

Electronic Structure Theory

ab-initio simulations of materials properties

Davide Romanin

Department of Applied Science (DISAT)
Politecnico di Torino, Torino

May 11, 2020

Table of Contents

- Introduction
- Density Functional Theory: the Hohenberg-Kohn theorems
- Density Functional Theory: the Kohn-Sham equations
- The exchange-correlation functional
- Plane-wave basis set
- Pseudopotentials
- Density Functional Perturbation Theory

Vibrational properties from ab-initio simulations

Vibrational spectroscopy is a very important tool for the characterization of materials. Vibrational frequencies are measured mainly using infrared and Raman spectroscopy as well as inelastic neutron scattering.

We would like to have a nice way to simulate vibrational properties. We will examine two main approaches:

- Density functional perturbation theory (DFPT);
- Frozen phonons;

Introduction

Consider a periodic solid of volume $V = N\Omega$ (Ω is the volume of the unitary cell, N is the number of cells) such that:

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

with $s = 1, \dots, N_{at}$, $\mu = 1, \dots, N$ and:

- $\mathbf{R}_\mu \rightarrow$ position of the μ -th cell;
- $\mathbf{d}_s \rightarrow$ position of the s -th atom inside the cell;

At time t each atom is displaced from the equilibrium position by $\mathbf{u}_I(t)$, $I = \{\mu, s\}$.

The harmonic approximation

Due to differences between electron's and ion's masses, electrons can be thought to be moving in an environment where ions' positions $\{\mathbf{R}\}$ are fixed and considered as parameters.

Electrons move in a frozen-phonon picture and we find their ground-state energy. After that we study the lattice dynamical properties in this **Born-Oppenheimer energy surface** $E_{tot}(\mathbf{R}_I + \mathbf{u}_I)$.

If $|\mathbf{u}_I| \ll 0$ in the harmonic approximation:

$$\begin{aligned}
 E_{tot}(\mathbf{R}_I + \mathbf{u}_I) \approx & E_{tot}(\mathbf{R}_I) + \sum_{I,\alpha} \left. \frac{\partial E_{tot}}{\partial u_{I,\alpha}} \right|_{u_{I,\alpha}=0} \cdot u_{I,\alpha} + \\
 & + \sum_{IJ,\alpha\beta} \left. \frac{\partial^2 E_{tot}}{\partial u_{I,\alpha} \partial u_{J,\beta}} \right|_{u_{I,\alpha}=0, u_{J,\beta}=0} \cdot u_{I,\alpha} u_{J,\beta}
 \end{aligned} \tag{2}$$

The equilibrium geometry is such that:

$$\mathbf{F}_I = - \left. \frac{\partial E_{tot}}{\partial \mathbf{u}_I} \right|_{\mathbf{u}_I=0} = 0 \quad (3)$$

Therefore, the harmonic hamiltonian for ions is:

$$H = \sum_{I,\alpha} \frac{P_{I\alpha}^2}{2M_I} + \sum_{IJ,\alpha\beta} \left. \frac{\partial^2 E_{tot}}{\partial u_{I,\alpha} \partial u_{J,\beta}} \right|_{u_{I,\alpha}=0, u_{J,\beta}=0} \cdot u_{I,\alpha} u_{J,\beta} \quad (4)$$

Using Hamilton's equations of motion we get the $3 \times N_{at} \times N$ equations:

$$M_I \ddot{u}_{I,\alpha} = - \sum_{J,\beta} \left. \frac{\partial^2 E_{tot}}{\partial u_{I,\alpha} \partial u_{J,\beta}} \right|_{u_{I,\alpha}=0, u_{J,\beta}=0} \cdot u_{J,\beta} \quad (5)$$

The Phonon solution

We look for a solution in the form of phonons;

$$u_{\mu,s,\alpha}(t) = \frac{1}{\sqrt{M_s}} \mathcal{R}e \left\{ u_{s,\alpha}(\mathbf{q}) e^{i(\mathbf{q} \cdot \mathbf{R}_\mu - \omega_{\mathbf{q}} t)} \right\} \quad (6)$$

If we insert it in the equations of motion we obtain the eigenvalue problem:

$$\omega_{\mathbf{q}}^2 u_{s,\alpha}(\mathbf{q}) = \sum_{s'\beta} D_{s\alpha,s'\beta}(\mathbf{q}) u_{s',\beta}(\mathbf{q}) \quad (7)$$

where we have define the dynamical matrix as:

$$D_{s\alpha,s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \left. \frac{\partial^2 E_{tot}}{\partial u_{\mu,s,\alpha} \partial u_{\nu,s',\beta}} \right|_{u_{\mu,s,\alpha}=0, u_{\nu,s',\beta}=0} \cdot e^{i\mathbf{q} \cdot (\mathbf{R}_\mu - \mathbf{R}_\nu)} \quad (8)$$

Linear response

Recall that within DFT, the ground-state energy is given by:

$$E_{tot} = -\frac{\hbar^2}{2m_e} \langle \psi_i | \nabla^2 | \psi_i \rangle + E_H[\rho] + E_{XC}[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{II} \quad (9)$$

with $\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$ and $\hat{H}|\psi_i\rangle = \epsilon_i|\psi_i\rangle$ for the electron problem.

Equilibrium geometry and vibrational properties are related to first and second derivatives of E_{tot} , which can be evaluated using the Hellman-Feynman theorem.

V_{KS} , ψ_i and ϵ_i depend on $u_{\nu,s',\beta}$. We can expand them:

$$\begin{aligned}
 V_{KS}(\mathbf{r}; u_{\nu,s',\beta}) &= V_{KS}(\mathbf{r}; 0) + \left. \frac{\partial V_{KS}}{\partial u_{\nu,s',\beta}} \right|_{u_{\nu,s',\beta}=0} \cdot u_{\nu,s',\beta} \\
 \psi_i(\mathbf{r}; u_{\nu,s',\beta}) &= \psi_i(\mathbf{r}; 0) + \left. \frac{\partial \psi_i}{\partial u_{\nu,s',\beta}} \right|_{u_{\nu,s',\beta}=0} \cdot u_{\nu,s',\beta} \\
 \epsilon_i(u_{\nu,s',\beta}) &= \epsilon_i(0) + \left. \frac{\partial \epsilon_i}{\partial u_{\nu,s',\beta}} \right|_{u_{\nu,s',\beta}=0} \cdot u_{\nu,s',\beta}
 \end{aligned} \tag{10}$$

In the end:

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{KS}(\mathbf{r}) - \epsilon_i \right] \frac{\partial \psi_i(\mathbf{r})}{\partial u_{\nu, s', \beta}} = -\frac{\partial V_{KS}(\mathbf{r})}{\partial u_{\nu, s', \beta}} \psi_i(\mathbf{r}) + \frac{\partial \epsilon_i}{\partial u_{\nu, s', \beta}} \psi_i(\mathbf{r}) \quad (11)$$

Notice that:

- $\frac{\partial V_{KS}(\mathbf{r})}{\partial u_{\nu, s', \beta}}$ depends self consistently on the induced charge density;
- the induced charge density depends only on the conduction submanifold;

Density Functional Perturbation Theory

We need to solve self consistently the following set of equations:

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{KS}(\mathbf{r}) - \epsilon_i \right] P_C \frac{\partial \psi_i(\mathbf{r})}{\partial u_{\nu, s', \beta}} = -P_C \frac{\partial V_{KS}(\mathbf{r})}{\partial u_{\nu, s', \beta}} \psi_i(\mathbf{r}) \quad (12)$$

$$\frac{\partial V_{KS}(\mathbf{r})}{\partial u_{\nu, s', \beta}} = \frac{\partial V_{\text{ext}}(\mathbf{r})}{\partial u_{\nu, s', \beta}} + \frac{\partial V_H(\mathbf{r})}{\partial u_{\nu, s', \beta}} + \frac{\partial V_{XC}(\mathbf{r})}{\partial u_{\nu, s', \beta}} \quad (13)$$

$$\frac{\partial \rho(\mathbf{r})}{\partial u_{\nu, s', \beta}} = \sum_i P_C \frac{\partial \psi_i^*(\mathbf{r})}{\partial u_{\nu, s', \beta}} \psi_i(\mathbf{r}) + \psi_i(\mathbf{r})^* P_C \frac{\partial \psi_i(\mathbf{r})}{\partial u_{\nu, s', \beta}} \quad (14)$$

Notice that conduction bands are never explicitly required.

Dynamical matrix at finite \mathbf{q}

We can write the dynamical matrix at a finite \mathbf{q} as an integral over the unit cell:

$$D_{s\alpha,s'\beta}(\mathbf{q}) = \int_{\Omega} d\mathbf{r} \frac{\partial^2 V_{\text{ext}}(\mathbf{r})}{\partial u_{s\alpha}^*(\mathbf{q}) \partial u_{s'\beta}(\mathbf{q})} + \int_{\Omega} d\mathbf{r} \left(\frac{\partial \tilde{V}_{\text{ext}}(\mathbf{r})}{\partial u_{s\alpha}(\mathbf{q})} \right)^* \frac{\partial \tilde{\rho}(\mathbf{r})}{\partial u_{s'\beta}(\mathbf{q})} \quad (15)$$

Dynamical matrix at finite \mathbf{q} - derivation I

Dynamical matrix at finite \mathbf{q} - derivation II

Dynamical matrix at finite \mathbf{q} - derivation III

Charge density response at finite \mathbf{q}

The lattice-periodic part of the charge density will be:

$$\frac{\partial \tilde{\rho}(\mathbf{r})}{\partial u_{s'\beta}(\mathbf{q})} = 2 \sum_{\mathbf{k}i} u_{\mathbf{k}i}^*(\mathbf{r}) P_C^{\mathbf{k}+\mathbf{q}} \frac{\partial \tilde{u}_{\mathbf{k}i}(\mathbf{r})}{\partial u_{s'\beta}(\mathbf{q})} \quad (16)$$

Charge density response at finite \mathbf{q} - derivation I

Charge density response at finite \mathbf{q} - derivation II

Charge density response at finite \mathbf{q} - derivation III

Charge density response at finite \mathbf{q} - derivation IV

Rewriting the DFPT eigenvalue problem

We will need to solve:

$$\left[H^{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}i} \right] P_C^{\mathbf{k}+\mathbf{q}} \frac{\partial \tilde{u}_{\mathbf{k}i}(\mathbf{r})}{\partial u_{s'\beta}(\mathbf{q})} = -P_C^{\mathbf{k}+\mathbf{q}} \frac{\partial \tilde{V}_{KS}}{\partial u_{s'\beta}(\mathbf{q})} u_{\mathbf{k}i}(\mathbf{r}) \quad (17)$$

where the linear response of the KS potential is given by:

$$\begin{aligned} \frac{\partial \tilde{V}_{KS}}{\partial u_{s'\beta}(\mathbf{q})} = & \frac{\partial \tilde{V}_{ext}}{\partial u_{s'\beta}(\mathbf{q})} + \int d\mathbf{r} \frac{e^{i\mathbf{q} \cdot (\mathbf{r}-\mathbf{r}')}}{|\mathbf{r}-\mathbf{r}'|} \frac{\partial \tilde{\rho}(\mathbf{r}')}{\partial u_{s'\beta}(\mathbf{q})} + \\ & + \frac{\partial V_{XC}}{\partial \rho} \frac{\partial \tilde{\rho}(\mathbf{r})}{\partial u_{s'\beta}(\mathbf{q})} \end{aligned} \quad (18)$$

Rewriting the DFPT eigenvalue problem - I

Rewriting the DFPT eigenvalue problem - II

Obtaining the phonon dispersion - the DFPT algorithm

We need to solve self-consistently the linear system of $3N_{at}$ perturbations at fixed \mathbf{q} .

The idea is:

$$\frac{\partial \rho(\mathbf{r})}{\partial u_{s'\beta}(\mathbf{q})} \Rightarrow D_{s\alpha,s'\beta}(\mathbf{q}) \Rightarrow \omega_{\mathbf{q}} \quad (19)$$

If we diagonalize the dynamical matrix on a grid of \mathbf{q} -points we obtain the $3N_{at}$ frequencies and we can reconstruct the phonon dispersion relation.

The dynamical matrix is a periodic function of \mathbf{q} , i.e.

$D_{s\alpha,s'\beta}(\mathbf{q} + \mathbf{G}) = D_{s\alpha,s'\beta}(\mathbf{q})$. Moreover it is the Fourier transform of a periodic function with Fourier components at discrete \mathbf{R}_ν values.

$$D_{s\alpha,s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \frac{\partial^2 E_{tot}}{\partial u_{\mu,s,\alpha} \partial u_{\nu,s',\beta}} e^{i\mathbf{q} \cdot (\mathbf{R}_\mu - \mathbf{R}_\nu)} \quad (20)$$

$$\frac{1}{\sqrt{M_s M_{s'}}} \frac{\partial^2 E_{tot}}{\partial u_{\mu,s,\alpha} \partial u_{\nu,s',\beta}} = \frac{\Omega}{(2\pi)^3} \int d\mathbf{q} D_{s\alpha,s'\beta}(\mathbf{q}) e^{i\mathbf{q} \cdot (\mathbf{R}_\nu - \mathbf{R}_\mu)} \quad (21)$$

we can use the properties of the discrete Fourier transform and sample the integral on a uniform mesh of \mathbf{q} -points.

Discrete Fourier transform in 1D

We define the interatomic force constants as:

$$C_{s\alpha,s'\beta}(\mathbf{R}) = \frac{\partial^2 E_{tot}}{\partial u_{\mu,s,\alpha} \partial u_{\nu,s',\beta}} \quad (22)$$

Therefore, the procedure becomes:

$$\begin{aligned} C_{s\alpha,s'\beta}(\mathbf{q}_i) &= \sqrt{M_s M_{s'}} D_{s\alpha,s'\beta}(\mathbf{q}_i) \\ C_{s\alpha,s'\beta}(\mathbf{R}) &= \frac{1}{N_q} \sum_{i=1}^{N_q} C_{s\alpha,s'\beta}(\mathbf{q}_i) e^{i\mathbf{q}_i \mathbf{R}} \\ C_{s\alpha,s'\beta}(\mathbf{q}_j) &= \sum_{\mathbf{R}} C_{s\alpha,s'\beta}(\mathbf{R}) e^{-i\mathbf{q}_j \mathbf{R}}, \text{ for } j \neq i \end{aligned} \quad (23)$$

Notice that this procedure fails:

- when there are Kohn anomalies;
- in polar insulators;

Frozen phonons technique

The DFPT method relies on collective modes arising from linear response to a monochromatic perturbation. The **frozen phonon** technique instead keeps all atoms locked at their equilibrium position and compute phonons by local perturbations, i.e. by slightly moving atom by atom from their starting position.

The calculation of the dynamical matrix at a generic point of the Brillouin zone has the problem that a crystal with a small distortion (i.e. *froze-in*) loses the original periodicity unless $\mathbf{q} = 0$. Computation of IFC at any $\mathbf{q} \neq 0$ require a supercell big enough to recover periodicity.

The computational effort needed to determine the forces grows as the cube of the supercell size. Therefore frozen phonon method is quite slow from the computational point of view.