Density functional perturbation theory for lattice dynamics

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Outline

1. Crystal lattice dynamics: phonons
2. Density functional perturbation theory
3. Dynamical matrix at finite $q$
Let’s consider a periodic solid. We indicate with

$$R_I = R_\mu + d_s$$

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 ($s = 1, \ldots, N_{at}$). 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

\[ E_{\text{tot}}(\mathbf{R}_I + \mathbf{u}_I) \]

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 \( E_{\text{tot}} \) in a Taylor series with respect to \( \mathbf{u}_I \). Within the *harmonic approximation*:

\[
E_{\text{tot}}(\mathbf{R}_I + \mathbf{u}_I) = E_{\text{tot}}(\mathbf{R}_I) + \sum_{I\alpha} \frac{\partial E_{\text{tot}}}{\partial \mathbf{u}_{I\alpha}} \mathbf{u}_{I\alpha} + \frac{1}{2} \sum_{I\alpha, J\beta} \frac{\partial^2 E_{\text{tot}}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{I\alpha} \mathbf{u}_{J\beta} + \ldots
\]

where the derivatives are calculated at \( \mathbf{u}_I = 0 \) 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:

\[
\begin{align*}
\dot{u}_{l\alpha} &= \frac{\partial H}{\partial P_{l\alpha}} \\
\dot{P}_{l\alpha} &= -\frac{\partial H}{\partial u_{l\alpha}}
\end{align*}
\]
Equations of motion-II

With our Hamiltonian:

\[ \dot{u}_{I \alpha} = \frac{P_{I \alpha}}{M_I} \]

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

or:

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

$$u_{\mu s \alpha}(t) = \frac{1}{\sqrt{M_s}} \text{Re} \left[ u_{s \alpha}(\mathbf{q}) e^{i(q R_{\mu} - \omega q t)} \right]$$

where the time dependence is given by simple phase factors $e^{\pm i \omega q t}$ and the displacement of the atoms in each cell identified by the Bravais lattice $R_{\mu}$ can be obtained from the displacements of the atoms in one unit cell, for instance the one that corresponds to $R_{\mu} = 0$: $\frac{1}{\sqrt{M_s}} u_{s \alpha}(\mathbf{q})$. 
Characteristic of a phonon - I

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

\[
e^{iqR} \begin{pmatrix} 1 & 1 & 1 & 1 & 1 \end{pmatrix} \quad q = 0
\]

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:

\[
e^{iqR} \begin{pmatrix} 1 & -1 & 1 & -1 \end{pmatrix} \quad q = \frac{2\pi}{a} \frac{1}{2}
\]
A phonon with $\mathbf{q} = \mathbf{q}_{ZB}/2$ has displacements which repeat every four unit cells:

$$e^{i\mathbf{q}\mathbf{R}} 1 i -1 -i 1 \mathbf{q} = \frac{2\pi}{a} \frac{1}{4}$$

A phonon at a general wavevector $\mathbf{q}$ could be incommensurate with the underlying lattice:

$$e^{i\mathbf{q}\mathbf{R}} 1 e^{i\frac{\pi}{2}\sqrt{2}} e^{i\pi\sqrt{2}} e^{i\frac{3\pi}{2}\sqrt{2}} e^{i2\pi\sqrt{2}} \mathbf{q} = \frac{2\pi\sqrt{2}}{a} \frac{1}{4}$$
The phonon solution-II

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

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

where:

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

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

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

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

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

and \( |\psi_i\rangle \) are the solutions of the Kohn and Sham equations. \( E_H \) is the Hartree energy, \( E_{xc} \) 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:

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

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

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

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

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:

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

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

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

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

\[
\varepsilon_i(\mu) = \varepsilon_i(\mu = 0) + \frac{\partial \varepsilon_i}{\partial \mu} \mu + \ldots
\]
Inserting these equations and keeping only the 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

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

$$\frac{\partial V_{xc}}{\partial \mu} = \frac{d V_{xc}}{d \rho} \frac{\partial \rho(r)}{\partial \mu}$$

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:

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

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

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

The dynamical matrix is:

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

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

$$D_{s\alpha s'\beta}(q) = \frac{1}{\sqrt{M_s M_{s'}}} \left[ \frac{1}{N} \int_V d^3r \sum_{\mu \nu} \left( e^{-i q R_{\mu}} \frac{\partial^2 V_{\text{loc}}(r)}{\partial u_{\mu s \alpha} \partial u_{\nu s' \beta}} e^{i q R_{\nu}} \right) \rho(r) \right]$$

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

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

Defining:

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

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

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

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

\[ \frac{\partial V_{\text{loc}}(\mathbf{r})}{\partial \mathbf{u}_{\alpha}(\mathbf{q})} = \sum_{\mu} \frac{\partial V_{\text{loc}}(\mathbf{r})}{\partial \mathbf{u}_{\mu \alpha}(\mathbf{q})} e^{iq\mathbf{R}_{\mu}} \]

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

\[
D_{\alpha \beta}(q) = \frac{1}{\sqrt{M_{\alpha}M_{\beta}}} \left[ \int_{\Omega} d^3 r \frac{\partial^2 V_{\text{loc}}(\mathbf{r})}{\partial \mathbf{u}_{\alpha}(\mathbf{q}) \partial \mathbf{u}_{\beta}(\mathbf{q})} \rho(\mathbf{r}) \right. \\
+ \left. \int_{\Omega} d^3 r \left( \frac{\partial \tilde{V}_{\text{loc}}(\mathbf{r})}{\partial \mathbf{u}_{\alpha}(\mathbf{q})} \right)^* \frac{\partial \tilde{\rho}(\mathbf{r})}{\partial \mathbf{u}_{\beta}(\mathbf{q})} \right] + D_{\alpha \beta}^{I,I}(q). \]
Dynamical matrix at finite $q$ - IV

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

is a lattice-periodic function because the local potential can be written as $V_{loc}(r) = \sum_{\mu} \sum_s v^s_{loc}(r - R_\mu - d_s - u_{\mu s})$, and $\frac{\partial^2 V_{loc}(r)}{\partial u_{\mu s \alpha} \partial u_{\nu s' \beta}}$ 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:

\[ \frac{\partial^2 V_{loc}(r)}{\partial u_{s \alpha}^*(q) \partial u_{s' \beta}(q)} = \delta_{s, s'} \sum_{\mu} \frac{\partial^2 v^s_{loc}(r - R_\mu - d_s - u_{\mu s})}{\partial u_{\mu s \alpha} \partial u_{\mu s \beta}} \bigg|_{u=0} \]
Dynamical matrix at finite $q - V$

In order to show that:

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

where $\frac{\tilde{\partial \rho(r)}}{\partial u_{s'}^{\beta}(q)}$ 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

$$\frac{\partial \rho}{\partial u_{s'}^{\beta}(q)}(k) = \frac{1}{V} \int_{V} d^{3}r \ e^{-i\mathbf{kr}} \sum_{\nu} \frac{\partial \rho(r)}{\partial u_{\nu s'}^{\beta}} e^{i\mathbf{qR}_{\nu}}.$$
Dynamical matrix at finite $\mathbf{q}$ - 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 $\mathbf{r}$, or we displace in the same direction the atom $s'$ in the cell $\nu$ and probe the charge at the point $\mathbf{r} + \mathbf{R}_\nu$, we should find the same value. Therefore

$$
\frac{\partial \rho (\mathbf{r} + \mathbf{R}_\nu)}{\partial \mathbf{u}_{\nu s' \beta}} = \frac{\partial \rho (\mathbf{r})}{\partial \mathbf{u}_{0s' \beta}}
$$

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

$$
\frac{\partial \rho}{\partial \mathbf{u}_{s' \beta}}(\mathbf{q})(\mathbf{k}) = \frac{1}{V} \int_V d^3 \mathbf{r} \ e^{-i\mathbf{k}\mathbf{r}} \sum_\nu \frac{\partial \rho (\mathbf{r} - \mathbf{R}_\nu)}{\partial \mathbf{u}_{0s' \beta}} e^{i\mathbf{q}\mathbf{R}_\nu}.
$$
Dynamical matrix at finite \( q \) - VII

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:

\[
\frac{\partial \rho(r)}{\partial u_{s'\beta}(q)} = e^{iqr} \sum_G \frac{\partial \rho}{\partial u_{s'\beta}(q)}(q + G)e^{iGr}
\]

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 \( V_{KS}(r + R_\mu) = V_{KS}(r) \):

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

can be indexed by a \( k \)-vector in the first Brillouin zone and by a band index \( \nu \), and:

\[
\psi_{k\nu}(r + R_\mu) = e^{ikR_\mu} \psi_{k\nu}(r),
\]

\[
\psi_{k\nu}(r) = e^{ikr} u_{k\nu}(r),
\]

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

\[
\psi^*_{-k\nu}(r) = \psi_{k\nu}(r).
\]
Charge density response at finite $\mathbf{q}$ - I

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

\[
\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{s',\beta}(\mathbf{q})} = 2 \sum_{\mathbf{k}\nu} \left[ \left( P_c \sum_{\nu} \frac{\partial \psi_{\mathbf{k}\nu}(\mathbf{r})}{\partial \mathbf{u}_{\nu}s'\beta} e^{-i\mathbf{q}\mathbf{R}_\nu} \right)^* \psi_{\mathbf{k}\nu}(\mathbf{r}) \right. \\
+ \left. \psi^*_{\mathbf{k}\nu}(\mathbf{r}) P_c \left( \sum_{\nu} \frac{\partial \psi_{\mathbf{k}\nu}(\mathbf{r})}{\partial \mathbf{u}_{\nu}s'\beta} e^{i\mathbf{q}\mathbf{R}_\nu} \right) \right].
\]

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

\[
\frac{\partial \psi_{\mathbf{k}\nu}(\mathbf{r})}{\partial \mathbf{u}_{s',\beta}(\mathbf{q})} = \sum_{\nu} \frac{\partial \psi_{\mathbf{k}\nu}(\mathbf{r})}{\partial \mathbf{u}_{\nu}s'\beta} e^{i\mathbf{q}\mathbf{R}_\nu},
\]
Charge density response at finite $\mathbf{q}$ - II

we have:

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

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

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

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

where $\frac{\tilde{\partial} u_{\mathbf{k} \nu}(\mathbf{r})}{\partial u_{s' \beta}(\mathbf{q})}$ is a lattice-periodic function.
The projector in the conduction band $P_c = 1 - P_v$ is:

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

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

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

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:

\[
\tilde{\partial}_\beta \rho(r) \frac{\partial}{\partial u_{s'}(q)} = 4 \sum_{k\nu} u_{k\nu}^*(r) P^k_{c+q} \frac{\tilde{\partial} u_{k\nu}(r)}{\partial u_{s'}(q)}.
\]
First-order derivative of the wavefunctions - I

\( \tilde{u}_{kv}(r) \) 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:

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

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

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

Using the translational invariance of the solid we can write

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

where $\tilde{\frac{\partial V_{KS}(\mathbf{r})}{\partial u_{s'\beta}(\mathbf{q})}}$ is a lattice-periodic function. The right-hand side of the linear system becomes:

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

In the left-hand side we have

\[ P_c \sum_\nu \frac{\partial \psi_{kv}(\mathbf{r})}{\partial u_{\nu s' \beta}} e^{i\mathbf{q}_\nu} = e^{i(k+\mathbf{q})_r} P_c^{k+\mathbf{q}} \frac{\partial u_{kv}(\mathbf{r})}{\partial u_{s' \beta}(\mathbf{q})}, \]

and defining

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

we obtain the linear system:

\[ \left[ H^{k+\mathbf{q}} - \epsilon_{kv} \right] P_c^{k+\mathbf{q}} \frac{\partial u_{kv}(\mathbf{r})}{\partial u_{s' \beta}(\mathbf{q})} = -P_c^{k+\mathbf{q}} \frac{\partial V_{KS}(\mathbf{r})}{\partial u_{s' \beta}(\mathbf{q})} u_{kv}(\mathbf{r}). \]
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:

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

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

\[
\frac{\partial V_{KS}(\mathbf{r})}{\partial \mathbf{u}_{s' \beta}(\mathbf{q})} = \frac{\partial V_{loc}(\mathbf{r})}{\partial \mathbf{u}_{s' \beta}(\mathbf{q})} + \int d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial \rho(\mathbf{r}')}{\partial \mathbf{u}_{s' \beta}(\mathbf{q})} + \frac{\partial V_{xc}}{\partial \rho} \frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{s' \beta}(\mathbf{q})}.
\]
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Keeping only the lattice periodic parts gives:

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

or equivalently:

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

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Bibliography


