Density Functional Perturbation Theory

and

Phonons Calculations
Outline

1. Crystal lattice dynamics: phonons
2. Density functional perturbation theory
3. Codes for phonon dispersions
Description of a solid

Let’s consider a periodic solid. We indicate with

$$R_I = R_\mu + d_s$$

the equilibrium positions of the atoms. $R_\mu$ indicate the Bravais lattice vectors and $d_s$ the positions of the atoms in one unit cell ($s = 1, \ldots, N_{at}$).

We take $N$ unit cells with Born-von Karman periodic boundary conditions. $\Omega$ is the volume of one cell and $V = N\Omega$ the volume of the solid.

At time $t$, each atom is displaced from its equilibrium position. $u_I(t)$ is the displacement of the atom $I$. 
Within the *Born-Oppenheimer adiabatic approximation* the nuclei move in a potential energy given by the total energy of the electron system calculated (for instance within DFT) at fixed nuclei. We call

\[ E_{tot}(R_l + u_l) \]

this energy. The electrons are assumed to be in the ground state for each nuclear configuration.

If \(|u_l|\) is small, we can expand \(E_{tot}\) in a Taylor series with respect to \(u_l\). Within the *harmonic approximation*:

\[ E_{tot}(R_l + u_l) = E_{tot}(R_l) + \sum_{l\alpha} \frac{\partial E_{tot}}{\partial u_{l\alpha}} u_{l\alpha} + \frac{1}{2} \sum_{l\alpha,j\beta} \frac{\partial^2 E_{tot}}{\partial u_{l\alpha} \partial u_{j\beta}} u_{l\alpha} u_{j\beta} + \ldots \]

where the derivatives are calculated at \(u_l = 0\) and \(\alpha\) and \(\beta\) indicate the three Cartesian coordinates.
Equations of motion

At equilibrium $\frac{\partial E_{\text{tot}}}{\partial u_{l\alpha}} = 0$, so the Hamiltonian of the ions becomes:

$$H = \sum_{l\alpha} \frac{P_{l\alpha}^2}{2M_l} + \frac{1}{2} \sum_{l\alpha, J\beta} \frac{\partial^2 E_{\text{tot}}}{\partial u_{l\alpha} \partial u_{J\beta}} u_{l\alpha} u_{J\beta}$$

where $P_l$ are the momenta of the nuclei and $M_l$ their masses. The classical motion of the nuclei is given by the $N \times 3 \times N_{\text{at}}$ functions $u_{l\alpha}(t)$. These functions are the solutions of the Hamilton equations:

$$\dot{u}_{l\alpha} = \frac{\partial H}{\partial P_{l\alpha}}$$

$$\dot{P}_{l\alpha} = -\frac{\partial H}{\partial u_{l\alpha}}$$
Vibrational properties

\[(R + \tau_s)_{eq} \rightarrow (R + \tau_s)_{eq} + u_{Rs}
\]

\[
\sum_{R s \alpha} \frac{P_{Rs\alpha}^2}{2M_s} + \frac{1}{2} \sum_{R s' \alpha'} u_{Rs\alpha} \frac{\partial^2 E_{el+ion}}{\partial u_{Rs\alpha} \partial u_{R's'\alpha'}} u_{R's'\alpha'}
\]

\[e^{i q R} 1 1 1 1 1 q=0\]
The phonon solution

We can search the solution in the form of a phonon. Let's introduce a vector $\mathbf{q}$ in the first Brillouin zone. For each $\mathbf{q}$ we can write:

$$ u_{\mu, s\alpha}(t) = \frac{1}{\sqrt{M_s}} \text{Re} \left[ u_{s\alpha}(\mathbf{q}) e^{i(\mathbf{q}\mathbf{R}_\mu - \omega_q t)} \right] $$

where the time dependence is given by simple phase factors $e^{\pm i\omega_q t}$ and the displacement of the atoms in each cell identified by the Bravais lattice $\mathbf{R}_\mu$ can be obtained from the displacements of the atoms in one unit cell, for instance the one that corresponds to $\mathbf{R}_\mu = 0$: $\frac{1}{\sqrt{M_s}} u_{s\alpha}(\mathbf{q})$. 
Vibrational properties

\[(R + \tau_s)_{eq} \rightarrow (R + \tau_s)_{eq} + u_s^q \frac{e^{iqR}}{\sqrt{N}}\]

\[\sum_{s\alpha} \frac{P_{s\alpha}^2}{2M_s} + \frac{1}{2} \sum_{s'\alpha'} u_{s\alpha}^q * \frac{\partial^2 E_{el+ion}}{\partial u_{s\alpha}^q \partial u_{s'\alpha'}^q} u_{s'\alpha'}^q\]

\[e^{iqR} \begin{array}{cccccc} 1 & 1 & 1 & 1 & 1 & 1 \\ a \end{array} \]

\[\Delta V_{ext}(r) = \sum_{Rs} \frac{\partial V_s}{\partial R} (|r - R - \tau_s|) u_s^q \frac{e^{iqR}}{\sqrt{N}}\]
Vibrational properties

\[(\mathbf{R} + \mathbf{\tau}_s)_{eq} \rightarrow (\mathbf{R} + \mathbf{\tau}_s)_{eq} + \mathbf{u}_s^q \frac{e^{i\mathbf{q}\cdot\mathbf{R}}}{\sqrt{N}}\]

\[
\sum_{s\alpha} \frac{P_{s\alpha}^2}{2M_s} + \frac{1}{2} \sum_{s' \alpha'} \mathbf{u}_{s\alpha}^q * \frac{\partial^2 E_{el+ion}}{\partial \mathbf{u}_{s\alpha}^q * \partial \mathbf{u}_{s'\alpha'}^q} \mathbf{u}_{s'\alpha'}^q
\]

\[e^{i\mathbf{q}\cdot\mathbf{R}} 1 -1 1 -1 1 q = \frac{2\pi}{a} \frac{1}{2}\]

\[\Delta V_{ext}(r) = \sum_{\mathbf{R}_s} \frac{\partial V_s}{\partial \mathbf{R}}(|r - \mathbf{R} - \mathbf{\tau}_s|) \mathbf{u}_s^q \frac{e^{i\mathbf{q}\cdot\mathbf{R}}}{\sqrt{N}}\]
Vibrational properties

\[(\mathbf{R} + \tau_s)_{eq} \rightarrow (\mathbf{R} + \tau_s)_{eq} + \mathbf{u}_s^q \frac{e^{iq\mathbf{R}}}{\sqrt{N}}\]

\[\sum_{s\alpha} \frac{p_{s\alpha}^2}{2M_s} + \frac{1}{2} \sum_{s\alpha} u_{s\alpha}^q \ast \frac{\partial^2 E_{el+ion}}{\partial u_{s\alpha}^q \ast \partial u_{s'\alpha'}^q} u_{s'\alpha'}^q\]

\[e^{iq\mathbf{R}} 1 \; i \; -1 \; -i \; 1 \quad q = \frac{2\pi}{a} \frac{1}{4}\]

\[\Delta V_{ext}(r) = \sum_{R_s} \frac{\partial V_s}{\partial \mathbf{R}}(|r - \mathbf{R} - \tau_s|) \mathbf{u}_s^q \frac{e^{iq\mathbf{R}}}{\sqrt{N}}\]
The phonon solution-II

Inserting this solution in the equations of motion and writing \( l = (\mu, s), J = (\nu, s') \) we obtain an eigenvalue problem for the \( 3 \times N_{at} \) variables \( u_{s\alpha}(q) \):

\[
\omega_q^2 u_{s\alpha}(q) = \sum_{s' \beta} D_{s\alpha s'\beta}(q) u_{s'\beta}(q)
\]

where:

\[
D_{s\alpha s'\beta}(q) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \frac{\partial^2 E_{tot}}{\partial u_{\mu s\alpha} \partial u_{\nu s'\beta}} e^{i q (R_\nu - R_\mu)}
\]

is the dynamical matrix of the solid.
KS self-consistent equations

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i \right] \varphi_i(r) = 0
\]
KS self-consistent equations

\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i\right] \varphi_i(r) = 0
\]

\[
\rho(r) = \sum_i |\varphi_i(r)|^2
\]
KS self-consistent equations

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i \right] \varphi_i(r) = 0
\]

\[\rho(r) = \sum_i |\varphi_i(r)|^2\]

\[V_{KS}(r) = V_{\text{ext}}(r) + V_H(r) + v_{xc}(r)\]
KS self-consistent equations

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i \right] \varphi_i(r) = 0 \]

\[ \rho(r) = \sum_i |\varphi_i(r)|^2 \]

\[ V_{KS}(r) = V_{ext}(r) + V_H(r) + u_{xc}(r) \]

\[ \rightarrow V_{KS}(r) \rightarrow \varphi_i(r) \rightarrow \rho(r) \]
Structure of a self-consistent type code

1. construct $V_{\text{ext}}$
2. guess $\rho_{\text{in}}$
3. compute $V_{\text{KS}}$
4. diagonalize $H_{\text{KS}}$
5. compute $\rho_{\text{out}}$

- $\rho_{\text{in}} = \rho_{\text{out}}$?
  - yes: compute forces, stress, and other properties
  - no: mix to get new $\rho_{\text{in}}$
Total KS energy

\[ E_{el+ion} = -\frac{\hbar^2}{2m} \sum_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \int V_{ext}(r) \rho(r) \, dr + E_H[\rho] + E_{xc}[\rho] + E_{WLD} \]
Total KS energy

\[ E_{el+ion} = -\frac{\hbar^2}{2m} \sum_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \int V_{ext}(r) \rho(r) dr + \]
\[ E_H[\rho] + E_{xc}[\rho] + E_{WLD} \]

Hellmann-Feynman Theorem

\[ F_{I\alpha} = -\frac{\partial E_{el+ion}}{\partial R_{I\alpha}} = -\int \frac{\partial V_{ext}(r)}{\partial R_{I\alpha}} \rho(r) dr - \frac{\partial E_{WLD}}{\partial R_{I\alpha}} \]

\[ \frac{\partial E_{el+ion}}{\partial \lambda} = \int \frac{\partial V_{ext}(r)}{\partial \lambda} \rho(r) dr + \frac{\partial E_{WLD}}{\partial \lambda} \]

the linear variation of the GS density is not needed
KS energy expansion

\[ E_{el+ion} = -\frac{\hbar^2}{2m} \sum_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \int V_{ext}(r) \rho(r) dr + E_H[\rho] + E_{xc}[\rho] + E_{WLD} \]

\[ \frac{\partial E_{el+ion}}{\partial \lambda} = \int \frac{\partial V_{ext}(r)}{\partial \lambda} \rho(r) dr + \frac{\partial E_{WLD}}{\partial \lambda} \]
KS energy expansion

\[ E_{el+ion} = -\frac{\hbar^2}{2m} \sum_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \int V_{ext}(r) \rho(r) dr + E_H[\rho] + E_{xc}[\rho] + E_{WLD} \]

\[ \frac{\partial E_{el+ion}}{\partial \lambda} = \int \frac{\partial V_{ext}(r)}{\partial \lambda} \rho(r) dr + \frac{\partial E_{WLD}}{\partial \lambda} \]

\[ \frac{\partial^2 E_{el+ion}}{\partial \lambda \partial \mu} = \int \frac{\partial^2 V_{ext}(r)}{\partial \lambda \partial \mu} \rho(r) dr + \int \frac{\partial V_{ext}(r)}{\partial \lambda} \frac{\partial \rho(r)}{\partial \mu} dr + \frac{\partial^2 E_{WLD}}{\partial \lambda \partial \mu} \]

the linear variation of the GS density is needed
KS self-consistent equations

\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i \right] \varphi_i(r) = 0
\]

\[
\rho(r) = \sum_i |\varphi_i(r)|^2
\]

\[
V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)
\]
DFPT self-consistent equations

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i \right] \varphi_i(r) = 0
\]

\[
\rho(r) = \sum_i |\varphi_i(r)|^2
\]

\[
V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)
\]
DFPT self-consistent equations

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i \right] \Delta \varphi_i(r) = - (\Delta V_{KS} - \Delta \varepsilon_i) \varphi_i(r)
\]

\[
\rho(r) = \sum_i |\varphi_i(r)|^2
\]

\[
V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)
\]
DFPT self-consistent equations

\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i\right] \Delta \varphi_i(r) = - (\Delta V_{KS} - \Delta \varepsilon_i) \varphi_i(r)
\]

\[
\Delta \rho(r) = 2 \sum_i \varphi_i^*(r) \Delta \varphi_i(r)
\]

\[
V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)
\]
DFPT self-consistent equations

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i \right] \Delta \tilde{\varphi}_i(r) = -P_c \Delta V_{KS}(r) \varphi_i(r) \]

\[ \Delta \rho(r) = 2 \sum_i \varphi_i^*(r) \Delta \tilde{\varphi}_i(r) \]

\[ V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r) \]
DFPT self-consistent equations

\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i \right] \Delta \tilde{\varphi}_i(r) = -P_c \Delta V_{KS}(r) \varphi_i(r)
\]

\[
\Delta \rho(r) = 2 \sum_i \varphi_i^*(r) \Delta \tilde{\varphi}_i(r)
\]

\[
\Delta V_{KS}(r) = \Delta V_{ext}(r) + \Delta V_H(r) + \Delta v_{xc}(r)
\]
DFPT self-consistent equations

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i\right] \Delta \tilde{\varphi}_i(r) = -P_c \Delta V_{KS}(r) \varphi_i(r)$$

$$\Delta \rho(r) = 2 \sum_i \varphi^*_i(r) \Delta \tilde{\varphi}_i(r)$$

$$\Delta V_{KS}(r) = \Delta V_{ext}(r) + e^2 \int \frac{\Delta \rho(r')}{|r - r'|} \, dr' + \int \frac{\delta v_{xc}(r)}{\delta \rho(r')} \Delta \rho(r') \, dr'$$
DFPT self-consistent equations

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i \right] \Delta \tilde{\varphi}_i(r) = -P_c \Delta V_{KS}(r) \varphi_i(r)
\]

\[
\Delta \rho(r) = 2 \sum_i \varphi_i^*(r) \Delta \tilde{\varphi}_i(r)
\]

\[
\Delta V_{KS}(r) = \Delta V_{ext}(r) + e^2 \int \frac{\Delta \rho(r')}{|r - r'|} dr' + \int f_{xc} \Delta \rho(r') dr'
\]
DFPT self-consistent equations

\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i \right]\Delta \tilde{\phi}_i(r) = -P_c \Delta V_{KS}(r) \varphi_i(r)
\]

\[
\Delta \rho(r) = 2 \sum_i \varphi_i^*(r) \Delta \tilde{\phi}_i(r)
\]

\[
\Delta V_{KS}(r) = \Delta V_{ext}(r) + e^2 \int \frac{\Delta \rho(r')}{|r - r'|} dr' + \int f_{xc} \Delta \rho(r') dr'
\]

\[\Delta V_{KS} \rightarrow \Delta \tilde{\phi}_i(r) \rightarrow \Delta \rho(r)\]
DFPT self-consistent equations

\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) - \varepsilon_i\right] \Delta \tilde{\varphi}_i(r) = -P_c \Delta V_{KS}(r) \varphi_i(r)
\]

\[
\Delta \rho(r) = 2 \sum_i \varphi_i^*(r) \Delta \tilde{\varphi}_i(r)
\]

\[
\Delta V_{KS}(r) = \Delta V_{ext}(r) + e^2 \int \frac{\Delta \rho(r')}{|r - r'|} dr' + \int f_{xc} \Delta \rho(r') dr'
\]

\[
\Rightarrow \Delta V_{KS} \rightarrow \Delta \tilde{\varphi}_i(r) \rightarrow \Delta \rho(r)
\]

Evaluate the dynamical matrix

\[
\frac{\partial^2 E_{el+ion}}{\partial \lambda \partial \mu} = \int \frac{\partial^2 V_{ext}(r)}{\partial \lambda \partial \mu} \rho(r) dr + \int \frac{\partial V_{ext}(r)}{\partial \lambda} \frac{\partial \rho(r)}{\partial \mu} dr + \frac{\partial^2 E_{WLD}}{\partial \lambda \partial \mu}
\]
Dynamical matrix at finite $q$ - II

Defining:

$$\frac{\partial^2 V_{loc}(r)}{\partial u_{s\alpha}^*(q) \partial u_{s'\beta}(q)} = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\mu \nu} e^{-i q R_\mu} \frac{\partial^2 V_{loc}(r)}{\partial u_{\mu s\alpha} \partial u_{\nu s'\beta}} e^{i q R_\nu}$$

we can show (see below) that $\frac{\partial^2 V_{loc}(r)}{\partial u_{s\alpha}^*(q) \partial u_{s'\beta}(q)}$ is a lattice-periodic function. Then we can define

$$\frac{\partial \rho(r)}{\partial u_{s'\beta}(q)} = \frac{1}{\sqrt{M_{s'}}} \sum_{\nu} \frac{\partial \rho(r)}{\partial u_{\nu s'\beta}} e^{i q R_\nu}$$

and show that $\frac{\partial \rho(r)}{\partial u_{s'\beta}(q)} = e^{i q r} \frac{\partial \tilde{\rho}(r)}{\partial u_{s'\beta}(q)}$, where $\frac{\partial \tilde{\rho}(r)}{\partial u_{s'\beta}(q)}$ is a lattice-periodic function.
Dynamical matrix at finite $q$ - III

In the same manner, by defining

$$
\left( \frac{\partial V_{loc}(r)}{\partial u_{s\alpha}(q)} \right)^* = \frac{1}{\sqrt{M_s}} \sum_{\mu} e^{-iqR_\mu} \frac{\partial V_{loc}(r)}{\partial u_{\mu s\alpha}}
$$

and showing that $\frac{\partial V_{loc}(r)}{\partial u_{s\alpha}(q)} = e^{iqr} \frac{\partial \tilde{V}_{loc}(r)}{\partial u_{s\alpha}(q)}$, where $\frac{\partial \tilde{V}_{loc}(r)}{\partial u_{s\alpha}(q)}$ is a lattice-periodic function, we can write the dynamical matrix at finite $q$ as:

$$
D_{s\alpha s'\beta}(q) = \int_{\Omega} d^3r \frac{\partial^2 V_{loc}(r)}{\partial u_{s\alpha}(q)\partial u_{s'\beta}(q)} \rho(r)
$$

$$
+ \int_{\Omega} d^3r \left( \frac{\partial \tilde{V}_{loc}(r)}{\partial u_{s\alpha}(q)} \right)^* \left( \frac{\partial \tilde{\rho}(r)}{\partial u_{s'\beta}(q)} \right).
$$
The program \texttt{ph.x} solves this self-consistent linear system for \(3 \times N_{at}\) perturbations at a fixed vector \(\mathbf{q}\). With \(\frac{\partial \rho(\mathbf{r})}{\partial u_{s' \beta}(\mathbf{q})}\) for all perturbations, it calculates the dynamical matrix

\[
D_{s\alpha s' \beta}(\mathbf{q})
\]

at the given \(\mathbf{q}\) as discussed above. Diagonalizing this matrix we obtain \(3 \times N_{at}\) frequencies \(\omega_{\mathbf{q}}\). By repeating this procedure for several \(\mathbf{q}\) we could plot \(\omega_{\mathbf{q}}\) as a function of \(\mathbf{q}\) and display the phonon dispersions. However, it is more convenient to adopt a different approach that requires the calculation of the dynamical matrix in a small set of vectors \(\mathbf{q}\).
Phonon dispersions

The dynamical matrix of the solid:

\[ D_{s\alpha s'\beta}(q) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \frac{\partial^2 E_{tot}}{\partial u_{\mu s\alpha} \partial u_{\nu s'\beta}} e^{i\mathbf{q}(\mathbf{R}_\nu - \mathbf{R}_\mu)} \]  \hspace{1cm} (1)

is a periodic function of \( \mathbf{q} \) with \( D_{s\alpha s'\beta}(\mathbf{q} + \mathbf{G}) = D_{s\alpha s'\beta}(\mathbf{q}) \) for any reciprocal lattice vector \( \mathbf{G} \). Furthermore, due to the translational invariance of the solid, it does not depend on \( \mu \).

Eq.1 is a Fourier expansion of a three dimensional periodic function. We have Fourier components only at the discrete values \( \mathbf{R}_\nu \) of the Bravais lattice and we can write:

\[ \frac{1}{\sqrt{M_s M_{s'}}} \frac{\partial^2 E_{tot}}{\partial u_{\mu s\alpha} \partial u_{\nu s'\beta}} = \frac{\Omega}{(2\pi)^3} \int d^3q D_{s\alpha s'\beta}(q) e^{-i\mathbf{q}(\mathbf{R}_\nu - \mathbf{R}_\mu)}. \]
Discrete Fourier transform

We can use the properties of the discrete Fourier transform and sample the integral in a uniform mesh of \( \mathbf{q} \) vectors. This will give the inter-atomic force constants only for a certain range of values of \( \mathbf{R}_\nu \) neighbors of \( \mathbf{R}_\mu \).

In order to recall the main properties of the discrete Fourier transform, let us consider a one dimensional periodic function \( f(x + a) = f(x) \) with period \( a \). This function can be expanded in a Fourier series and will have a discrete set of Fourier components at \( k_n = \frac{2\pi}{a} n \), where \( n \) is an integer (positive, negative or zero).

\[
f(x) = \sum_{n} c_n e^{ik_n x}
\]

where the coefficients of the expansion are:
\[ c_n = \frac{1}{a} \int_0^a f(x) e^{-ik_n x} \, dx. \]

In general, if \( f(x) \) is a sufficiently smooth function, \( c_n \to 0 \) at large \( n \). Now suppose that we discretize \( f(x) \) in a uniform set of \( N \) points \( x_j = j\Delta x \) where \( \Delta x = a/N \) and \( j = 0, \ldots, N - 1 \), then we can calculate:

\[ \tilde{c}_n = \frac{1}{N} \sum_{j=0}^{N-1} f(x_j) e^{-i \frac{2\pi}{N} n j}, \]

\( \tilde{c}_n \) is a periodic function of \( n \) and \( \tilde{c}_{n+N} = \tilde{c}_n \). So, if \( N \) is sufficiently large that \( c_n = 0 \) when \( |n| \geq N/2 \), \( \tilde{c}_n \) is a good approximation of \( c_n \) for \( |n| < N/2 \) and the function
\[ C_{s\alpha s' \beta}(\mathbf{R}) = \frac{\partial^2 E_{\text{tot}}}{\partial u_{\mu s\alpha} \partial u_{\nu s' \beta}} \text{ and write the relationship:} \]

\[ C_{s\alpha s' \beta}(\mathbf{R}) = \frac{1}{N_q} \sum_{i=1}^{N_q} C_{s\alpha s' \beta}(\mathbf{q}_i) e^{i\mathbf{q}_i \cdot \mathbf{R}}. \]

The code \texttt{q2r.x} reads a set of dynamical matrices obtained for a uniform mesh of \(\mathbf{q}_i\) vectors and calculates, using this equation, the inter-atomic force constants for some neighbors of the point \(\mathbf{R} = 0\).
matdyn.x

If the dynamical matrix is a sufficiently smooth function of \( q \), the inter-atomic force constants decay sufficiently rapidly in real space and we can use Eq. 1 limiting the sum over \( \nu \) to the few neighbors of \( R_\mu \) for which we have calculated the inter-atomic force constants. With the present notation Eq. 1 becomes:

\[
C_{s\alpha s'\beta}(q) = \sum_R C_{s\alpha s'\beta}(R) e^{-i q R},
\]

(3)

a relationship that allows the interpolation of the dynamical matrix at arbitrary \( q \), by a few inter-atomic force constants. The program \texttt{matdyn.x} reads the inter-atomic force constants calculated by \texttt{q2r.x} and calculates the dynamical matrices at an arbitrary \( q \) using this equation.
This procedure fails in two cases:

- In metals when there are Kohn anomalies. In this case $D_{s\alpha s'\beta}(q)$ is not a smooth function of $q$ and the inter-atomic force constants are long range.

- In polar insulators where the atomic displacements generate long range electrostatic interactions and the dynamical matrix is non analytic for $q \to 0$. This case, however, can be dealt with by calculating the Born effective charges and the dielectric constant of the material.
Use of symmetry

Phonon dispersions require the DFPT calculation on a uniform mesh $N_{q_1} \times N_{q_2} \times N_{q_3} = N_q$ of $\mathbf{q}$ vectors. The CPU time can be roughly estimated as

$$N_q \times 3 \times N_{\text{at}} \times T_{\text{scf}}$$

where $T_{\text{scf}}$ is the CPU time of a single self-consistent calculation. Using symmetry the $\mathbf{q}$-vector mesh is reduced to a set of $\tilde{N}_q$ non equivalent $\mathbf{q}$ vectors. The calculation of the dynamical matrix at each $\mathbf{q}$ vector requires an amount of CPU time roughly proportional to the size of its star of $\mathbf{q}$ vectors. So low symmetry $\mathbf{q}$ vectors require much more CPU time than high symmetry $\mathbf{q}$ vectors mainly because $\mathbf{p}\cdot\mathbf{h}$ uses only the symmetries of the small group of $\mathbf{q}$ to reduce the $\mathbf{k}$ points.
Use of symmetry - II

On the other hand, from the dynamical matrix at \( \mathbf{q} \) we can obtain, for free, the dynamical matrices of the star of \( \mathbf{q} \) that is larger for low symmetry \( \mathbf{q} \). Not all the \( 3 \times N_{\text{at}} \) perturbations have to be calculated simultaneously at each \( \mathbf{q} \). Choosing displacement patterns that transform according to an irreducible representation (irrep) of the small group of \( \mathbf{q} \), the number of patterns that transform among themselves is equal to the dimension of the irreducible representation. For standard point groups the maximum dimension is 3, while for \( \mathbf{q} \) at zone border and nonsymmmorphic point groups the maximum dimension could be larger, up to 6.
THE END