Density functional perturbation theory for lattice dynamics

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Outline

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

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

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*:

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

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:

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

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:

$$\begin{aligned} \dot{\mathbf{u}}_{I\alpha} &= \frac{\partial H}{\partial \mathbf{P}_{I\alpha}}, \\ \dot{\mathbf{P}}_{I\alpha} &= -\frac{\partial H}{\partial \mathbf{u}_{I\alpha}}. \end{aligned}$$

Equations of motion-II

With our Hamiltonian:

$$\begin{aligned} \dot{\mathbf{u}}_{I\alpha} &= \frac{\mathbf{P}_{I\alpha}}{M_I}, \\ \dot{\mathbf{P}}_{I\alpha} &= -\sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta}, \end{aligned}$$

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

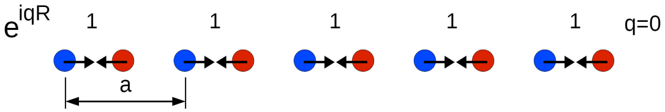
We can search the solution in the form of a phonon. Let's introduce a vector **q** in the first Brillouin zone. For each **q** we can write:

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

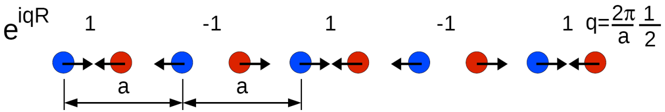
where the amplitude $A(\mathbf{q},t)$ of the displacement depends on time and the displacement of the atoms in each cell identified by the Bravais lattice $\mathbf{R}_\mu$ can be obtained from the displacements of the atoms in one unit cell, for instance the one that corresponds to $\mathbf{R}_\mu = 0$ ($\frac{A(\mathbf{q},t)}{\sqrt{M_s}}\tilde{\mathbf{u}}_{s\alpha}(\mathbf{q})$) multiplying by a phase factor.

Characteristic of a phonon - I

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

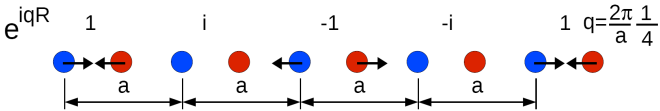


A zone border phonon with $\mathbf{q}_{ZB} = \mathbf{G}/2$, where $\mathbf{G}$ is a reciprocal lattice vector, has displacements which repeat periodically every two unit cells:

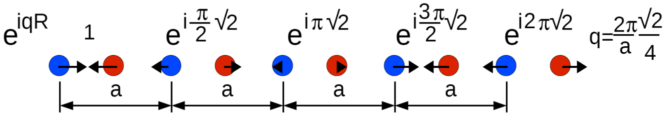


Characteristic of a phonon - II

A phonon with $\mathbf{q} = \mathbf{q}_{ZB}/2$ has displacements which repeat every four unit cells:



A phonon at a general wavevector **q** could be incommensurate with the underlying lattice:



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

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

where:

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

is the dynamical matrix of the solid.

The phonon solution-III

Diagonalizing the dynamical matrix:

$$\sum_{s'\beta} D_{s\alpha s'\beta}(\mathbf{q})\mathbf{e}^{\eta}_{s'\beta}(\mathbf{q}) = \omega^2_{\mathbf{q},\eta}\mathbf{e}^{\eta}_{s\alpha}(\mathbf{q}),$$

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

$$\frac{d^2 A^{\eta}(\mathbf{q},t)}{dt^2} = -\omega^2_{\mathbf{q},\eta} A^{\eta}(\mathbf{q},t),$$

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

$$A^{\eta}(\mathbf{q},t) = A^{\eta}_{\mathbf{q}} \sin\left(\omega_{\mathbf{q},\eta} t - \delta^{\eta}_{\mathbf{q}}\right),$$

where $A^{\eta}_{\mathbf{q}}$ and $\delta^{\eta}_{\mathbf{q}}$ depends on the initial conditions.

The phonon solution-IV

The final solution of the problem is:

$$\mathbf{u}_{\mu s\alpha}(t) = \sum_{\mathbf{q},\eta} \frac{1}{\sqrt{M_s}} A^{\eta}_{\mathbf{q}} \sin\left(\omega_{\mathbf{q},\eta} t - \delta^{\eta}_{\mathbf{q}}\right) \mathbf{e}^{\eta}_{s\alpha}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_{\mu}}.$$

Density functional theory

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

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

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:

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

E_{xc} is the exchange and correlation energy and U_{II} is the ion-ion interaction.

Hellmann-Feynman theorem

According to the Hellmann-Feynman theorem, the first order derivative of the ground state energy with respect to an external parameter is:

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

Deriving with respect to a second parameter μ:

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

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 $\lambda = \mathbf{u}_{\mu s\alpha}$ and $\mu = \mathbf{u}_{\nu s'\beta}$

The wavefunctions obey the following equation:

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

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:

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

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

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

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

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

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

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:

$$\begin{aligned} \frac{\partial \rho(\mathbf{r})}{\partial \mu} &= 2\sum_i \left[\left(P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \right)^* \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \right] \\ &+ 2\sum_i \left[\left(P_v \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \right)^* \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) P_v \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \right]. \end{aligned}$$

$$\begin{aligned} \frac{\partial \rho(\mathbf{r})}{\partial \mu} &= 2\sum_i \left[\left(P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \right)^* \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \right] \\ &+ 2\sum_{ij} \psi_j^*(\mathbf{r}) \psi_i(\mathbf{r}) \left(\langle \frac{\partial \psi_i}{\partial \mu} | \psi_j \rangle + \langle \psi_i | \frac{\partial \psi_j}{\partial \mu} \rangle \right). \end{aligned}$$

DFPT

Therefore we can solve the self-consistent linear system:

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

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:

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

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

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

We now show that these integrals can be done over Ω.

Dynamical matrix at finite q - II

Defining:

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

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

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

and show that $\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = e^{i\mathbf{q}\mathbf{r}} \frac{\partial \tilde{\rho}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}$, where $\frac{\partial \tilde{\rho}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}$ is a lattice-periodic function.

Dynamical matrix at finite **q** - III

In the same manner, by defining

$$\frac{\partial V_{loc}(\mathbf{r})}{\partial \mathbf{u}_{s\alpha}(\mathbf{q})} = \sum_{\mu} \frac{\partial V_{loc}(\mathbf{r})}{\partial \mathbf{u}_{\mu s\alpha}} e^{i\mathbf{q}\mathbf{R}_{\mu}}$$

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

$$\begin{aligned} D_{s\alpha s'\beta}(\mathbf{q}) &= \frac{1}{\sqrt{M_s M_{s'}}} \left[\int_{\Omega} d^3r \frac{\partial^2 V_{loc}(\mathbf{r})}{\partial \mathbf{u}^*_{s\alpha}(\mathbf{q}) \partial \mathbf{u}_{s'\beta}(\mathbf{q})} \rho(\mathbf{r}) \right. \\ &+ \left. \int_{\Omega} d^3r \left(\frac{\partial \tilde{V}_{loc}(\mathbf{r})}{\partial \mathbf{u}_{s\alpha}(\mathbf{q})} \right)^* \frac{\tilde{\partial} \rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} \right] + D^{I,I}_{s\alpha s'\beta}(\mathbf{q}). \end{aligned}$$

Dynamical matrix at finite **q** - IV

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

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

$$\frac{\partial^2 V_{loc}(\mathbf{r})}{\partial \mathbf{u}^*_{s\alpha}(\mathbf{q}) \partial \mathbf{u}_{s'\beta}(\mathbf{q})} = \delta_{s,s'} \sum_{\mu} \left. \frac{\partial^2 v^s_{loc}(\mathbf{r} - \mathbf{R}_\mu - \mathbf{d}_s - \mathbf{u}_{\mu s})}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\mu s\beta}} \right|_{\mathbf{u}=0}.$$

Dynamical matrix at finite **q** - V

In order to show that:

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

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

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

Dynamical matrix at finite **q** - VI

Due to the translational invariance of the solid, if we displace the atom s' in the direction β 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 ν and probe the charge at the point $\mathbf{r} + \mathbf{R}_\nu$, we should find the same value. Therefore

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

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

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

Dynamical matrix at finite **q** - VII

Changing variable in the integral setting $\mathbf{r}' = \mathbf{r} - \mathbf{R}_\nu$, we have

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

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

$$\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = e^{i\mathbf{q}\mathbf{r}} \sum_{\mathbf{G}} \frac{\partial \rho}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}(\mathbf{q}+\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}$$

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 $V_{KS}(\mathbf{r}+\mathbf{R}_\mu) = V_{KS}(\mathbf{r})$:

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

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

$$\psi_{\mathbf{k}v}(\mathbf{r}+\mathbf{R}_\mu) = e^{i\mathbf{k}\mathbf{R}_\mu}\psi_{\mathbf{k}v}(\mathbf{r}),$$

$$\psi_{\mathbf{k}v}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}u_{\mathbf{k}v}(\mathbf{r}),$$

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

$$\psi^*_{-\mathbf{k}v}(\mathbf{r}) = \psi_{\mathbf{k}v}(\mathbf{r}).$$

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:

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

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

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

Charge density response at finite **q** - II

we have:

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

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

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

where $\frac{\tilde{\partial} u_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}$ is a lattice-periodic function.

Charge density response at finite **q** - III

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

$$\begin{aligned} P_c &= \sum_{\mathbf{k}'c} \psi_{\mathbf{k}'c}(\mathbf{r})\psi^*_{\mathbf{k}'c}(\mathbf{r}') \\ &= \sum_{\mathbf{k}'c} e^{i\mathbf{k}'\mathbf{r}} u_{\mathbf{k}'c}(\mathbf{r}) u^*_{\mathbf{k}'c}(\mathbf{r}') e^{-i\mathbf{k}'\mathbf{r}'} \\ &= \sum_{\mathbf{k}'} e^{i\mathbf{k}'\mathbf{r}} P_c^{\mathbf{k}'} e^{-i\mathbf{k}'\mathbf{r}'}, \end{aligned}$$

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

$$\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = e^{i\mathbf{q}\mathbf{r}} 4 \sum_{\mathbf{k}v} u^*_{\mathbf{k}v}(\mathbf{r}) P_c^{\mathbf{k}+\mathbf{q}} \frac{\tilde{\partial} u_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})},$$

Charge density response at finite **q** - IV

so the lattice-periodic part of the induced charge density, written in terms of lattice-periodic functions is:

$$\frac{\partial\tilde{\rho}(\mathbf{r})}{\partial\mathbf{u}_{s'\beta}(\mathbf{q})} = 4\sum_{\mathbf{k}v} u^{*}_{\mathbf{k}v}(\mathbf{r}) P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial\tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial\mathbf{u}_{s'\beta}(\mathbf{q})}.$$

First-order derivative of the wavefunctions - I

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

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

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

$$\begin{aligned}\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) - \epsilon_{\mathbf{k}v}\right] \quad P_c \quad & \frac{\partial \psi_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} \\ = \quad & -P_c \frac{\partial V_{KS}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} \psi_{\mathbf{k}v}(\mathbf{r}).\end{aligned}$$

First-order derivative of the wavefunctions - II

Using the translational invariance of the solid we can write

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

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

$$-e^{i(\mathbf{k}+\mathbf{q})\mathbf{r}} P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial \tilde{V}_{KS}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} u_{\mathbf{k}v}(\mathbf{r}).$$

First-order derivative of the wavefunctions - III

In the left-hand side we have

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

and defining

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

we obtain the linear system:

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

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 $e^{i\mathbf{q}\mathbf{R}_\nu}$ and summing on ν, we obtain:

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

Linear response: the self-consistent potential - II

Keeping only the lattice periodic parts gives:

$$e^{i\mathbf{qr}}\frac{\partial \tilde{V}_{KS}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = e^{i\mathbf{qr}}\frac{\partial \tilde{V}_{loc}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} + \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|} e^{i\mathbf{qr}'} \frac{\tilde{\partial}\rho(\mathbf{r}')}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} + \frac{\partial V_{xc}}{\partial \rho} e^{i\mathbf{qr}} \frac{\tilde{\partial}\rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})},$$

or equivalently:

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

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