An introduction to linear response and phonon calculations

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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 the electronic response.
Their calculation is however a nontrivial many-body problem.

Density-Functional Linear Response

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, including a factor of 2 for spin deg.)

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 can 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 is

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

and the one of the charge density (after some manipulations):

$$\delta n(\mathbf{r}) = \sum_i f_i[\delta\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) + c.c.] + \delta f_i|\psi_i(\mathbf{r})|^2 = \sum_{i,j} \frac{f_i - f_j}{\epsilon_i - \epsilon_j}\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\langle\psi_j|\delta V_{KS}|\psi_i\rangle$$

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

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

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

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

which can be recast into the form

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

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

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

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

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

$\Delta\psi_v$ 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:

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

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

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

(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

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

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

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

and the energy functional into powers of λ:

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

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

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

Energy functional expansion terms

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

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

The result can be generalized to mixed derivatives:

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

(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 $\partial n/\partial\lambda$.

Density Functional Perturbation Theory

and

Phonons Calculations

Outline

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

Description of a solid

Let's consider a periodic solid. We indicate with

$$\mathbf{R}_l = \mathbf{R}_\mu + \mathbf{d}_s$$

the equilibrium positions of the atoms. $\mathbf{R}_\mu$ indicate the Bravais lattice vectors and $\mathbf{d}_s$ the positions of the atoms in one unit cell ($s = 1, \ldots, N_{at}$).
We take N unit cells with Born-von Karman periodic boundary conditions. Ω is the volume of one cell and $V = N\Omega$ the volume of the solid.
At time t, each atom is displaced from its equilibrium position. $\mathbf{u}_l(t)$ is the displacement of the atom l.

Within the *Born-Oppenheimer adiabatic approximation* the nuclei move in a potential energy given by the total energy of the electron system calculated (for instance within DFT) at fixed nuclei. We call

$$E_{tot}(\mathbf{R}_I + \mathbf{u}_I)$$

this energy. The electrons are assumed to be in the ground state for each nuclear configuration.
If $|\mathbf{u}_I|$ is small, we can expand E_{tot} in a Taylor series with respect to $\mathbf{u}_I$. Within the *harmonic approximation*:

$$E_{tot}(\mathbf{R}_I+\mathbf{u}_I) = E_{tot}(\mathbf{R}_I)+\sum_{I\alpha} \frac{\partial E_{tot}}{\partial \mathbf{u}_{I\alpha}}\mathbf{u}_{I\alpha}+\frac{1}{2}\sum_{I\alpha,J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha}\partial \mathbf{u}_{J\beta}}\mathbf{u}_{I\alpha}\mathbf{u}_{J\beta}+...$$

where the derivatives are calculated at $\mathbf{u}_I = 0$ and α and β indicate the three Cartesian coordinates.

Equations of motion

At equilibrium $\frac{\partial E_{tot}}{\partial \mathbf{u}_{I\alpha}} = 0$, so the Hamiltonian of the ions becomes:

$$H = \sum_{I\alpha} \frac{\mathbf{P}_{I\alpha}^2}{2M_I} + \frac{1}{2} \sum_{I\alpha, J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{I\alpha} \mathbf{u}_{J\beta}$$

where $\mathbf{P}_I$ are the momenta of the nuclei and M_I their masses. The classical motion of the nuclei is given by the $N \times 3 \times N_{at}$ functions $\mathbf{u}_{I\alpha}(t)$. These functions are the solutions of the Hamilton equations:

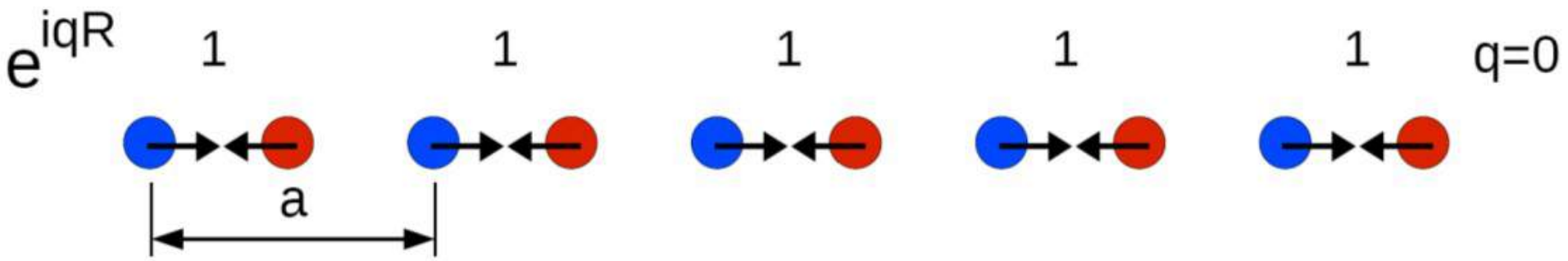
$$\dot{\mathbf{u}}_{I\alpha} = \frac{\partial H}{\partial \mathbf{P}_{I\alpha}}$$

$$\dot{\mathbf{P}}_{I\alpha} = -\frac{\partial H}{\partial \mathbf{u}_{I\alpha}}$$

Vibrational properties

$$(\mathbf{R}+\tau_s)_{eq} \longrightarrow (\mathbf{R}+\tau_s)_{eq} + \mathbf{u}_{\mathbf{R}s}$$

$$\sum_{Rs\alpha} \frac{\mathbf{P}^2_{Rs\alpha}}{2M_s} + \frac{1}{2} \sum_{\substack{Rs\alpha \\ R's'\alpha'}} \mathbf{u}_{Rs\alpha} \frac{\partial^2 E_{el+ion}}{\partial \mathbf{u}_{Rs\alpha} \partial \mathbf{u}_{R's'\alpha'}} \mathbf{u}_{R's'\alpha'}$$



The phonon solution

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

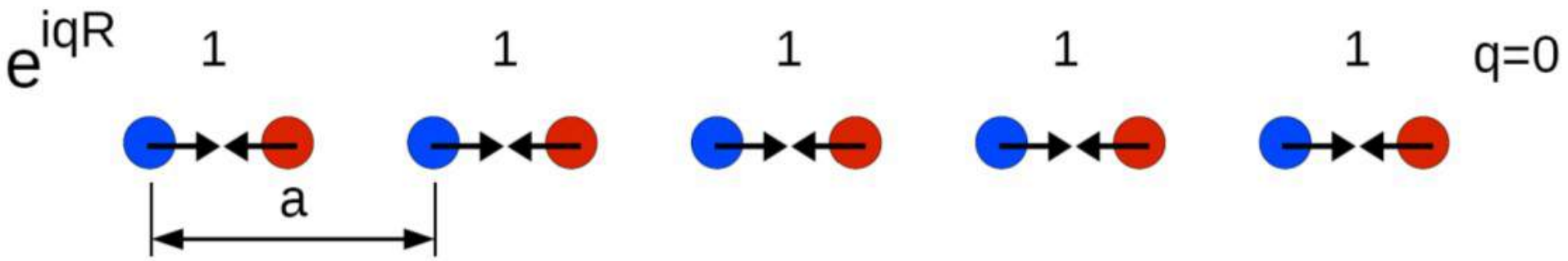
$$\mathbf{u}_{\mu s\alpha}(t) = \frac{1}{\sqrt{M_s}} \mathrm{Re}\left[\mathbf{u}_{s\alpha}(\mathbf{q}) e^{i(\mathbf{q}\mathbf{R}_\mu - \omega_{\mathbf{q}} t)}\right]$$

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

Vibrational properties

$$(\mathbf{R}+\tau_s)_{eq} \longrightarrow (\mathbf{R}+\tau_s)_{eq} + \mathbf{u}_s^{\mathbf{q}} \frac{e^{i\mathbf{qR}}}{\sqrt{N}}$$

$$\sum_{s\alpha} \frac{\mathbf{P}_{s\alpha}^2}{2M_s} + \frac{1}{2} \sum_{\substack{s\alpha \\ ' s'\alpha'}} \mathbf{u}_{s\alpha}^{\mathbf{q}} * \frac{\partial^2 E_{el+ion}}{\partial \mathbf{u}_{s\alpha}^{\mathbf{q}} * \partial \mathbf{u}_{' s'\alpha'}^{\mathbf{q}}} \mathbf{u}_{' s'\alpha'}^{\mathbf{q}}$$



$$\Delta V_{ext}(r) = \sum_{\mathbf{R}s} \frac{\partial V_s}{\partial \mathbf{R}} (|r - \mathbf{R} - \tau_s|) \, \mathbf{u}_s^{\mathbf{q}} \frac{e^{i\mathbf{qR}}}{\sqrt{N}}$$

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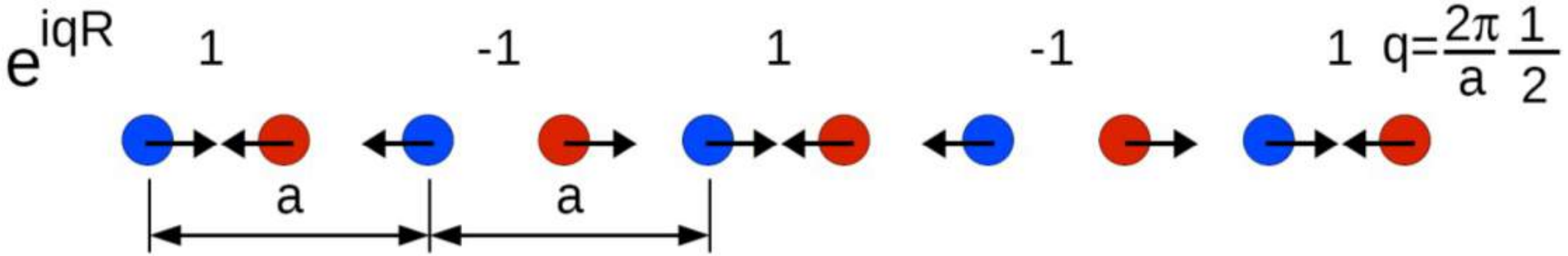

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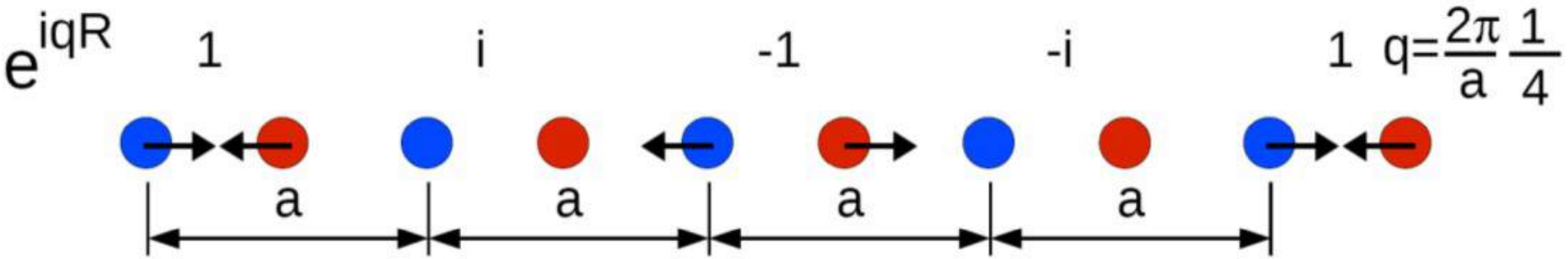

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The phonon solution-II

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

$$\omega^2_{\mathbf{q}} \mathbf{u}_{s\alpha}(\mathbf{q}) = \sum_{s'\beta} D_{s\alpha s'\beta}(\mathbf{q}) \mathbf{u}_{s'\beta}(\mathbf{q})$$

where:

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

is the dynamical matrix of the solid.

KS self-consistent equations

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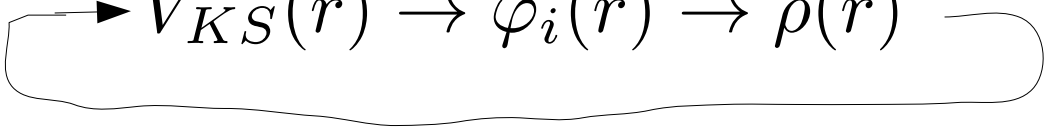
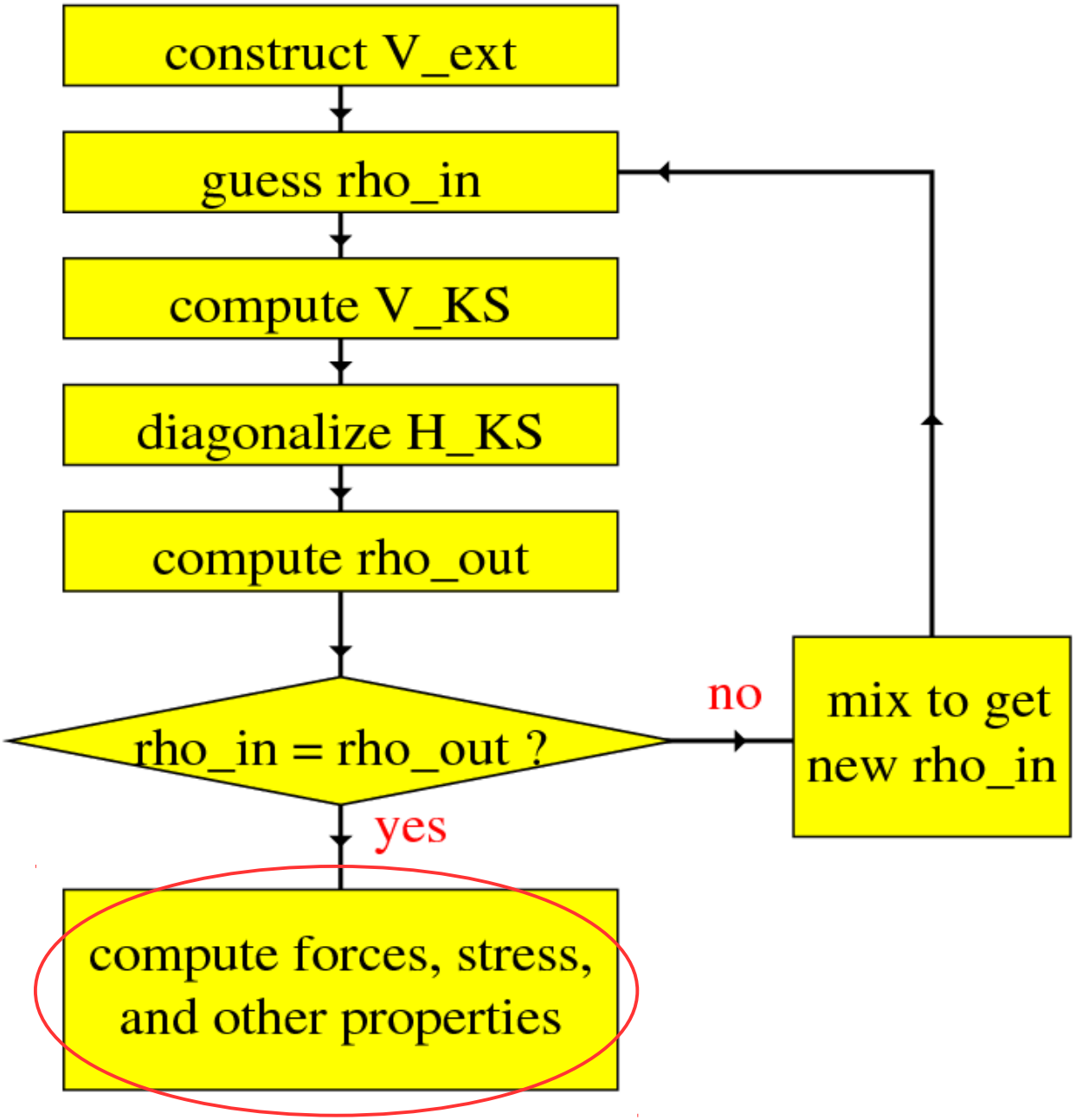


Structure of a self-consistent type code



Total KS energy

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

Total KS energy

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Hellmann-Feynman Theorem

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

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

the linear variation of the GS density is not needed

KS energy expansion

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

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

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

the linear variation of the GS density is needed

KS self-consistent equations

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

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

DFPT self-consistent equations

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DFPT self-consistent equations

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

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DFPT self-consistent equations

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

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

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

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DFPT self-consistent equations

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$$\Delta V_{KS} \rightarrow \Delta\tilde{\varphi}_i(r) \rightarrow \Delta\rho(r)$$

Evaluate the dynamical matrix

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

Dynamical matrix at finite **q** - II

Defining:

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

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

$$\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = \frac{1}{\sqrt{M_{s'}}} \sum_{\nu} \frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}\mathbf{R}_\nu}$$

and show that $\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = e^{i\mathbf{q}\mathbf{r}} \frac{\partial \tilde{\rho}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}$, where $\frac{\partial \tilde{\rho}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}$ is a lattice-periodic function.

Dynamical matrix at finite **q** - III

In the same manner, by defining

$$\left(\frac{\partial V_{loc}(\mathbf{r})}{\partial \mathbf{u}_{s\alpha}(\mathbf{q})}\right)^* = \frac{1}{\sqrt{M_s}} \sum_{\mu} e^{-i\mathbf{q}\mathbf{R}_\mu} \frac{\partial V_{loc}(\mathbf{r})}{\partial \mathbf{u}_{\mu s\alpha}}$$

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

$$\begin{aligned} D_{s\alpha s'\beta}(\mathbf{q}) &= \int_\Omega d^3r \frac{\partial^2 V_{loc}(\mathbf{r})}{\partial \mathbf{u}^*_{s\alpha}(\mathbf{q}) \partial \mathbf{u}_{s'\beta}(\mathbf{q})} \rho(\mathbf{r}) \\ &+ \int_\Omega d^3r \left(\frac{\partial \tilde{V}_{loc}(\mathbf{r})}{\partial \mathbf{u}_{s\alpha}(\mathbf{q})}\right)^* \left(\frac{\tilde{\partial}\rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}\right). \end{aligned}$$

ph.x

The program `ph.x` solves this self-consistent linear system for $3 \times N_{at}$ perturbations at a fixed vector $\mathbf{q}$. With $\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}$ for all perturbations, it calculates the dynamical matrix

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

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

Phonon dispersions

The dynamical matrix of the solid:

$$D_{s\alpha s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}(\mathbf{R}_\nu - \mathbf{R}_\mu)} \qquad (1)$$

is a periodic function of $\mathbf{q}$ with $D_{s\alpha s'\beta}(\mathbf{q}+\mathbf{G}) = D_{s\alpha s'\beta}(\mathbf{q})$ for any reciprocal lattice vector $\mathbf{G}$. Furthermore, due to the translational invariance of the solid, it does not depend on μ. Eq.1 is a Fourier expansion of a three dimensional periodic function. We have Fourier components only at the discrete values $\mathbf{R}_\nu$ of the Bravais lattice and we can write:

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

Discrete Fourier transform

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

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

$$f(x) = \sum_n c_n e^{ik_n x}$$

where the coefficients of the expansion are:

Discrete Fourier transform - II

$$c_n = \frac{1}{a}\int_0^a f(x)e^{-ik_n x}dx.$$

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

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

$\tilde{c}_n$ is a periodic function of n and $\tilde{c}_{n+N} = \tilde{c}_n$. So, if N is sufficiently large that $c_n = 0$ when $|n| \geq N/2$, $\tilde{c}_n$ is a good approximation of c_n for $|n| < N/2$ and the function

Inter-atomic force constants in real space

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. For non polar system, inter-atomic force constants are short-ranged and require a moderate number of calculations at dif $\mathbf{q}$.

Inter-atomic force constants in real space (2)

In simple semiconductors like Si and Ge, **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.

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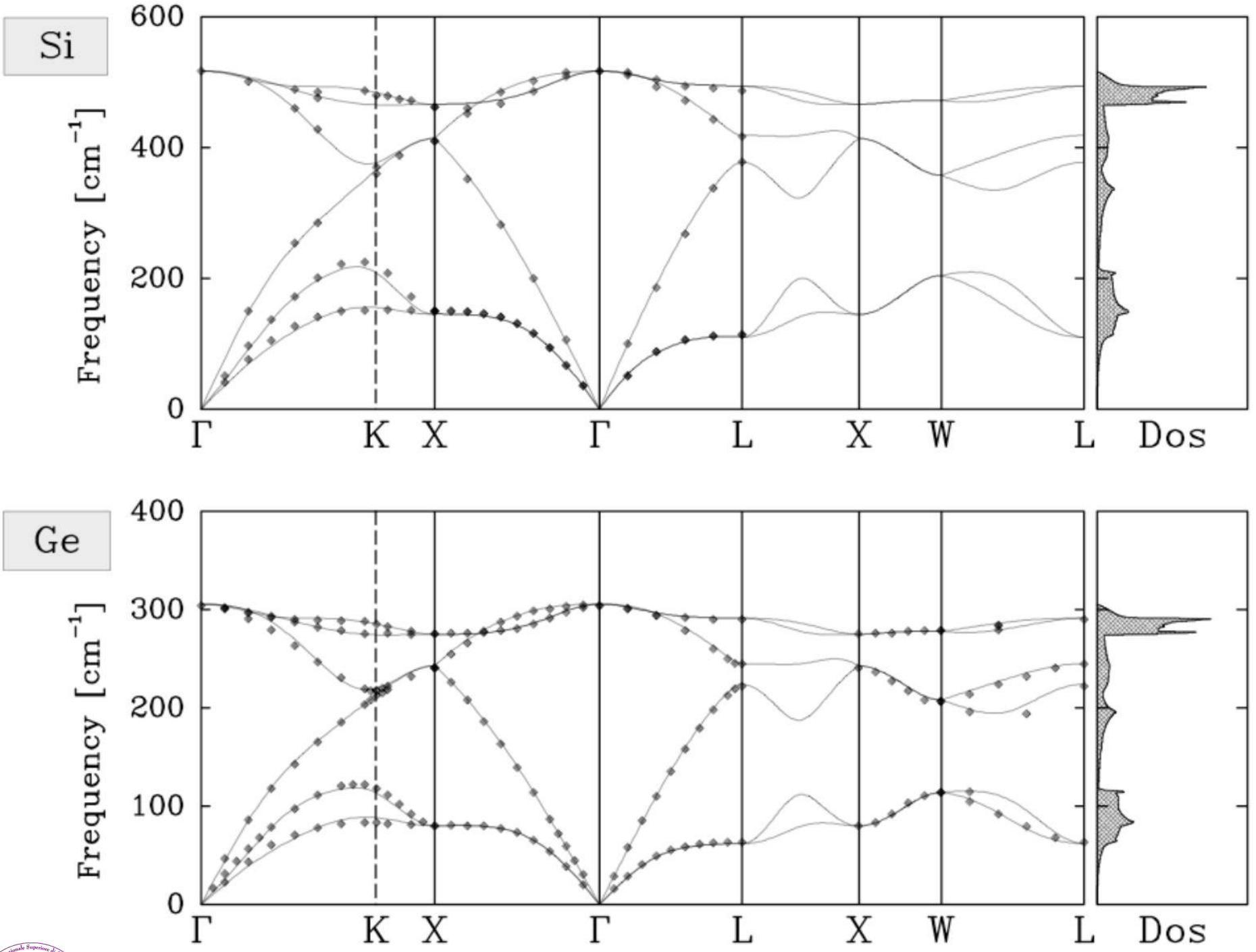
Si
Frequency [cm^{-1}]
600
400
200
0
Γ
K
X
Γ
L
X
W
L
Dos
Ge
Frequency [cm^{-1}]
400
300
200
100
0
Γ
K
X
Γ
L
X
W
L
Dos

q2r.x

$C_{s\alpha s'\beta}(\mathbf{R}) = \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}}$ and write the relationship:

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

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

matdyn.x

If the dynamical matrix is a sufficiently smooth function of **q**, the inter-atomic force constants decay sufficiently rapidly in real space and we can use Eq. 1 limiting the sum over ν to the few neighbors of $\mathbf{R}_\mu$ for which we have calculated the inter-atomic force constants. With the present notation Eq. 1 becomes:

$$C_{s\alpha s'\beta}(\mathbf{q}) = \sum_{\mathbf{R}} C_{s\alpha s'\beta}(\mathbf{R}) e^{-i\mathbf{q}\mathbf{R}}, \tag{3}$$

a relationship that allows the interpolation of the dynamical matrix at arbitrary **q**, by a few inter-atomic force constants. The program `matdyn.x` reads the inter-atomic force constants calculated by `q2r.x` and calculates the dynamical matrices at an arbitrary **q** using this equation.

This procedure fails in two cases:

- In metals when there are Kohn anomalies. In this case $D_{s\alpha s'\beta}(\mathbf{q})$ is not a smooth function of $\mathbf{q}$ and the inter-atomic force constants are long range.
- In polar insulators where the atomic displacements generate long range electrostatic interactions and the dynamical matrix is non analytic for $\mathbf{q} \to 0$. This case, however, can be dealt with by calculating the Born effective charges and the dielectric constant of the material.

Use of symmetry

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

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

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

Use of symmetry - II

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

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THE END

Scuola Internazionale Superiore di Studi Avanzati
- tra per seguir virtute e conoscenza -