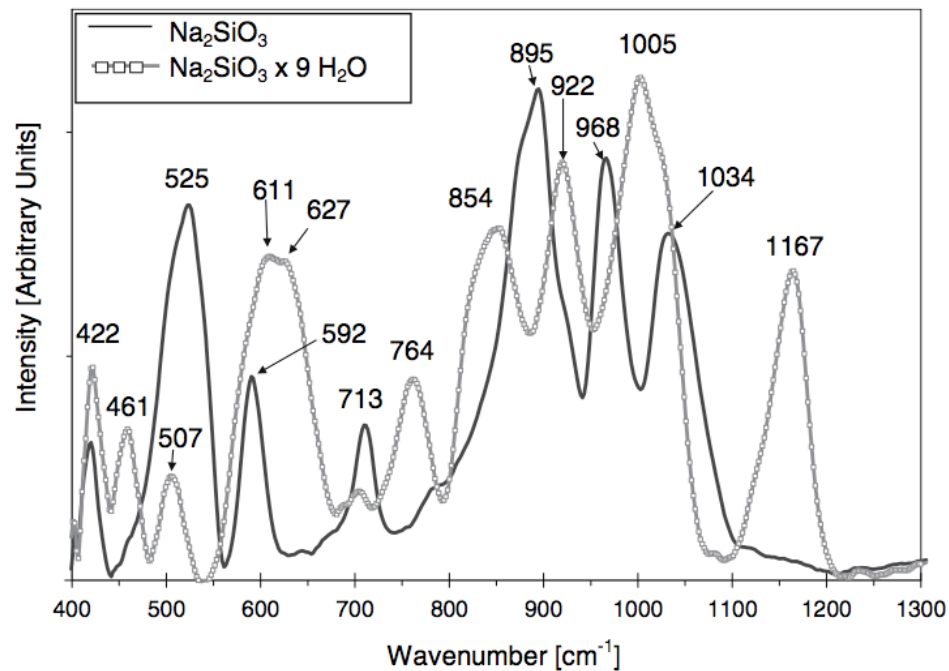# Introduction to the calculation of phonons and of vibrational spectra

P. Giannozzi

Università di Udine and Democritos National Simulation Center, Italy

September 23, 2009

Vibrational Spectroscopy: experiments

- Observation of vibrational modes:

  - *phonons* in crystals,
  - *normal modes* in molecules,

  is a powerful tool in materials characterization

- Vibrational spectroscopy is a sensitive probe of the atomic structure and of the chemical bonding and thus of the electronic structure

- Most frequently used experimental techniques:

  - *Neutron* scattering (technically difficult, the entire dispersion is observable)
  - *Infrared* (IR) spectroscopy (simple, only some modes are observable)
  - *Raman* spectroscopy (simple, a different subset of modes is observable)

Theoretical calculation of vibrational mode frequencies and intensities from first principles is very helpful in analyzing vibrational spectra

Basic theory: 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 $M_I >> m$):

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

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

Basic theory: 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: $\mathbf{r} \equiv (\mathbf{r}_1, .., \mathbf{r}_N)$, $\mathbf{R} \equiv (\mathbf{R}_1, .., \mathbf{R}_n)$

Normal vibrational modes in molecules and crystals

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*, i.e. second derivatives of the energy with respect to atomic positions:

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

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 equations:

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

Practical calculation of vibrational modes

Common methods – based on Density-functional Theory – to calculate vibrational modes (via Interatomic Force Constants):

- *Frozen-phonon* technique: finite differentiation of forces

- *Density-functional Perturbation Theory* (DFPT): direct calculation of second-order derivatives of the energy

Alternative method (not using Interatomic Force Constants):

- *Molecular Dynamics*: spectra can be extracted from Molecular Dynamics runs, via the Fourier Transform of the velocity-velocity autocorrelation function

$$f(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} \sum_I \frac{\langle \mathbf{v}_I(t) \cdot \mathbf{v}_I(0) \rangle}{\langle \mathbf{v}_I(0) \cdot \mathbf{v}_I(0) \rangle} \, dt, \qquad (1)$$

Function $f(\omega)$ has peaks at the vibrational frequencies.

Let us focus on the case of phonons in crystals.

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:

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

Quantum ESPRESSO calculates them 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,

Fourier transform of force constants at **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, $n = 2, 3, 4, ...$, 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 **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 $\widetilde{C}_{st}^{\alpha\beta}(\mathbf{q})$ on a discrete (n_1, n_2, n_3) grid of $\mathbf{q}$-vectors:

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

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

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

$l = -n_1/2, ..., n_1/2$ 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. Inter-atomic force constants are short-ranged and require a moderate number of calculations at different $\mathbf{q}$ (for polar systems, see later).

Density-Functional Perturbation Theory

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

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

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

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

and the energy functional into powers of λ:

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

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

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

Density-Functional Perturbation Theory II

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

Calculation of the Linear Response

The minimization of the second-order functional, or alternatively the linearization of Kohn-Sham equations, yields a set of equations:

$$(H_{KS} - \epsilon_i)\frac{\partial\psi_i(\mathbf{r})}{\partial\lambda} + \sum_j K_{ij}\frac{\partial\psi_j}{\partial\lambda} = -P_c\frac{\partial V}{\partial\lambda}|\psi_i\rangle$$
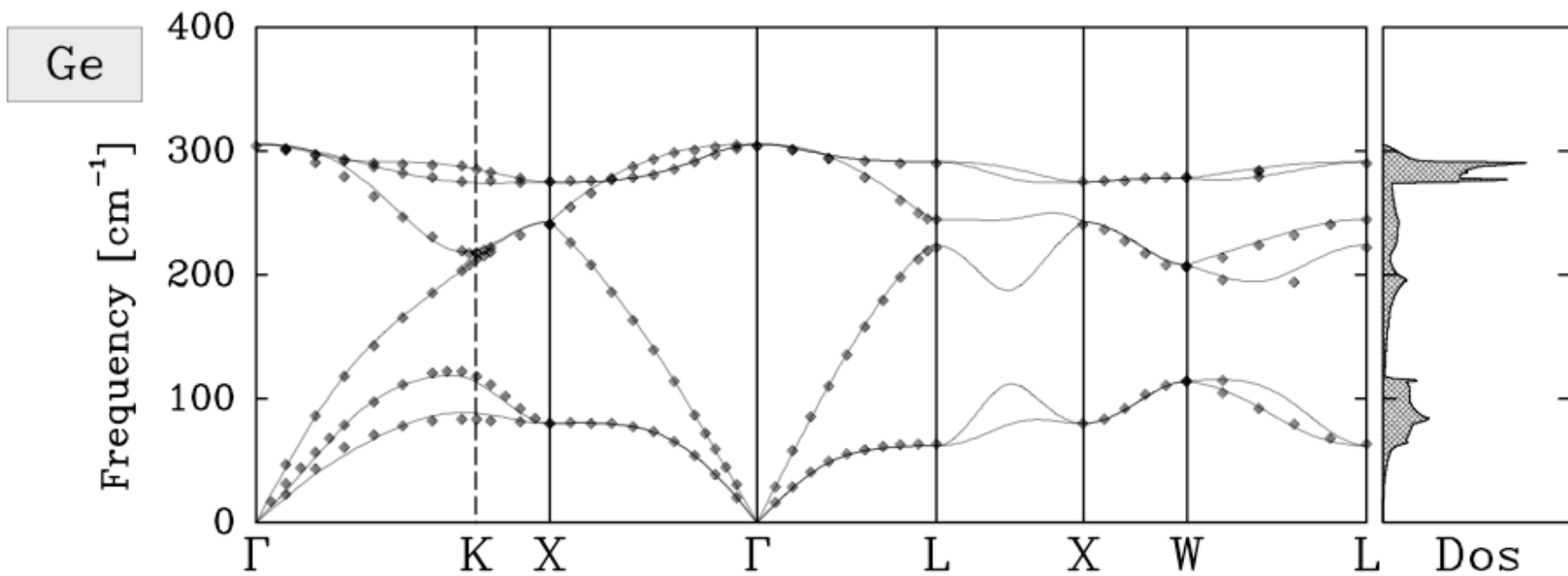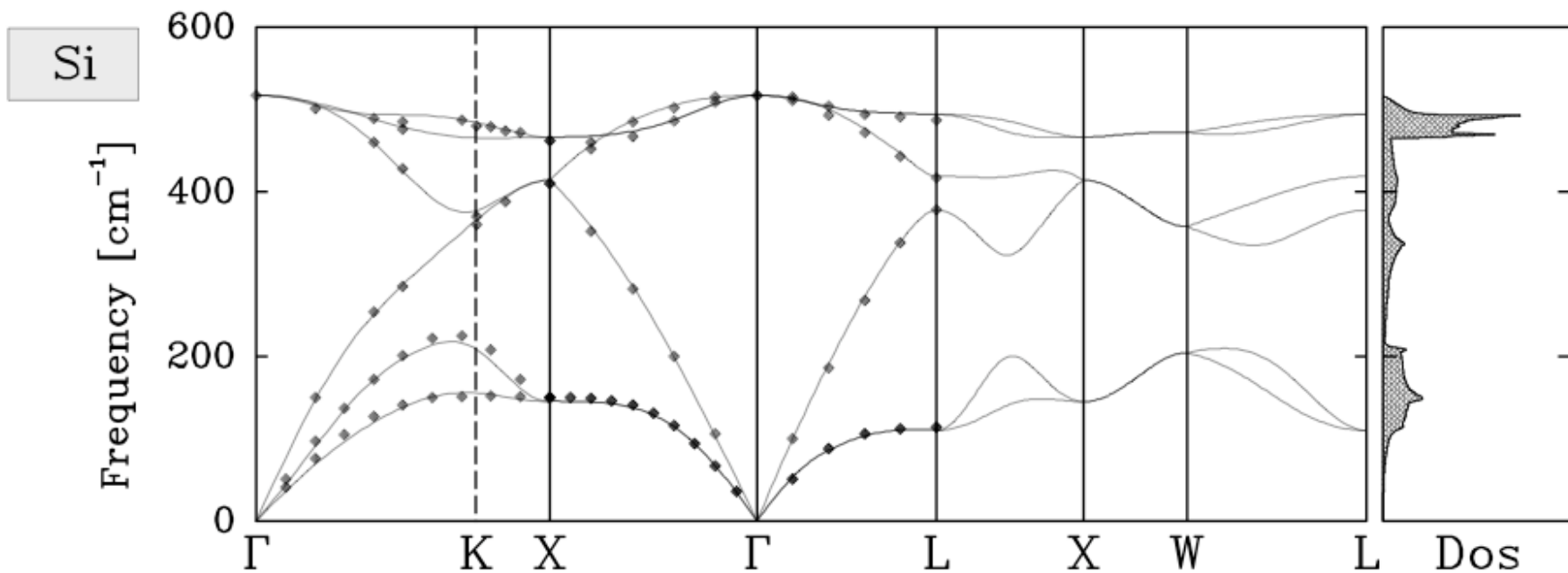
where P_c is the projector over unoccupied states, K_{ij} is a nonlocal operator:

$$\left(K_{ij}\frac{\partial\psi_j}{\partial\lambda}\right)(\mathbf{r}) = 4\int\psi_i(\mathbf{r})\left(\frac{e^2}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta v_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')}\right)\psi_j^*(\mathbf{r}')\frac{\partial\psi_j}{\partial\lambda}(\mathbf{r}')d\mathbf{r}'$$

and the linear charge response:

$$\frac{\partial n(\mathbf{r})}{\partial\lambda} = 2\mathrm{Re}\sum_i\psi_i^*(\mathbf{r})\frac{\partial\psi_i(\mathbf{r})}{\partial\lambda}$$

These equations can be solved as a linear system for all $\partial\psi_i(\mathbf{r})/\partial\lambda$, or else as many linear systems for each $\partial\psi_i(\mathbf{r})/\partial\lambda$ followed by self-consistency

Phonons and macroscopic electric fields

Polar materials in the **q**=0 limit: a macroscopic electric field appear as a consequence of long-rangeness of Coulomb interactions. Incompatible with Periodic Boundary Conditions! Macroscopic electric fields contribute a non-analytic term to the dynamical matrix:

$$^{na}\widetilde{C}_{st}^{\alpha\beta} = \frac{4\pi}{\Omega} \frac{(\mathbf{q} \cdot \mathbf{Z}^{\star}{}_{s})_{\alpha} (\mathbf{q} \cdot \mathbf{Z}^{\star}{}_{t})_{\beta}}{\mathbf{q} \cdot \epsilon_{\infty} \cdot \mathbf{q}}$$
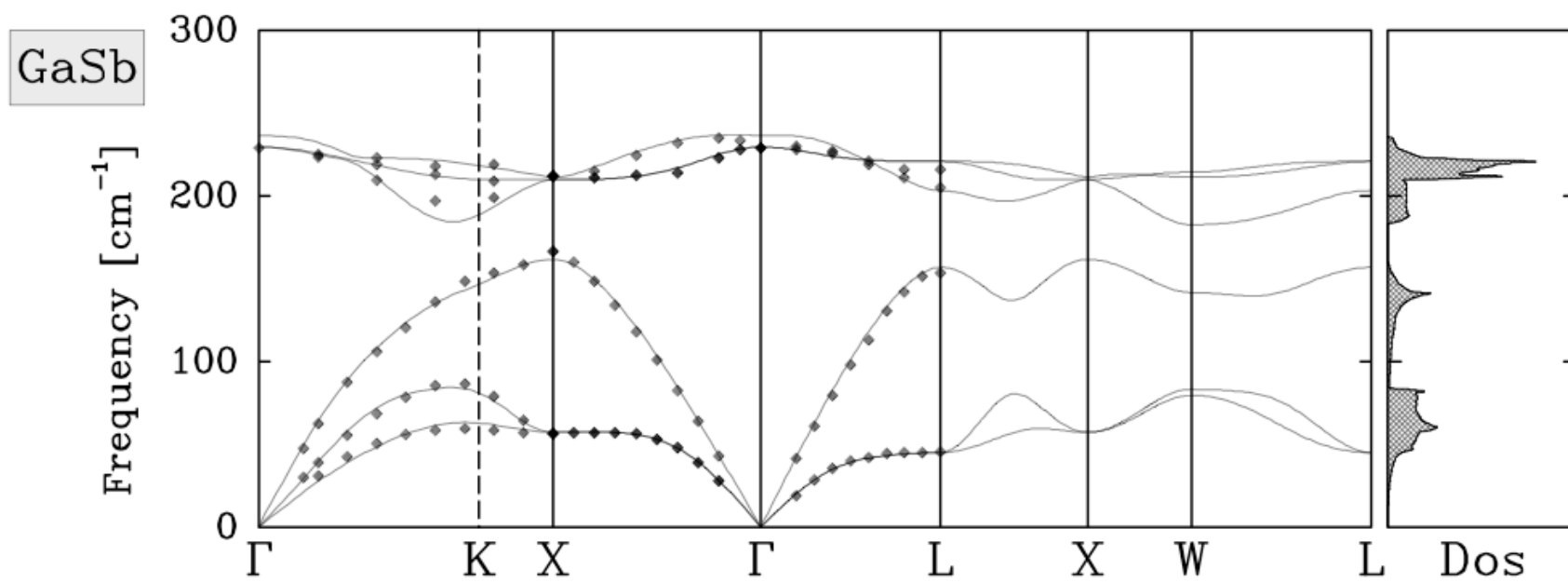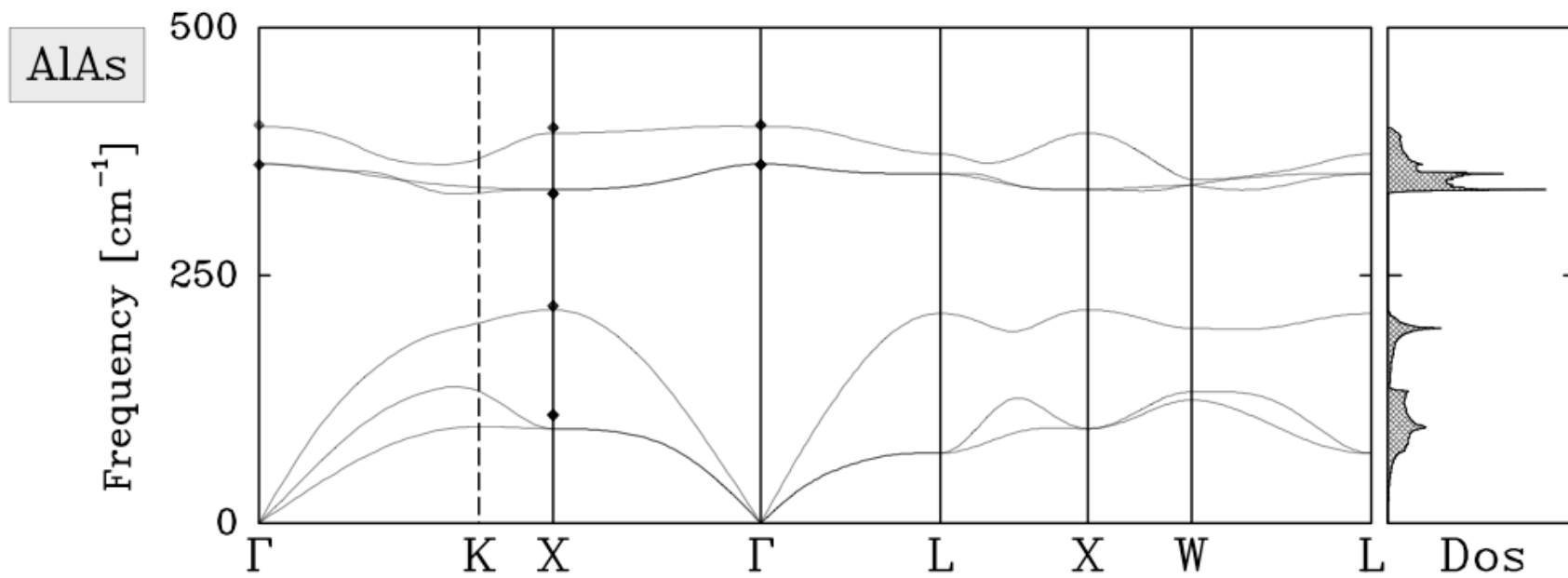
Effective charges $\mathbf{Z}^{\star}$ are related to polarization P induced by a lattice distortion:

$$Z^{\star}{}_{s}^{\alpha\beta} = \Omega \frac{\partial \mathsf{P}_{\alpha}}{\partial u_{s}^{\beta}(\mathbf{q} = 0)}$$

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

$$\epsilon_{\infty}^{\alpha\beta} = \delta_{\alpha\beta} + 4\pi \left. \frac{\partial \mathsf{P}_{\alpha}}{\partial \mathsf{E}_{\beta}} \right|_{\mathbf{u}_{s}(\mathbf{q}=0)=0}.$$

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

Practical calculations for electric fields

We need the response to a macroscopic electric field E: $\partial V/\partial E_\alpha = -er_\alpha$.
This 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:

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

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:

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

(V_{NL} is the nonlocal term of the potential if present).
Alternative technique: differentiation wrt Bloch vector (numerically performed)

Calculation of Infrared Cross Sections

Infrared spectroscopy (absorption/reflectivity, energy loss spectroscopy, FTIR): $\lambda >> a$, the electromagnetic field can be considered macroscopic. Selection rules:

- Only phonons close to the Γ-point ($\mathbf{q} = 0$) are involved, i.e. *IR-active*

- Only phonons that induce a nonzero dipole are IR-active

The IR intensity is proportional to the square of the dipole induced by the phonon that is excited by the IR radiation:
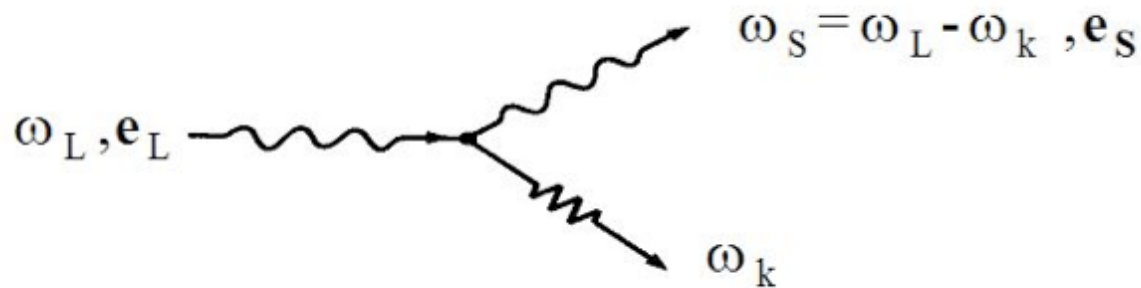
$$ I_{IR}(\nu) = \sum_{\alpha} \left| \sum_{I\beta} Z^{\star\alpha\beta}_{I} U^{\beta}_{I}(\nu) \right|^2 . $$

This is a trivial byproduct of a phonon calculation.
Alternative technique: effective charges are expressed via the *Berry's phase*.

Calculation of Raman Cross Sections

Non-resonant, resonant, surface-enhanced Raman scattering: an inelastic process in which light is scattered and a phonon or normal mode is created or destroyed

Again, only phonons near Γ ($\mathbf{k} = 0$) contribute.

Stokes process: $\omega_S = \omega_L - \omega_{\mathbf{k}}$
Anti-Stokes process: $\omega_S = \omega_L + \omega_{\mathbf{k}}$

Resonant Raman: $\omega_{L,S} \sim \omega_{el} = $ typical electronic excitation frequencies
Non-resonant Raman: $\omega_{L,S} << \omega_{el}$. This is the simpler case.

Calculation of Raman Cross Sections (2)

Non-resonant Raman intensities in the *Placzek approximation*:

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

χ = electric polarizability, $u^{(\nu)}$ = normal mode coordinate along mode ν. The *Raman tensor* $r_{\alpha\beta}(\nu)$ is a third-order derivative of the energy that can be calculated using:

- DFPT for χ + Frozen-phonon (finite differences)

- DFPT using the $(2n+1)$ *theorem:* the $(2n+1)$−th derivative of energy depends only on derivatives up to order n of the charge density (not implemented).

- DFPT + Second-order response to electric field (imlpemented)

- Finite electric fields + Frozen phonon

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 $U(\mathbf{q}=0)$ (`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^∞). For non resonant Raman: specify option `lraman=.true.`
  - Impose Acoustic Sum Rule (ASR), add the nonanalytic LO-TO splitting, calculate cross sections (if data available) (code `dynmat.x`)

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 $C(\mathbf{q}_1)$ (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 using code `matdyn.x`

Fast algorithm for specific cases

If you sample the Brillouin Zone with only the Γ point (e.g. molecules, large unit cells) and you need phonon modes only at Γ, you can use a simplified and faster algorithm.

- scf calculation at equilibrium positions *with $\Gamma-$point tricks*: performed by `pw.x` with 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`

Restrictions: no Raman, no Ultrasoft Pseudopotentials