

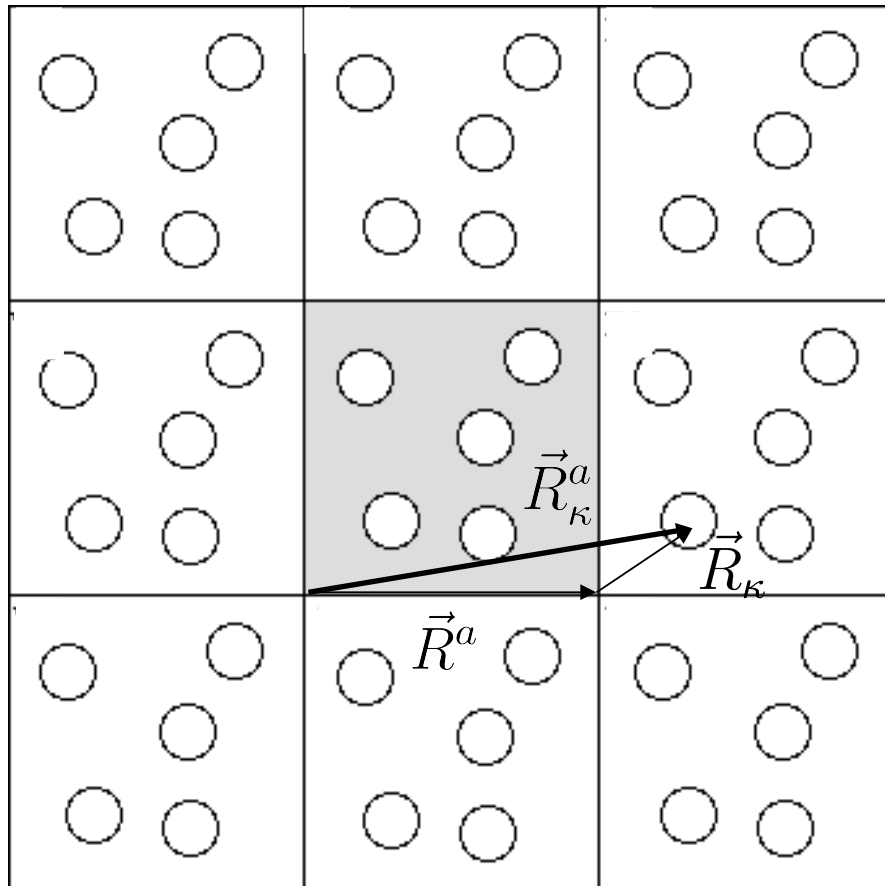
Lattice Dynamics

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Notation

Greek characters (κ) refer to atoms within the unit cell

Latin characters (a) refer to the different replicas of the unit cell



Assuming periodic boundary conditions

$\vec{R}^a$ **Vector defining the position of unit cell a**

$\vec{R}_\kappa$ **Position of atom κ within the unit cell**

$\vec{R}_\kappa^a$ **Position of atom κ in unit cell a**

$$\vec{R}_\kappa^a = \left(\vec{R}^a + \vec{R}_\kappa \right)$$

Total energy for periodic & small distortions

We shall remain in the adiabatic approximation, in which it is considered that the electrons are in their ground state for any instantaneous ionic configuration

$$E_{e+i} \left(\{ \vec{R}_{\kappa}^{\alpha}(t) \} \right) = E_{e+i} \left(\{ \vec{R}_{\kappa}^{\alpha} \} \right) + \sum_{a\kappa\alpha} \left(\frac{\partial E_{e+i}}{\partial u_{\kappa\alpha}^a} \right) u_{\kappa\alpha}^a(t) + \sum_{a\kappa\alpha} \sum_{b\kappa'\beta} \frac{1}{2} \left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\beta}^b} \right) u_{\kappa\alpha}^a u_{\kappa'\beta}^b + \dots$$

1. In principle, if we take all the orders in the expansion this expression is exact.
2. All the derivatives are taken at the mean equilibrium positions. They are constants in the expansion.
3. Since, the derivatives are taken at the equilibrium positions, the first derivatives in the previous expansion vanish.

$$E_{e+i} \left(\{ \vec{R}_{\kappa}^{\alpha}(t) \} \right) = E_{e+i} \left(\{ \vec{R}_{\kappa}^{\alpha} \} \right) + \sum_{a\kappa\alpha} \sum_{b\kappa'\beta} \frac{1}{2} \left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\beta}^b} \right) u_{\kappa\alpha}^a u_{\kappa'\beta}^b + \dots$$

Interatomic force Constant in Real Space

The second derivatives of the energy, coupling constants, are defined as the interatomic force constants in real space:

$$C_{\kappa\alpha,\kappa'\beta}(a,b) = \left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\beta}^b} \right)$$

They must satisfy a number of conditions that arise from

Isotropy of space

Point group symmetry

Translation invariance upon displacement of the lattice by an arbitrary lattice constant: the second derivative of the energy can only depend on the difference between a and b

$$\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\beta}^b} = \frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^0 \partial u_{\kappa'\beta}^{b-a}}$$

Classical equation of Motion

For each atom, there are three equations of motion of this type (one for each cartesian direction). In total, $3 \times N_{atoms}$

$$M_{\kappa} \frac{\partial^2 u_{\kappa\alpha}^a}{\partial t^2} = - \sum_{b\kappa'\beta} \left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\beta}^b} \right) u_{\kappa'\beta}^b$$

The equations of motion are coupled

To know the displacement of atom κ ,
in unit cell a ,
along cartesian direction α ,
 $u_{\kappa\alpha}^a$

We require the displacement of atom κ' ,
in unit cell b ,
along cartesian direction β ,
 $u_{\kappa'\beta}^b$

We seek for general solutions where all the displacements have a temporal dependency of the form $e^{-i\omega_m t}$

$$u_{\kappa\alpha}^a(t) = \eta_m^a(\kappa\alpha) e^{-i\omega_m t}$$

Properties and Consequences

For periodic structures, we can write the displacements in terms of a plane wave with respect to cell coordinates

$$u_{\kappa\alpha}^a(t) = \eta_{m\vec{q}}(\kappa\alpha) e^{i\vec{q}\cdot\vec{R}_a} e^{-i\omega_{m\vec{q}}t}$$

The vibration of the ions have been classified according to a wave vector $\vec{q}$

- Approach equivalent to that taken for the electrons through the Bloch theorem**
- If the solid is simulated by a supercell composed of N unit cells + Born-von Karman boundary conditions, then only compatible $\vec{q}$ points can be used in the previous expression.**

**There are as many allowed values as unit cells there are in the supercell
In contrast to a normal plane wave, this wave is only defined at the lattice points**

$\eta_{m\vec{q}}(\kappa\alpha)$ is the component along direction α of a vector called the polarization vector of the normal mode

Algebra

$$-M_\kappa \omega_{m\vec{q}}^2 \eta_{m\vec{q}}(\kappa\alpha) e^{i\vec{q}\cdot\vec{R}_a} e^{-i\omega_{m\vec{q}}t} = - \sum_{b\kappa'\beta} \left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\beta}^b} \right) \eta_{m\vec{q}}(\kappa'\beta) e^{i\vec{q}\cdot\vec{R}_b} e^{-i\omega_{m\vec{q}}t}$$

Multiplying both sides by $e^{i\omega_{m\vec{q}}t}$

$$M_\kappa \omega_{m\vec{q}}^2 \eta_{m\vec{q}}(\kappa\alpha) e^{i\vec{q}\cdot\vec{R}_a} = \sum_{b\kappa'\beta} \left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\beta}^b} \right) \eta_{m\vec{q}}(\kappa'\beta) e^{i\vec{q}\cdot\vec{R}_b} e^{-i\vec{q}\cdot\vec{R}_a}$$

Reordering the sums, and multiplying both sides by

$$M_\kappa \omega_{m\vec{q}}^2 \eta_{m\vec{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \left[\sum_b \left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\beta}^b} \right) e^{i\vec{q}\cdot(\vec{R}_b - \vec{R}_a)} \right] \eta_{m\vec{q}}(\kappa'\beta)$$

$$C_{\kappa\alpha, \kappa'\beta}(a, b) = \left(\frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^a \partial u_{\kappa'\beta}^b} \right)$$

$$M_\kappa \omega_{m\vec{q}}^2 \eta_{m\vec{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \left[\sum_b C_{\kappa\alpha, \kappa'\beta}(0, b) e^{i\vec{q}\cdot\vec{R}_b} \right] \eta_{m\vec{q}}(\kappa'\beta)$$

Fourier Transform

$$M_{\kappa} \omega_{m\vec{q}}^2 \eta_{m\vec{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \left[\sum_b C_{\kappa\alpha, \kappa'\beta}(0, b) e^{i\vec{q} \cdot \vec{R}_b} \right] \eta_{m\vec{q}}(\kappa'\beta)$$

The term in brackets is nothing else than the discrete Fourier transform of the interatomic force constant in real space

$$\begin{aligned} \tilde{C}_{\kappa\alpha, \kappa'\beta}(\vec{q}) &= \frac{1}{N} \sum_{a,b} C_{\kappa\alpha, \kappa'\beta}(a, b) e^{-i\vec{q} \cdot (\vec{R}_a - \vec{R}_b)} \\ &= \sum_b C_{\kappa\alpha, \kappa'\beta}(0, b) e^{i\vec{q} \cdot \vec{R}_b} \end{aligned}$$

Therefore, the movement of the atoms can be defined in terms of the following dynamical equations

$$M_{\kappa} \omega_{m\vec{q}}^2 \eta_{m\vec{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \tilde{C}_{\kappa\alpha, \kappa'\beta}(\vec{q}) \eta_{m\vec{q}}(\kappa'\beta)$$

Matrix Form

$$M_{\kappa} \omega_{m\vec{q}}^2 \eta_{m\vec{q}}(\kappa\alpha) = \sum_{\kappa' \beta} \tilde{C}_{\kappa\alpha, \kappa' \beta}(\vec{q}) \eta_{m\vec{q}}(\kappa' \beta)$$

For each $\vec{q}$ vector, we have a linear homogenous system of equations, that in matrix form can be read as

$$\begin{pmatrix} \tilde{C}(\vec{q}) \end{pmatrix} \begin{pmatrix} \eta(\vec{q}) \end{pmatrix} = \omega^2(\vec{q}) \begin{pmatrix} M_{\kappa} \delta_{\kappa\kappa'} \delta_{\alpha\beta} \end{pmatrix} \begin{pmatrix} \eta(\vec{q}) \end{pmatrix}$$

$(3 \times N_{\text{atoms unit cell}})$
 $\times$
 $(3 \times N_{\text{atoms unit cell}})$

$(3 \times N_{\text{atoms unit cell}})$
 $\times$
 1

$(3 \times N_{\text{atoms unit cell}})$
 $\times$
 $(3 \times N_{\text{atoms unit cell}})$

$(3 \times N_{\text{atoms unit cell}})$
 $\times$
 1

**Fourier transform of
the interatomic force
constants**

**Phonon
eigendisplacements**

**Phonon
frequencies**

Mass matrix

**Phonon
eigendisplacements**

The mass matrix

$$M_{\kappa} \delta_{\kappa\kappa'} \delta_{\alpha\beta}$$

	Atom 1 Direction x	Atom 1 Direction y	Atom 1 Direction z	Atom 2 Direction x	Atom 2 Direction y	Atom 2 Direction z
Atom 1 Direction x	M_1	0	0	0	0	0
Atom 1 Direction y	0	M_1	0	0	0	0
Atom 1 Direction z	0	0	M_1	0	0	0
Atom 2 Direction x	0	0	0	M_2	0	0
Atom 2 Direction y	0	0	0	0	M_2	0
Atom 2 Direction z	0	0	0	0	0	M_2

Renormalization

$$\begin{pmatrix} \tilde{C}(\vec{q}) \end{pmatrix} \begin{pmatrix} \eta(\vec{q}) \end{pmatrix} = \omega^2(\vec{q}) \begin{pmatrix} M_\kappa \delta_{\kappa\kappa'} \delta_{\alpha\beta} \end{pmatrix} \begin{pmatrix} \eta(\vec{q}) \end{pmatrix}$$

This is not a standard eigenvalue problem due to the presence of the mass matrix (somehow the “eigenvalue” changes from one row to the other...)

We can recover an standard eigenvalue problem redefining the eigenvectors incorporating the square root of mass

$$u_{\kappa\alpha}^a(t) = \frac{1}{\sqrt{M_\kappa}} \gamma_{m\vec{q}}(\kappa\alpha) e^{i\vec{q}\cdot\vec{R}_a} e^{-i\omega_{m\vec{q}}t}$$

The Dynamical Matrix

Redoing previous algebra

$$\omega_{m\vec{q}}^2 \gamma_{m\vec{q}}(\kappa\alpha) = \sum_{\kappa'\beta} \frac{\tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q})}{\sqrt{M_\kappa M_{\kappa'}}} \gamma_{m\vec{q}}(\kappa'\beta)$$

We define the dynamical matrix as

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q})$$

So finally the dynamical equation reduces to

$$\sum_{\kappa'\beta} \tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q}) \gamma_{m\vec{q}}(\kappa'\beta) = \omega_{m\vec{q}}^2 \gamma_{m\vec{q}}(\kappa\alpha)$$

Renormalized displacements

Redoing previous algebra

$$\sum_{\kappa' \beta} \tilde{D}_{\kappa\alpha, \kappa' \beta}(\vec{q}) \gamma_{m\vec{q}}(\kappa' \beta) = \omega_{m\vec{q}}^2 \gamma_{m\vec{q}}(\kappa\alpha)$$

In matrix form

$$\begin{pmatrix} \tilde{D}(\vec{q}) \end{pmatrix}_{\substack{(3 \times N_{\text{atoms unit cell}}) \\ \times \\ (3 \times N_{\text{atoms unit cell}})}} \begin{pmatrix} \gamma(\vec{q}) \end{pmatrix}_{\substack{(3 \times N_{\text{atoms unit cell}}) \\ \times \\ 1}} = \omega^2(\vec{q}) \begin{pmatrix} \gamma(\vec{q}) \end{pmatrix}_{\substack{(3 \times N_{\text{atoms unit cell}}) \\ \times \\ 1}}$$

Dynamical matrix

**Phonon
eigenvectors**

**Phonon
frequencies**

**Phonon
eigenvectors**

Phonon eigenvectors and phonon eigendisplacements

In a standard code, the dynamical matrix is diagonalized, and the solutions are the phonon eigenvectors

$$\gamma_{m\vec{q}}(\kappa\alpha)$$

However, to compute many properties related with the lattice dynamics, we require the phonon eigendisplacements.

For instance, the mode polarity

$$p_{m\alpha} = \sum_{\kappa\beta} Z_{\kappa,\alpha\beta}^* \eta_m(\kappa\beta)$$

Required to compute, for instance, the static dielectric constant

$$\varepsilon_{\alpha\beta}^0 = \varepsilon_{\alpha\beta}^\infty + \frac{4\pi}{\Omega_0} \sum_m \frac{p_{m\alpha} \cdot p_{m\beta}}{\omega_m^2}$$

The phonon eigendisplacements and phonon eigenvectors are related by

$$\eta_{m\vec{q}}(\kappa\alpha) = \frac{1}{\sqrt{M_\kappa}} \gamma_{m\vec{q}}(\kappa\alpha)$$

Constant Matrix in real space: finite displacement

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q}) = \frac{\tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q})}{\sqrt{M_{\kappa}M_{\kappa'}}} = \frac{1}{\sqrt{M_{\kappa}M_{\kappa'}}} \sum_b C_{\kappa\alpha,\kappa'\beta}(0, b) e^{i\vec{q} \cdot \vec{R}_b}$$

We can compute the dynamical matrix for every q-point

Knowing the force constant matrix in real space

$$C_{\kappa\alpha,\kappa'\beta}(0, a) = \frac{\partial^2 E_{e+i}}{\partial u_{\kappa\alpha}^0 \partial u_{\kappa'\beta}^a} = \frac{\partial}{\partial u_{\kappa\alpha}^0} \left(\frac{\partial E_{e+i}}{\partial u_{\kappa'\beta}^a} \right) = - \frac{\partial F_{\kappa'\beta}^a}{\partial u_{\kappa\alpha}^0}$$

We displace the atom κ in the unit cell along direction α , and compute how changes the force on atom κ' in unit cell a along direction β

The derivative is computed by finite differences

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q}) = \frac{\tilde{C}_{\kappa\alpha,\kappa'\beta}(\vec{q})}{\sqrt{M_{\kappa}M_{\kappa'}}} = \frac{1}{\sqrt{M_{\kappa}M_{\kappa'}}} \sum_b C_{\kappa\alpha,\kappa'\beta}(0, b) e^{i\vec{q} \cdot \vec{R}_b}$$

**We compute the dynamical matrix
for every q-point**

**Knowing the force constant matrix
in real space**

In principle, we should displace the atoms in the unit cell one by one in all the three cartesian directions, and look at the force on the atom of our choice, that might be in a unit cell very far away.

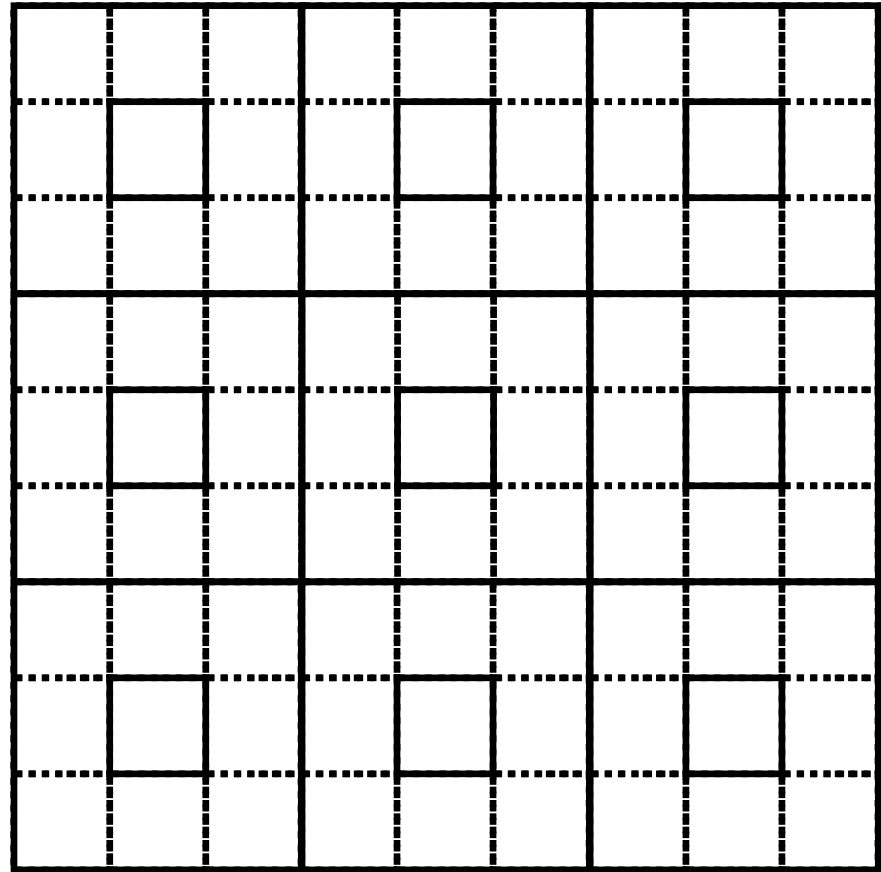
From a practical point of view, the values of the force constant matrix in real space decay with the distance between the atoms. Practically the previous sum is cut to include only a given number of distant neighbours

$$\frac{1}{\sqrt{M_{\kappa}M_{\kappa'}}} \sum_b^{\infty} C_{\kappa\alpha,\kappa'\beta}(0, b) e^{i\vec{q} \cdot \vec{R}_b} \approx \frac{1}{\sqrt{M_{\kappa}M_{\kappa'}}} \sum_b^{b_{\text{cut}}} C_{\kappa\alpha,\kappa'\beta}(0, b) e^{i\vec{q} \cdot \vec{R}_b}$$

(1) Phonons with SIESTA/Vibra

Supercell in real space

Unit cell in real space



```

#
# General system descriptors
#

SystemName      Bulk Silicon in the diamond structure
#              building the supercell to compute the phonons

SystemLabel      Si
NumberOfSpecies  1
NumberOfAtoms    2
%block ChemicalSpeciesLabel
  1 14 Si
%endblock ChemicalSpeciesLabel

#
# Lattice, coordinates, k-sampling
#

LatticeConstant  5.546406 Ang      # Theor. lattice parameter of bulk Si
%block LatticeVectors
  0.00  0.50  0.50
  0.50  0.00  0.50
  0.50  0.50  0.00
%endblock LatticeVectors

AtomicCoordinatesFormat  Fractional
%block AtomicCoordinatesAndAtomicSpecies
  -0.125 -0.125 -0.125  1  28.086
   0.125  0.125  0.125  1  28.086
%endblock AtomicCoordinatesAndAtomicSpecies

kgrid_cutoff      8.0 Ang

#
# Options to generate the supercell
#

SuperCell_1  3  # number of shells in which the unit cell is
                # repeated in the direction of the first lattice vector.
SuperCell_2  3  # Idem for the second lattice vector.
SuperCell_3  3  # Idem for the third lattice vector.

```

We prepare an input file to run fcbuild and generate the supercell. Let's call this input file **Si.fcbuild.fdf**

Variables to define the unit cell in real space

Variables to define the supercell in real space

Building the Supercell

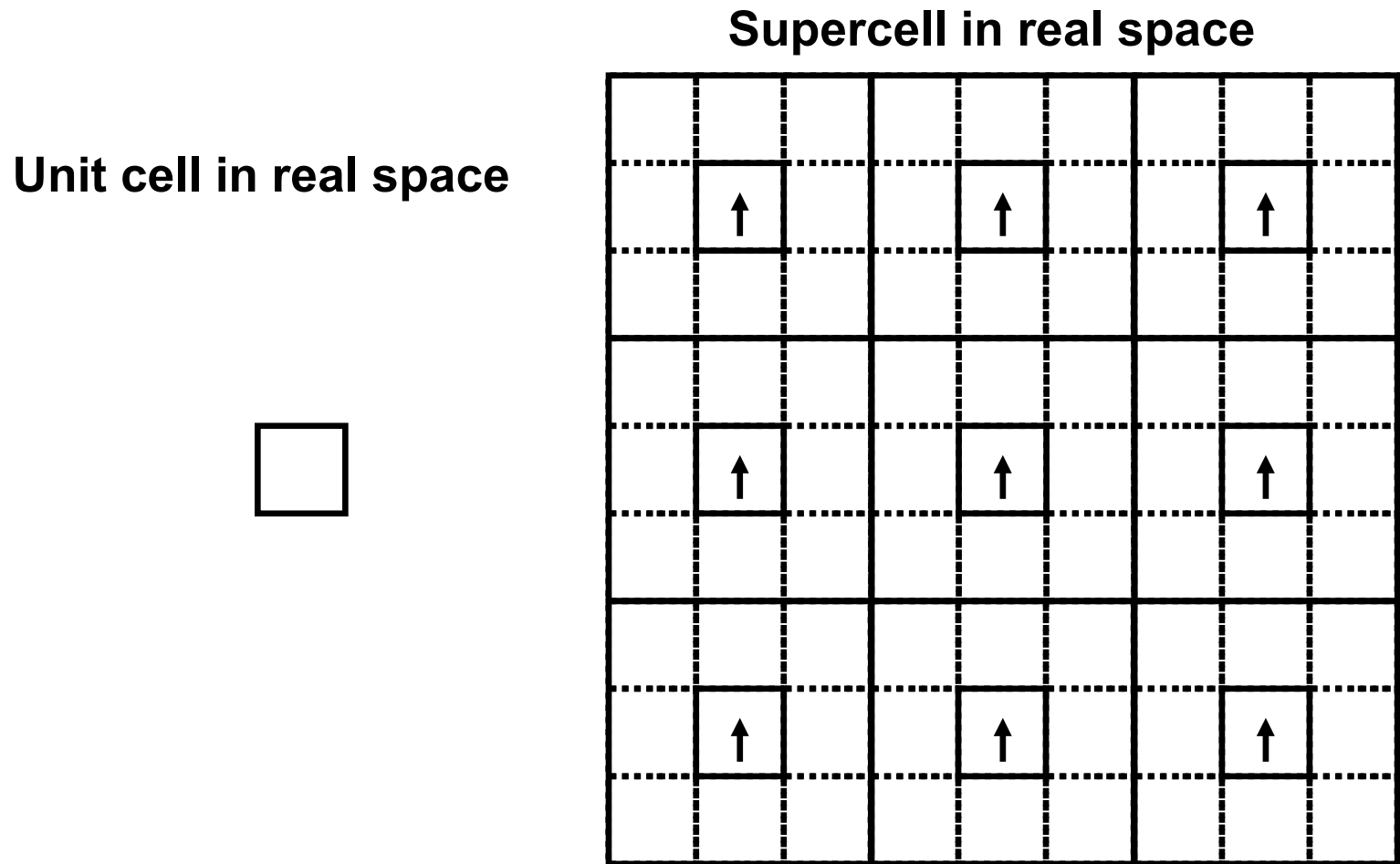
`$siesta/Utils/Vibra/Src/fcbuild < Si.fcbuild.fdf`

This will generate a file called FC.fdf with:

- The structural data of the supercell (supercell lattice vectors, atomic coordinates,...)**
- The atoms that will be displaced to compute the interatomic force constants in real space**
- The amount that the atoms will be displaced**

The supercell should contain enough atoms so that all non-negleageable elements of the force constant matrix are computed. The range in real space in which the force constant matrix decays to zero varies widely from system to system!!.

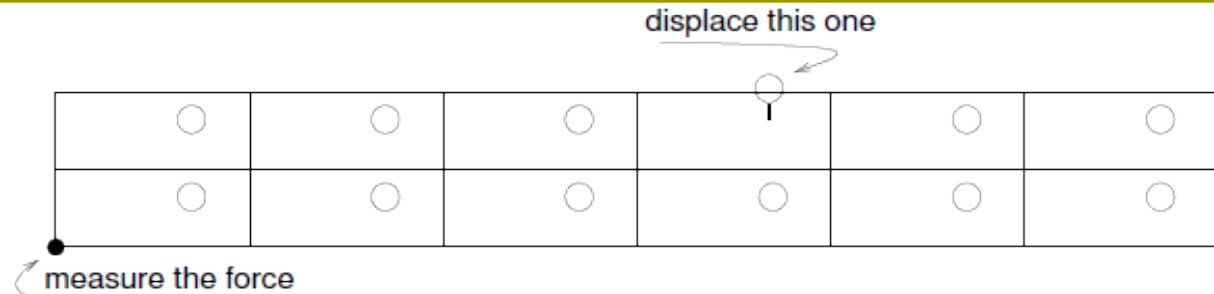
(2) Displace the atoms and compute IFC



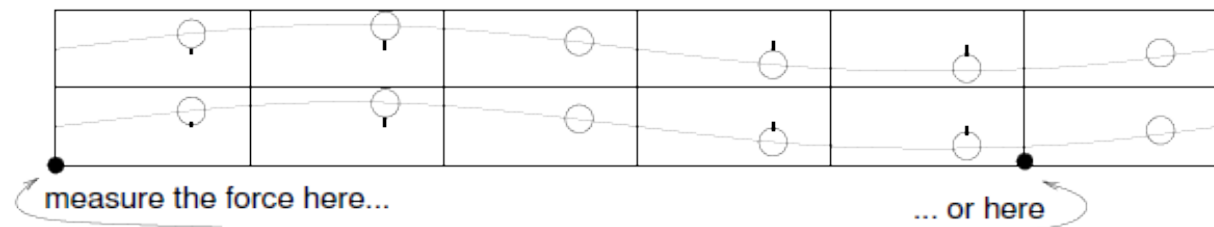
In principle, we should displace only the atoms in the unit cell, but this is not possible when using periodic boundary conditions... again, it is important to converge the size of the supercell

Another view point

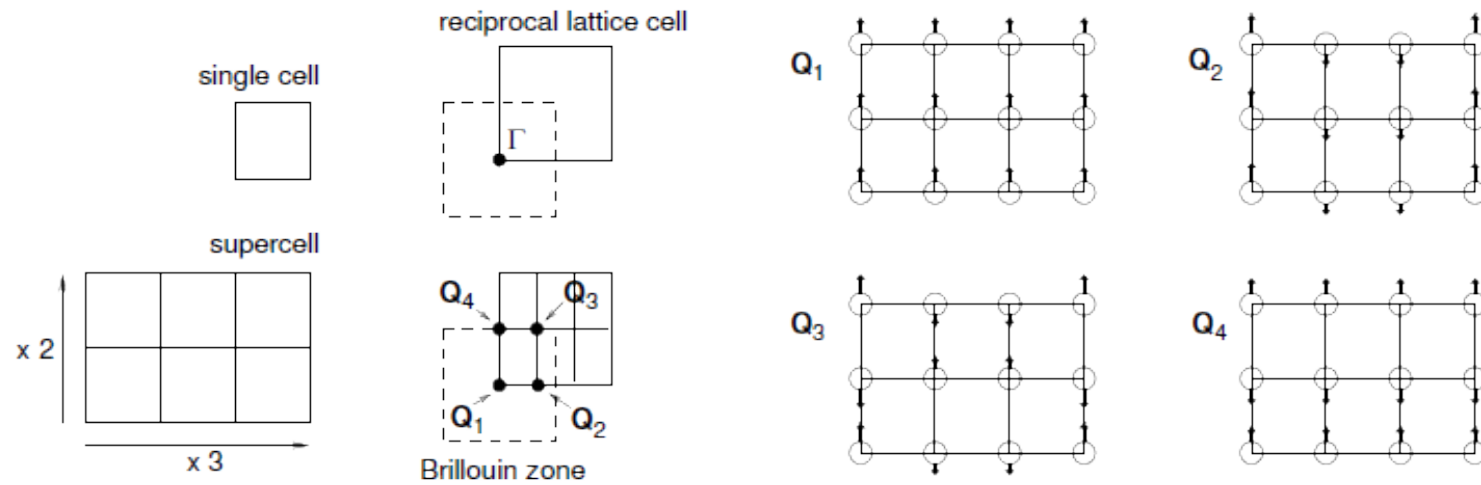
How to obtain
real-space force
constants $F_{\alpha\beta}^{ij}$:



or, Fourier-
transformed
ones $F_{ss'}^{ij}(\mathbf{q})$:



Γ phonon in a supercell scans different $\mathbf{q}$ values:



```

#
# General system descriptors
#

SystemName      Bulk Silicon in the diamond structure
#              building the supercell to compute the phonons

SystemLabel      Si
NumberOfSpecies  1
NumberOfAtoms    < FC.fdf
%block ChemicalSpeciesLabel
  1 14 Si
%endblock ChemicalSpeciesLabel

#
# Lattice, coordinates, k-sampling
#

LatticeConstant  < FC.fdf
LatticeVectors   < FC.fdf

AtomicCoordinatesFormat < FC.fdf
AtomicCoordinatesAndAtomicSpecies < FC.fdf

kgrid_cutoff     8.0 Ang

#
# Grid
#

MeshCutoff       200 Ry

#
# Basis definition
#

PAO.BasisSize    SZ

#
# Options to compute the interatomic force constants in real space
#

MD.TypeOfRun     < FC.fdf
MD.FCfirst       < FC.fdf
MD.FClast        < FC.fdf
MD.FCdispl       < FC.fdf
# Compute the interatomic force constants matrix
# Index of first atom to displace
# Index of the last atom to displace
# Displacement to use for the computation of the
# interatomic force constant matrix
# (Remember that the second derivative of the
# energy with respect the displacement of two
# atoms is computed by means of a
# finite difference derivative of the forces)

```

**We prepare an input file to run siesta
and compute the interatomic force
constant matrix. Let's call this input file**
Si.ifc.fdf

**Many variables are taken directly from
the file where the supercell is described**

**Only the atoms of the
unit cell are displaced**

The IFC

\$siesta < Si.ifc.fdf > Si.ifc.out

This will generate a file called SystemLabel.FC with the interatomic force constant matrix

Force constants matrix

-0.0312701	0.0482093	0.0482093
0.0351977	-0.0006070	-0.0006070
-0.0321113	0.0487602	-0.0469701
0.0616160	-0.0701156	0.0616651
-0.0423482	0.0009719	-0.0000591
0.0529542	-0.0654082	-0.0593842
-0.0321113	-0.0469701	0.0487602
0.0616160	0.0616651	-0.0701156
0.4098112	-0.1418340	-0.1418340
-3.9652498	2.9318623	2.9318623
-0.1379968	0.1480754	0.1571662
0.0449045	0.0580579	-0.0614154
...	...	...

Displace atom 1 along direction -x

**As many lines as atoms in the supercell,
force on the atom j in the supercell
(in eV/Å)**

**Then loop on the directions along
which the atom 1 is displaced:**

-x, +x, -y, +y, -z, +z

Finally, loop on the atoms in the unit cell

(III) Computing the dynamical matrix and diagonalize

Once the interatomic force constant matrix has been computed, a Fourier transform is carried out at different k-points to calculate the dynamical matrix

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q}) \approx \frac{1}{\sqrt{M_{\kappa}M_{\kappa'}}} \sum_b^{b_{\text{cut}}} C_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\vec{q}\cdot\vec{R}_b}$$

The k-points are defined in the same way as to compute the electronic band structure in the same file used to define the supercell (Si.fcbuild.fdf)

```
#
# High symmetry lines to plot the phonon band structure
#
BandLinesScale      pi/a
%block BandLines
1  0.0  0.0  0.0  \Gamma    # Begin at Gamma
45 2.0  0.0  0.0  X          # 45 points from Gamma to X
17 2.0  0.5  0.5  K          # 17 points from X to K
48 2.0  2.0  2.0  \Gamma    # 48 points from K to Gamma
41 1.0  1.0  1.0  L          # 41 points from Gamma to L
%endblock BandLines
```

(III) Dynamical matrix

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\vec{q}) \approx \frac{1}{\sqrt{M_{\kappa}M_{\kappa'}}} \sum_b^{b_{\text{cut}}} C_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\vec{q}\cdot\vec{R}_b}$$

`$siesta/Utils/Vibra/Src/vibrator < Si.fcbuild.fdf`

Output:

SystemLabel.bands: **mode frequencies (in cm⁻¹)**
(Same structure as the electronic band structure)

SystemLabel.vectors: **eigenmodes for each k-point**
(format self-explained)

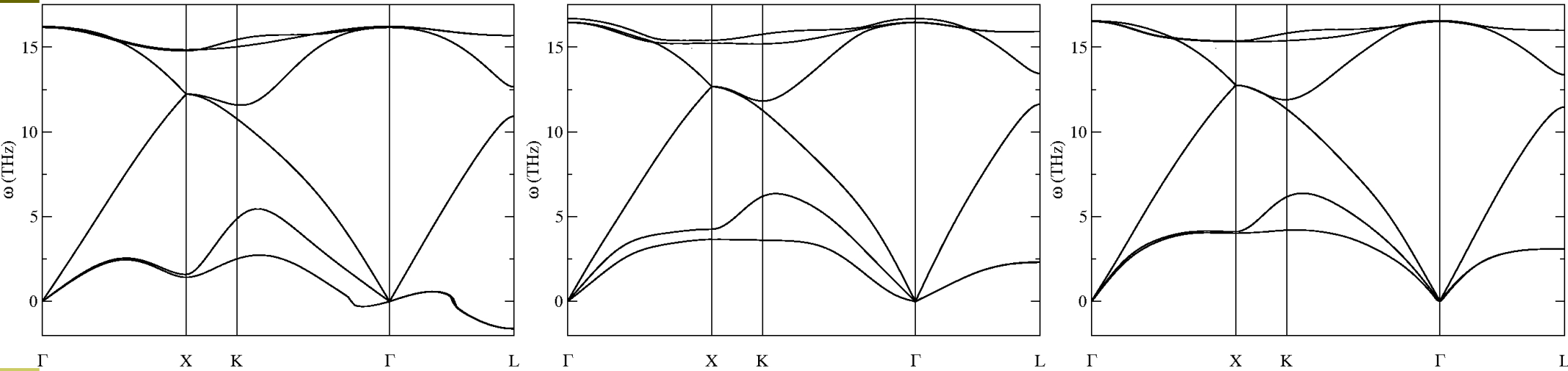
To plot the phonon band structure:

`$gnubands < Si.bands > Si.bands.dat`

`$gnuplot`

`$plot "Si.bands.dat" using 1:2 with lines`

Convergence for different Supercells



Plane waves + pseudopotentials

Dots represent experimental points

P. E. Van Camp *et al.*, Phys. Rev. B 31, 4089 (1985)

