

An introduction to linear response and to phonon calculations

P. Giannozzi

Università di Udine and IOM-Democritos, Trieste

March 28, 2018

Reference: *Phonons and related crystal properties from density-functional perturbation theory*, S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515-562 (2001).

Electronic screening

Consider a static *perturbation* $\delta V_0(\mathbf{r})$ to a system of electrons under an external (nuclear) potential $V_0(\mathbf{r})$. At linear order,

$$\delta n(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') \delta V_0(\mathbf{r}') d\mathbf{r}'$$

where $\chi(\mathbf{r}, \mathbf{r}')$ is the *density response* of the system.

The polarization charge $\delta n(\mathbf{r})$ produces an electrostatic field that *screens* the perturbing potential $\delta V_0(\mathbf{r})$:

$$\delta V(\mathbf{r}) = \delta V_0(\mathbf{r}) + e^2 \int \frac{\delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

that is:

$$\delta V(\mathbf{r}) = \int \left(\delta(\mathbf{r} - \mathbf{r}') + e^2 \int \frac{\chi(\mathbf{r}'', \mathbf{r}')}{|\mathbf{r} - \mathbf{r}''|} d\mathbf{r}'' \right) \delta V_0(\mathbf{r}') d\mathbf{r}' \equiv \int \epsilon^{-1}(\mathbf{r}, \mathbf{r}') \delta V_0(\mathbf{r}') d\mathbf{r}'.$$

$\epsilon^{-1}(\mathbf{r}, \mathbf{r}')$ is the *dielectric response function* as usually defined in electrostatics.

Linear Response functions

- $\chi(\mathbf{r}, \mathbf{r}')$
yields the charge response to a bare (external) perturbing potential via

$$\delta n(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') \delta V_0(\mathbf{r}') d\mathbf{r}'$$

- $\epsilon^{-1}(\mathbf{r}, \mathbf{r}')$
yields the screened potential from the bare one via

$$\delta V(\mathbf{r}) = \int \epsilon^{-1}(\mathbf{r}, \mathbf{r}') \delta V_0(\mathbf{r}') d\mathbf{r}'.$$

and is related to $\chi(\mathbf{r}, \mathbf{r}')$ via

$$\epsilon^{-1}(\mathbf{r}, \mathbf{r}') \equiv \delta(\mathbf{r} - \mathbf{r}') + e^2 \int \frac{\chi(\mathbf{r}'', \mathbf{r}')}{|\mathbf{r} - \mathbf{r}''|} d\mathbf{r}''$$

These are the functions that determine electronic response. Their calculation is however a nontrivial many-body problem.

Density-Functional Linear Response

We assume that the system obeys Kohn-Sham (KS) equations:

$$(H_{KS} - \epsilon_i) \psi_i(\mathbf{r}) = 0, \quad H_{KS} = -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(\mathbf{r})$$

where $V_{KS}(\mathbf{r}) = V_0(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}[n(\mathbf{r})]$ and the charge is given by

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$$

(general case of noninteger occupancy f_i).

Let us add an external $\delta V_0(\mathbf{r})$ to $V_0(\mathbf{r})$: the potential V_{KS} will be modified by $\delta V_{KS} = \delta V_0(\mathbf{r}) + \delta V_H(\mathbf{r}) + \delta V_{xc}[n(\mathbf{r})]$. Let us consider first order (linear response). We introduce the *independent-particle polarizability* $\chi_0(\mathbf{r}, \mathbf{r}')$ via

$$\delta n(\mathbf{r}) = \int \chi_0(\mathbf{r}, \mathbf{r}') \delta V_{KS}(\mathbf{r}') d\mathbf{r}'.$$

Unlike $\chi(\mathbf{r}, \mathbf{r}')$, this quantity can be easily calculated using perturbation theory.

Independent-particle polarizability

The first-order variation of KS orbitals:

$$\delta\psi_i(\mathbf{r}) = \sum_{j \neq i} \psi_j(\mathbf{r}) \frac{\langle \psi_j | \delta V_{KS} | \psi_i \rangle}{\epsilon_i - \epsilon_j}$$

and of the charge density (after some manipulations):

$$\delta n(\mathbf{r}) = \sum_i f_i \delta\psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) + c.c. = \sum_{i,j,i \neq j} \frac{f_i - f_j}{\epsilon_i - \epsilon_j} \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) \langle \psi_j | \delta V_{KS} | \psi_i \rangle$$

Note that contribution from i, j states vanishes if both are fully occupied. For a closed-shell (insulating) system:

$$\delta n(\mathbf{r}) = 4\text{Re} \sum_{v,c} \psi_v^*(\mathbf{r}) \psi_c(\mathbf{r}) \frac{\langle \psi_c | \delta V_{KS} | \psi_v \rangle}{\epsilon_v - \epsilon_c}$$

v = filled (valence) states, c = empty (conduction) states, a factor 2 from spin.

Independent-particle polarizability II

We can write the independent-particle polarizability $\chi_0(\mathbf{r}, \mathbf{r}')$ as

$$\chi_0(\mathbf{r}, \mathbf{r}') = 4\text{Re} \sum_{v,c} \frac{\psi_v^*(\mathbf{r})\psi_c(\mathbf{r})\psi_c^*(\mathbf{r}')\psi_v(\mathbf{r}')}{\epsilon_v - \epsilon_c}.$$

which can be recast into the form

$$\chi_0(\mathbf{r}, \mathbf{r}') = 4\text{Re} \sum_v \psi_v^*(\mathbf{r}) P_c \frac{1}{\epsilon_v - H_{KS}} P_c \psi_v(\mathbf{r}')$$

where P_c is the projector operator over conduction states.

Note that:

- this expression is valid only if $V_{KS} \equiv V_{KS}(\mathbf{r})$, i.e. is a local potential:
- $\chi_0(\mathbf{r}, \mathbf{r}')$ is a *ground-state property*: it yields the difference between two ground states, even if it seems to depend on excited-state energies ϵ_c

Physical Response Operator

...but we need $\chi(\mathbf{r}, \mathbf{r}')$, not $\chi_0(\mathbf{r}, \mathbf{r}')$! How can we get from χ_0 to χ ?

In operator notations: $\delta n = \hat{\chi} \delta V_0 = \hat{\chi}_0 \delta V_{KS}$, and $\delta V_{KS} = \delta V_0 + \delta V_H + \delta V_{XC}$.

Screening from Hartree potential:

$$\delta V_H(\mathbf{r}) = e^2 \int \frac{\delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \equiv \hat{v}_c \delta n, \quad \text{where} \quad v_c(\mathbf{r}, \mathbf{r}') = \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}$$

Screening from exchange-correlation:

$$\delta V_{xc}(\mathbf{r}) = \int f_{xc}(\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}') d\mathbf{r}' \equiv \hat{f}_{xc} \delta n, \quad \text{where} \quad f_{xc}(\mathbf{r}, \mathbf{r}') = \frac{\delta V_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')}$$

After some algebra (remember that these are operators!):

$$\hat{\chi} = \hat{\chi}_0 + \hat{\chi}_0 (\hat{v}_c + \hat{f}_{xc}) \hat{\chi}$$

and finally

$$\hat{\chi} = \left(\hat{\chi}_0^{-1} - \hat{v}_c - \hat{f}_{xc} \right)^{-1}$$

Physical Response Operator in practice

Major problem: how to invert the operators!

In solids, the response function $\chi_0(\mathbf{r}, \mathbf{r}')$ can be expressed in reciprocal space as a matrix, the *dielectric matrix*: $\chi_0(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}')$, for the response to an external perturbation of wavevector \mathbf{q} . Operators become infinite matrix. By truncating them at an appropriate \mathbf{G}_{cut} one has a practical scheme for calculating response operators.

Local-field effects: those due to the presence of $\mathbf{G} \neq 0$ terms.

Random Phase Approximation (RPA): neglect the f_{xc} term. Note that the addition of LDA exchange-correlation is straightforward: f_{xc} is a local operator

$$f_{xc}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \left. \frac{dV_{xc}(n)}{dn} \right|_{n=n(\mathbf{r})} .$$

The *dielectric matrix* approach yields the response to *all* possible perturbations, but only *local* ones (i.e. δV local), and is computationally heavy. However we are often interested to the response to a *specific* and/or *nonlocal* perturbation.

Self-consistent Linear Response

We consider the basic equations, to be self-consistently solved:

$$\delta V_{KS} = \delta V_0 + \hat{v}_c \delta n + \hat{f}_{xc} \delta n$$

and

$$\delta n(\mathbf{r}) = 4\text{Re} \sum_{v,c} \psi_v^*(\mathbf{r}) \psi_c(\mathbf{r}) \frac{\langle \psi_c | \delta V_{KS} | \psi_v \rangle}{\epsilon_v - \epsilon_c} = 4\text{Re} \sum_v \psi_v^*(\mathbf{r}) P_c \frac{1}{\epsilon_v - H_{KS}} P_c \delta V_{KS} \psi_v.$$

The variation of the charge density can be recast into the form

$$\delta n(\mathbf{r}) = 4\text{Re} \sum_v \psi_v^*(\mathbf{r}) \Delta \psi_v(\mathbf{r}), \quad \text{where} \quad \Delta \psi_v = P_c \frac{1}{\epsilon_v - H_{KS}} P_c \delta V_{KS} \psi_v$$

$\Delta \psi_v$ can be obtained from the solution of a linear equation:

$$(\epsilon_v - H_{KS}) P_c \Delta \psi_v = P_c \delta V_{KS} \psi_v.$$

The above equations define a self-consistent procedure that can be solved by iteration, much in the same way as in the solution of KS equations.

Linear Response to an Electric Field

If the perturbing potential represents a macroscopic electric field δE :

$$\delta V_0 = -e\delta E_0 \cdot \mathbf{r}$$

it is ill-defined in a crystal, because \mathbf{r} is not a lattice-periodic operator! it can however be recast into a well-defined expression using the following trick:

$$\langle \psi_c | \mathbf{r} | \psi_v \rangle = \frac{\langle \psi_c | [H_{KS}, \mathbf{r}] | \psi_v \rangle}{\epsilon_c - \epsilon_v} \quad \text{for } c \neq v.$$

We can rewrite $|\bar{\psi}_v^\alpha\rangle = P_c r_\alpha |\psi_v\rangle$ as the solution of a linear system:

$$(H_{KS} - \epsilon_v) |\bar{\psi}_v^\alpha\rangle = P_c [H_{KS}, \mathbf{r}_\alpha] |\psi_v\rangle,$$

where the commutator can be calculated from the following expression:

$$[H_{KS}, \mathbf{r}] = -\frac{\hbar^2}{m} \frac{\partial}{\partial \mathbf{r}} + [\hat{V}_{NL}, \mathbf{r}].$$

(V_{NL} is the nonlocal term of the potential if present).

Macroscopic Polarization

The bare macroscopic electric field will be screened according to electrostatic: $\mathbf{E}_0^\alpha = \sum_\beta \epsilon_\infty^{\alpha,\beta} \mathbf{E}_\beta$, where ϵ_∞ is the electronic (clamped-nuclei) contribution to the dielectric tensor. This is related to the induced *polarization* \mathbf{P} via $\mathbf{E}_0 = \mathbf{E} + 4\pi\mathbf{P}$ so that

$$\epsilon_\infty^{\alpha,\beta} = \delta_{\alpha,\beta} + 4\pi \frac{\delta \mathbf{P}_\alpha}{\delta \mathbf{E}_\beta}$$

The macroscopic induced polarization can be calculated as

$$\delta \mathbf{P}_\alpha = -\frac{e}{N_c \Omega} \int \mathbf{r}_\alpha \delta n(\mathbf{r}) d\mathbf{r} = \frac{e}{N_c \Omega} \sum_v \langle \bar{\psi}_v^\alpha | \Delta \psi_v \rangle.$$

(N_c is the number of cells of volume Ω_c , $N_c \Omega$ is the crystal volume) using the same trick as shown before. In practical calculations, the (screened) electric field \mathbf{E} is kept fixed, iteration is performed on the microscopic terms of the potential:

$$\delta V_{KS}(\mathbf{r}) = -e \delta \mathbf{E}_\alpha \mathbf{r}_\alpha + \int \left(\frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta v_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \right) \delta n(\mathbf{r}').$$

Linear Response and Phonons

An important advantage of the self-consistent approach to Linear Response: the typical PW-PP technology can be straightforwardly applied. Note that the projector over empty states can be written as

$$P_c = 1 - P_v = 1 - \sum_v |\psi_v\rangle\langle\psi_v|$$

so that conduction bands are never explicitly required.

Typical application: calculation of normal vibrational modes, and especially phonons in crystals. The "perturbing potential" is in this case the displacement of a nuclear potential (or of a group of them). Once $\delta n(\mathbf{r})$ is (are) calculated, the dynamical matrix can be easily derived, along with phonon modes and frequencies. To this end, we need to know the form of the second-order expansion term of the energy.

Such procedure is often called *Density-Functional Perturbation Theory* (DFPT).

(in the following, notations change: derivatives replace infinitesimal increments)

Density-Functional Perturbation Theory

Let us assume that the external potential depends on some parameter λ

$$V_\lambda(\mathbf{r}) \simeq V(\mathbf{r}) + \lambda \frac{\partial V(\mathbf{r})}{\partial \lambda} + \frac{1}{2} \lambda^2 \frac{\partial^2 V(\mathbf{r})}{\partial \lambda^2} + \dots$$

(all derivatives calculated at $\lambda = 0$) and expand the charge density

$$n_\lambda(\mathbf{r}) \simeq n(\mathbf{r}) + \lambda \frac{\partial n(\mathbf{r})}{\partial \lambda} + \frac{1}{2} \lambda^2 \frac{\partial^2 n(\mathbf{r})}{\partial \lambda^2} + \dots$$

and the energy functional into powers of λ :

$$E_\lambda \simeq E + \lambda \frac{\partial E}{\partial \lambda} + \frac{1}{2} \lambda^2 \frac{\partial^2 E}{\partial \lambda^2} + \dots$$

The first-order derivative $\partial E / \partial \lambda$ does not depend on any derivative of $n(\mathbf{r})$ (*Hellmann-Feynman theorem*):

$$\frac{\partial E}{\partial \lambda} = \int n(\mathbf{r}) \frac{\partial V(\mathbf{r})}{\partial \lambda} d\mathbf{r}$$

Energy functional expansion terms

The second-order derivative $\partial^2 E / \partial \lambda^2$ depends on the first-order derivative of the charge density, $\partial n(\mathbf{r}) / \partial \lambda$:

$$\frac{\partial^2 E}{\partial \lambda^2} = \int \frac{\partial V(\mathbf{r})}{\partial \lambda} \frac{\partial n(\mathbf{r})}{\partial \lambda} d\mathbf{r} + \int n(\mathbf{r}) \frac{\partial^2 V(\mathbf{r})}{\partial \lambda^2} d\mathbf{r}$$

The result can be generalized to mixed derivatives:

$$\frac{\partial^2 E}{\partial \lambda \partial \mu} = \int \frac{\partial V(\mathbf{r})}{\partial \lambda} \frac{\partial n(\mathbf{r})}{\partial \mu} d\mathbf{r} + \int n(\mathbf{r}) \frac{\partial^2 V(\mathbf{r})}{\partial \lambda \partial \mu} d\mathbf{r}$$

(the order of derivatives can be exchanged)

In general, the $(2n + 1)$ -th derivative of energy depends only on derivatives up to order n of the charge density ($(2n + 1)$ *theorem*) due to its variational character.

$\partial n / \partial \lambda$ can be calculated either by the self-consistent procedure shown above, or by direct minimization of the 2nd-order energy, written as a functional of $\partial n / \partial \lambda$.

Born-Oppenheimer approximation

The behavior of a system of interacting electrons \mathbf{r} and nuclei \mathbf{R} is determined by the solutions of the *time-dependent Schrödinger equation*:

$$i\hbar \frac{\partial \hat{\Phi}(\mathbf{r}, \mathbf{R}; t)}{\partial t} = \left(- \sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial \mathbf{R}_I^2} - \sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} + V(\mathbf{r}, \mathbf{R}) \right) \hat{\Phi}(\mathbf{r}, \mathbf{R}; t)$$

where $V(\mathbf{r}, \mathbf{R})$ is the potential describing the coulombian interactions:

$$\begin{aligned} V(\mathbf{r}, \mathbf{R}) &= \sum_{I>J} \frac{Z_i Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i>j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &\equiv V_{nn}(\mathbf{R}) + V_{ne}(\mathbf{r}, \mathbf{R}) + V_{ee}(\mathbf{r}) \end{aligned}$$

Born-Oppenheimer (or adiabatic) approximation (valid for $M_I \gg m$):

$$\hat{\Phi}(\mathbf{r}, \mathbf{R}; t) \simeq \Phi(\mathbf{R}) \Psi(\mathbf{r}|\mathbf{R}) e^{-i\hat{E}t/\hbar}$$

NB: $\mathbf{r} \equiv (\mathbf{r}_1, \dots, \mathbf{r}_N)$, $\mathbf{R} \equiv (\mathbf{R}_1, \dots, \mathbf{R}_n)$

Potential Energy Surface

The Born-Oppenheimer approximation allows to split the problem into an electronic problem depending upon nuclear positions:

$$\left(- \sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} + V(\mathbf{r}, \mathbf{R}) \right) \Psi(\mathbf{r}|\mathbf{R}) = E(\mathbf{R})\Psi(\mathbf{r}|\mathbf{R})$$

and a nuclear problem under an effective interatomic potential determined by the electrons:

$$\left(- \sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial \mathbf{R}_I^2} + E(\mathbf{R}) \right) \Phi(\mathbf{R}) = \hat{E}\Phi(\mathbf{R})$$

$E(\mathbf{R})$ determines the *Potential Energy Surface* and the equilibrium geometry. At equilibrium, forces \mathbf{F}_I on nuclei vanish:

$$\mathbf{F}_I = -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_I} = 0$$

NB: $\mathbf{r} \equiv (\mathbf{r}_1, \dots, \mathbf{r}_N)$, $\mathbf{R} \equiv (\mathbf{R}_1, \dots, \mathbf{R}_n)$

Normal vibrational modes in crystals and molecules

Harmonic approximation: the interatomic potential energy is expanded to 2nd order. The resulting Hamiltonian transforms into a sum of independent oscillators.

Normal mode frequencies, ω , and displacement patterns, U_I^α for cartesian component α of atom I , at atomic position \mathbf{R}_I , are determined by the secular equation:

$$\sum_{J,\beta} \left(C_{IJ}^{\alpha\beta} - M_I \omega^2 \delta_{IJ} \delta_{\alpha\beta} \right) U_J^\beta = 0,$$

where $C_{IJ}^{\alpha\beta}$ is the matrix of *inter-atomic force constants* (IFC), i.e. second derivatives of the energy with respect to atomic positions:

$$C_{IJ}^{\alpha\beta} \equiv \frac{\partial^2 E(\{\mathbf{R}\})}{\partial R_I^\alpha \partial R_J^\beta}.$$

In crystals, normal modes are classified by a wave-vector \mathbf{q} . Phonon frequencies, $\omega(\mathbf{q})$, and displacement patterns, $U_s^\alpha(\mathbf{q})$, are determined by the secular equation:

$$\sum_{t,\beta} \left(\tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) - M_s \omega^2(\mathbf{q}) \delta_{st} \delta_{\alpha\beta} \right) U_t^\beta(\mathbf{q}) = 0$$

Calculation of phonon spectra

Introduce monochromatic perturbation \mathbf{u} to atomic positions $\mathbf{R}_I = \mathbf{R}_l + \boldsymbol{\tau}_s$ as

$$\mathbf{R}_I[\mathbf{u}_s(\mathbf{q})] = \mathbf{R}_l + \boldsymbol{\tau}_s + \mathbf{u}_s(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}_l}.$$

(\mathbf{R}_l =lattice vector, $\boldsymbol{\tau}_s$ =equilibrium position of the s -th atom in the unit cell).

Fourier transform of force constants at \mathbf{q} are second derivatives of the energy with respect to such monochromatic perturbations:

$$\tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) \equiv \sum_{\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} C_{st}^{\alpha\beta}(\mathbf{R}) = \frac{1}{N_c} \frac{\partial^2 E}{\partial u_s^{*\alpha}(\mathbf{q}) \partial u_t^\beta(\mathbf{q})}$$

This can be calculated from the knowledge of the linear response $\partial n(\mathbf{r})/\partial u_s^\alpha(\mathbf{q})$ and diagonalized to get phonon modes at \mathbf{q} . Note that:

- the linear response has the same wave vector \mathbf{q} of the perturbation: this algorithm will work for *any* \mathbf{q} without any supercell involved
- in the spirit of adiabatic approximation, one can use *static* response.

Frozen phonon

Frozen phonons is an older and alternative way to calculate phonons. The monochromatic perturbation is *frozen in* with a finite amplitude in the system, which is described by a *supercell* having \mathbf{q} as reciprocal lattice vector.

Fourier transform of force constants at \mathbf{q} are calculated from *finite differences of forces* induced on all the atoms of the supercell by the monochromatic perturbation.

Advantages:

- straightforward to implement

Disadvantages:

- limited to small supercells, i.e. $\mathbf{q} = \mathbf{G}/n$, where \mathbf{G} is a reciprocal lattice vector of the original cell, $n = 2, 3, 4, \dots$, but in any case a small number.

Note that this is *not* the algorithm used by QUANTUM ESPRESSO!

What if we want the entire dispersions for all \mathbf{q} -vectors in the Brillouin Zone?

Phonons and macroscopic electric fields

Polar materials in the $\mathbf{q}=0$ (long-wavelength) limit: a macroscopic (finite and constant) electric field is present. Gives rise to observable *TO-LO splitting*. Macroscopic electric field incompatible with Periodic Boundary Conditions! Must be separately treated.

Phenomenological expression for the energy as a function of atomic displacements, \mathbf{u}_s , and of macroscopic electric field, \mathbf{E} (Born and Huang long-wavelength limit):

$$E(\{\mathbf{u}\}, \mathbf{E}) = \frac{1}{2} \sum_{st} \sum_{\alpha\beta} \mathbf{u}_s \cdot {}^{an}\tilde{\mathbf{C}}_{st} \cdot \mathbf{u}_t - \frac{\Omega}{8\pi} \mathbf{E} \cdot \boldsymbol{\epsilon}_\infty \cdot \mathbf{E} - e \sum_s \mathbf{u}_s \cdot \mathbf{Z}_s^* \cdot \mathbf{E},$$

(${}^{an}\tilde{\mathbf{C}}_{st}$ force constants, $\boldsymbol{\epsilon}_\infty$ dielectric tensor, \mathbf{Z}_s^* Born effective charge tensor).

Under which circumstances is an electric field \mathbf{E} generated by atomic displacements \mathbf{u} ? Which consequences does it have? The answer comes from electrostatics.

Phonons and macroscopic electric fields (2)

Let us consider *electric induction* $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$ (where \mathbf{P} is the polarization):

$$\mathbf{D} = \mathbf{E} + \mathbf{P}_{el} + \mathbf{P}_{ion} = \boldsymbol{\epsilon}_{\infty} \cdot \mathbf{E} + \frac{4\pi}{\Omega} e \sum_s \mathbf{u}_s \cdot \mathbf{Z}_s^*$$

Maxwell equations tell us $\mathbf{q} \cdot \mathbf{D} = 0$ and $\mathbf{q} \times \mathbf{E} = 0 \implies \mathbf{E} = \mathbf{q}(\mathbf{q} \cdot \mathbf{E})$, hence

$$\mathbf{E} = -\frac{4\pi e}{\Omega} \sum_t \frac{\mathbf{q}(\mathbf{q} \cdot \mathbf{Z}_t^* \mathbf{u}_t)}{\mathbf{q} \cdot \boldsymbol{\epsilon}_{\infty} \cdot \mathbf{q}}$$

and

$$E(\{\mathbf{u}\}) = \frac{1}{2} \sum_{st} \sum_{\alpha\beta} \mathbf{u}_s \cdot \tilde{\mathbf{C}}_{st} \cdot \mathbf{u}_t, \quad \tilde{\mathbf{C}}_{st} = {}^{an}\tilde{\mathbf{C}}_{st} + {}^{na}\tilde{\mathbf{C}}_{st}$$

where

$${}^{na}\tilde{\mathbf{C}}_{st} = \frac{4\pi}{\Omega} \frac{(\mathbf{q} \cdot \mathbf{Z}_s^*)_{\alpha} (\mathbf{q} \cdot \mathbf{Z}_t^*)_{\beta}}{\mathbf{q} \cdot \boldsymbol{\epsilon}_{\infty} \cdot \mathbf{q}}$$

A "non-analytical" term has appeared in the force constants!

Effective charges and dielectric tensor

Effective charges Z^* are related to polarization P induced by a lattice distortion:

$$Z_s^{*\alpha\beta} = \frac{\Omega}{e} \frac{\partial P_\alpha}{\partial u_s^\beta(\mathbf{q} = 0)}.$$

Dielectric tensor $\epsilon_\infty^{\alpha\beta}$ are related to polarization induced by an electric field E :

$$\epsilon_\infty^{\alpha\beta} = \delta_{\alpha\beta} + 4\pi \left. \frac{\partial P_\alpha}{\partial E_\beta} \right|_{\mathbf{u}_s(\mathbf{q}=0)=0}.$$

One can observe that such quantities are second derivatives of the energy as well:

$$Z_s^{*\alpha\beta} = Z_s \delta_{\alpha\beta} - \frac{1}{N_c} \frac{\partial^2 E}{\partial E_\alpha \partial u_s^\beta(\mathbf{q} = 0)},$$

(N_c number of cells in crystal)

$$\epsilon_\infty^{\alpha\beta} = \delta_{\alpha\beta} + \frac{1}{N_c} \frac{\partial^2 E}{\partial E_\alpha \partial E_\beta}.$$

Calculation of effective charges

Polarization induced by an atomic displacement:

$$\frac{\partial P_\alpha}{\partial u_s^\beta(\mathbf{q} = 0)} = -\frac{e}{N_c \Omega} \int \mathbf{r} \frac{\partial n(\mathbf{r})}{\partial u_s(\mathbf{q} = 0)} d\mathbf{r} + \frac{e}{\Omega} Z_s \delta_{\alpha\beta}.$$

Integral is ill-defined for a crystal with Periodic Boundary Conditions! Can use a trick:

$$\langle \psi_m | \mathbf{r} | \psi_n \rangle = \frac{\langle \psi_m | [H_{SCF}, \mathbf{r}] | \psi_n \rangle}{\epsilon_m - \epsilon_n}, \quad \forall m \neq n$$

(in fact, only non-diagonal matrix elements are needed). The commutator is well defined:

$$[H_{SCF}, \mathbf{r}] = -\frac{\hbar^2}{m} \frac{\partial}{\partial \mathbf{r}} + [V_{NL}, \mathbf{r}]$$

(momentum operator, plus a contribution from nonlocal pseudopotentials). Let us define $|\bar{\psi}_n^\alpha\rangle = r_\alpha |\psi_n\rangle$ the solution of linear system:

$$(H_{SCF} - \epsilon_n) |\bar{\psi}_n^\alpha\rangle = P_c [H_{SCF}, r_\alpha] |\psi_n\rangle$$

(P_c is the projector over conduction states).

Calculation of effective charges (2)

Effective charges are then given by:

$$Z_s^{*\alpha\beta} = Z_s + \frac{4}{N_c} \sum_{n=1}^{N/2} \left\langle \bar{\psi}_n^\alpha \left| \frac{\partial \psi_n}{\partial u_\beta(\mathbf{q} = 0)} \right. \right\rangle.$$

using the linear response to an atomic perturbation.

Alternatively, effective charges are given by the force linearly induced on an atom by an electric field:

$$Z_s^{*\alpha\beta} = Z_s + \frac{4}{N_c} \sum_{n=1}^{N/2} \left\langle \psi_n \left| \frac{\partial V}{\partial u_\beta(\mathbf{q} = 0)} \right| \frac{\partial \psi_n}{\partial \mathbf{E}_\alpha} \right\rangle.$$

using the linear response to an electric field (this is so because the Z^* are mixed second derivatives of the energy). QUANTUM ESPRESSO can do both types of calculations (they yield the same result within numerical accuracy!)

Calculation of dielectric tensor

The linear response to a macroscopic electric field can be calculated using the same trick as above. In fact, $V(\mathbf{r}) = e\mathbf{E} \cdot \mathbf{r}$ is ill-defined but we need only non-diagonal matrix elements. The convenient way to solve the linear-response equations is to iterate over $V_{SCF}(\mathbf{r})$ while keeping \mathbf{E} fixed:

$$\frac{\partial V_{SCF}(\mathbf{r})}{\partial \mathbf{E}} = \frac{\partial V(\mathbf{r})}{\partial \mathbf{E}} + \int \left(\frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta v_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \right) \frac{\partial n(\mathbf{r}')}{\partial \mathbf{E}} d\mathbf{r}'.$$

Finally:

$$\epsilon_{\infty}^{\alpha\beta} = \delta_{\alpha\beta} - \frac{16\pi e}{N_c \Omega} \sum_{n=1}^{N/2} \left\langle \bar{\psi}_n^{\alpha} \left| \frac{\partial \psi_n}{\partial E_{\beta}} \right. \right\rangle.$$

In the end, all we need to properly deal with LO-TO splitting in phonons are three additional linear-response calculations to an electric field

Final note: alternative techniques based on the *modern theory of polarizability* (Berry's phase) exist for the calculation of effective charges (also implemented in QUANTUM ESPRESSO)

Inter-atomic force constants in real space

Inter-atomic force constants in real space, $C_{st}^{\alpha\beta}(\mathbf{R})$, are obtained by

- calculating $\tilde{C}_{st}^{\alpha\beta}(\mathbf{q})$ on a discrete (n_1, n_2, n_3) grid of \mathbf{q} -vectors:

$$\mathbf{q}_{ijk} = \frac{i-1}{n_1}\mathbf{G}_1 + \frac{j-1}{n_2}\mathbf{G}_2 + \frac{k-1}{n_3}\mathbf{G}_3, \quad i = 1, \dots, n_1, \text{ and the like for } j, k;$$

- Fourier-transforming to the corresponding real-space grid:

$$C(\mathbf{q}_{ijk}) \iff C(\mathbf{R}_{lmn}), \quad \mathbf{R}_{lmn} = l\mathbf{R}_1 + m\mathbf{R}_2 + n\mathbf{R}_3$$

$$l = -n_1/2, \dots, n_1/2 \text{ and the like for } m, n.$$

The denser the grid of \mathbf{q} -vectors, the larger the vectors \mathbf{R}_{lmn} for which the inter-atomic force constants are calculated. For non polar system, inter-atomic force constants are short-ranged and require a moderate number of calculations at different \mathbf{q} .

Inter-atomic force constants in real space (2)

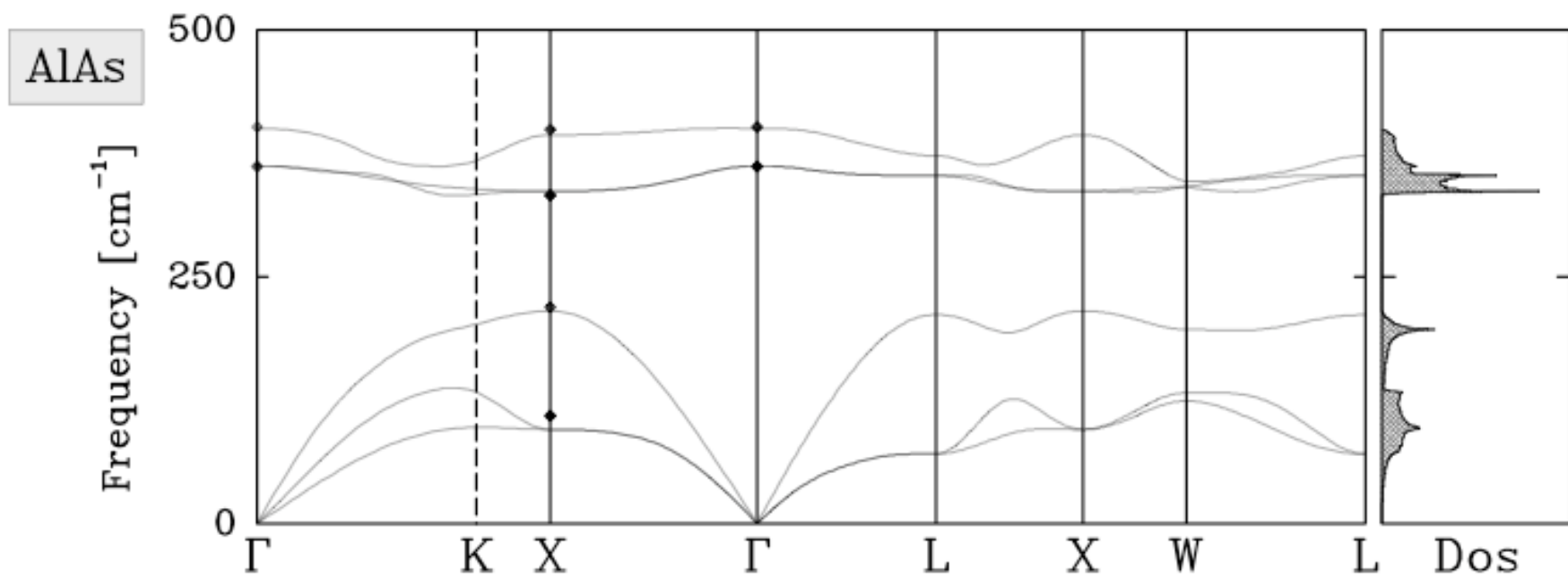
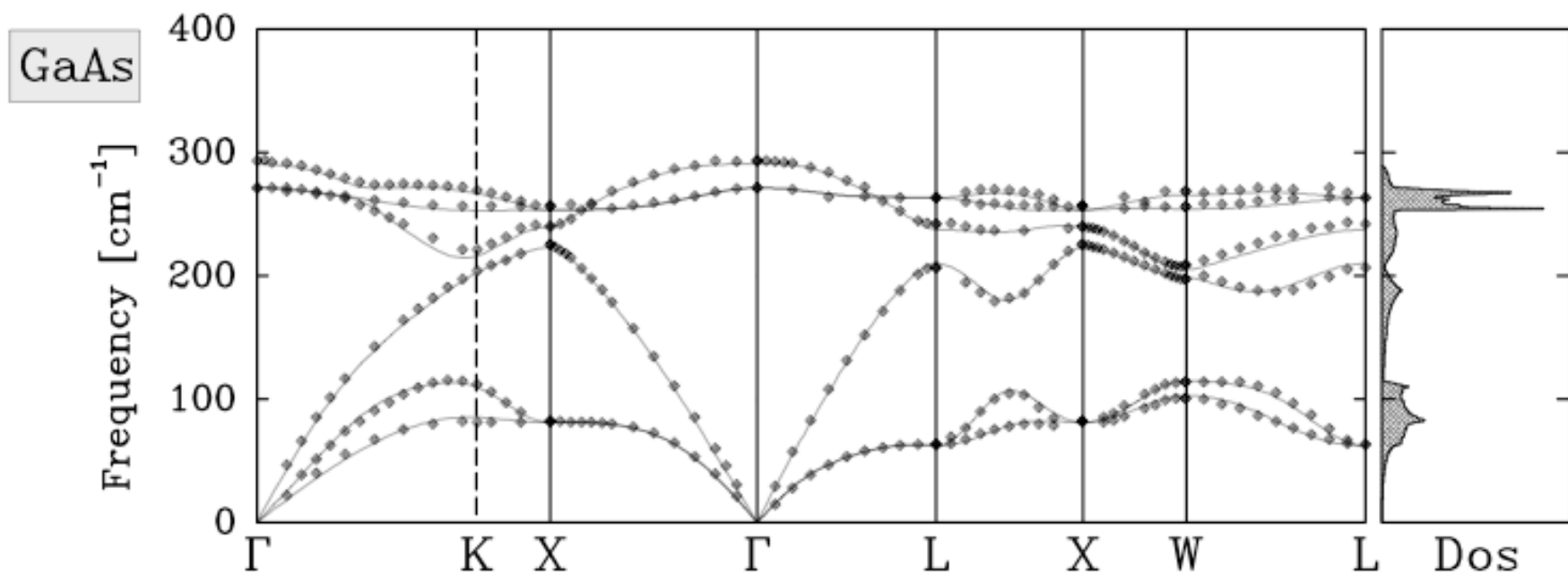
In simple semiconductors like Si and Ge, \mathbf{q} -point grids like $4 \times 4 \times 4$ already yield rather converged force constants in real space. Symmetry is used to reduce the number of needed linear-response calculations.

Once inter-atomic force constants are known, the entire phonon dispersion at any \mathbf{q} can be straightforwardly calculated.

References: *Phonons and related crystal properties from density-functional perturbation theory*, S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515-562 (2001).

Density-Functional Perturbation Theory, P. Giannozzi and S. Baroni, in *Handbook of Materials Modeling*, Vol.1: "Methods and Models", Editor S. Yip, Volume Editors: E. Kaxiras, N. Marzari, and B. Trout (Springer, 2005), p.195-214

Thermal Properties of Materials from ab-initio Quasi-Harmonic Phonons, S. Baroni, P. Giannozzi, and E. Isaev, Rev. Mineral. Geochem. **71**, 39-57 (2010)



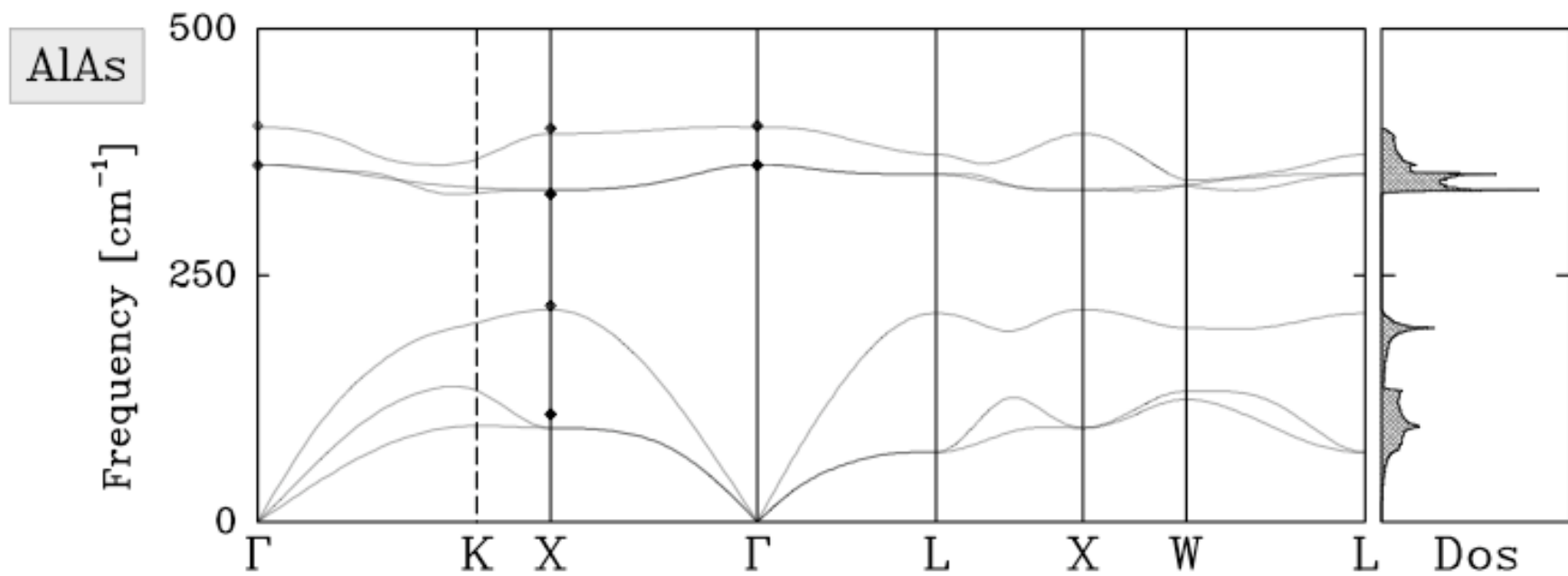
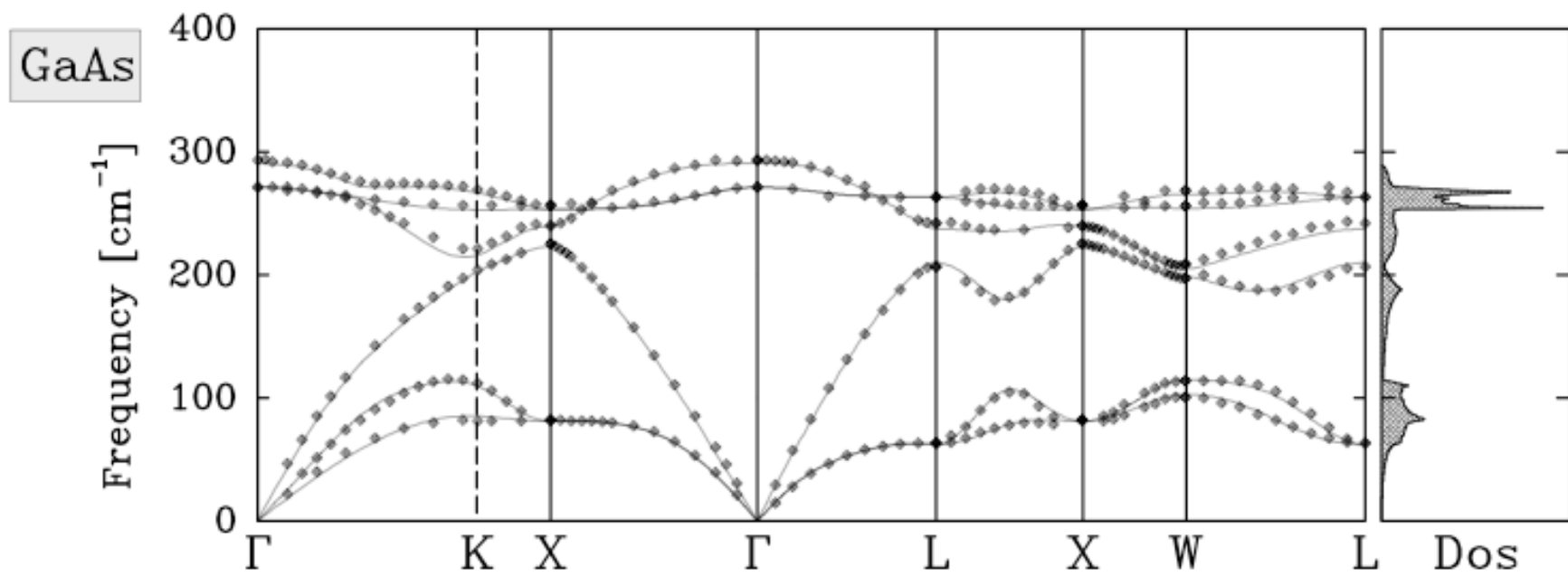
Interatomic force constants in polar materials

For materials having a TO-LO splitting (e.g.: polar semiconductors), the non-analytic term in the force constants makes inter-atomic force constants in real space *no longer short-ranged*. Fourier-interpolation is no longer possible. Solution:

- Subtract from $\tilde{C}_{st}^{\alpha\beta}(\mathbf{q}_{ijk})$ a term that has the same $\mathbf{q} \rightarrow 0$ limit of the non-analytic term ${}^{na}\tilde{C}_{st}^{\alpha\beta}(\mathbf{q})$ (and that is easy to calculate)
- Fourier-transform from reciprocal to real space as for the non-polar case: force constants in real space are now short-ranged.
- When force constants at a general \mathbf{q} are re-calculated from those in real space, re-add the term removed before the Fourier transform.

QUANTUM ESPRESSO uses the same term as the one described in:

X. Gonze *et al.*, Phys. Rev **B** 50, 13035 (1994)



Calculation of IR and Raman Intensities

Infrared Intensities:

$$I_{IR}(\nu) = \sum_{\alpha} \left| \sum_{s\beta} Z_s^{*\alpha\beta} U_s^{\beta}(\nu) \right|^2$$

can be calculated directly from effective charges and phonon displacement patterns.

Non-resonant Raman intensities:

$$I_{\text{Stokes}}(\nu) \propto \frac{(\omega_i - \omega_{\nu})^4}{\omega_{\nu}} r_{\alpha\beta}(\nu), \quad r_{\alpha\beta}(\nu) = \left| \frac{\partial \chi_{\alpha\beta}}{\partial U(\nu)} \right|^2$$

where χ is the electric polarizability of the system.

Raman coefficients are third-order derivatives of the energy that can be calculated in various ways. The most convenient way is to use second-order response to an electric field: M.Lazzeri and F.Mauri, Phys. Rev. Lett. 90, 036401 (2003). Implemented (but not for USPP or PAW) in QUANTUM ESPRESSO.

Superconducting T_c and electron-phonon interaction

Electron-phonon interaction λ :

$$\lambda = \sum_{\mathbf{q}\nu} \lambda_{\mathbf{q}\nu} = \sum_{\mathbf{q}\nu} \frac{\gamma_{\mathbf{q}\nu}}{\pi\hbar N(\epsilon_F)\omega_{\mathbf{q}\nu}^2}$$

where $N(\epsilon_F)$ is the DOS at the Fermi level, and for phonon mode ν at wavevector \mathbf{q} :

$$\gamma_{\mathbf{q}\nu} = 2\pi\omega_{\mathbf{q}\nu} \sum_{ij} \int \frac{d^3k}{\Omega_{BZ}} |g_{\mathbf{q}\nu}(\mathbf{k}, i, j)|^2 \delta(\epsilon_{\mathbf{q},i} - \epsilon_F) \delta(\epsilon_{\mathbf{k}+\mathbf{q},j} - \epsilon_F),$$

$$g_{\mathbf{q}\nu}(\mathbf{k}, i, j) = \left(\frac{\hbar}{2M\omega_{\mathbf{q}\nu}} \right)^{1/2} \langle \psi_{i,\mathbf{k}} | \frac{\partial V_{SCF}}{\partial U^{(\nu)}(\mathbf{q})} | \psi_{j,\mathbf{k}+\mathbf{q}} \rangle.$$

$U(\nu)$ is a displacement along phonon ν . This quantity can be easily calculated using DFPT. McMillan formula for T_c :

$$T_c = \frac{\Theta_D}{1.45} \exp \left[\frac{-1.04(1 + \lambda)}{\lambda(1 - 0.62\mu^*) - \mu^*} \right]$$

Practical phonon calculation in QUANTUM ESPRESSO

First step: scf calculation *at equilibrium positions* (performed by `pw.x`)

- Single phonon calculation at finite wave-vector \mathbf{q}
 - Generate $\psi_{\mathbf{k},v}$ and $\psi_{\mathbf{k}+\mathbf{q},v}$ in the Irreducible Brillouin Zone relative to the small group of \mathbf{q} ; Calculate $C(\mathbf{q})$, diagonalize, produce $\omega(\mathbf{q})$ and $U(\mathbf{q})$ (code `ph.x`)
- Single phonon calculation at Γ wave-vector ($\mathbf{q}=0$)
 - Calculate $C(\mathbf{q} = 0)$, diagonalize, produce $\omega(\mathbf{q} = 0)$ and $U(\mathbf{q} = 0)$ (code `ph.x`)
For polar materials: calculate non-analytical terms that are missing from $C(\mathbf{q} = 0)$ (LO-TO splitting are absent from $\omega(\mathbf{q} = 0)$): specify option `epsil=.true.` to `ph.x` (will calculate and store in output file Z^* and ϵ^∞).
 - Impose Acoustic Sum Rule (ASR), add the nonanalytic LO-TO splitting, calculate cross sections (code `dynmat.x`)

Sample input files in `examples_phon.tar.gz`

Practical phonon dispersions calculation

First step as before: scf calculation *at equilibrium positions* (performed by `pw.x`)

- Perform many single-phonon calculations on a uniform grid of wave-vectors \mathbf{q}_i , including $\mathbf{q} = 0$ (if system is polar, calculate in the latter case Z^* and ϵ^∞); save all $C(\mathbf{q}_i)$ (and Z^* , ϵ^∞) (code `ph.x` with option `ldisp=.true.`)
- Perform inverse FFT of the $C(\mathbf{q}_i)$, obtain interatomic force constants in real space $C(\mathbf{R})$. For polar materials: a term having the same behaviour for $\mathbf{q} \rightarrow 0$ as the non-analytic term is subtracted from $C(\mathbf{q}_i)$ before the Fourier Transform and re-added to $C(\mathbf{R})$, so that no problem related to non-analytic behaviour and related long-rangeness arises in the Fourier Transform (code `q2r.x`)
- Calculate phonons at any wave-vector, diagonalizing the dynamical matrix:

$$D_{st}^{\alpha\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_{\mathbf{R}} C_{st}^{\alpha\beta}(\mathbf{R}) \exp(i\mathbf{q} \cdot \mathbf{R})$$

using code `matdyn.x`

Sample input files in `examples_disp.tar.gz`

Fast algorithm for specific cases

A simplified, faster algorithm exists if i) you sample the Brillouin Zone with only the Γ point (e.g. molecules, large unit cells), ii) you need phonon modes only at Γ , and iii) you use only norm-conserving pseudopotentials (no USPP or PAW).

- Perform the scf calculation at equilibrium positions *with Γ -point tricks*: code `pw.x` with input card
`K_POINTS gamma`
- use specialized code `phcg.x` to find $C(\mathbf{q} = 0)$; specify option `epsil=.true.` to calculate Z^* and ϵ^∞ .
- Impose Acoustic Sum Rule (ASR), add the nonanalytic LO-TO splitting, calculate IR cross sections with code `dynmat.x`

Nonlinear quantities (e.g. Raman) not implemented.