An introduction to linear response and to phonon calculations

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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:

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

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 little 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 $\delta\mathsf{E}$:

$$\delta V_0 = -e\delta\mathsf{E}_0 \cdot \mathbf{r}$$

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:

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

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).

Macroscopic Polarization

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

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

The macroscopic induced polarization can be calculated as

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

(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 E is kept fixed, iteration is performed on the microscopic terms of the potential:

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

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

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

(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*):

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

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 $M_I >> m$):

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

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

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 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:

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

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:

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

This can be calculated from the knowledge of the linear response $\partial n(\mathbf{r})/\partial u^{\alpha}_s(\mathbf{q})$ 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, $n = 2, 3, 4, ...$, 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 $\widetilde{C}_{st}^{\alpha\beta}(\mathbf{q})$ on a discrete (n_1, n_2, n_3) grid of **q**-vectors:

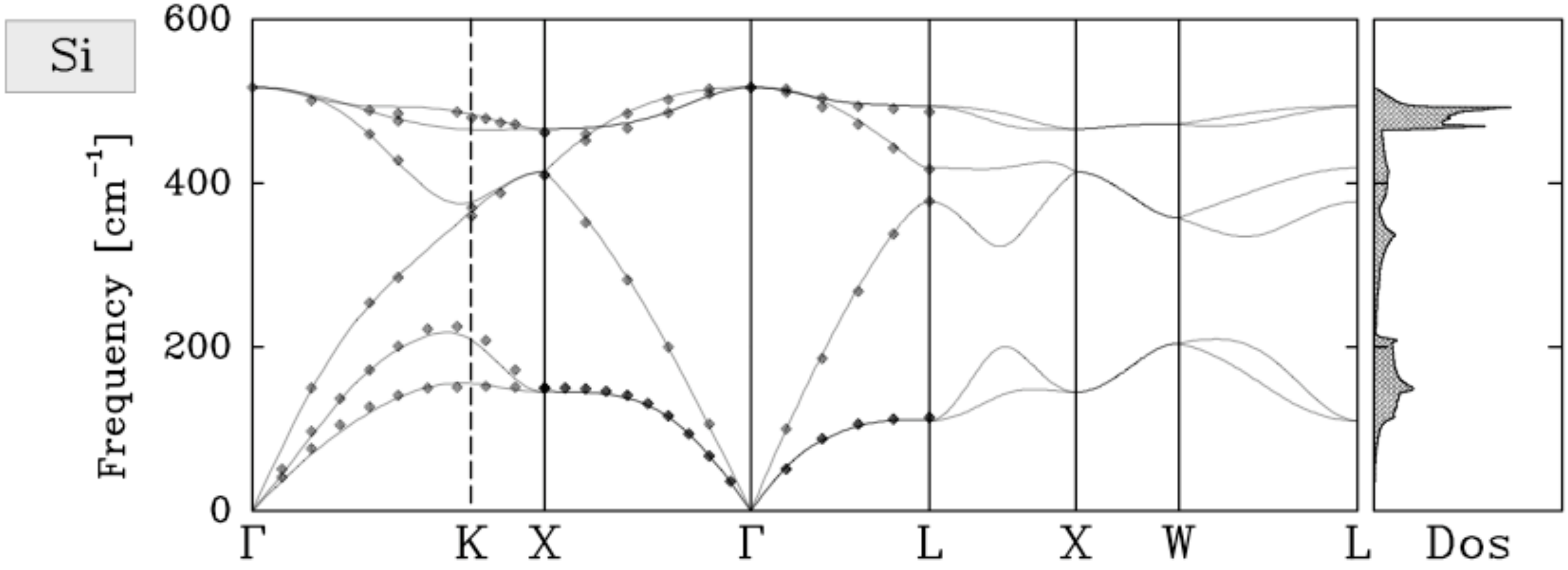
$$\mathbf{q}_{ijk} = \frac{i-1}{n_1}\mathbf{G}_1 + \frac{j-1}{n_2}\mathbf{G}_2 + \frac{k-1}{n_3}\mathbf{G}_3, \qquad i = 1, .., n_1, \text{and the like for } j, k;$$

- 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 **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 **q**.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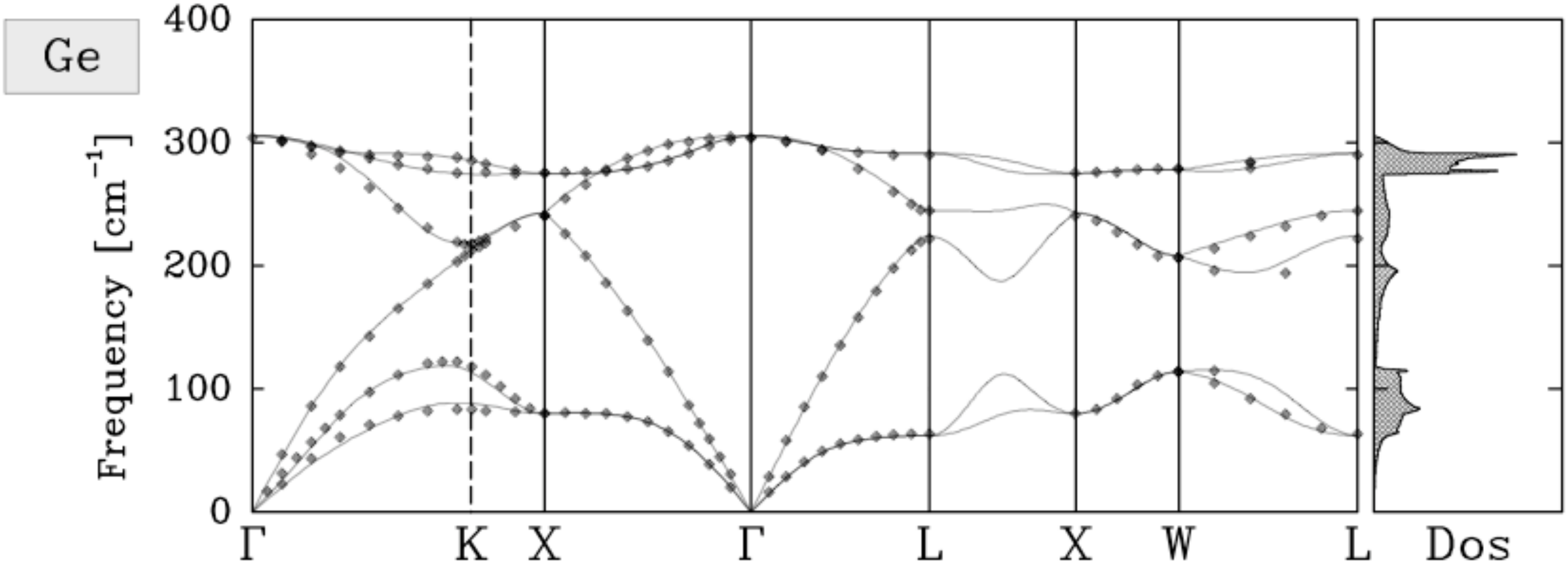
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Phonons and macroscopic electric fields

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 $\mathbf{q} = \mathbf{0}$:

$$\mathbf{F}_s = -\sum_t {}^{an}\widetilde{C}_{st}\mathbf{u}_t + e\mathbf{Z}^\star{}_s\mathsf{E}$$

$$\mathsf{D} \quad = \quad E + 4\pi\mathsf{P}_{el} + 4\pi\mathsf{P}_{ion} \quad = \quad \epsilon_\infty\mathsf{E} + \frac{4\pi e}{\Omega}\sum_t \mathbf{Z}^\star{}_t\mathbf{u}_t$$

now Maxwel equations tell us

$$\mathbf{q}\cdot\mathsf{D} = 0 \quad \text{and} \quad \mathbf{q}\times\mathsf{E} = 0 \quad \Longrightarrow \quad \mathsf{E} = \mathbf{q}(\mathbf{q}\cdot\mathsf{E})$$

hence

$$\mathsf{E} = -\frac{4\pi e}{\Omega}\sum_t \frac{\mathbf{q}(\mathbf{q}\cdot\mathbf{Z}^\star{}_t\mathbf{u}_t)}{\mathbf{q}\cdot\epsilon_\infty\cdot\mathbf{q}}$$

Putting things together

$$\mathbf{F}_s = -\sum_t \left({}^{an}\widetilde{C}_{st}\mathbf{u}_t + \frac{4\pi e^2}{\Omega}\frac{(\mathbf{Z}^\star{}_s\cdot\mathbf{q})\,(\mathbf{q}\cdot\mathbf{Z}^\star{}_t)}{\mathbf{q}\cdot\epsilon_\infty\cdot\mathbf{q}} \right)\mathbf{u}_t$$

Macroscopic electric fields contribute a non-analytic term to the dynamical matrix

$$ {}^{na}\widetilde{C}_{st}^{\alpha\beta} = \frac{4\pi}{\Omega} \frac{(\mathbf{q}\cdot\mathbf{Z}^{\star}{}_{s})_{\alpha}\,(\mathbf{q}\cdot\mathbf{Z}^{\star}{}_{t})_{\beta}}{\mathbf{q}\cdot\epsilon_{\infty}\cdot\mathbf{q}} $$

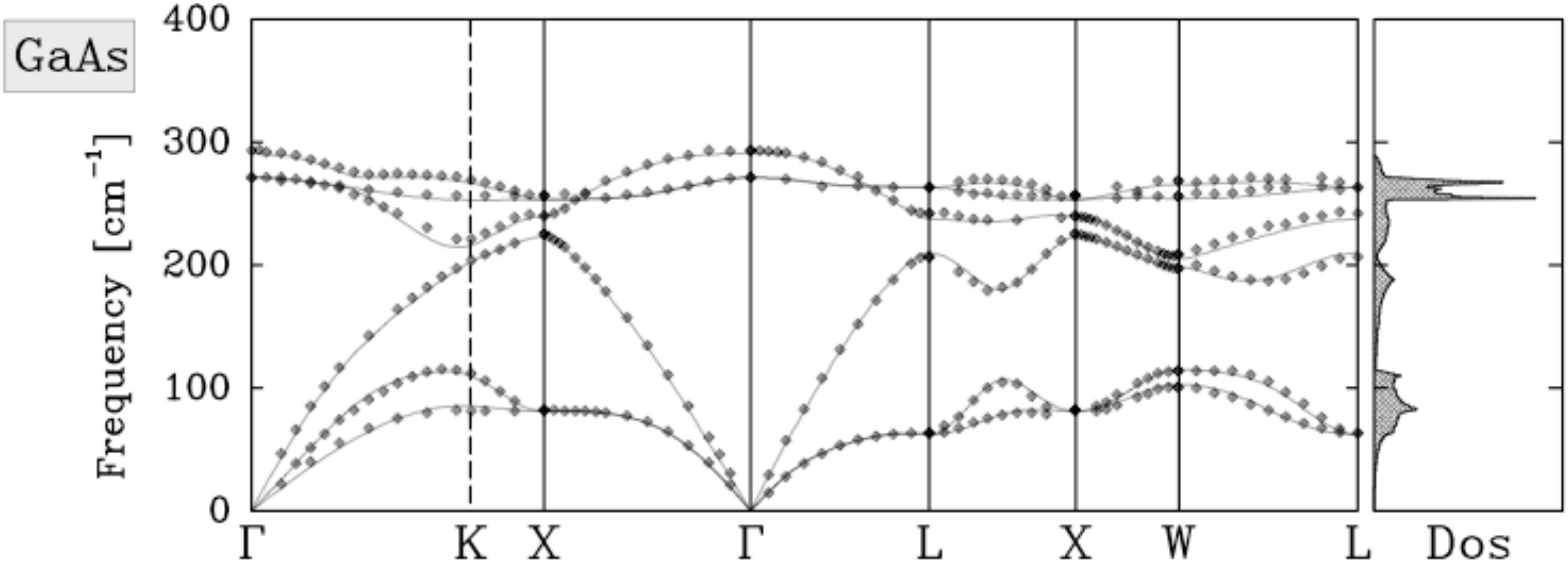
Effective charges $\mathbf{Z}^{\star}$ are related to polarization P induced by a lattice distortion:

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

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.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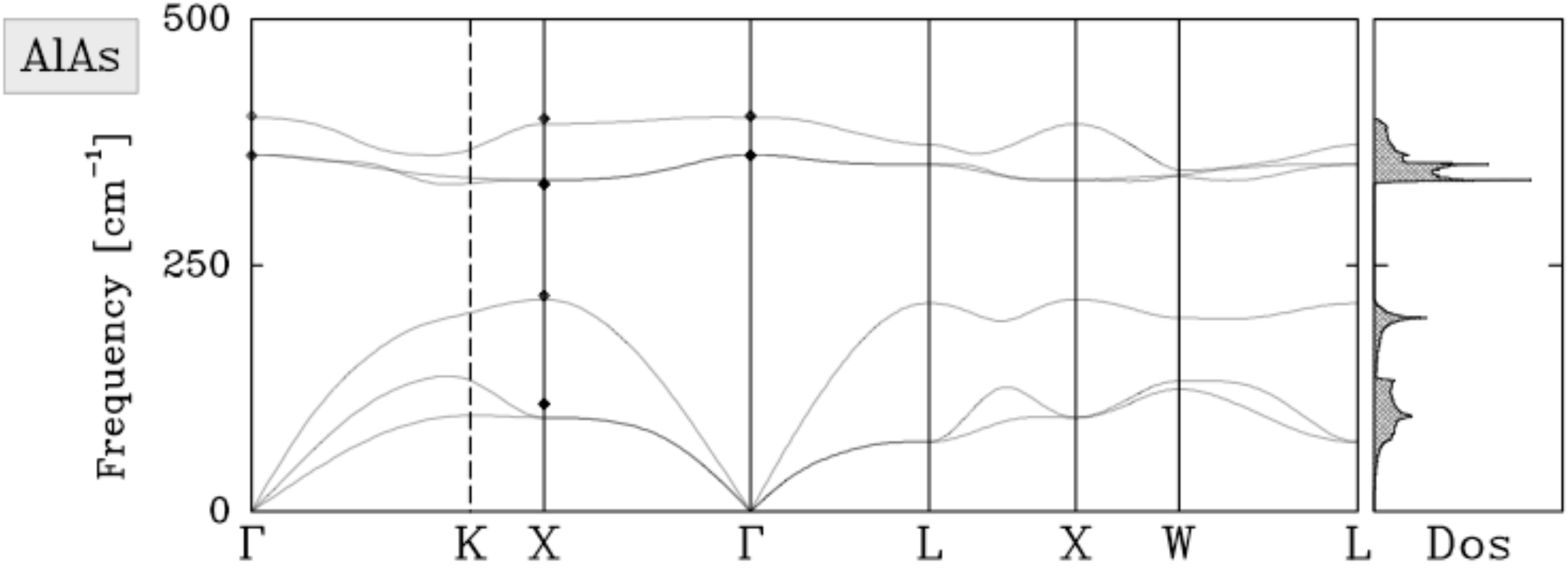
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Calculation of IR and Raman Intensities

Infrared Intensities:

$$I_{IR}(\nu) = \sum_{\alpha} \left| \sum_{s\beta} Z^{\star}{}_{s}^{\alpha\beta} U_{s}^{\beta}(\nu) \right|^2$$

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

Non-resonant Raman intensities:

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

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).

Superconducting T_c and electron-phonon interaction

Electron-phonon interaction λ:

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

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:

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

Practical phonon calculation 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 $\mathbf{q}$; 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 Sume 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 $C(\mathbf{q}_1)$ (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 $\mathbf{q} \to 0$ 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`

Sample input files in `examples_disp.tar.gz`

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