Density functional perturbation theory for lattice dynamics

Andrea Dal Corso

SISSA and IOM-CNR
Trieste (Italy)
Outline

1. Crystal lattice dynamics: phonons
2. Density functional perturbation theory
3. Dynamical matrix at finite \( q \)
Description of a solid

Let’s consider a periodic solid. We indicate with

\[ \mathbf{R}_I = \mathbf{R}_\mu + \mathbf{d}_s \]

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. \( \Omega \) 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. \( \mathbf{u}_I(t) \) 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

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

this energy. The electrons are assumed to be in the ground state for each nuclear configuration.

If \(|u_I|\) is small, we can expand \(E_{tot}\) in a Taylor series with respect to \(u_I\). Within the *harmonic approximation*:

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

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

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

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

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

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

$$\dot{p}_{l\alpha} = -\frac{\partial H}{\partial u_{l\alpha}}.$$
Equations of motion-II

With our Hamiltonian:

\[ \dot{\mathbf{u}}_{I\alpha} = \frac{\mathbf{P}_{I\alpha}}{M_I}, \]

\[ \dot{\mathbf{P}}_{I\alpha} = -\sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta}, \]

or:

\[ M_I \ddot{\mathbf{u}}_{I\alpha} = -\sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta} \]
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:

$$u_{\mu s\alpha}(t) = \frac{A(\mathbf{q}, t)}{\sqrt{M_s}} \tilde{u}_{s\alpha}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}_\mu} = u_{s\alpha}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}_\mu}$$

where the amplitude $A(\mathbf{q}, t)$ of the displacement depends on time 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 $\mathbf{R}_\mu = 0$ ($A(\mathbf{q}, t) \tilde{u}_{s\alpha}(\mathbf{q})$) multiplying by a phase factor.
Characteristic of a phonon - 1

A $\Gamma$-point phonon has the same displacements in all unit cells ($q = 0$):

$$e^{iqR}$$

1 1 1 1 1 q=0

A zone border phonon with $q_{ZB} = G/2$, where $G$ is a reciprocal lattice vector, has displacements which repeat periodically every two unit cells:

$$e^{iqR}$$

1 -1 1 -1 1 q=$\frac{2\pi}{a} \frac{1}{2}$
Characteristic of a phonon - II

A phonon with \( q = q_{ZB}/2 \) has displacements which repeat every four unit cells:

\[ e^{i q R} \]

\[ \begin{array}{cccccc}
1 & i & -1 & -i & 1 \\
a & a & a & a & a \\
\end{array} \quad q = \frac{2\pi}{a} \frac{1}{4} \]

A phonon at a general wavevector \( q \) could be incommensurate with the underlying lattice:

\[ e^{i q R} \]

\[ \begin{array}{cccccc}
1 & e^{i\frac{\pi}{2}\sqrt{2}} & e^{i\pi\sqrt{2}} & e^{i\frac{3\pi}{2}\sqrt{2}} & e^{i2\pi\sqrt{2}} \\
a & a & a & a & a \\
\end{array} \quad q = \frac{2\pi\sqrt{2}}{a} \frac{1}{4} \]
The phonon solution-II

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

\[
\frac{d^2 A(q, t)}{dt^2} \tilde{u}_{s\alpha}(q) = -A(q, t) \sum_{s'\beta} D_{s\alpha s'\beta}(q) \tilde{u}_{s'\beta}(q),
\]

where:

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

is the dynamical matrix of the solid.
The phonon solution-III

Diagonalizing the dynamical matrix:

\[
\sum_{s', \beta} D_{s\alpha s' \beta}(q) e_{s' \beta}^\eta(q) = \omega_{q, \eta}^2 e_{s\alpha}^\eta(q),
\]

we find the eigenvalues \( \omega_{q, \eta}^2 \) and eigenvectors \( e_{s\alpha}^\eta(q) \). Setting \( \tilde{u}_{s\alpha}(q) = e_{s\alpha}^\eta(q) \) the equations of motion become:

\[
\frac{d^2 A_{\eta}(q, t)}{dt^2} = -\omega_{q, \eta}^2 A_{\eta}(q, t),
\]

which are (for each \( q \)) the equations of \( 3 \times N_{at} \) decoupled harmonic oscillators whose solutions are for instance:

\[
A_{\eta}(q, t) = A_{q}^\eta \sin \left( \omega_{q, \eta} t - \delta_{q}^\eta \right),
\]

where \( A_{q}^\eta \) and \( \delta_{q}^\eta \) depends on the initial conditions.
The final solution of the problem is:

$$u_{\mu s\alpha}(t) = \sum_{q,\eta} \frac{1}{\sqrt{M_s}} A_{q}^{\eta} \sin \left( \omega_{q,\eta} t - \delta_{q}^{\eta} \right) e_{s\alpha}^{\eta}(q) e^{i q \cdot R_{\mu}}.$$
Density functional theory

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

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

where \( \rho(\mathbf{r}) \) is the density of the electron gas (2 sums over spins):

\[ \rho(\mathbf{r}) = 2 \sum_i |\psi_i(\mathbf{r})|^2, \]

and \( |\psi_i\rangle \) are the wavefunctions. \( E_H \) is the Hartree energy:

\[ E_H = \frac{1}{2} \int d^3 r d^3 r' \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \]

\( E_{\text{xc}} \) 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:

\[
\frac{\partial E_{\text{tot}}}{\partial \lambda} = \int \frac{\partial V_{\text{loc}}(\mathbf{r})}{\partial \lambda} \rho(\mathbf{r}) d^3 \mathbf{r} + \frac{\partial U_{\text{II}}}{\partial \lambda},
\]
Deriving with respect to a second parameter $\mu$:

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

\[
+ \int \frac{\partial V_{loc}(\mathbf{r})}{\partial \lambda} \frac{\partial \rho(\mathbf{r})}{\partial \mu} d^3 r.
\]

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

\[
\frac{\partial \rho(\mathbf{r})}{\partial \mu} = 2 \sum_i \left[ \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mu} \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \right].
\]

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:

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

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:

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

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

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

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

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

\[
\frac{\partial V_H}{\partial \mu} = \int \frac{1}{|r - r'|} \frac{\partial \rho(r')}{\partial \mu} d^3 r',
\]

\[
\frac{\partial V_{xc}}{\partial \mu} = \frac{dV_{xc}}{d\rho} \frac{\partial \rho(r)}{\partial \mu}
\]

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:

$$\frac{\partial \rho(r)}{\partial \mu} = 2 \sum_i \left[ \left( P_c \frac{\partial \psi_i(r)}{\partial \mu} \right)^* \psi_i(r) + \psi_i^*(r) P_c \frac{\partial \psi_i(r)}{\partial \mu} \right]$$

$$+ 2 \sum_i \left[ \left( P_v \frac{\partial \psi_i(r)}{\partial \mu} \right)^* \psi_i(r) + \psi_i^*(r) P_v \frac{\partial \psi_i(r)}{\partial \mu} \right].$$

$$\frac{\partial \rho(r)}{\partial \mu} = 2 \sum_i \left[ \left( P_c \frac{\partial \psi_i(r)}{\partial \mu} \right)^* \psi_i(r) + \psi_i^*(r) P_c \frac{\partial \psi_i(r)}{\partial \mu} \right]$$

$$+ 2 \sum_{ij} \psi_j^*(r) \psi_i(r) \left( \langle \frac{\partial \psi_i}{\partial \mu} | \psi_j \rangle + \langle \psi_i | \frac{\partial \psi_j}{\partial \mu} \rangle \right).$$
Therefore we can solve the self-consistent linear system:

\[
\begin{bmatrix}
-\frac{1}{2} \nabla^2 + V_{KS}(\mathbf{r}) - \varepsilon_i
\end{bmatrix}
\begin{bmatrix}
P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu}
\end{bmatrix}
= -P_c \frac{\partial V_{KS}}{\partial \mu} \psi_i(\mathbf{r}),
\]

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

\[
\frac{\partial \rho(\mathbf{r})}{\partial \mu} = 2 \sum_i \left[ \left( P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \right)^* \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \right].
\]
Dynamical matrix at finite $q$ - I

The dynamical matrix is:

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

Inserting the expression of the second derivative of the total energy we have (neglecting the ion-ion term):

$$D_{s\alpha s'\beta}(q) = \frac{1}{\sqrt{M_sM_{s'}}} \left[ \frac{1}{N} \int_V d^3 r \sum_{\mu\nu} \left( e^{-i q R_\mu} \frac{\partial^2 V_{loc}(r)}{\partial u_{\mu s\alpha} \partial u_{\nu s'\beta}} e^{i q R_\nu} \right) \rho(r) \right] + D^{I,I}_{s\alpha s'\beta}(q).$$

We now show that these integrals can be done over $\Omega$. 
Dynamical matrix at finite $q$ - II

Defining:

$$\frac{\partial^2 V_{\text{loc}}(r)}{\partial u^*_s \partial u'_{s' \beta}(q)} = \sum_{\mu \nu} e^{-i q R_\mu} \frac{\partial^2 V_{\text{loc}}(r)}{\partial u_{\mu s} \partial u_{\nu s' \beta}(q)} e^{i q R_\nu}$$

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

$$\frac{\partial \rho(r)}{\partial u_{s' \beta}(q)} = \sum_\nu \frac{\partial \rho(r)}{\partial u_{\nu s' \beta}} e^{i q R_\nu}$$

and show that $\frac{\partial \rho(r)}{\partial u_{s' \beta}(q)} = e^{i q r} \frac{\tilde{\rho}(r)}{\partial u_{s' \beta}(q)}$, where $\frac{\tilde{\rho}(r)}{\partial u_{s' \beta}(q)}$ is a lattice-periodic function.
In the same manner, by defining

$$\frac{\partial V_{loc}(r)}{\partial u_{s\alpha}(q)} = \sum_{\mu} \frac{\partial V_{loc}(r)}{\partial u_{\mu s\alpha}} e^{iqR_{\mu}}$$

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

$$D_{s\alpha s'\beta}(q) = \frac{1}{\sqrt{M_s M_{s'}}} \left[ \int_{\Omega} d^3r \frac{\partial^2 V_{loc}(r)}{\partial u_{s\alpha}^*(q) \partial u_{s'\beta}(q)} \rho(r) ight. + \int_{\Omega} d^3r \left( \frac{\partial \tilde{V}_{loc}(r)}{\partial u_{s\alpha}(q)} \right)^* \tilde{\rho}(r) \frac{\partial \tilde{\rho}(r)}{\partial u_{s'\beta}(q)} \left. + D_{s\alpha s'\beta}^{II}(q) \right].$$
Dynamical matrix at finite $q$ - IV

\[
\frac{\partial^2 V_{\text{loc}}(\mathbf{r})}{\partial u^*_{\alpha \sigma}(q) \partial u_{\beta s'}(q)} = \sum_{\mu \nu} e^{-i q R_{\mu}} \frac{\partial^2 V_{\text{loc}}(\mathbf{r})}{\partial u_{\mu s\alpha} \partial u_{\nu s' \beta}} e^{i q R_{\nu}}
\]

is a lattice-periodic function because the local potential can be written as

\[
V_{\text{loc}}(\mathbf{r}) = \sum_{\mu} \sum_{s} V_{\text{loc}}^s(\mathbf{r} - R_{\mu} - d_s - u_{\mu s}),
\]

and

\[
\frac{\partial^2 V_{\text{loc}}(\mathbf{r})}{\partial u_{\mu s\alpha} \partial u_{\nu s' \beta}}
\]

vanishes if $\mu \neq \nu$ or $s \neq s'$. Since $\mu = \nu$ the two phase factors cancel, and we remain with a lattice-periodic function:

\[
\frac{\partial^2 V_{\text{loc}}(\mathbf{r})}{\partial u^*_{\alpha \sigma}(q) \partial u_{\beta s'}(q)} = \delta_{s s'} \sum_{\mu} \frac{\partial^2 V_{\text{loc}}^s(\mathbf{r} - R_{\mu} - d_s - u_{\mu s})}{\partial u_{\mu s\alpha} \partial u_{\mu s \beta}} \bigg|_{\mathbf{u}=0}.
\]
In order to show that:

\[
\frac{\partial \rho(r)}{\partial u_{s'\beta}(q)} = \sum_{\nu} \frac{\partial \rho(r)}{\partial u_{\nu s'\beta}} e^{i q R_{\nu}} = e^{i qr} \tilde{\frac{\partial \rho(r)}{\partial u_{s'\beta}(q)}}
\]

where \( \tilde{\frac{\partial \rho(r)}{\partial u_{s'\beta}(q)}} \) is a lattice-periodic function, we can calculate the Fourier transform of \( \frac{\partial \rho(r)}{\partial u_{s'\beta}(q)} \) and show that it is different from zero only at vectors \( q + G \), where \( G \) is a reciprocal lattice vector. We have

\[
\frac{\partial \rho}{\partial u_{s'\beta}(q)}(k) = \frac{1}{V} \int_{V} d^3r \ e^{-ikr} \sum_{\nu} \frac{\partial \rho(r)}{\partial u_{\nu s'\beta}} e^{i q R_{\nu}}.
\]
Dynamical matrix at finite \( q \) - VI

Due to the translational invariance of the solid, if we displace the atom \( s' \) in the direction \( \beta \) in the cell \( \nu = 0 \) and probe the charge at the point \( r \), or we displace in the same direction the atom \( s' \) in the cell \( \nu \) and probe the charge at the point \( r + R_\nu \), we should find the same value. Therefore

\[
\frac{\partial \rho(r + R_\nu)}{\partial u_{\nu s' \beta}} = \frac{\partial \rho(r)}{\partial u_{0 s' \beta}}
\]

or, taking \( r = r' - R_\nu \), we have \( \frac{\partial \rho(r')}{\partial u_{\nu s' \beta}} = \frac{\partial \rho(r' - R_\nu)}{\partial u_{0 s' \beta}} \) which can be inserted in the expression of the Fourier transform to give:

\[
\frac{\partial \rho}{\partial u_{s' \beta}(q)}(k) = \frac{1}{V} \int_V d^3r \ e^{-ikr} \sum_\nu \frac{\partial \rho(r - R_\nu)}{\partial u_{0 s' \beta}} e^{iQ_\nu}.
\]
Changing variable in the integral setting $r' = r - R_\nu$, we have

$$\frac{\partial \rho}{\partial u_{s'\beta}(q)}(k) = \frac{1}{V} \int_V d^3 r' e^{-i k r'} \sum_\nu \frac{\partial \rho(r')}{\partial u_{0s'\beta}} e^{i(q-k)R_\nu}. $$

The sum over $\nu$: $\sum_\nu e^{i(q-k)R_\nu}$ gives $N$ if $k = q + G$ and $0$ otherwise. Hence $\frac{\partial \rho}{\partial u_{s'\beta}(q)}(k)$ is non-vanishing only at $k = q + G$. It follows that:

$$\frac{\partial \rho(r)}{\partial u_{s'\beta}(q)} = e^{i qr} \sum_G \frac{\partial \rho}{\partial u_{s'\beta}(q)}(q + G) e^{i Gr}$$

and the sum over $G$ gives a lattice-periodic function.
Properties of the wavefunctions: Bloch theorem

According to the Bloch theorem, the solution of the Kohn and Sham equations in a periodic potential $V_{KS}(r + R_{\mu}) = V_{KS}(r)$:

$$\left[ -\frac{1}{2} \nabla^2 + V_{KS}(r) \right] \psi_{kv}(r) = \epsilon_{kv} \psi_{kv}(r)$$

can be indexed by a $k$-vector in the first Brillouin zone and by a band index $v$, and:

$$\psi_{kv}(r + R_{\mu}) = e^{ikR_{\mu}} \psi_{kv}(r),$$

$$\psi_{kv}(r) = e^{ikr} u_{kv}(r),$$

where $u_{kv}(r)$ is a lattice-periodic function. By time reversal symmetry, we also have:

$$\psi_{-kv}(r) = \psi_{kv}(r).$$
Charge density response at finite $q$ - I

The lattice-periodic part of the induced charge density at finite $q$ can be calculated as follows. We have:

$$
\frac{\partial \rho(r)}{\partial u_{s'\beta}(q)} = 2 \sum_{k\nu} \left[ \left( P_c \sum_{\nu} \frac{\partial \psi_{k\nu}(r)}{\partial u_{\nu s'\beta}} e^{-i q R_\nu} \right)^* \psi_{k\nu}(r) \right. \\
+ \left. \psi_{k\nu}^{*}(r) P_c \left( \sum_{\nu} \frac{\partial \psi_{k\nu}(r)}{\partial u_{\nu s'\beta}} e^{i q R_\nu} \right) \right].
$$

Changing $k$ with $-k$ in the first term, using time reversal symmetry $\psi_{-k\nu}(r) = \psi_{k\nu}^{*}(r)$, and defining:

$$
\frac{\partial \psi_{k\nu}(r)}{\partial u_{s'\beta}(q)} = \sum_{\nu} \frac{\partial \psi_{k\nu}(r)}{\partial u_{\nu s'\beta}} e^{i q R_\nu},
$$
Charge density response at finite $\mathbf{q} - \text{II}$

we have:

$$
\frac{\partial \rho(\mathbf{r})}{\partial u_{s'\beta}(\mathbf{q})} = 4 \sum_{k\nu} \psi^*_{k\nu}(\mathbf{r}) P_c \frac{\partial \psi_{k\nu}(\mathbf{r})}{\partial u_{s'\beta}(\mathbf{q})}.
$$

We can now use the following identities to extract the periodic part of the induced charge density:

$$
\frac{\partial \psi_{k\nu}(\mathbf{r})}{\partial u_{s'\beta}(\mathbf{q})} = e^{i\mathbf{k}\mathbf{r}} \frac{\partial u_{k\nu}(\mathbf{r})}{\partial u_{s'\beta}(\mathbf{q})} = e^{i\mathbf{k}\mathbf{r}} \sum_{\nu} \frac{\partial u_{k\nu}(\mathbf{r})}{\partial u_{\nu s'\beta}} e^{i\mathbf{q}\mathbf{R}_\nu} = e^{i(k+\mathbf{q})\mathbf{r}} \frac{\tilde{\partial} u_{k\nu}(\mathbf{r})}{\partial u_{s'\beta}(\mathbf{q})},
$$

where $\frac{\tilde{\partial} u_{k\nu}(\mathbf{r})}{\partial u_{s'\beta}(\mathbf{q})}$ is a lattice-periodic function.
Charge density response at finite $q$ - III

The projector in the conduction band $P_c = 1 - P_v$ is:

$$
P_c = \sum_{k'c} \psi_{k'c}(r) \psi^*_{k'c}(r')
$$

$$
= \sum_{k'c} e^{ik'r} u_{k'c}(r) u^*_{k'c}(r') e^{-ik'r'}
$$

$$
= \sum_{k'} e^{ik'r} P_{k'} c e^{-ik'r'},
$$

but only the term $k' = k + q$ gives a non zero contribution when applied to $\frac{\partial \psi_{kv}(r)}{\partial u_{s'\beta}(q)}$. We have therefore:

$$
\frac{\partial \rho(r)}{\partial u_{s'\beta}(q)} = e^{iqr} 4 \sum_{kv} u^*_{kv}(r) P_{c+k+q} \frac{\tilde{u}_{kv}(r)}{\partial u_{s'\beta}(q)},
$$
so the lattice-periodic part of the induced charge density, written in terms of lattice-periodic functions is:

$$\frac{\tilde{\partial}\rho(r)}{\partial u_{s'\beta}(q)} = 4 \sum_{k\nu} u^*_{k\nu}(r) P^k_{c+q} \frac{\tilde{\partial}u_{k\nu}(r)}{\partial u_{s'\beta}(q)}.$$

Andrea Dal Corso  
Density functional perturbation theory
First-order derivative of the wavefunctions - 1

\[ \frac{\partial u_{k\nu}(r)}{\partial u_{s'\beta}(q)} \] is a lattice-periodic function which can be calculated with the following considerations. From first order perturbation theory we get, for each displacement \( u_{\nu s'\beta} \), the equation:

\[
\left[-\frac{1}{2} \nabla^2 + V_{KS}(r) - \epsilon_{k\nu} \right] P_c \frac{\partial \psi_{k\nu}(r)}{\partial u_{\nu s'\beta}} = -P_c \frac{\partial V_{KS}(r)}{\partial u_{\nu s'\beta}} \psi_{k\nu}(r).
\]

Multiplying every equation by \( e^{i\mathbf{q}\mathbf{R}_\nu} \) and summing on \( \nu \), we get:

\[
\left[-\frac{1}{2} \nabla^2 + V_{KS}(r) - \epsilon_{k\nu} \right] P_c \frac{\partial \psi_{k\nu}(r)}{\partial u_{s'\beta}(q)} = -P_c \frac{\partial V_{KS}(r)}{\partial u_{s'\beta}(q)} \psi_{k\nu}(r).
\]
First-order derivative of the wavefunctions - II

Using the translational invariance of the solid we can write

\[
\frac{\partial V_{KS}(r)}{\partial u_{s'\beta}(q)} = \sum_{\nu} \frac{\partial V_{KS}(r)}{\partial u_{\nu s'\beta}} e^{iqr_{\nu}} = e^{iqr} \tilde{\partial} V_{KS}(r) \frac{\partial u_{s'\beta}(q)}{\partial u_{s'\beta}(q)},
\]

where \(\tilde{\partial} V_{KS}(r)\) is a lattice-periodic function. The right-hand side of the linear system becomes:

\[
- e^{i(k+q)r} P_{c}^{k+q} \tilde{\partial} V_{KS}(r) \frac{\partial u_{s'\beta}(q)}{\partial u_{s'\beta}(q)} u_{k\nu}(r).
\]
First-order derivative of the wavefunctions - III

In the left-hand side we have

\[ P_c \sum_\nu \frac{\partial \psi_{k\nu}(r)}{\partial u_{\nu s'\beta}} e^{i q R_{\nu}} = e^{i(k+q)R} P_c^{k+q} \frac{\partial \tilde{u}_{k\nu}(r)}{\partial u_{s'\beta}(q)}, \]

and defining

\[ H^{k+q} = e^{-i(k+q)r} \left[ -\frac{1}{2} \nabla^2 + V_{KS}(r) \right] e^{i(k+q)r}, \]

we obtain the linear system:

\[ \left[ H^{k+q} - \varepsilon_{k\nu} \right] P_c^{k+q} \frac{\partial \tilde{u}_{k\nu}(r)}{\partial u_{s'\beta}(q)} = -P_c^{k+q} \frac{\partial V_{KS}(r)}{\partial u_{s'\beta}(q)} u_{k\nu}(r). \]
Linear response: the self-consistent potential - I

The lattice-periodic component of the self-consistent potential can be obtained with the same techniques seen above. We have:

\[
\frac{\partial V_{KS}(r)}{\partial u_{\nu s'\beta}} = \frac{\partial V_{loc}(r)}{\partial u_{\nu s'\beta}} + \int d^3 r' \frac{1}{|r - r'|} \frac{\partial \rho(r')}{\partial u_{\nu s'\beta}} + \frac{\partial V_{xc}}{\partial \rho} \frac{\partial \rho(r)}{\partial u_{\nu s'\beta}}.
\]

Multiplying by \( e^{i q R_{\nu}} \) and summing on \( \nu \), we obtain:

\[
\frac{\partial V_{KS}(r)}{\partial u_{s'\beta}(q)} = \frac{\partial V_{loc}(r)}{\partial u_{s'\beta}(q)} + \int d^3 r' \frac{1}{|r - r'|} \frac{\partial \rho(r')}{\partial u_{s'\beta}(q)} + \frac{\partial V_{xc}}{\partial \rho} \frac{\partial \rho(r)}{\partial u_{s'\beta}(q)}.
\]
Linear response: the self-consistent potential - II

Keeping only the lattice periodic parts gives:

$$e^{iqr} \frac{\partial \tilde{V}_{KS}(r)}{\partial u_{s' \beta}(q)} = e^{iqr} \frac{\partial \tilde{V}_{loc}(r)}{\partial u_{s' \beta}(q)} + \int d^3 r' \frac{1}{|r - r'|} e^{iqr'} \frac{\partial \tilde{\rho}(r')}{\partial u_{s' \beta}(q)}$$

$$+ \frac{\partial V_{xc}(r)}{\partial \rho} e^{iqr} \frac{\partial \tilde{\rho}(r)}{\partial u_{s' \beta}(q)},$$

or equivalently:

$$\frac{\partial \tilde{V}_{KS}(r)}{\partial u_{s' \beta}(q)} = \frac{\partial \tilde{V}_{loc}(r)}{\partial u_{s' \beta}(q)} + \int d^3 r' \frac{1}{|r - r'|} e^{iq(r' - r)} \frac{\partial \tilde{\rho}(r')}{\partial u_{s' \beta}(q)}$$

$$+ \frac{\partial V_{xc}(r)}{\partial \rho} \frac{\partial \tilde{\rho}(r)}{\partial u_{s' \beta}(q)}.$$
Bibliography


