

Secular equation (elementary solid state physics)

Let us consider a molecule and its normal mode for the lattice vibration. The secular equation provides a way to obtain the frequency ω and the displacement patterns U_τ^α for cartesian component α of atom τ :

$$\sum_{\tau',\beta} (C_{\tau\tau'}^{\alpha\beta} - M_\tau \omega^2 \delta_{\tau\tau'} \delta_{\alpha\beta}) U_{\tau'}^\beta = 0,$$

where $C_{\tau\tau'}^{\alpha\beta}$ is the inter-atomic force constant given by

$$C_{\tau\tau'}^{\alpha\beta} \equiv \frac{\partial^2 E}{\partial R_\tau^\alpha \partial R_{\tau'}^\beta} = -\frac{\partial F_{\alpha\tau}}{\partial R_{\tau'}^\beta}.$$

The secular equation for finite systems given above can be extended for crystals as

$$\sum_{\tau',\beta} (\tilde{C}_{\tau\tau'}^{\alpha\beta}(\mathbf{q}) - M_\tau \omega^2(\mathbf{q}) \delta_{\tau\tau'} \delta_{\alpha\beta}) U_{\tau'}^\beta(\mathbf{q}) = 0,$$

where \mathbf{q} is the wave vector.

Dynamical matrix

Here we describe the atomic position \mathbf{R}_I as a sum of the lattice vector \mathbf{R}_μ and the position the atom within a unicell \mathbf{d}_s , i.e. $\mathbf{R}_I = \mathbf{R}_\mu + \mathbf{d}_s$, following the convention of QE community; sorry for duplicate use of \mathbf{R} . Here s is the atomic species and μ is the index of the lattice vector. The atomic position is displaced coherently according to the wave vector \mathbf{q} as

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

The secular equation is

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

where D is the dynamical matrix obtained using the force constant as

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

Since the energy is given as a functional of the density, $\partial n(\mathbf{r}) / \partial \mathbf{u}_{\mu s \alpha}$ needs to be calculated; in this respect, DFT calculation is distinct from others.

Density functional perturbation theory

Now let us consider the associated change in the energy, which will be used to get the phonon dispersion curve. We will use the density functional perturbation theory (DFPT). DFPT is different from the conventional perturbation theory in that we take into account that all the quantities are functional of the density. The energy

$$E = \sum_i \langle \varphi_i | \hat{T} | \varphi_i \rangle + \int d^3r n(\mathbf{r}) V_{\text{loc}}(\mathbf{r}) + E_{\text{Hxc}}[n] + U_{\text{ion-ion}}$$

is changed through variation of the local potential and ion-ion interaction terms by

$$\frac{\partial E}{\partial \lambda} = \int d^3r n(\mathbf{r}) \frac{\partial V_{\text{loc}}}{\partial \lambda} + \frac{\partial U_{\text{ion-ion}}}{\partial \lambda},$$

where Hellmann-Feynman theorem was used. The second derivative is

$$\frac{\partial^2 E}{\partial \lambda \partial \mu} = \int d^3r n(\mathbf{r}) \frac{\partial^2 V_{\text{loc}}}{\partial \lambda \partial \mu} + \int d^3r \frac{\partial n(\mathbf{r})}{\partial \mu} \frac{\partial V_{\text{loc}}}{\partial \lambda} + \frac{\partial^2 U_{\text{ion-ion}}}{\partial \lambda \partial \mu}.$$

Therefore, we need the quantity, which is inherent to DFPT,

$$\frac{\partial n(\mathbf{r})}{\partial \mu} = \sum_{i \in \text{occ}} \left[\frac{\partial \varphi_i^*(\mathbf{r})}{\partial \mu} \varphi_i(\mathbf{r}) + \varphi_i^*(\mathbf{r}) \frac{\partial \varphi_i(\mathbf{r})}{\partial \mu} \right]$$

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

To take the derivative of KS orbital, we take derivative of the KS equation

$$[\hat{T} + V_{\text{eff}}(\mathbf{r})] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}),$$

so that we get

$$[\hat{T} + V_{\text{eff}}(\mathbf{r}) - \varepsilon_i] \frac{\partial \varphi_i(\mathbf{r})}{\partial \mu} = - \frac{\partial V_{\text{eff}}}{\partial \mu} \varphi_i(\mathbf{r}) + \frac{\partial \varepsilon_i}{\partial \mu} \varphi_i(\mathbf{r}),$$

where

$$\frac{\partial V_{\text{eff}}}{\partial \mu} = \frac{\partial V_{\text{loc}}}{\partial \mu} + \frac{\partial V_{\text{Hxc}}}{\partial \mu}$$

can be written with slightly more detailed expression

$$= \frac{\partial V_{\text{loc}}}{\partial \mu} + \int d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial n(\mathbf{r}')}{\partial \mu} + \frac{\partial V_{\text{xc}}}{\partial n} \frac{\partial n(\mathbf{r})}{\partial \mu}.$$

We notice that the derivative of the occupied KS orbitals can be decomposed into two spaces, the one spanned by occupied orbitals and the other spanned the unoccupied orbitals. For this purpose, we introduce the projection operators P_v and P_c , where

$$P_v = \sum_{i=1}^{\text{occ}} |\varphi_i\rangle \langle \varphi_i|$$

and $P_c = 1 - P_v$. With them, we can rewrite the derivative as

$$\begin{aligned} \frac{\partial n(\mathbf{r})}{\partial \mu} &= \sum_i P_c \frac{\partial \varphi_i^*(\mathbf{r})}{\partial \mu} \varphi_i(\mathbf{r}) + \varphi_i^*(\mathbf{r}) P_c \frac{\partial \varphi_i(\mathbf{r})}{\partial \mu} + \sum_{ij} \varphi_i(\mathbf{r}) \varphi_j^*(\mathbf{r}) \left(\int d^3r' \frac{\partial \varphi_i^*(\mathbf{r}')}{\partial \mu} \varphi_j(\mathbf{r}') \right) \\ &\quad + \varphi_i(\mathbf{r}) \varphi_j^*(\mathbf{r}) \left(\int d^3r' \frac{\partial \varphi_j(\mathbf{r}')}{\partial \mu} \varphi_i^*(\mathbf{r}') \right). \end{aligned}$$

Since the last two terms are zero because of the orthonormality of Ks orbitals,

$$= \sum_i P_c \frac{\partial \varphi_i^*(\mathbf{r})}{\partial \mu} \varphi_i(\mathbf{r}) + \varphi_i^*(\mathbf{r}) P_c \frac{\partial \varphi_i(\mathbf{r})}{\partial \mu}.$$

By applying $P_c \frac{\partial}{\partial \mu}$ to the KS equation from the left, we get, after some simplification,

$$[\hat{T} + V_{\text{eff}}(\mathbf{r}) - \varepsilon_i] P_c \frac{\partial \varphi_i(\mathbf{r})}{\partial \mu} = -P_c \frac{\partial V_{\text{eff}}}{\partial \mu} \varphi_i(\mathbf{r}).$$

This is the equation that we have to solve in DFPT. Therefore, we have to solve the self-consistent equations

$$\begin{cases} \frac{\partial n(\mathbf{r})}{\partial \mu} = \sum_i P_c \frac{\partial \varphi_i^*(\mathbf{r})}{\partial \mu} \varphi_i(\mathbf{r}) + \varphi_i^*(\mathbf{r}) P_c \frac{\partial \varphi_i(\mathbf{r})}{\partial \mu} \\ [\hat{T} + V_{\text{eff}}(\mathbf{r}) - \varepsilon_i] P_c \frac{\partial \varphi_i(\mathbf{r})}{\partial \mu} = -P_c \frac{\partial V_{\text{eff}}}{\partial \mu} \varphi_i(\mathbf{r}) \\ \frac{\partial V_{\text{eff}}}{\partial \mu} = \frac{\partial V_{\text{loc}}}{\partial \mu} + \int d^3 r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial n(\mathbf{r}')}{\partial \mu} + \frac{\partial V_{\text{xc}}}{\partial n} \frac{\partial n(\mathbf{r})}{\partial \mu} \end{cases}$$

The program ph.x of QE solves this equation for different $\mu = \mathbf{u}_{\nu\alpha}$ at fixed \mathbf{q} . The output is $D_{sas'\beta}(\mathbf{q})$.

Since the dynamical matrix D is periodic in reciprocal space as $D(\mathbf{q} + \mathbf{G}) = D(\mathbf{q})$, one can Fourier transform (discrete FT) this as

$$\frac{\Omega}{(2\pi)^3} \int d^3 q D_{sas'\beta}(\mathbf{q}) e^{-i\mathbf{q} \cdot (\mathbf{R}_\nu - \mathbf{R}_\mu)}.$$

This can be shown to be equal to the force constant

$$\frac{1}{\sqrt{M_s M_{s'}}} \frac{\partial^2 E}{\partial \mathbf{u}_{\mu\alpha} \partial \mathbf{u}_{\nu\beta}},$$

namely

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

With q2r.x of QE, one can transform the dynamical matrix obtained for a uniform mesh point for \mathbf{q} to the interatomic force constants.

When the dynamical matrix is smooth in the reciprocal space, we need small number of the pair $\{\mathbf{R}_\nu, \mathbf{R}_\mu\}$, with $|\mathbf{R}_\nu - \mathbf{R}_\mu| \leq R_{\text{cut}}$: The value is zero otherwise. Using the force constant thus obtained, one can use Fourier transformation to obtain the dynamical matrix $D_{sas'\beta}(\mathbf{q})$ in finer mesh points of \mathbf{q} . This Frouier technique allows one to reduce the computational time. The program matdyn.x of QE can be used to calculate the dynamical matrix using the force constant.