Density functional perturbation theory II: phonon dispersions

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Outline

A periodic solid

We study a periodic solid indicating with

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

the equilibrium positions of the atoms. $\mathbf{R}_\mu$ label 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. 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.

A phonon

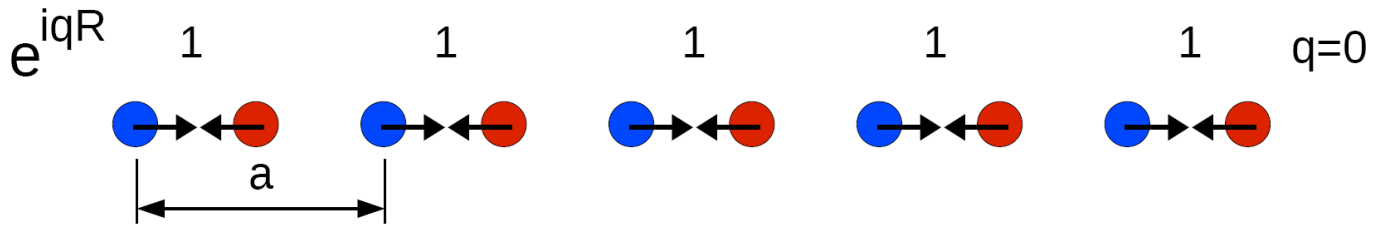
In a phonon of wave-vector **q** the displacement of the atom $I = (\mu, s)$ is:

$$\mathbf{u}_{\mu s\alpha}(t) = \mathrm{Re}\left(\frac{1}{\sqrt{M_s}}\mathbf{u}_{s\alpha}(\mathbf{q})e^{i(\mathbf{q}\mathbf{R}_\mu - \omega_\mathbf{q} t)}\right),$$

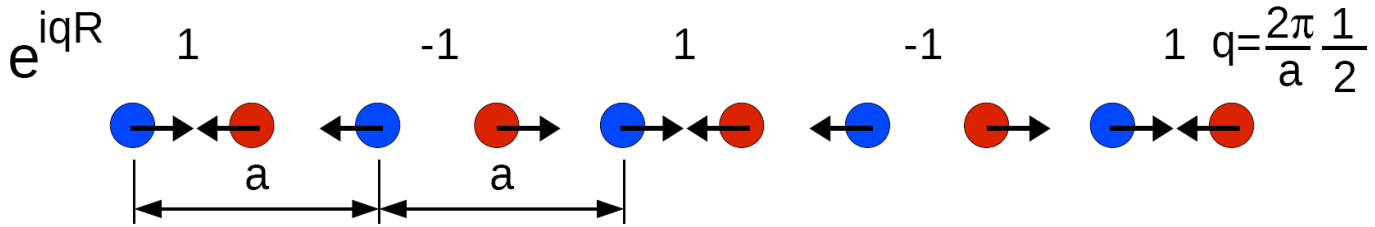
where the time dependence is given by a complex phase $e^{\pm i\omega_\mathbf{q} t}$ and α indicates the cartesian coodinate. The displacements of the atoms in a cell identified by the Bravais lattice $\mathbf{R}_\mu$ can be obtained from the displacements of the atoms in a chosen unit cell, for instance the one identified by $\mathbf{R}_\mu = 0$: $\frac{1}{\sqrt{M_s}}\mathbf{u}_{s\alpha}(\mathbf{q})$.

Characteristic of a phonon - I

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

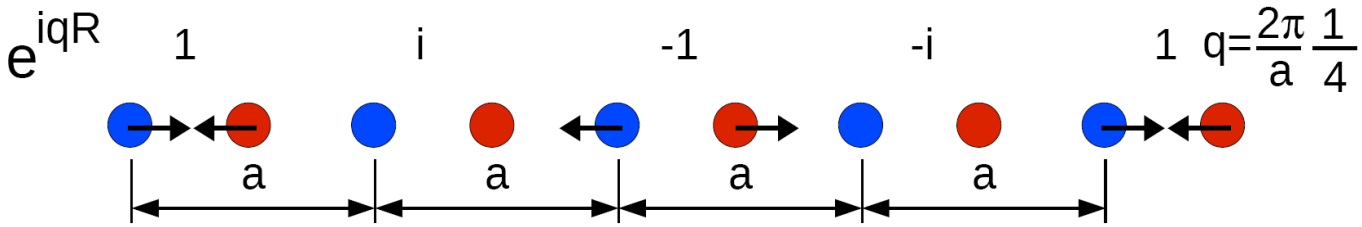


A zone border phonon with $\mathbf{q}_{ZB} = \mathbf{G}/2$, where **G** is a reciprocal lattice vector, has displacements which repeat periodically every two unit cells:

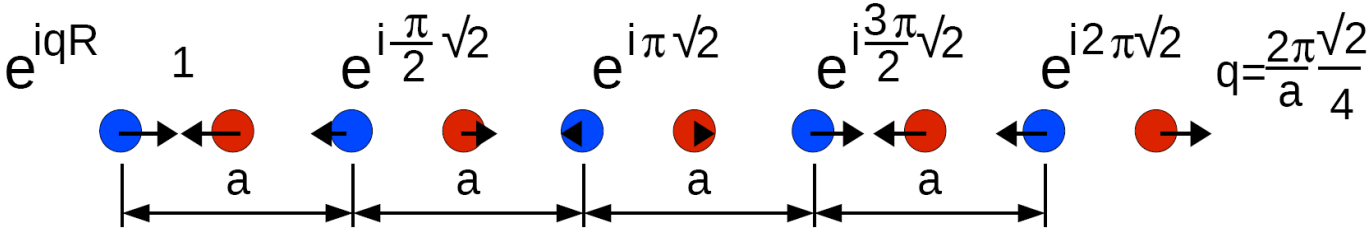


Characteristic of a phonon - II

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:



Dynamical matrix at finite **q** - I

The dynamical matrix is:

$$D_{s\alpha s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} e^{-i\mathbf{q}\mathbf{R}_\mu} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}} \bigg|_{\mathbf{u}=0} e^{i\mathbf{q}\mathbf{R}_\nu}.$$

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

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

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

Dynamical matrix at finite **q** - II

Defining:

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

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

$$\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = \frac{1}{\sqrt{M_{s'}}} \sum_{\nu} \frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}\mathbf{R}_\nu}$$

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

Dynamical matrix at finite **q** - III

In the same manner, by defining

$$\left(\frac{\partial V_{loc}(\mathbf{r})}{\partial \mathbf{u}_{s\alpha}(\mathbf{q})}\right)^* = \frac{1}{\sqrt{M_s}} \sum_{\mu} e^{-i\mathbf{q}\mathbf{R}_\mu} \frac{\partial V_{loc}(\mathbf{r})}{\partial \mathbf{u}_{\mu s\alpha}}$$

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:

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

Dynamical matrix at finite **q** - IV

$$\frac{\partial^2 V_{loc}(\mathbf{r})}{\partial \mathbf{u}^*_{s\alpha}(\mathbf{q}) \partial \mathbf{u}_{s'\beta}(\mathbf{q})} = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\mu\nu} e^{-i\mathbf{q}\mathbf{R}_\mu} \frac{\partial^2 V_{loc}(\mathbf{r})}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}} \bigg|_{\mathbf{u}=0} e^{i\mathbf{q}\mathbf{R}_\nu}$$

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 simplify, and we remain with a lattice-periodic function:

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

Dynamical matrix at finite **q** - V

In order to show that:

$$\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = \frac{1}{\sqrt{M_{s'}}} \sum_{\nu} \frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}\mathbf{R}_\nu} = e^{i\mathbf{q}\mathbf{r}} \frac{\partial \tilde{\rho}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}$$

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

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

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 $\mathbf{r}$, 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:

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

Dynamical matrix at finite **q** - VII

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

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

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:

$$\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = \frac{1}{\sqrt{M_{s'}}} \sum_{\mathbf{k}v} \left[P_c \left(\sum_{\nu} \frac{\partial \psi^*_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}\mathbf{R}_\nu} \right) \psi_{\mathbf{k}v}(\mathbf{r}) + \psi^*_{\mathbf{k}v}(\mathbf{r}) P_c \left(\sum_{\nu} \frac{\partial \psi_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}\mathbf{R}_\nu} \right) \right].$$

Changing $\mathbf{k}$ 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:

$$\frac{\partial \psi_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = \frac{1}{\sqrt{M_{s'}}} \sum_{\nu} \frac{\partial \psi_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}\mathbf{R}_\nu},$$

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

we have:

$$\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = 2 \sum_{\mathbf{k}v} \psi^*_{\mathbf{k}v}(\mathbf{r}) P_c \frac{\partial \psi_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}.$$

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

$$\begin{aligned} \frac{\partial \psi_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} &= e^{i\mathbf{k}\mathbf{r}} \frac{\partial u_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = e^{i\mathbf{k}\mathbf{r}} \frac{1}{\sqrt{M_{s'}}} \sum_{\nu} \frac{\partial u_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}\mathbf{R}_\nu} \\ &= e^{i(\mathbf{k}+\mathbf{q})\mathbf{r}} \frac{\tilde{\partial} u_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}, \end{aligned}$$

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:

$$\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = e^{i\mathbf{q}\mathbf{r}} 2 \sum_{\mathbf{k}v} u^*_{\mathbf{k}v}(\mathbf{r}) P_c^{\mathbf{k}+\mathbf{q}} \frac{\tilde{\partial} u_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})},$$

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:

$$\frac{\tilde{\partial}\rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = 2\sum_{\mathbf{k}v} u^*_{\mathbf{k}v}(\mathbf{r}) P_c^{\mathbf{k}+\mathbf{q}} \frac{\tilde{\partial} u_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}.$$

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 $\frac{1}{\sqrt{M_{s'}}} e^{i\mathbf{q}\mathbf{R}_\nu}$ and summing on ν, we get:

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

First-order derivative of the wavefunctions - II

Using the translational invariance of the solid we can write

$$\frac{\partial V_{KS}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})} = \frac{1}{\sqrt{M_{s'}}} \sum_{\nu} \frac{\partial V_{KS}(\mathbf{r})}{\partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}\mathbf{R}_\nu} = e^{i\mathbf{q}\mathbf{r}} \frac{\partial \tilde{V}_{KS}(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})},$$

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

$$P_c \frac{1}{\sqrt{M_{s'}}} \sum_{\nu} \frac{\partial \psi_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{\nu s' \beta}} e^{i\mathbf{q}\mathbf{R}_\nu} = e^{i(\mathbf{k}+\mathbf{q})\mathbf{r}} P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial \tilde{u}_{\mathbf{k}v}(\mathbf{r})}{\partial \mathbf{u}_{s' \beta}(\mathbf{q})},$$

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:

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

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:

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

Multiplying by $\frac{1}{\sqrt{M_{s'}}} e^{i\mathbf{q}\mathbf{R}_\nu}$ and adding, we obtain:

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

Linear response: the self-consistent potential - II

Keeping only the lattice periodic parts gives:

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

or equivalently:

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

`ph.x`

The program `ph.x` solves the self-consistent linear system for $3 \times N_{at}$ perturbations at a fixed $\mathbf{q}$ vector. Having $\frac{\tilde{\partial}\rho(\mathbf{r})}{\partial \mathbf{u}_{s'\beta}(\mathbf{q})}$ for all the perturbations it can calculate the dynamical matrix $D_{s\alpha s'\beta}(\mathbf{q})$ at the given $\mathbf{q}$ which can be diagonalized to obtain $3 \times N_{at}$ frequencies $\omega_{\mathbf{q}}$. By repeating this procedure for several $\mathbf{q}$ we could plot $\omega_{\mathbf{q}}$ as a function of $\mathbf{q}$ 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 $\mathbf{q}$.

PHONON DISPERSIONS

The dynamical matrix of the solid:

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

is a periodic function of $\mathbf{q}$ with $D_{s\alpha s'\beta}(\mathbf{q}+\mathbf{G}) = D_{s\alpha s'\beta}(\mathbf{q})$ for any reciprocal lattice vector $\mathbf{G}$. Furthermore, due to the translational invariance of the solid it does not depend on μ. Eq.1 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:

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

DISCRETE FOURIER TRANSFORM - I

We can use the properties of the discrete Fourier transform and sample the integral in a uniform mesh of points **q**. This will give the inter-atomic force constants only for a certain range of values of $\mathbf{R}_\nu$ neighbors of $\mathbf{R}_\mu$.
In order to recall the main properties of the discrete Fourier transform, 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 points $k_n = \frac{2\pi}{a} n$, where n is an integer (positive, negative or zero).

$$f(x) = \sum_n c_n e^{ik_n x}$$

where the coefficients of the expansion are:

DISCRETE FOURIER TRANSFORM - II

$$c_n = \frac{1}{a}\int_0^a f(x)e^{-ik_n x}dx.$$

In general, if $f(x)$ is a sufficiently smooth function, $c_n \to 0$ at large n. Now suppose that we discretize $f(x)$ 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:

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

$\tilde{c}_n$ 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 $|n| \geq N/2$, $\tilde{c}_n$ is a good approximation of c_n for $|n| < N/2$ and the function

DISCRETE FOURIER TRANSFORM - III

$$f(x) = \sum_{n=-N/2}^{n=N/2} \tilde{c}_n e^{ik_n x}$$

is a good approximation of the function $f(x)$ also on the points x different from x_j. In three dimensions the discretization of Eq. 2 on a uniform mesh of $\mathbf{q}_i$ points is:

$$\frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s \alpha} \partial \mathbf{u}_{\nu s' \beta}} = \frac{1}{N_q} \sum_{i=1}^{N_q} C_{s\alpha s'\beta}(\mathbf{q}_i) e^{-i\mathbf{q}_i(\mathbf{R}_\nu - \mathbf{R}_\mu)}, \qquad (3)$$

where we defined $C_{s\alpha s'\beta}(\mathbf{q}) = \sqrt{M_s M_{s'}} D_{s\alpha s'\beta}(\mathbf{q})$. Since $\frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s \alpha} \partial \mathbf{u}_{\nu s' \beta}}$ depends only on the vector $\mathbf{R} = \mathbf{R}_\mu - \mathbf{R}_\nu$, we can call

q2r.x

$C_{s\alpha s'\beta}(\mathbf{R}) = \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}}$ and write the relationship:

$$C_{s\alpha s'\beta}(\mathbf{R}) = \frac{1}{N_q} \sum_{i=1}^{N_q} C_{s\alpha s'\beta}(\mathbf{q}_i) e^{i\mathbf{q}_i \mathbf{R}}.$$

The code `q2r.x` reads a set of dynamical matrices obtained for a uniform mesh of $\mathbf{q}_i$ points and calculates, using this equation, the inter-atomic force constants for some neighbors of the point $\mathbf{R} = 0$.

matdyn.x

If the dynamical matrix is a sufficiently smooth function of **q**, the inter-atomic force constants decay sufficiently rapidly in real space and we can use Eq. 1 limiting the sum over ν to the few neighbors of $\mathbf{R}_\mu$ for which we have calculated the interatomic force constants. With the present notation Eq. 1 becomes:

$$C_{s\alpha s'\beta}(\mathbf{q}) = \sum_{\mathbf{R}} C_{s\alpha s'\beta}(\mathbf{R}) e^{-i\mathbf{q}\mathbf{R}}, \tag{4}$$

a relationship that allows the interpolation of the dynamical matrix at arbitrary **q**, by a few interatomic force constants. The program `matdyn.x` reads the inter-atomic force constants calculated by `q2r.x` and calculates the dynamical matrices at an arbitrary **q** using this equation.

This procedure fails in two cases:

- In metals when there are Kohn anomalies. In this case $D_{s\alpha s'\beta}(\mathbf{q})$ is not a smooth function of $\mathbf{q}$ and the inter-atomic 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 $\mathbf{q} \to 0$. This case, however, can be dealt with by calculating the Born effective charges and the dielectric constant of the material.

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