently close to the equilibrium inter-atomic distance  $R_e$  the energy is quadratic in  $(R - R_e)$ .

↓

Small molecule vibrations behave like a one-dimensional quantum harmonic oscillator.

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{\mu\omega^2}{2}\hat{x}^2$$



# Concept of phonon

Take  $H_2$  as a toy model system.

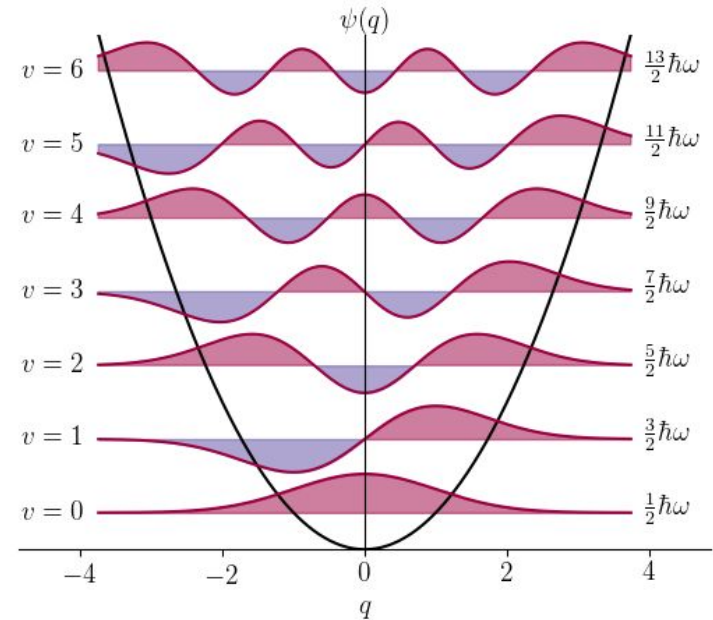
Small molecule vibrations behave like a one-dimensional quantum harmonic oscillator.

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{\mu\omega^2}{2}\hat{x}^2$$

which has the eigenvalues

$$E_\nu = \hbar\omega\left(\nu + \frac{1}{2}\right)$$

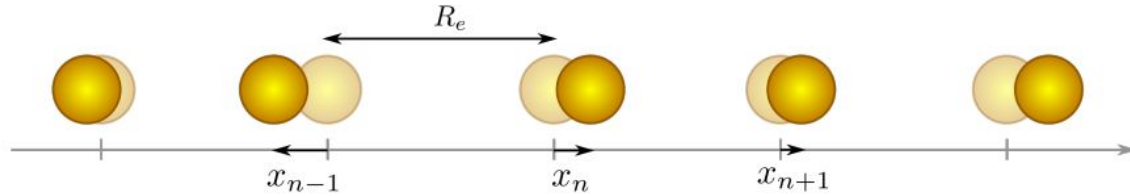
and eigenstates on the right.



Quantum modes of vibration

# Concept of phonon

Atomic vibrations in a solid can (to first approximation) be modelled as a set of coupled harmonic oscillators. For a 1D chain of quantum harmonic oscillators



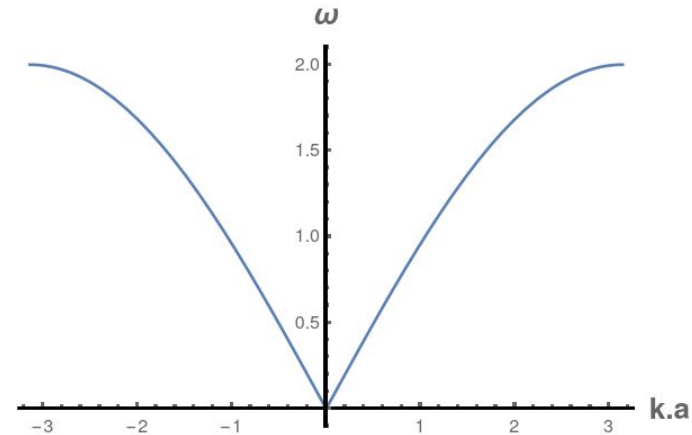
the hamiltonian reads

$$\hat{H} = \sum_{n=1}^N \left[ \frac{\hat{p}_n^2}{2m} + \frac{1}{2} m \omega^2 (\hat{x}_{n+1} - \hat{x}_n)^2 \right]$$

and the eigen-energies can be shown to be

$$\hat{H} = \sum_{k_\nu = -\frac{\pi}{a}}^{\frac{\pi}{a}} \hbar \Omega(k_\nu) \left[ \hat{a}^\dagger(k_\nu) \hat{a}(k_\nu) + \frac{1}{2} \right]$$

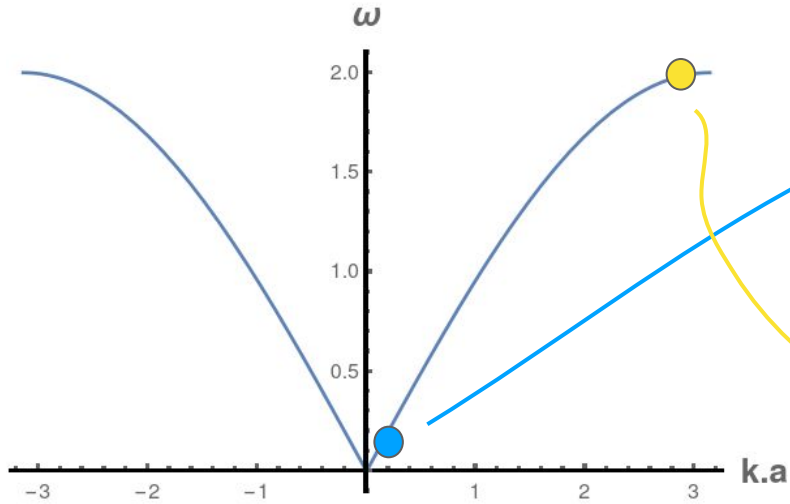
where  $\Omega(k)^2 = [2\omega \sin(ka/2)]^2$



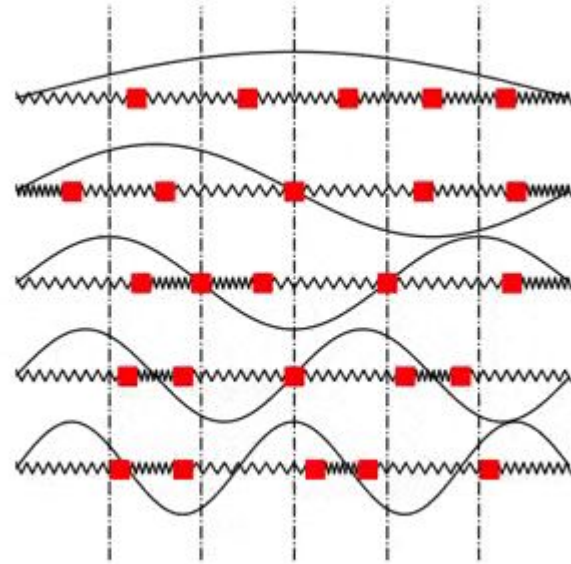


# Concept of phonon

Classical picture of phonon modes.

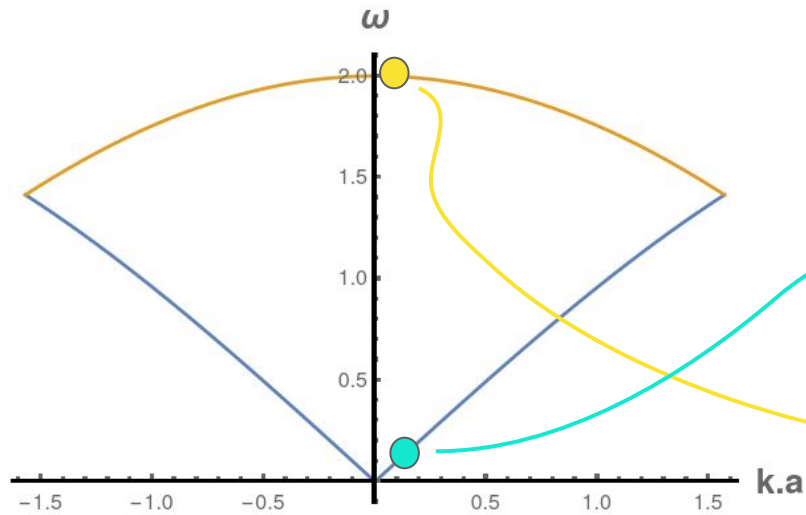


©2017, Bhaskar Kamble

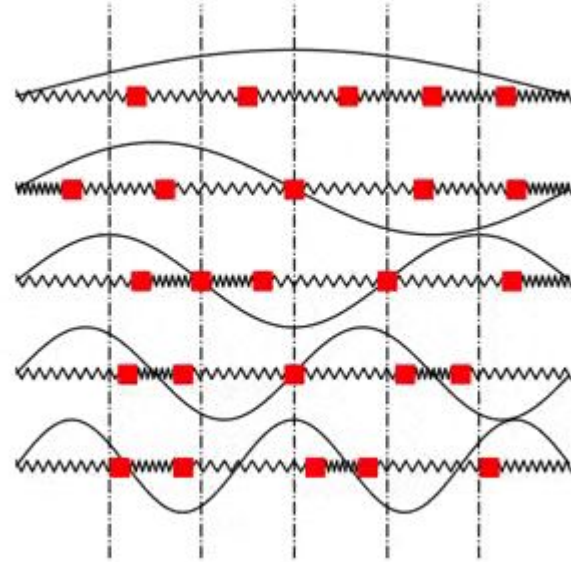


# Concept of phonon

Classical picture of phonon modes for an (artificially) doubled unit cell.



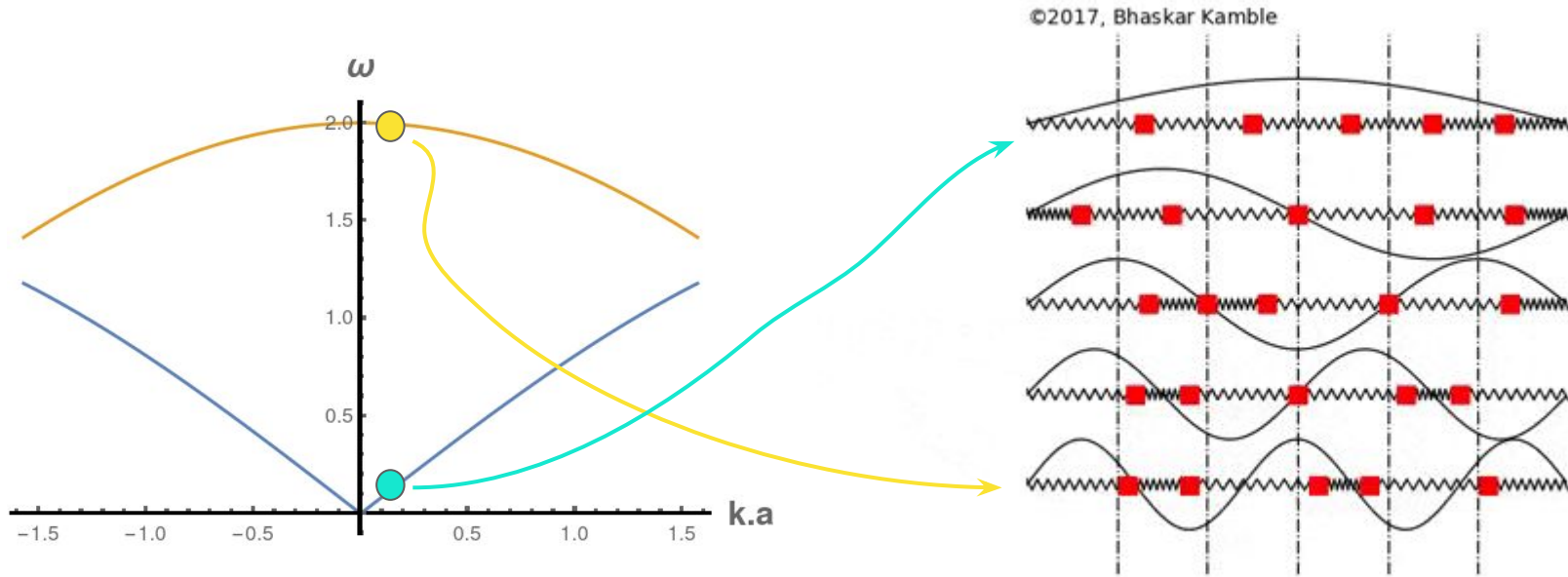
©2017, Bhaskar Kamble



These are called acoustic modes and optical modes.

# Concept of phonon

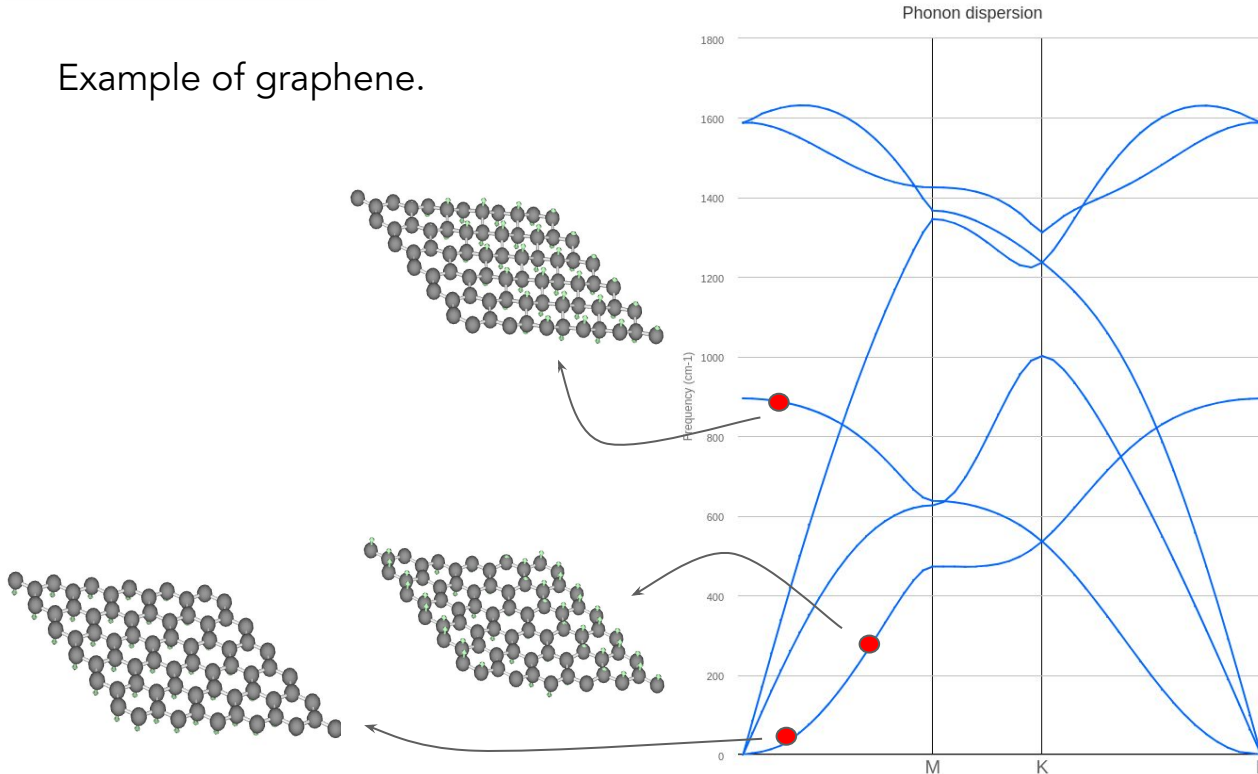
Classical picture of phonon modes for a AB chain of quantum harmonic oscillators.



These are called acoustic modes and optical modes.

# Concept of phonon

Example of graphene.



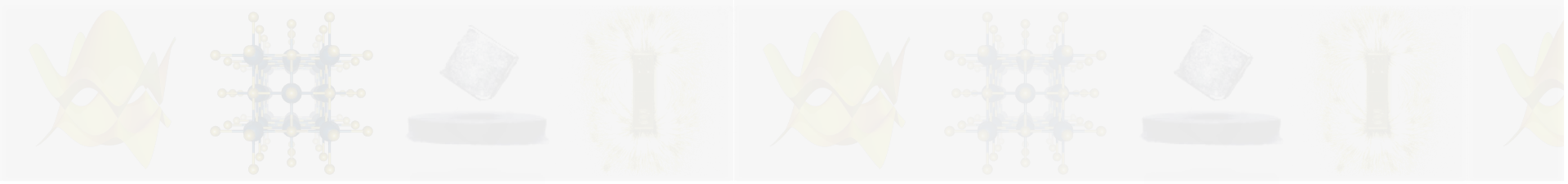
If spatial dimension is  $d$  and there are  $M$  atoms inside the unit cell:

- there will be  $d$  acoustic modes.
- there will be  $d \cdot (M - 1)$  optical modes.

Case of Graphene: 2D material "living" in 3D; with 2 atoms in the unit cell:

- 3 acoustic modes.
- 3 optical modes.

Check: <https://henriquemiranda.github.io/phononwebsite/phonon.html>



How can we compute a material's phonon spectrum?

# How can we compute a material's phonon spectrum?

We have to compute the frequencies  $\omega$  characterizing the **curvature of the ground state energy close to the equilibrium** atomic configuration in the multidimensional space of atomic displacements.

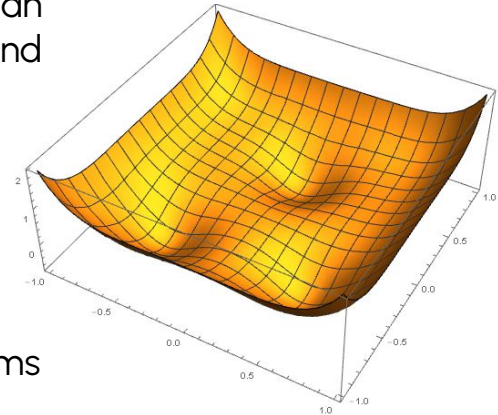
The g.s. energy is a multivariate function of the position of all the ions. We can expand it around the equilibrium position in terms of atom displacements

$$\Phi = \Phi_0 + \sum_{l\kappa} \sum_{\alpha} \Phi_{\alpha}(l\kappa) \mathbf{u}_{\alpha}(l\kappa) + \sum_{l\kappa, l'\kappa'} \sum_{\alpha\beta} \Phi_{\alpha\beta}(l\kappa, l'\kappa') \mathbf{u}_{\alpha}(l\kappa) \mathbf{u}_{\beta}(l'\kappa') + \dots$$

where  $\mathbf{u}_{\alpha}(l\kappa)$  identifies the displacement of the atom  $\kappa$  of unit cell  $l$  along cartesian direction  $\alpha$ . The coefficients  $\Phi_0$ ,  $\Phi_{\alpha}(l\kappa)$  and  $\Phi_{\alpha\beta}(l\kappa, l'\kappa')$  stand for the zeroth, first and second order force constants since

$$\Phi_{\alpha}(l\kappa) = \frac{\partial \Phi}{\partial \mathbf{u}_{\alpha}(l\kappa)}$$
$$\Phi_{\alpha\beta}(l\kappa, l'\kappa') = \frac{\partial^2 \Phi}{\partial \mathbf{u}_{\alpha}(l\kappa) \partial \mathbf{u}_{\beta}(l'\kappa')}$$

can be written in terms of the forces  $F_{\alpha}(l\kappa) = -\Phi_{\alpha}(l\kappa)$ . As we are displacing the atoms around an equilibrium position, the first order terms  $\Phi_{\alpha}(l\kappa)$  will all be zero.



# How can we compute a material's phonon spectrum?

We work with the **harmonic approximation**, i.e. we keep only terms up to second order in atomic displacement.

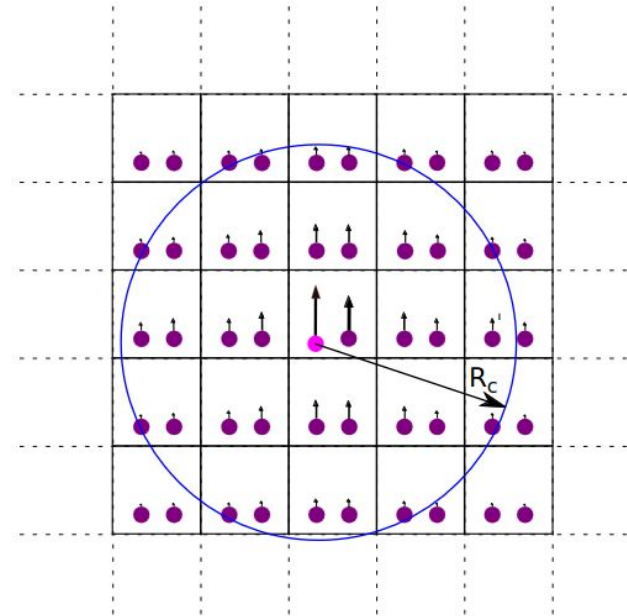
We can show (using periodicity of the crystal lattice) that the normal modes of vibration are given by solving the eigenvalue equation

$$\sum_{\beta\kappa'} D_{\kappa\kappa'}^{\alpha\beta}(\mathbf{q}) \mathbf{e}_{\mathbf{q}j}^{\beta\kappa'} = \omega_{\mathbf{q}j}^2 \mathbf{e}_{\mathbf{q}j}^{\alpha\kappa}$$

where the matrix  $D(\mathbf{q})$  is known as dynamic matrix

$$D_{\kappa\kappa'}^{\alpha\beta}(\mathbf{q}) = \sum_{l'} \frac{\Phi_{\alpha\beta}(0\kappa, l'\kappa')}{\sqrt{m_{\kappa} m_{\kappa'}}} e^{i\mathbf{q}\cdot[\mathbf{r}(l'\kappa') - \mathbf{r}(0\kappa)]}$$

The eigenvalues  $\omega_{\mathbf{q}j}$  will be the phonon frequencies (of wave number  $\mathbf{q}$ ;  $j$  is the phonon band index), while the  $\mathbf{e}_{\mathbf{q}j}$  are the polarization vectors (give information on how the atoms move in that vibrational mode).



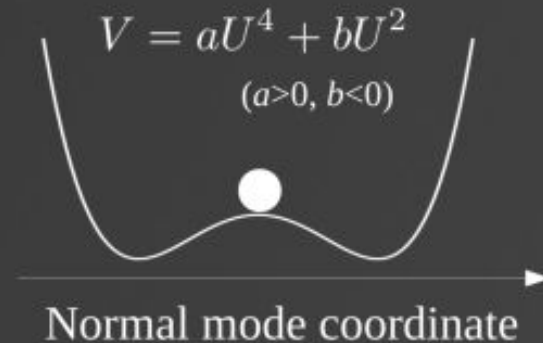
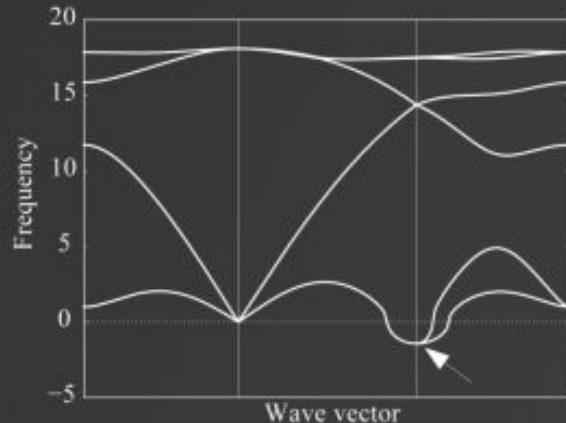
# Imaginary mode

$$\omega^2 < 0$$

Imaginary frequency appears when crystal structure is dynamically unstable through the imaginary mode.

Sometimes it relates to phase transition, or may be used to check if virtual crystal structure is stable or not.

\*In phonopy output, imaginary frequencies are shown as negative values.





# How can we compute a material's phonon spectrum?

The **central challenge** is to determine the dynamic matrix  $D(\mathbf{q})$  in the huge space of possible crystal deformations (each atom can move along three directions).

Example: For a  $2 \times 2 \times 2$  supercell of  $\text{YIn}_3$  we have  $8 \times 4 \times 3$  linearly independent directions in deformation space. The force matrix will be a  $96 \times 96$  matrix. The dynamic matrix (which is the Fourier transform of the force matrix) will be  $12 \times 12$  matrix.

For *ab initio* calculations the dynamic matrix  $D(\mathbf{q})$  can be calculated using two methods:

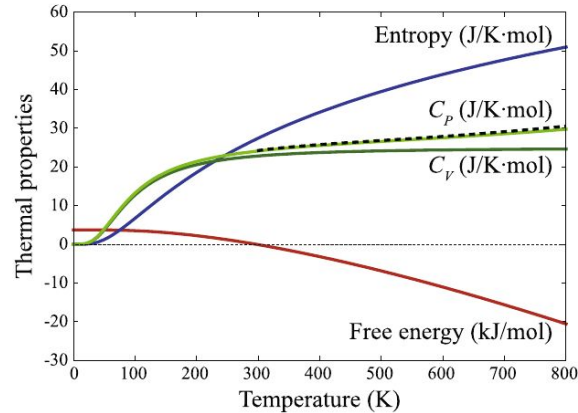
- Finite displacement method: displace atoms slightly out of the equilibrium position and calculate that crystal configuration's total energy. Get the derivative of the forces on each atom from there;
- Perturbation theory: uses Hellmann-Feynman theorem and PT.

We will use the Finite Displacement method in the calculations ahead (with the code Phonopy).

# How can we compute a material's phonon spectrum?

Once we have the phonon dispersion  $\omega_{\mathbf{q}j}$  we can compute several physical properties:

- Phonon's density of states (DOS);
- Average vibrational energy of a system (i.e. due to phonons);
- Constant volume specific heat,  $C_V$ ;
- Free energy,  $F$ ;
- Entropy,  $S$ ;



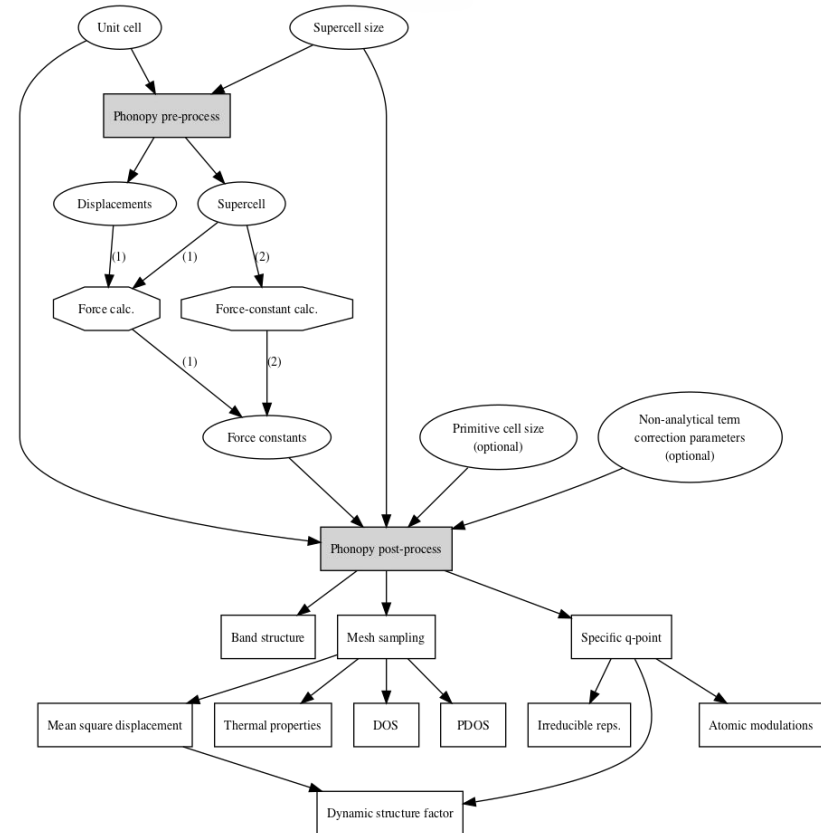
**Fig. 2.** Thermal properties of Al. Entropy,  $C_V$ , and Helmholtz free energy were calculated with harmonic approximation (Section 2). QHA was employed to obtain  $C_p$  (Section 4). Physical units are shown with labels of the physical properties, and the value of the vertical axis is shared by them. Dotted curve depicts the experiment of  $C_p$  [35].

# How can we compute a material's phonon spectrum?

We will use [Phonopy](#)+QuantumEspresso to do the finite displacement method.

## Basic steps of **Phonopy workflow**:

1. Structural relaxation (with stricter convergence thresholds).
2. Create SCF input archive with optimized lattice parameters and atomic positions.
3. Generation of supercells with displaced atoms. (Phonopy does this already taking into account crystal symmetry.)
4. Run SCF calculations for each of those systems.
5. Use Phonopy to collect forces on each SCF output file, generate the force matrix and compute the dynamic matrix eigenvalues .
6. Plot phonon dispersion, DOS, etc..





# Phonon calculation Workflow

- Step 1:**        **Structural relaxation** (with stricter convergence thresholds).
- Step 2:**        Create SCF input archive with optimized lattice parameters and atomic positions.
- Step 3:**        Generate **supercells with displaced atoms**. (Phonopy does this already taking into account crystal symmetry.)
- Step 4:**        **Run SCF calculations** for each of those systems.
- Step 5:**        Use Phonopy to **collect forces** on each SCF output file, generate the **force matrix** and compute the **dynamic matrix** eigenvalues .
- Step 6:**        Plot phonon dispersion, DOS, etc..

# YIn<sub>3</sub> phonon spectrum calculation

1. We start by doing a structural relaxation with stricter convergence parameters. Inside your scratch `"/scratch/efmc24/your_username/"` do:

```
>> cp -r ../HandsOn_Material/day3 .  
>> cd day3/1_vc-relax/  
>> grep "conv_thr" vc-relax.in  
  
etot_conv_thr = 6.0d-07  
forc_conv_thr = 1.0d-06
```

Compare with the values from previous structural optimization:

```
>> grep "conv_thr" ../../day1/3_vc-relax/cell1dm_0.75/vc-relax.in  
  
etot_conv_thr = 6.0d-05  
forc_conv_thr = 1.0d-04
```

# YIn<sub>3</sub> phonon spectrum calculation

2. Submit the job:

```
>> sbatch sub.srm
```

Wait for the calculation to finish:

```
>> tail vc-relax.out
```

```
This run was terminated on: 21:49:24 10Jul2024
```

```
-----  
JOB DONE.  
-----
```

# YIn<sub>3</sub> phonon spectrum calculation

3. Set up a SCF calculation input file with the converged structure:
  - a. To find the relaxed structure, look for "Begin final coordinates" at the vc-relax.out file:

```
>> grep -16 Begin vc-relax.out
```

```
File ./yin3.bfgs deleted, as requested
Begin final coordinates
new unit-cell volume = 680.36332 a.u.^3 ( 100.81944 Ang^3
density = 7.13762 g/cm^3

CELL_PARAMETERS (angstrom)
 4.654232739 0.000000000 0.000000000
 0.000000000 4.654232739 0.000000000
 0.000000000 0.000000000 4.654232739

ATOMIC_POSITIONS (crystal)
Y      0.0000000000 -0.0000000000 0.0000000000
In     0.5000000000 0.5000000000 -0.0000000000
In     0.5000000000 0.0000000000 0.5000000000
In     0.0000000000 0.5000000000 0.5000000000

End final coordinates
```

This is your optimized structure: Copy this information!

# YIn<sub>3</sub> phonon spectrum calculation

3. Set up a SCF calculation input file with the converged structure:
  - b. Generate a new input file with the optimized structure:


```
>> cp vc-relax.in scf.in  
>> nano scf.in
```

Remove the information from the previous structure (CELL\_PARAMETERS and ATOMIC\_POSITIONS) and copy the information from the new (optimized) structure, as is in the blue box in the previous slide.



# YIn<sub>3</sub> phonon spectrum calculation

```
&CONTROL
  calculation = 'scf'
  outdir = './'
  prefix = 'yin3'
  pseudo_dir = '/scratch/efmc24/
HandsOn_Material/Pseudos/'
/
&SYSTEM
  ecutwfc = 90
  ibrav = 0
  nat = 4
  ntyp = 2
/
&ELECTRONS
/
&IONS
/
&CELL
/
```



```
ATOMIC_SPECIES
In 207.2 In.rel-pbe-dn-kjpaw_psl.1.0.0.UPF
Y 88.90585 Y.rel-pbe-spn-kjpaw_psl.1.0.0.UPF
```

```
CELL_PARAMETERS (angstrom)
4.654232739 0.000000000 0.000000000
0.000000000 4.654232739 0.000000000
0.000000000 0.000000000 4.654232739
```

```
ATOMIC_POSITIONS (crystal)
Pb 0.50 0.50 0.00
Pb 0.50 0.00 0.50
Pb 0.00 0.50 0.50
Y 0.00 0.00 0.00
```

This is your optimized structure!

```
K_POINTS automatic
2 2 2 0 0 0
```

# YIn<sub>3</sub> phonon spectrum calculation

4. Generate supercells with displacements from your scf.in file:
  - a. We chose a 2x2x2 supercell, but it could be larger, depending on the type of material you are working.

```
>> phonopy --qe -d --dim="2 2 2" -c scf.in
```

If you list your files (command ls), you will see that the following files were generated:

```
>> ls
>> supercell-001.in  supercell-002.in
```

They contain the atomic coordinates and lattice vectors of a 2x2x2 supercell with a small displacement in one of the atoms. Check the differences between them:

```
>> vimdiff supercell-001.in  supercell-002.in
```

# YIn<sub>3</sub> phonon spectrum calculation

5. Generate an scf.in file for each displacement:

a. Generate an scf.in file inside the 2\_supercells/disp001 and 2\_supercells/disp002 folders. From the 1\_vc-relax folder:

```
.....  
: >> cp scf.in ../2_supercell/disp001  
: >> cp scf.in ../2_supercell/disp002  
: .....
```

b. Copy the coordinates from the supercell-001.in and supercell-002.in into these new scf.in files.

6. Submit the jobs:

a. From the 2\_supercell/disp001 folder:

```
.....  
: >> sbatch sub.srm  
: .....
```

# YIn<sub>3</sub> phonon spectrum calculation

6. Submit the jobs:

b. From the 2\_supercell/disp002 folder:

```
>> sbatch sub.srm
```

7. Once the calculations are done: generate forces file. From the 2\_supercells folder:

```
>> phonopy -f disp001/scf.out disp002/scf.out
```

If you list your files (command ls), you will see that the following file were generated:

```
>> ls  
>> FORCE_SETS
```

More info about this file can be found [here!](#)

# YIn<sub>3</sub> phonon spectrum calculation

8. Once you have the `FORCE_SETS` file: generate phonon bands and phonon DOS.  
From the `2_supercells` folder:

↳ Plotting phonon band dispersion:

```
:>> phonopy --qe -c scf.in -p -s band.conf
```

↳ Plotting phonon bands + dos dispersion:

```
:>> phonopy --qe -c scf.in -p -s mesh.conf
```

## **BONUS!**

↳ Plotting thermal properties:

```
:>> phonopy -t -p -s mesh.conf
```

# YIn<sub>3</sub> phonon spectrum calculation

::::::::::::

mesh.conf

::::::::::::

ATOM\_NAME = Y In

DIM = 2 2 2

BAND = 0.0 0.0 0.0 0.0 0.5 0.0 0.5 0.5 0.0 0.0 0.0 0.0

0.0 0.0 0.5 0.0 0.5 0.0

BAND\_LABELS= Z  $\Gamma$  X M  $\Gamma$  R X

MP = 8 8 8

PDOS = AUTO

::::::::::::

band.conf

::::::::::::

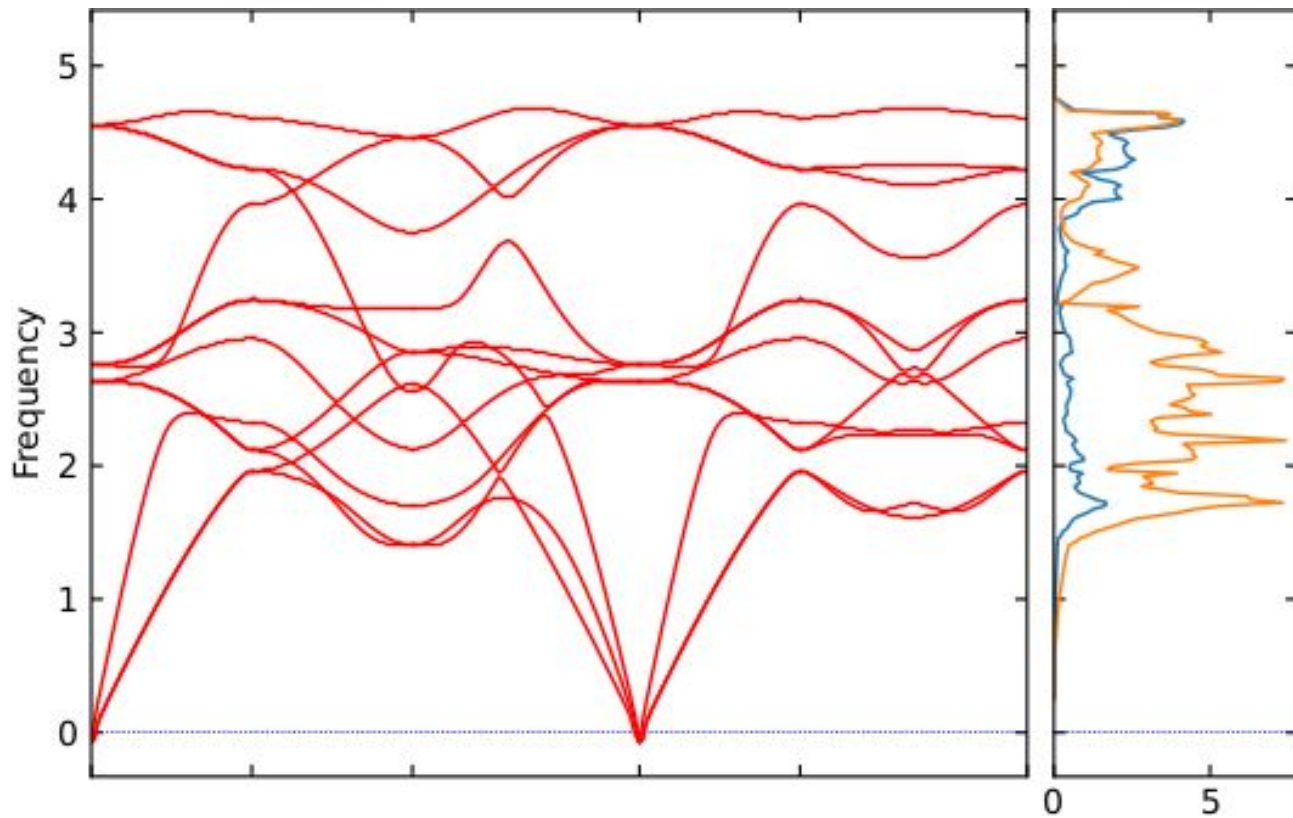
ATOM\_NAME = Y In

DIM = 2 2 2

BAND = 0.0 0.0 0.0 0.0 0.5 0.0 0.5 0.5 0.0 0.0 0.0 0.0

0.0 0.0 0.5 0.0 0.5 0.0

# YIn<sub>3</sub> phonon spectrum



# YIn<sub>3</sub> phonon spectrum calculation

## Materials:

Bulk MoTe<sub>2</sub>  
Graphene  
Bulk MoS<sub>2</sub>  
Layer MoS<sub>2</sub>  
Layer MoTe<sub>2</sub>  
Bulk TiSe<sub>2</sub>  
Bulk hBN

- [1] H. Miranda, [localdb](#) (2015)
- [2] M. Calandra, F. Mauri, [PRL](#) (2011)
- [3] F. Paleari, (2018)

## Amplitude:



## Vectors:



## Speed:

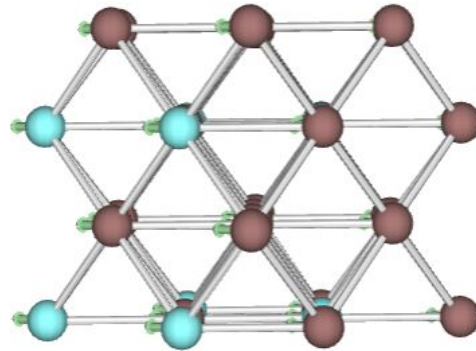


## Covalent radii:

Y 1.9  
update reset

288 FPS (2-325)

## Y1In3



## Phonon dispersion

