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:

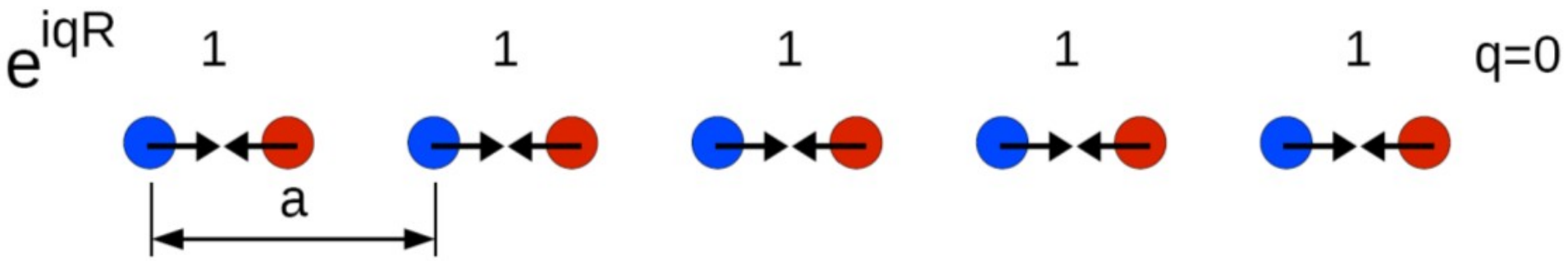
$$\dot{\mathbf{u}}_{I\alpha} = \frac{\partial H}{\partial \mathbf{P}_{I\alpha}}$$

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

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:

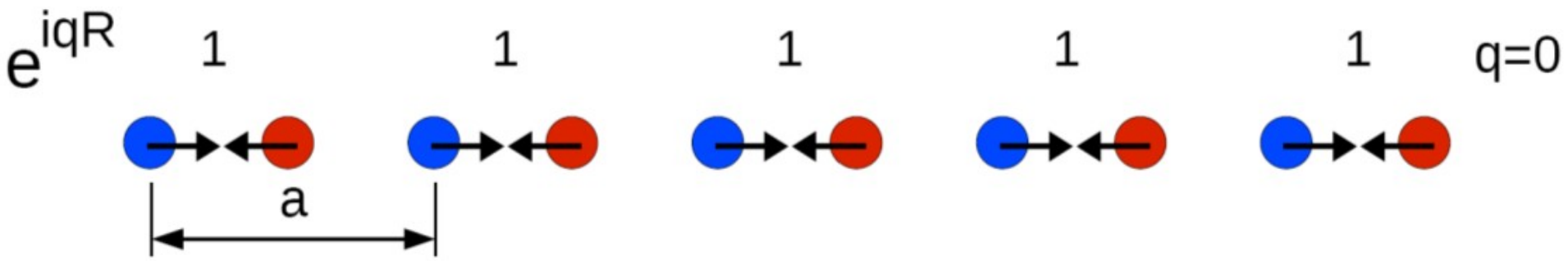
$$\mathbf{u}_{\mu s\alpha}(t) = \frac{1}{\sqrt{M_s}} \mathrm{Re}\left[\mathbf{u}_{s\alpha}(\mathbf{q}) e^{i(\mathbf{q}\mathbf{R}_\mu - \omega_{\mathbf{q}} t)}\right]$$

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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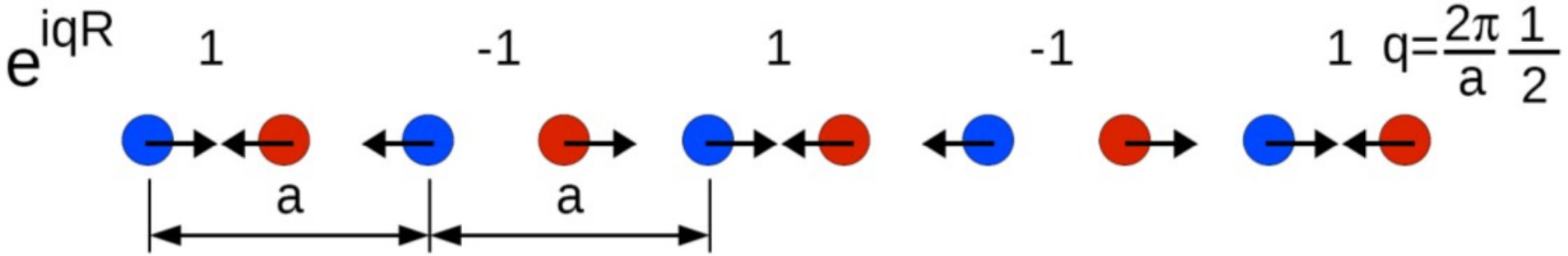

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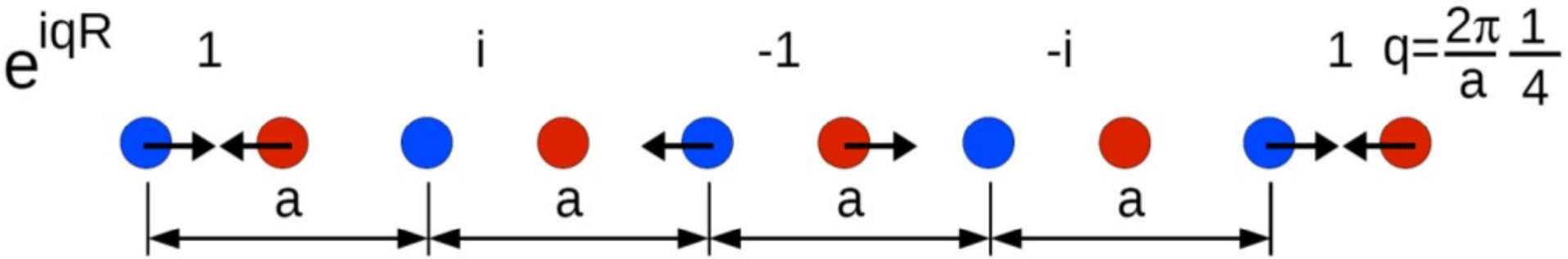

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The phonon solution-II

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

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

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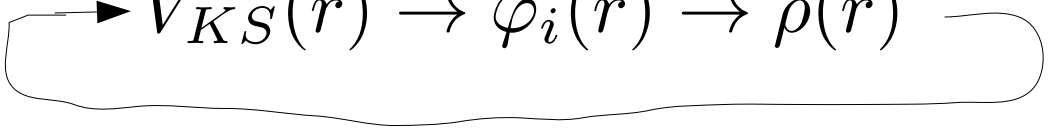
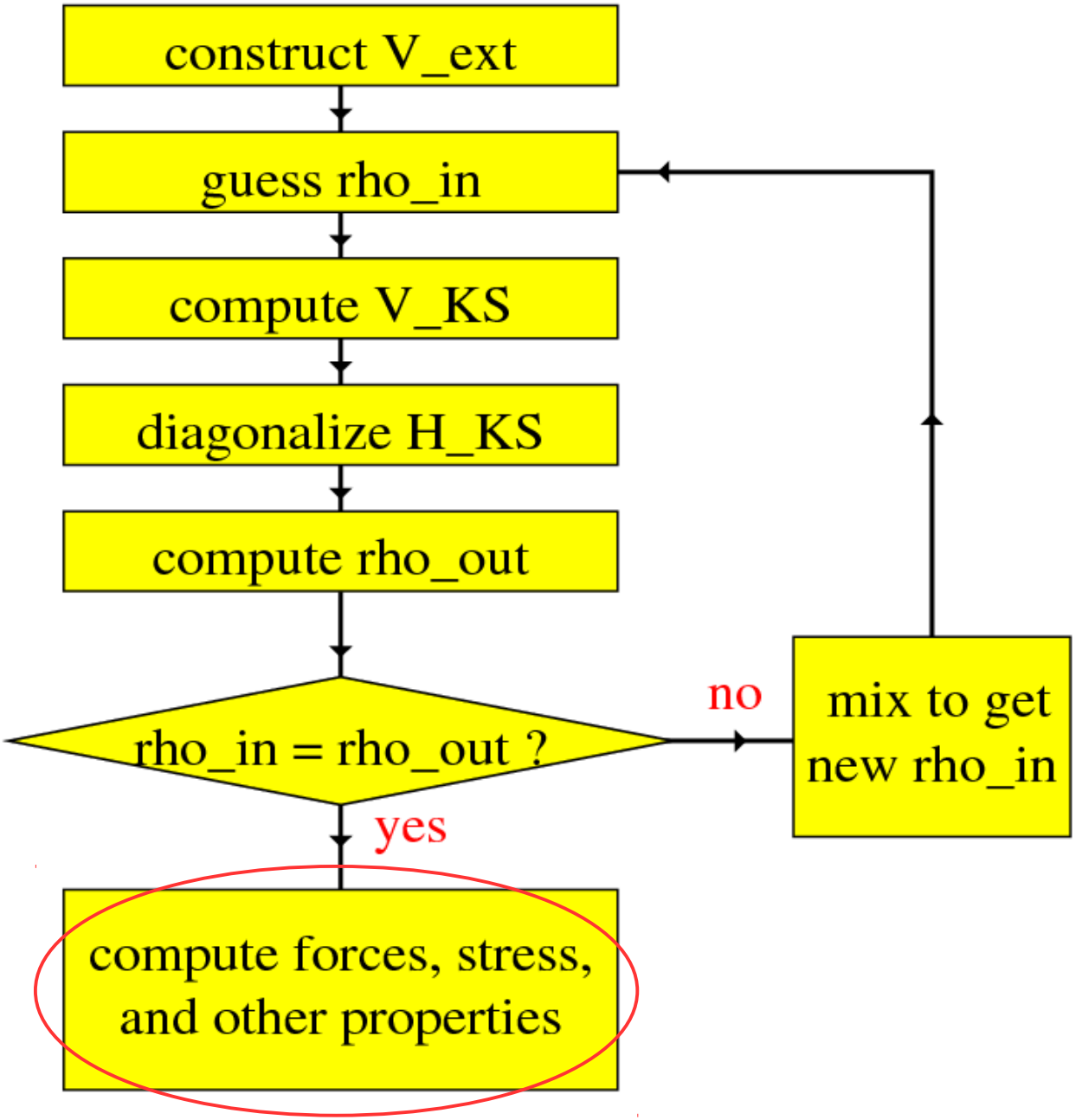


Structure of a self-consistent type code



Total KS energy

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

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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

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

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

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

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

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DFPT self-consistent equations

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

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$$\Delta\rho(r) = 2\sum_i \varphi_i^*(r)\,\Delta\varphi_i(r)$$

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DFPT self-consistent equations

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

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

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

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 $\mathbf{q} \longrightarrow 0$. 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.

Bibliography

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THE END


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