Introduction to density functional perturbation theory for lattice dynamics

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Let’s consider a periodic solid. We indicate with

$$R_I = R_\mu + d_s$$  \hspace{1cm} (1)

the equilibrium positions of the atoms. $R_\mu$ indicate the Bravais lattice vectors and $d_s$ the positions of the atoms in one unit cell ($s = 1, \ldots, N_{\text{at}}$).

We take $N$ unit cells with Born-von Karman periodic boundary conditions. $\Omega$ 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. $u_I(t)$ 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

\[ E_{\text{tot}}(R_I + u_I) \]  

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

\[
E_{\text{tot}}(R_I + u_I) = E_{\text{tot}}(R_I) + \sum_{l\alpha} \frac{\partial E_{\text{tot}}}{\partial u_{l\alpha}} u_{l\alpha} + \frac{1}{2} \sum_{l\alpha, J\beta} \frac{\partial^2 E_{\text{tot}}}{\partial u_{l\alpha} \partial u_{J\beta}} u_{l\alpha} u_{J\beta} + \ldots
\]

where the derivatives are calculated at \(u_I = 0\) and \(\alpha\) and \(\beta\) indicate the three cartesian coordinates.
Equations of motion

At equilibrium $\frac{\partial E_{tot}}{\partial u_{l\alpha}} = 0$, so the Hamiltonian of the ions becomes:

$$H = \sum_{l\alpha} \frac{P_{l\alpha}^2}{2M_l} + \frac{1}{2} \sum_{l\alpha,J\beta} \frac{\partial^2 E_{tot}}{\partial u_{l\alpha} \partial u_{J\beta}} u_{l\alpha} u_{J\beta}$$

(4)

where $P_l$ are the momenta of the nuclei and $M_l$ their masses. The classical motion of the nuclei is given by the $N \times 3 \times N_{at}$ functions $u_{l\alpha}(t)$. These functions are the solutions of the Hamilton equations:

$$\dot{u}_{l\alpha} = \frac{\partial H}{\partial P_{l\alpha}}$$

$$\dot{P}_{l\alpha} = -\frac{\partial H}{\partial u_{l\alpha}}$$

(5)
Equations of motion-II

With our Hamiltonian:

\[ \dot{u}_{l\alpha} = \frac{P_{l\alpha}}{M_l} \]
\[ \dot{P}_{l\alpha} = -\sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial u_{l\alpha} \partial u_{J\beta}} u_{J\beta} \]  

or:

\[ M_l \ddot{u}_{l\alpha} = -\sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial u_{l\alpha} \partial u_{J\beta}} u_{J\beta} \]
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:

$$u_{\mu s\alpha}(t) = \frac{1}{\sqrt{M_s}} u_{s\alpha}(\mathbf{q}) e^{i(\mathbf{qR}_\mu - \omega q t)}$$

(8)

where the time dependence is given by a simple exponential $e^{i\omega q t}$ 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 $\mathbf{R}_\mu = 0$: $\frac{1}{\sqrt{M_s}} u_{s\alpha}(\mathbf{q})$. 
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 $u_{s\alpha}(q)$:

$$
\omega_q^2 u_{s\alpha}(q) = \sum_{s' \beta} D_{s\alpha s' \beta}(q) u_{s' \beta}(q)
$$

(9)

where:

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

(10)

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

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

(11)

where \( \rho(r) \) is the density of the electron gas:

\[ \rho(r) = \sum_i |\psi_i(r)|^2 \]  

(12)

and \( |\psi_i\rangle \) are the solution of the Kohn and Sham equations. \( E_H \) is the Hartree energy, \( E_{\text{xc}} \) is the exchange and correlation energy and \( U_{\text{II}} \) 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:

\[ \frac{\partial E_{\text{tot}}}{\partial \lambda} = \int \frac{\partial V_{\text{loc}}(r)}{\partial \lambda} \rho(r) d^3 r + \frac{\partial U_{\text{II}}}{\partial \lambda} \]  

(13)
Deriving with respect to a second parameter $\mu$:

\[
\frac{\partial^2 E_{\text{tot}}}{\partial \mu \partial \lambda} = \int \frac{\partial^2 V_{\text{loc}}(r)}{\partial \mu \partial \lambda} \rho(r) d^3 r + \frac{\partial^2 U_{\text{II}}}{\partial \mu \partial \lambda} + \int \frac{\partial V_{\text{loc}}(r)}{\partial \lambda} \frac{\partial \rho(r)}{\partial \mu} d^3 r \tag{14}
\]

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

\[
\frac{\partial \rho(r)}{\partial \mu} = \sum_i \frac{\partial \psi_i^*(r)}{\partial \mu} \psi_i(r) + \psi_i^*(r) \frac{\partial \psi_i(r)}{\partial \mu} \tag{15}
\]

To fix the ideas we can think that $\lambda = u_{\mu s\alpha}$ and $\mu = u_{\nu s'\beta}$.
The wavefunctions obey the following equation:

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

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

\[
V_{KS}(\mathbf{r}, \mu) = V_{KS}(\mathbf{r}, \mu = 0) + \mu \frac{\partial V_{KS}(\mathbf{r})}{\partial \mu} + \ldots
\]

\[
\psi_i(\mathbf{r}, \mu) = \psi_i(\mathbf{r}, \mu = 0) + \mu \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} + \ldots
\]

\[
\varepsilon_i(\mu) = \varepsilon_i(\mu = 0) + \mu \frac{\partial \varepsilon_i}{\partial \mu} + \ldots \tag{17}
\]
Inserting these equations and keeping only the first order in $\mu$ we obtain:

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

where:

\[
\frac{\partial V_{KS}}{\partial \mu} = \frac{\partial V_{loc}}{\partial \mu} + \frac{\partial V_{H}}{\partial \mu} + \frac{\partial V_{xc}}{\partial \mu} \quad \text{and}
\]

\[
\frac{\partial V_{H}}{\partial \mu} = \int \frac{1}{|r - r'|} \frac{\partial \rho(r')}{\partial \mu} \text{d}^3 r' \\
\frac{\partial V_{xc}}{\partial \mu} = \frac{dV_{xc}}{d\rho} \frac{\partial \rho(r)}{\partial \mu} \tag{19}
\]

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:

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

$$+ \sum_i P_v \frac{\partial \psi_i^*(r)}{\partial \mu} \psi_i(r) + \psi_i^*(r) P_v \frac{\partial \psi_i(r)}{\partial \mu}$$

(20)

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

$$+ \sum_{ij} \psi_j^*(r) \psi_i(r) \left( \langle \frac{\partial \psi_i}{\partial \mu} | \psi_j \rangle + \langle \psi_i | \frac{\partial \psi_j}{\partial \mu} \rangle \right)$$

(21)
Therefore we can solve the self-consistent linear system:

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

where

\[
\frac{\partial V_{KS}}{\partial \mu} = \frac{\partial V_{loc}}{\partial \mu} + \frac{\partial V_H}{\partial \mu} + \frac{\partial V_{xc}}{\partial \mu} \tag{23}
\]

and

\[
\frac{\partial \rho(r)}{\partial \mu} = \sum_i P_c \frac{\partial \psi^*_i(r)}{\partial \mu} \psi_i(r) + \psi^*_i(r) P_c \frac{\partial \psi_i(r)}{\partial \mu} \tag{24}
\]
The program `ph.x` solves this self-consistent linear system for $3 \times N_{\text{at}}$ perturbations at a fixed vector $q$. With $\frac{\partial \rho(r)}{\partial \mu}$ for all the perturbations it calculates the dynamical matrix

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

at the given $q$. Diagonalizing this matrix we obtain $3 \times N_{\text{at}}$ frequencies $\omega_q$. By repeating this procedure for several $q$ we could plot $\omega_q$ as a function of $q$ 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 $q$. 
The dynamical matrix of the solid:

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

(26)

is a periodic function of \( \mathbf{q} \) with \( D_{\alpha\alpha'}^{\beta\beta'}(\mathbf{q} + \mathbf{G}) = D_{\alpha\alpha'}^{\beta\beta'}(\mathbf{q}) \) for any reciprocal lattice vector \( \mathbf{G} \). Moreover, since in a solid all Bravais lattice points are equivalent, it does not depend on \( \mu \). Eq.26 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:

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

(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 $\mathbf{R}_\nu$ neighbors of $\mathbf{R}_\mu$. The code $\texttt{q2r.x}$ 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).

\[
f(x) = \sum_n c_n e^{i k_n x}
\]  

(28)

where the coefficients of the expansion are:

\[
c_n = \frac{1}{a} \int_0^a f(x) e^{-i k_n x} \, dx
\]  

(29)

In general, if \( f(x) \) is a sufficiently smooth function, \( c_n \to 0 \) 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 \( j = 0, \ldots, N - 1 \),
then we can calculate:

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

(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

\[ f(x) = \sum_{n=-N/2}^{N/2} \tilde{c}_n e^{iknx} \]  

(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 \( \mathbf{R}_\nu \) neighbors of \( \mathbf{R}_\mu = 0 \). The program \texttt{matdyn.x} reads the interatomic force constants calculated by \texttt{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 $D_{s\alpha s'\beta}(q)$ is not a smooth function of $q$ 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 $q \to 0$. This case, however, can be dealt with by calculating the Born effective charges and the dielectric constant of the material.