

Introduction to density functional perturbation theory for lattice dynamics

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Let's consider a periodic solid. We indicate with

$$\mathbf{R}_I = \mathbf{R}_\mu + \mathbf{d}_s \quad (1)$$

the equilibrium positions of the atoms. \mathbf{R}_μ indicate the Bravais lattice vectors and \mathbf{d}_s the positions of the atoms in one unit cell ($s = 1, \dots, N_{at}$).

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. $\mathbf{u}_I(t)$ is the displacement of the atom I .

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

$$E_{tot}(\mathbf{R}_I + \mathbf{u}_I) \quad (2)$$

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*:

$$E_{tot}(\mathbf{R}_I + \mathbf{u}_I) = E_{tot}(\mathbf{R}_I) + \sum_{I\alpha} \frac{\partial E_{tot}}{\partial \mathbf{u}_{I\alpha}} \mathbf{u}_{I\alpha} + \frac{1}{2} \sum_{I\alpha, J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{I\alpha} \mathbf{u}_{J\beta} + \dots \quad (3)$$

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:

$$H = \sum_{I\alpha} \frac{\mathbf{P}_{I\alpha}^2}{2M_I} + \frac{1}{2} \sum_{I\alpha, J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{I\alpha} \mathbf{u}_{J\beta} \quad (4)$$

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:

$$\begin{aligned} \dot{\mathbf{u}}_{I\alpha} &= \frac{\partial H}{\partial \mathbf{P}_{I\alpha}} \\ \dot{\mathbf{P}}_{I\alpha} &= -\frac{\partial H}{\partial \mathbf{u}_{I\alpha}} \end{aligned} \quad (5)$$

Equations of motion-II

With our Hamiltonian:

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

$$\dot{\mathbf{P}}_{I\alpha} = - \sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta} \quad (6)$$

or:

$$M_I \ddot{\mathbf{u}}_{I\alpha} = - \sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta} \quad (7)$$

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:

$$\mathbf{u}_{\mu s\alpha}(t) = \frac{1}{\sqrt{M_s}} \mathbf{u}_{s\alpha}(\mathbf{q}) e^{i(\mathbf{q}\mathbf{R}_\mu - \omega_{\mathbf{q}}t)} \quad (8)$$

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

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 $\mathbf{u}_{s\alpha}(\mathbf{q})$:

$$\omega_{\mathbf{q}}^2 \mathbf{u}_{s\alpha}(\mathbf{q}) = \sum_{s'\beta} D_{s\alpha s'\beta}(\mathbf{q}) \mathbf{u}_{s'\beta}(\mathbf{q}) \quad (9)$$

where:

$$D_{s\alpha s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}(\mathbf{R}_{\nu} - \mathbf{R}_{\mu})} \quad (10)$$

is the dynamical matrix of the solid.

Within DFT the ground state total energy of the solid, calculated at fixed nuclei, is:

$$E_{tot} = \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{loc}(\mathbf{r}) \rho(\mathbf{r}) d^3r + E_H[\rho] + E_{xc}[\rho] + U_{II} \quad (11)$$

where $\rho(\mathbf{r})$ is the density of the electron gas:

$$\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \quad (12)$$

and $|\psi_i\rangle$ are the solution of the Kohn and Sham equations. E_H is the Hartree energy, E_{xc} is the exchange and correlation energy and U_{II} is the ion-ion interaction. According to the Hellmann-Feynman theorem, the first order derivative of the ground state energy with respect to an external parameter is:

$$\frac{\partial E_{tot}}{\partial \lambda} = \int \frac{\partial V_{loc}(\mathbf{r})}{\partial \lambda} \rho(\mathbf{r}) d^3r + \frac{\partial U_{II}}{\partial \lambda} \quad (13)$$

Deriving with respect to a second parameter μ :

$$\begin{aligned} \frac{\partial^2 E_{tot}}{\partial \mu \partial \lambda} &= \int \frac{\partial^2 V_{loc}(\mathbf{r})}{\partial \mu \partial \lambda} \rho(\mathbf{r}) d^3 r + \frac{\partial^2 U_{II}}{\partial \mu \partial \lambda} \\ &+ \int \frac{\partial V_{loc}(\mathbf{r})}{\partial \lambda} \frac{\partial \rho(\mathbf{r})}{\partial \mu} d^3 r \end{aligned} \quad (14)$$

So the new quantity that we need to calculate is the charge density induced, at first order, by the perturbation:

$$\frac{\partial \rho(\mathbf{r})}{\partial \mu} = \sum_i \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mu} \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \quad (15)$$

To fix the ideas we can think that $\lambda = \mathbf{u}_{\mu S \alpha}$ and $\mu = \mathbf{u}_{\nu S' \beta}$

The wavefunctions obey the following equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (16)$$

where $V_{KS} = V_{loc}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})$. $V_{KS}(\mathbf{r}, \mu)$ depends on μ so that also $\psi_i(\mathbf{r}, \mu)$, and $\varepsilon_i(\mu)$ depend on μ . We can expand these quantities in a Taylor series:

$$\begin{aligned} V_{KS}(\mathbf{r}, \mu) &= V_{KS}(\mathbf{r}, \mu = 0) + \mu \frac{\partial V_{KS}(\mathbf{r})}{\partial \mu} + \dots \\ \psi_i(\mathbf{r}, \mu) &= \psi_i(\mathbf{r}, \mu = 0) + \mu \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} + \dots \\ \varepsilon_i(\mu) &= \varepsilon_i(\mu = 0) + \mu \frac{\partial \varepsilon_i}{\partial \mu} + \dots \end{aligned} \quad (17)$$

Inserting these equations and keeping only the first order in μ we obtain:

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) - \varepsilon_i \right] \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} = -\frac{\partial V_{KS}}{\partial \mu} \psi_i(\mathbf{r}) + \frac{\partial \varepsilon_i}{\partial \mu} \psi_i(\mathbf{r}) \quad (18)$$

where: $\frac{\partial V_{KS}}{\partial \mu} = \frac{\partial V_{loc}}{\partial \mu} + \frac{\partial V_H}{\partial \mu} + \frac{\partial V_{xc}}{\partial \mu}$ and

$$\begin{aligned} \frac{\partial V_H}{\partial \mu} &= \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial \rho(\mathbf{r}')}{\partial \mu} d^3 r' \\ \frac{\partial V_{xc}}{\partial \mu} &= \frac{dV_{xc}}{d\rho} \frac{\partial \rho(\mathbf{r})}{\partial \mu} \end{aligned} \quad (19)$$

depend self-consistently on the charge density induced by the perturbation.

The induced charge density depends only on $P_c \frac{\partial \psi_i}{\partial \mu}$ where $P_c = 1 - P_v$ is the projector on the conduction bands and $P_v = \sum_i |\psi_i\rangle\langle\psi_i|$ is the projector on the valence bands. In fact:

$$\begin{aligned} \frac{\partial \rho(\mathbf{r})}{\partial \mu} &= \sum_i P_c \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mu} \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \\ &+ \sum_i P_v \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mu} \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) P_v \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \end{aligned} \quad (20)$$

$$\begin{aligned} \frac{\partial \rho(\mathbf{r})}{\partial \mu} &= \sum_i P_c \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mu} \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \\ &+ \sum_{ij} \psi_j^*(\mathbf{r}) \psi_i(\mathbf{r}) \left(\left\langle \frac{\partial \psi_j}{\partial \mu} \middle| \psi_j \right\rangle + \left\langle \psi_i \middle| \frac{\partial \psi_j}{\partial \mu} \right\rangle \right) \end{aligned} \quad (21)$$

DFPT

Therefore we can solve the self-consistent linear system:

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) - \varepsilon_i \right] P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} = -P_c \frac{\partial V_{KS}}{\partial \mu} \psi_i(\mathbf{r}) \quad (22)$$

where

$$\frac{\partial V_{KS}}{\partial \mu} = \frac{\partial V_{loc}}{\partial \mu} + \frac{\partial V_H}{\partial \mu} + \frac{\partial V_{xc}}{\partial \mu} \quad (23)$$

and

$$\frac{\partial \rho(\mathbf{r})}{\partial \mu} = \sum_i P_c \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mu} \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \quad (24)$$

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

$$D_{s\alpha s'\beta}(\mathbf{q}) \quad (25)$$

at the given \mathbf{q} . 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 points \mathbf{q} .

The dynamical matrix of the solid:

$$D_{s\alpha s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}(\mathbf{R}_{\nu} - \mathbf{R}_{\mu})} \quad (26)$$

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} . Moreover, since in a solid all Bravais lattice points are equivalent, it does not depend on μ . Eq.26 is a Fourier expansion of a three dimensional periodic function. We have Fourier components only at the discrete values \mathbf{R}_{ν} of the Bravais lattice and we can write:

$$\frac{1}{\sqrt{M_s M_{s'}}} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}} = \frac{\Omega}{(2\pi)^3} \int d^3 \mathbf{q} D_{s\alpha s'\beta}(\mathbf{q}) e^{-i\mathbf{q}(\mathbf{R}_{\nu} - \mathbf{R}_{\mu})} \quad (27)$$

We can use the properties of the discrete Fourier transform and sample the integral in a uniform mesh of points \mathbf{q} . This will give the interatomic force constants only for a set of \mathbf{R}_ν neighbors of \mathbf{R}_μ . The code `q2r.x` reads a set of dynamical matrices calculated in a uniform mesh of \mathbf{q} points and calculates, using Eq. 27, the interatomic force constants for a few neighbors of the point $\mathbf{R}_\mu = 0$.

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 the point $k_n = \frac{2\pi}{a}n$, where n is an integer (positive, negative or zero).

$$f(x) = \sum_n c_n e^{ik_n x} \quad (28)$$

where the coefficients of the expansion are:

$$c_n = \frac{1}{a} \int_0^a f(x) e^{-ik_n x} dx \quad (29)$$

In general, if $f(x)$ is a sufficiently smooth function, $c_n \rightarrow 0$ at large n . Now suppose that we know $f(x)$ only in a uniform set of N points $x_j = j\Delta x$ where $\Delta x = a/N$ and $j = 0, \dots, N - 1$,

then we can calculate:

$$\tilde{c}_n = \frac{1}{N} \sum_{j=0}^{N-1} f(x_j) e^{-i \frac{2\pi}{N} n j} \quad (30)$$

\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 $|n| \geq N/2$ then \tilde{c}_n is a good approximation of c_n for $|n| < N/2$ and the function

$$f(x) = \sum_{n=-N/2}^{n=N/2} \tilde{c}_n e^{i k_n x} \quad (31)$$

is a good approximation of the function $f(x)$ also on the points x different from x_j .

Therefore, if the dynamical matrix is a sufficiently smooth function of \mathbf{q} and the interatomic force constants decay sufficiently rapidly in real space, we can use Eq. 26 to calculate the dynamical matrix at arbitrary \mathbf{q} , limiting the sum to a few \mathbf{R}_ν neighbors of $\mathbf{R}_\mu = 0$. The program `matdyn.x` reads the interatomic force constants calculated by `q2r.x` and calculates the dynamical matrices at an arbitrary \mathbf{q} using Eq. 26.

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 interatomic 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 $\mathbf{q} \rightarrow 0$. This case, however, can be dealt with by calculating the Born effective charges and the dielectric constant of the material.