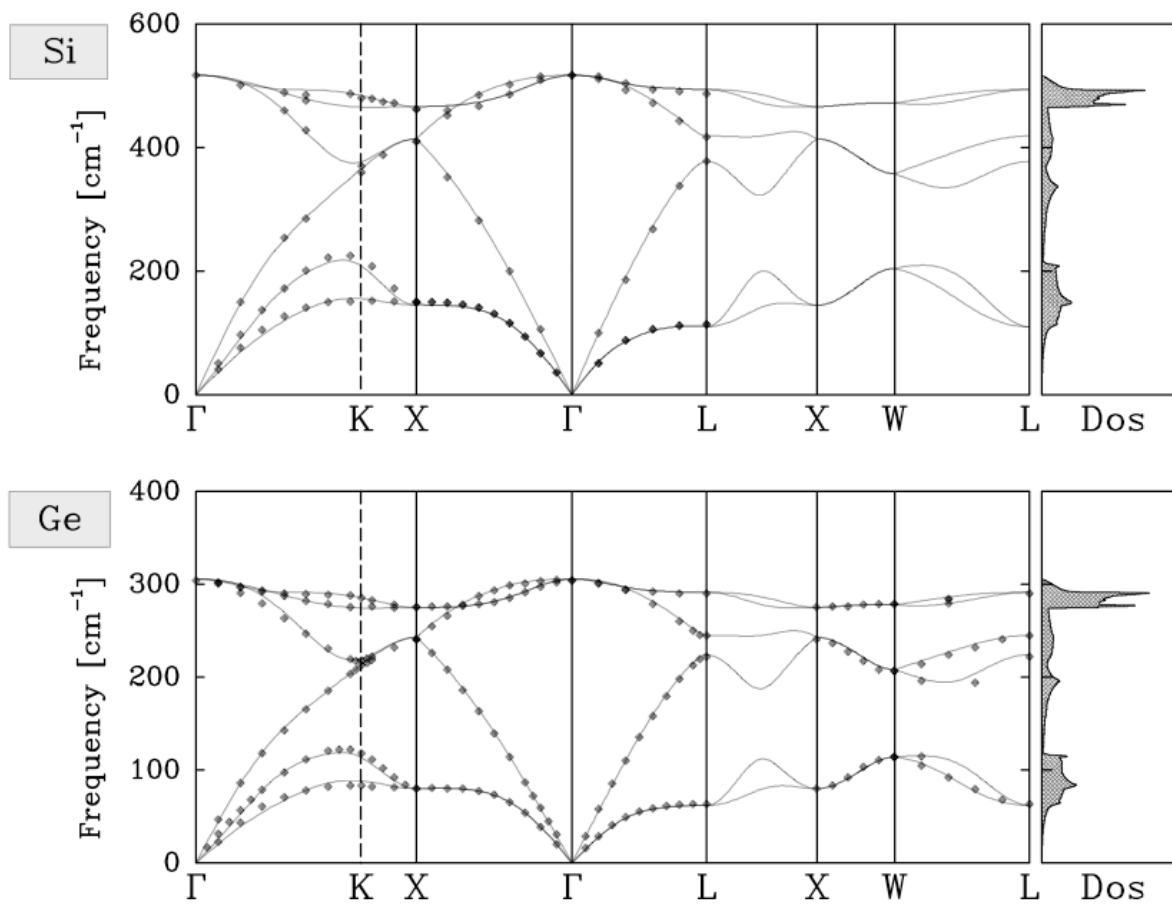


# Quantum-ESPRESSO

## An introduction to phonon calculations



## 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.

## Models for electronic screening

Several approximate models for dielectric screening are known. Let us consider a homogeneous and isotropic medium. We expect that  $\chi(\mathbf{r}, \mathbf{r}') = \chi(\mathbf{r} - \mathbf{r}')$  and the same for  $\epsilon$ . In reciprocal space we will have the so-called *diagonal screening*:

$$\delta n(\mathbf{k}) = \chi(\mathbf{k})\delta V_0(\mathbf{k}).$$

The corresponding dielectric response is

$$\epsilon^{-1}(\mathbf{k}) = 1 + \frac{4\pi e^2}{k^2}\chi(\mathbf{k}) \equiv \frac{1}{\epsilon(\mathbf{k})}$$

and the screened potential

$$\delta V(\mathbf{k}) = \frac{\delta V_0(\mathbf{k})}{\epsilon(\mathbf{k})}.$$

For metals, an approximate form for  $\epsilon(\mathbf{k})$  is given by Thomas-Fermi theory:

$$\epsilon(\mathbf{k}) = 1 + \frac{k_{TF}^2}{k^2}$$

where  $k_{TF}$  is a parameter depending on the homogeneous charge density.

# 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, 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  $\epsilon_c$

## Physical Response Operator

...but we need  $\chi(\mathbf{r}, \mathbf{r}')$ , not  $\chi_0(\mathbf{r}, \mathbf{r}')$  ! In operator notations:  $\delta n = \hat{\chi}_0 \delta V = \hat{\chi} \delta V_0$ .  
How can we get from  $\chi_0$  to  $\chi$  ?

We have  $\delta V = \delta V_0 + \delta V_H + \delta V_{XC}$ . 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!):

$$\delta n = \left( 1 - \hat{\chi}_0 \hat{v}_c - \hat{\chi}_0 \hat{f}_{xc} \right)^{-1} \hat{\chi}_0 \delta V_0 = \hat{\chi} \delta V$$

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.  $\delta V$  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

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

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

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

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

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

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  $\delta E$ :

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

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  $|\bar{\psi}_v^\alpha\rangle = r_\alpha |\psi_v\rangle$  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  $\epsilon_\infty$  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

$$\epsilon_\infty^{\alpha,\beta} = \delta_{\alpha,\beta} + 4\pi \frac{\delta P_\alpha}{\delta E_\beta}$$

The macroscopic induced polarization can be calculated as

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

( $N_c$  is the number of cells of volume  $\Omega_c$ ,  $N_c \Omega$  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  $\lambda$

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

(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  $\lambda$ :

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

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,  $\omega$ , and displacement patterns,  $U_I^\alpha$  for cartesian component  $\alpha$  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?

# Calculation of interatomic force constants

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:

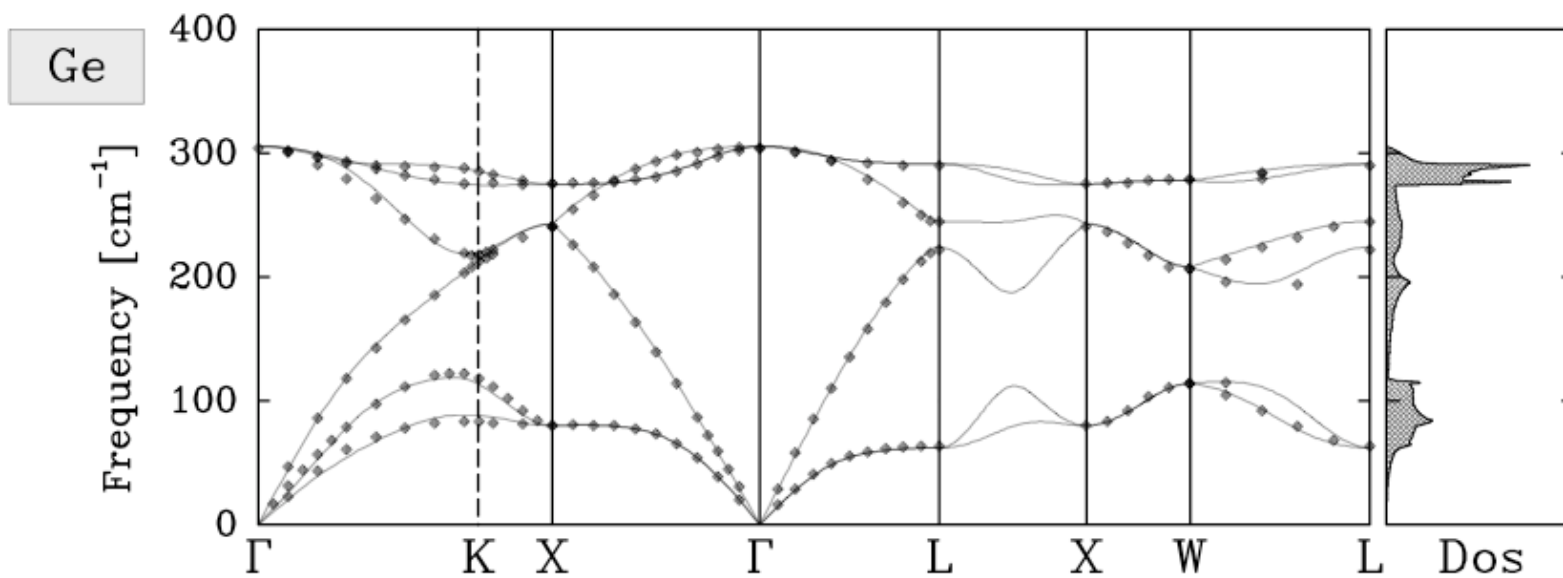
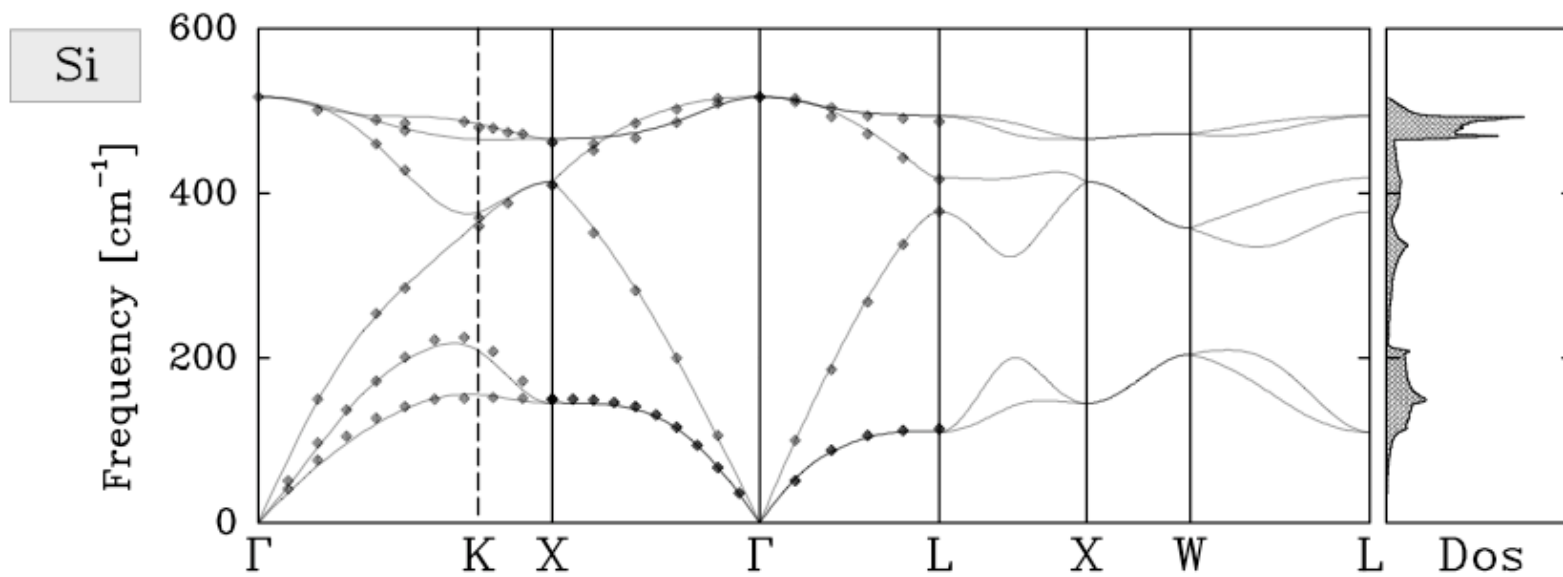
$$\mathbf{q}_{ijk} = \frac{i-1}{n_1}\mathbf{G}_1 + \frac{j-1}{n_2}\mathbf{G}_2 + \frac{k-1}{n_3}\mathbf{G}_3, \quad i = 1, \dots, n_1, \text{ and the like for } j, k;$$

- 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  $\mathbf{q}$ .



## Phonons and macroscopic electric fields

Polar materials in the  $\mathbf{q}=0$  limit: a macroscopic electric field appear as a consequence of long-rangeness of Coulomb interactions. Incompatible with Periodic Boundary Conditions! A non-analytic term must be added to force constants at  $\mathbf{q} = \mathbf{0}$ :

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

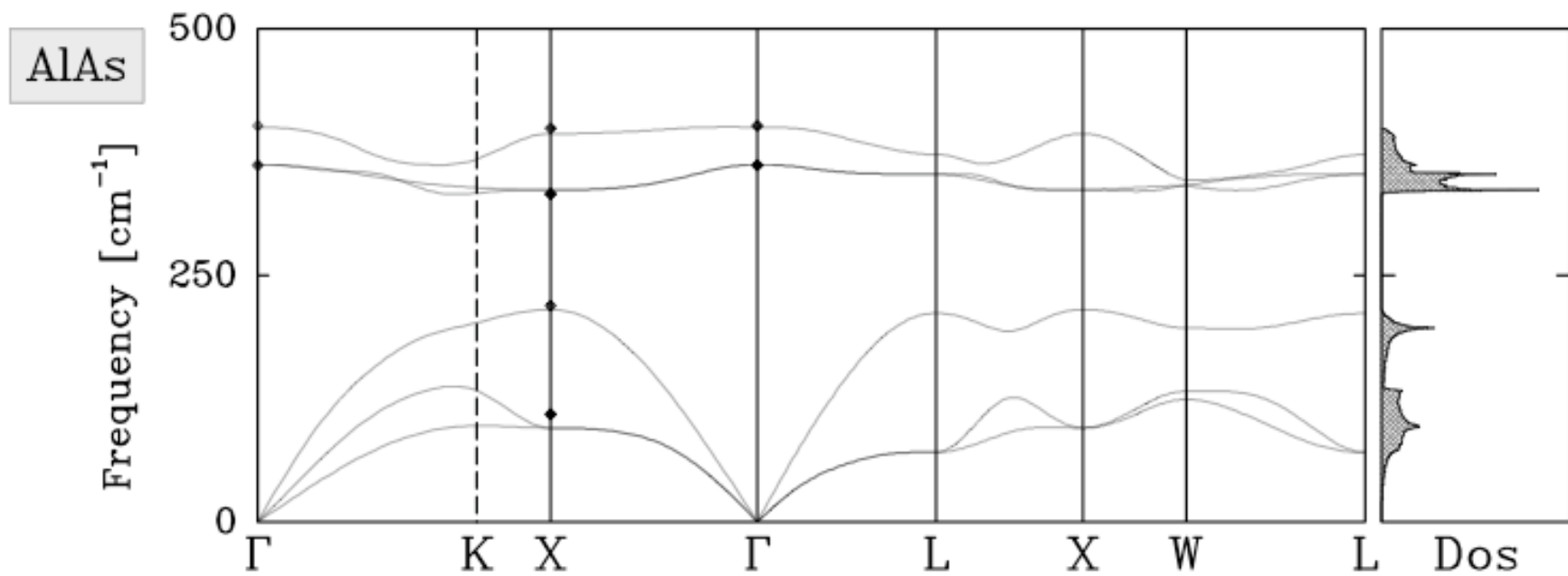
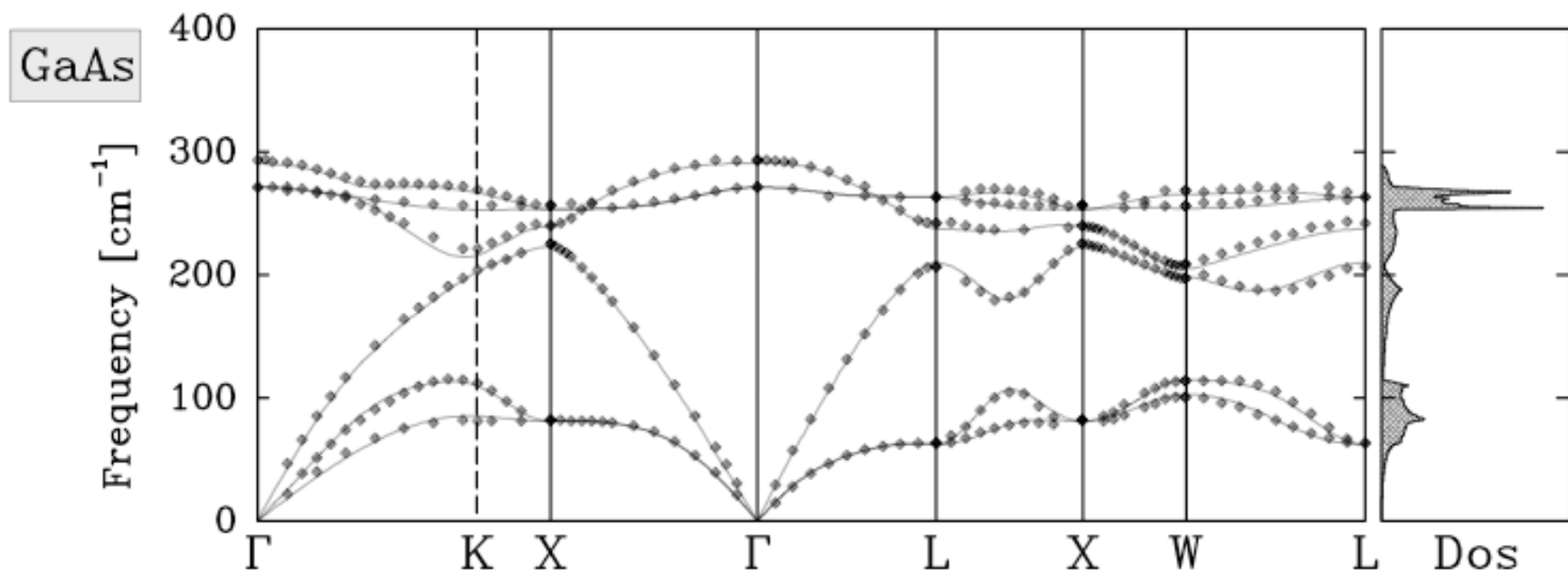
*Effective charges*  $\mathbf{Z}^*$  are related to polarization  $\mathbf{P}$  induced by a lattice distortion:

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

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

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

All of the above can be calculated from (mixed) second derivatives of the energy.





# 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  $\chi$  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).

# Superconducting $T_c$ and electron-phonon interaction

Electron-phonon interaction  $\lambda$ :

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

where  $N(\epsilon_F)$  is the DOS at the Fermi level, and for phonon mode  $\nu$  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  $\nu$ . 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 calculations in Q-E

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  $\mathbf{q}$  (option `lnscf=.true.` to `ph.x`)  
Calculate  $C(\mathbf{q})$ , diagonalize, produce  $\omega(\mathbf{q})$  and  $U(\mathbf{q})$  (performed by `ph.x`)
- Single phonon calculation at  $\Gamma$  wave-vector ( $\mathbf{q}=0$ )
  - Calculate  $C(\mathbf{q} = 0)$ , diagonalize, produce  $\omega(\mathbf{q} = 0)$  and  $U(\mathbf{q} = 0)$  (`ph.x`)  
For polar materials: calculate non-analytical terms that are missing from  $C(\mathbf{q} = 0)$  (LO-TO splitting are absent from  $\omega(\mathbf{q} = 0)$ ): done by `ph.x` with option `epsil=.true.` (will calculate and store in output file  $Z^*$  and  $\epsilon^\infty$ ).
  - Impose Acoustic Sum Rule (ASR), add the nonanalytic LO-TO splitting, further processing by code `dynmat.x`

Sample input files in `examples_phon.tar.gz`

# Practical phonon dispersions calculations

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  $\epsilon^\infty$ ); save all  $C(\mathbf{q}_1)$  (and  $Z^*$ ,  $\epsilon^\infty$ ) (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 whatever phonon property you want using code `matdyn.x`

Sample input files in `examples_disp.tar.gz`