Introduction to the Theory of Lattice Vibrations and their Ab Initio Calculation

Lecture 4: Calculation of harmonic phonons with density-functional theory or other methods

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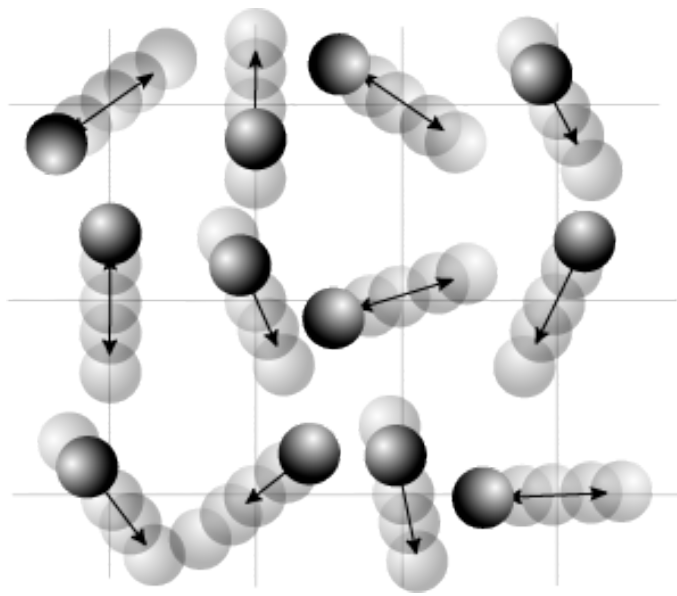

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Outline

The harmonic problem

- In order to obtain the phonon spectra we need to diagonalize the dynamical matrix
- In real space

$$\sum_b D_{ab} e^b_\mu = \omega^2_\mu e^a_\mu$$

with the dynamical matrix

$$D_{ab} = \frac{\overset{(2)}{\phi}_{ab}}{\sqrt{M_a M_b}}$$

- In reciprocal space

$$\sum_b D_{ab}(\boldsymbol{q}) e^b_\mu(\boldsymbol{q}) = \omega^2_\mu e^a_\mu(\boldsymbol{q})$$

with the dynamical matrix

$$D_{ab}(\boldsymbol{q}) = \sum_{\boldsymbol{T}} \frac{\overset{(2)}{\phi}_{ab}(\boldsymbol{T})}{\sqrt{M_a M_b}} e^{i\boldsymbol{q}\cdot\boldsymbol{T}}$$

- In order to get phonon frequencies we need to calculate the second-order force constants $\overset{(2)}{\phi}_{ab}$

Force-constants from DFT

- The calculation of the force constants require the calculation of second-derivatives of $V(\boldsymbol{R})$

$$\overset{(2)}{\phi}_{ab}(\boldsymbol{T}) = \left[\frac{\partial^2 V(\boldsymbol{R})}{\partial R_a(\boldsymbol{T})\partial R_b(0)}\right]_{\mathbf{R}=\boldsymbol{R}_0}$$

- There are two main approaches to obtain $\overset{(2)}{\phi}_{ab}(\boldsymbol{T})$ from DFT
  - **Finite displacements methods**
    Atoms are displaced from the equilibrium $\boldsymbol{R}_0$ position and the energies and/or forces are obtained with DFT to later calculate the force-constants taking numerical derivatives.
    These methods are valid also for empirical potentials
  - **Perturbative methods**
    Quantum mechanical perturbation theory is used to the change in the electronic density and wave functions, from which the force-constants can be calculated.
    Valid only for DFT approaches, not empirical potentials

Finite-displacements methods: Frozen phonon

- Let's assume we want to calculate the phonon frequency for phonon mode μ associated to a particular irrep for which we know the polarization vector $\boldsymbol{e}_\mu$
- We can move all the atoms according to the normal mode associated to it

$$u_a(Q_\mu) = \frac{e^a_\mu}{\sqrt{M_a}} Q_\mu$$

- The potential will be then parametrized as

$$V(Q_\mu) = \frac{1}{2} \sum_{ab} \overset{(2)}{\phi}_{ab} u_a(Q_\mu) u_b(Q_\mu) + \mathcal{O}(Q_\mu^3) = \frac{1}{2} \omega_\mu^2 Q_\mu^2 + \mathcal{O}(Q_\mu^3)$$

- Calculating the total energy as a function of Q_μ and taking the second derivative the phonon frequency can be obtained

$$\omega_\mu^2 = \left[\frac{d^2 V(Q_\mu)}{dQ_\mu^2} \right]_{Q_\mu = 0}$$

Finite-displacements methods: Frozen phonon

- In practice this is done in a supercell
- Let's assume we want to calculate the phonon frequency for phonon mode μ at $\boldsymbol{q}$ with polarization vector $\boldsymbol{e}_\mu(\boldsymbol{q})$
- The normal mode displacement in the is atoms of the crystal distort as

$$u_a(\boldsymbol{T}_a)(Q_\mu(\boldsymbol{q})) = \mathrm{Re}\left[e^{-i\boldsymbol{q}\cdot\boldsymbol{T}_a}\frac{\epsilon^a_\mu(\boldsymbol{q})}{\sqrt{M_s}}\right]Q_\mu(\boldsymbol{q})$$

- The $\boldsymbol{q}$ vector will determine the periodicity of the displacement pattern. If $\boldsymbol{a}^*$, $\boldsymbol{b}^*$, and $\boldsymbol{c}^*$ are reciprocal lattice vectors and

$$\boldsymbol{q} = \frac{(m_1-1)\boldsymbol{a}^*}{n_1} + \frac{(m_2-1)\boldsymbol{b}^*}{n_2} + \frac{(m3-1)\boldsymbol{c}^*}{n_3}, \quad m_i = \{1,\cdots,n_i\},$$

with n_1, n_2, and n_3 integers, then de displacement is commensurate in a $n_1 \times n_2 \times n_3$ supercell

- It can be shown that the total energy as a function of the normal mode $Q_\mu(\boldsymbol{q})$ is

$$V(Q_\mu(\boldsymbol{q})) = N\frac{1}{2}\omega^2_\mu(\boldsymbol{q})Q^2_\mu(\boldsymbol{q}),$$

thus,

$$\omega^2_\mu(\boldsymbol{q}) = \frac{d^2[V(Q_\mu(\boldsymbol{q}))/N]}{dQ_\mu(\boldsymbol{q})^2}$$

Finite-displacements methods: Frozen phonon

An example:

- Let's calculate the phonon frequency of the longitudinal (L) mode at X point of simple cubic Ca:

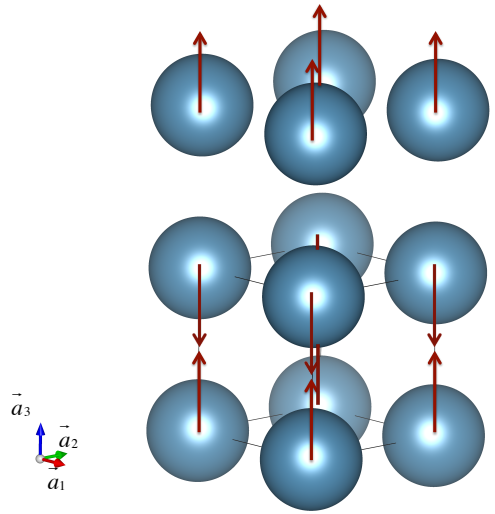
$$\begin{aligned} \boldsymbol{q}_X &= \boldsymbol{c}^*/2 \\ \boldsymbol{\epsilon}_L(\boldsymbol{q}_X) &= \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \end{aligned}$$

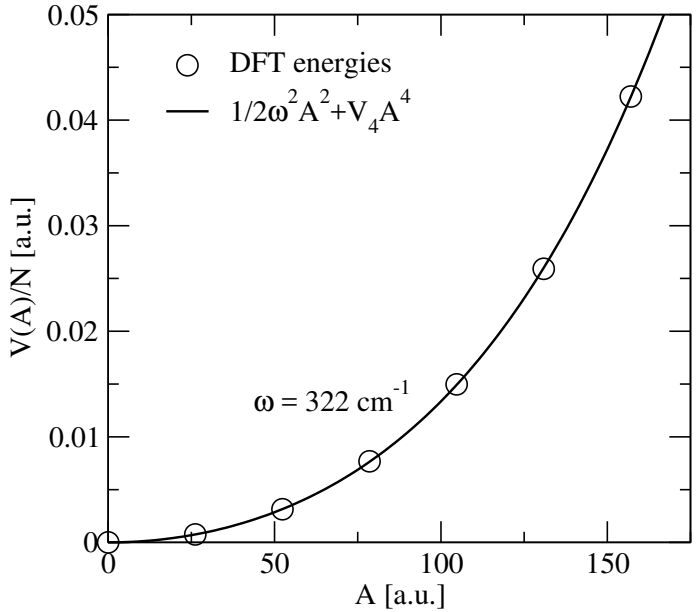
- We displace the atoms as

$$u^\alpha[L\boldsymbol{q}_X](\boldsymbol{T}) = e^{-i\boldsymbol{q}_X\cdot\boldsymbol{T}}\frac{\epsilon_L^\alpha(\boldsymbol{q}_X)}{\sqrt{M}}A$$

  and calculate the DFT energies as a function of A

- A $1\times1\times2$ supercell is enough to reproduce the pattern





Which are the problems of the frozen phonon approach? And benefits?

Finite-displacements methods: force-constants

- It is possible to directly obtain the force-constants matrix by calculating with DFT atomic forces in slightly distorted supercells
- In the harmonic approximation the force of an atom can be obtained from the force-constants as

$$f_a(\boldsymbol{T}_a) = -\sum_{b\boldsymbol{T}_b} \overset{(2)}{\phi}_{ab}(\boldsymbol{T}_a, \boldsymbol{T}_b) u_b(\boldsymbol{T}_b)$$

- Therefore, the force-constants are

$$\overset{(2)}{\phi}_{ab}(\boldsymbol{T}_a, \boldsymbol{T}_b) = -\frac{\partial f_a(\boldsymbol{T}_a)}{\partial u_b(\boldsymbol{T}_b)}$$

- Due to symmetries force constants can be generated by

$$\overset{(2)}{\phi}{}^{\beta_1\beta_2}_{s_1's_2'}(\boldsymbol{T}_1', \boldsymbol{T}_2') = \sum_{\alpha_1\alpha_2} S^{\beta_1\alpha_1} S^{\beta_2\alpha_2} \overset{(2)}{\phi}{}^{\alpha_1\alpha_2}_{s_1s_2}(\boldsymbol{T}_1, \boldsymbol{T}_2),$$

  which reduces the number of derivatives to be known
- As the force-constant only depend on $\boldsymbol{T} = \boldsymbol{T}_1 - \boldsymbol{T}_2$ it is sufficient to know

$$\overset{(2)}{\phi}_{ab}(\boldsymbol{T}) = -\frac{\partial f_a(\boldsymbol{T})}{\partial u_b(0)}$$

Finite-displacements methods: force-constants

- The idea is to calculate these derivatives by finite differences
- Take a supercell, displace one atom that belongs to the unit cell as $R_{b0}(0) + u_b(0)$, and calculate by DFT the forces on the atoms of the supercell. Then,

$$\overset{(2)}{\phi}_{ab}(\boldsymbol{T}) = -\frac{\partial f_a(\boldsymbol{T})}{\partial u_b(0)} = -\left[\frac{f_a(\boldsymbol{T}; R_{0b}(0) + u_b(0)) - f_a(\boldsymbol{T}; R_{0b}(0))}{u_b(0)}\right]$$

- Repeat the procedure for all the displacements needed to generate by symmetry all the force-constants for $\boldsymbol{T}_{sc}$ a lattice vector within the supercell
- Due to periodic boundary boundary conditions set by the supercell, the dynamical matrix can be calculated at any $\boldsymbol{q} \in 1BZ$ by Fourier transform

$$D_{ab}(\boldsymbol{q}) = \frac{1}{N_{sc}} \sum_{\boldsymbol{T}_{sc}} \frac{\overset{(2)}{\phi}_{ab}(\boldsymbol{T}_{sc})}{\sqrt{M_a} M_b} e^{i\boldsymbol{q}\cdot\boldsymbol{T}_{sc}},$$

  where the sum is limited to the N_{sc} $\boldsymbol{T}_{sc}$ vectors within the supercell
- The obtained dynamical matrix is correct if for a $n_1 \times n_2 \times n_3$ supercell

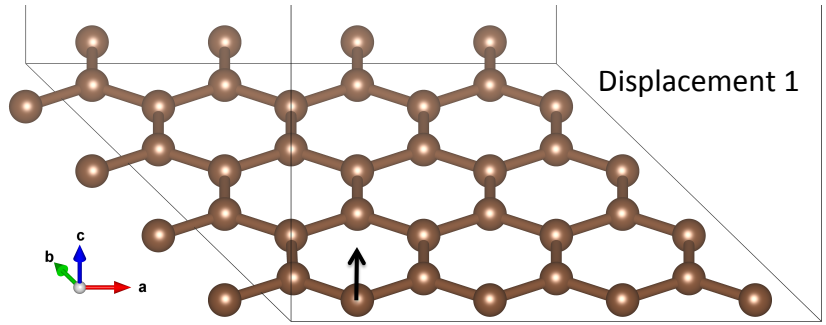
$$\boldsymbol{q} = \frac{(m_1 - 1)\mathbf{b}_1}{n_1} + \frac{(m_2 - 1)\mathbf{b}_2}{n_2} + \frac{(m3 - 1)\mathbf{b}_3}{n_3}, \quad m_i = \{1, \cdots, n_i\}.$$

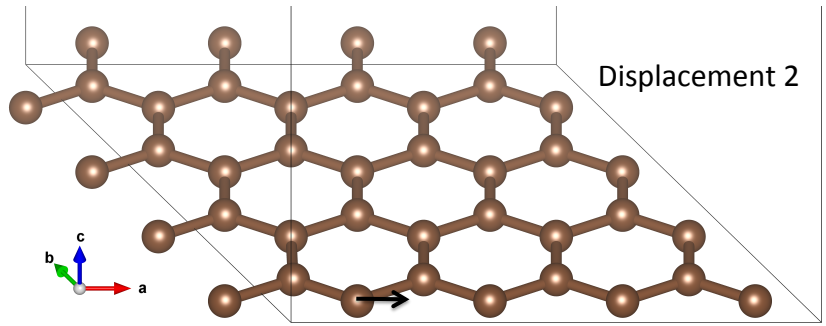
  If not $D(\boldsymbol{q})$ is approximated by the Fourier transform

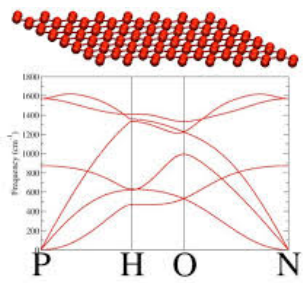
Finite-displacements methods: force-constants

An example:

- Force-constants for graphene in a $4 \times 4(\times 1)$ supercell
- Only two force calculations are needed to get the force-constants in the $4 \times 4(\times 1)$ supercell
- This method to calculate force-constants is implemented in many codes that can be used in conjunction with any DFT code:
  1. Calculate minimum distorsion patterns in the supercell
  2. Calculate the forces for these distorted structures with a DFT code
  3. Get the force-constants in the supercell







PHONOPY

Finite-displacements methods

Pros:

- Straightforwardly implemented in conjunction with any DFT code
- The frozen-phonon approach is very intuitive physically
- From the force-constants the dynamical matrix can be obtained at any $\boldsymbol{q}$ as long as the Fourier transform approximation works

Cons:

- Getting the exact dynamical matrix is limited to the $\boldsymbol{q}$'s commensurate with the supercell size
- If we want to calculate the phonon modes for a particular $\boldsymbol{q}$ point exactly, a huge (even infinite if the $\boldsymbol{q}$ is irrational) supercell might be needed
- Calculations using supercells in DFT are expensive

Is the choice of the displacement $u_b(0)$ relevant?

Perturbative methods

- Perturbative methods offer the way to calculate $D(\boldsymbol{q})$ for any $\boldsymbol{q}$ without creating any supercell
- The BOES energies are calculated as

$$V(\boldsymbol{R}) = \langle \Psi_0^e(\boldsymbol{R}) | H_e(\boldsymbol{R}) | \Psi_0^e(\boldsymbol{R}) \rangle,$$

  where the wave-function and the Hamiltonian depend parametrically on $\boldsymbol{R}$. We need its second derivative

- The first derivative (forces) can be calculated with the Hellmann-Feynman theorem

$$\frac{\partial V(\boldsymbol{R})}{\partial R_b} = -f_b = \langle \Psi_0^e(\boldsymbol{R}) | \frac{\partial H_e(\boldsymbol{R})}{\partial R_b} | \Psi_0^e(\boldsymbol{R}) \rangle = \frac{\partial V_{i-i}(\boldsymbol{R})}{\partial R_b} + \int d\boldsymbol{r} n(\boldsymbol{r}) \frac{\partial V_{e-i}(\boldsymbol{r})}{\partial R_b}$$

- The second derivative (force-constants)

$$\overset{(2)}{\phi}_{ab} = \left[\frac{\partial^2 V(\boldsymbol{R})}{\partial R_a \partial R_b} \right]_{\boldsymbol{R}=\boldsymbol{R}_0} = \left[\frac{\partial^2 V_{i-i}(\boldsymbol{R})}{\partial R_a \partial R_b} \right]_{\boldsymbol{R}=\boldsymbol{R}_0} +$$
$$\int d\boldsymbol{r} \left[\frac{\partial n(\boldsymbol{r})}{\partial R_a} \right]_{\boldsymbol{R}=\boldsymbol{R}_0} \left[\frac{\partial V_{e-i}(\boldsymbol{r})}{\partial R_b} \right]_{\boldsymbol{R}=\boldsymbol{R}_0} + \int d\boldsymbol{r} n(\boldsymbol{r}) \left[\frac{\partial^2 V_{e-i}(\boldsymbol{r})}{\partial R_a \partial R_b} \right]_{\boldsymbol{R}=\boldsymbol{R}_0}$$

Perturbative methods

$$\overset{(2)}{\phi}_{ab} = \left[\frac{\partial^2 V(\boldsymbol{R})}{\partial R_a \partial R_b}\right]_{\boldsymbol{R}=\boldsymbol{R}_0} = \left[\frac{\partial^2 V_{i-i}(\boldsymbol{R})}{\partial R_a \partial R_b}\right]_{\boldsymbol{R}=\boldsymbol{R}_0} +$$
$$\int d\boldsymbol{r} \left[\frac{\partial n(\boldsymbol{r})}{\partial R_a}\right]_{\boldsymbol{R}=\boldsymbol{R}_0} \left[\frac{\partial V_{e-i}(\boldsymbol{r})}{\partial R_b}\right]_{\boldsymbol{R}=\boldsymbol{R}_0} + \int d\boldsymbol{r} n(\boldsymbol{r}) \left[\frac{\partial^2 V_{e-i}(\boldsymbol{r})}{\partial R_a \partial R_b}\right]_{\boldsymbol{R}=\boldsymbol{R}_0}$$

The calculation of the force-constants matrix requires:

- The electroncic density at equilibrium $n(\boldsymbol{r})$
  Calculated from $|\Psi_0^e(\boldsymbol{R})\rangle$ in DFT
- The derivative of the electronic density $\left[\frac{\partial n(\boldsymbol{r})}{\partial R_a}\right]_{\boldsymbol{R}=\boldsymbol{R}_0}$

  Needs the calculation of $\frac{\partial |\Psi_0^e(\boldsymbol{R})\rangle}{\partial R_a}$, not obtained in a DFT run

Linear response theory

- A way to obtain the derivative of the density is through linear response theory and the density response function $\chi(\boldsymbol{r}, \boldsymbol{r}')$
- In fact the change in the electronic density by a change in the external potential of the system is

$$\delta n(\boldsymbol{r}) = \int d\boldsymbol{r}' \chi(\boldsymbol{r}, \boldsymbol{r}') \delta V_{ext}(\boldsymbol{r}')$$

- Considering that the external potential is the electron-ion interaction in our case

$$\left[\frac{\partial n(\boldsymbol{r})}{\partial R_a}\right]_{\boldsymbol{R}=\boldsymbol{R}_0} = \int d\boldsymbol{r}' \chi(\boldsymbol{r}, \boldsymbol{r}') \left[\frac{\partial V_{e-i}(\boldsymbol{r}')}{\partial R_a}\right]_{\boldsymbol{R}=\boldsymbol{R}_0}$$

- The force constants are

$$\begin{aligned}
\overset{(2)}{\phi}_{ab} &= \left[\frac{\partial^2 V(\boldsymbol{R})}{\partial R_a \partial R_b}\right]_{\boldsymbol{R}=\boldsymbol{R}_0} = \left[\frac{\partial^2 V_{i-i}(\boldsymbol{R})}{\partial R_a \partial R_b}\right]_{\boldsymbol{R}=\boldsymbol{R}_0} + \int d\boldsymbol{r} n(\boldsymbol{r}) \left[\frac{\partial^2 V_{e-i}(\boldsymbol{r})}{\partial R_a \partial R_b}\right]_{\boldsymbol{R}=\boldsymbol{R}_0} \\
&+ \int d\boldsymbol{r} d\boldsymbol{r}' \chi(\boldsymbol{r}, \boldsymbol{r}') \left[\frac{\partial V_{e-i}(\boldsymbol{r}')}{\partial R_a}\right]_{\boldsymbol{R}=\boldsymbol{R}_0} \left[\frac{\partial V_{e-i}(\boldsymbol{r})}{\partial R_b}\right]_{\boldsymbol{R}=\boldsymbol{R}_0} \\
&= \phi^{ii}_{ab} + \phi^{ei-nd}_{ab} + \phi^{ei}_{ab}
\end{aligned}$$

Linear response theory

- The static density response function can be calculated from the non-interacting density response function $\chi^0(\boldsymbol{r}, \boldsymbol{r}')$ from a Dyson equation

$$\chi(\boldsymbol{r}, \boldsymbol{r}') = \chi^0(\boldsymbol{r}, \boldsymbol{r}') + \int d\boldsymbol{\xi} d\boldsymbol{\xi}' \, \chi^0(\boldsymbol{r}, \boldsymbol{\xi}) \left[\frac{1}{|\boldsymbol{\xi} - \boldsymbol{\xi}'|} + f^{xc}(\boldsymbol{\xi}, \boldsymbol{\xi}') \right] \chi(\boldsymbol{\xi}', \boldsymbol{r}')$$

- $\chi^0(\boldsymbol{r}, \boldsymbol{r}')$ by definition is the change of the potential due to the change in the KS potential itself

$$\chi^0(\boldsymbol{r}, \boldsymbol{r}') = \frac{\delta n(\boldsymbol{r})}{\delta V_{KS}(\boldsymbol{r}')}$$

- It can be calculated as

$$\chi^0(\boldsymbol{r}, \boldsymbol{r}') = \sum_{ij, j \neq i} \frac{f_i - f_j}{E_i - E_j} \psi_j^*(\boldsymbol{r}') \psi_i(\boldsymbol{r}') \psi_i^*(\boldsymbol{r}) \psi_j(\boldsymbol{r})$$

  where $\psi_i(\boldsymbol{r})$ is a KS state and f_i the Fermi-Dirac occupation

- Calculating χ^0 requires a complex sum over excited states

Linear response theory and dimensionality

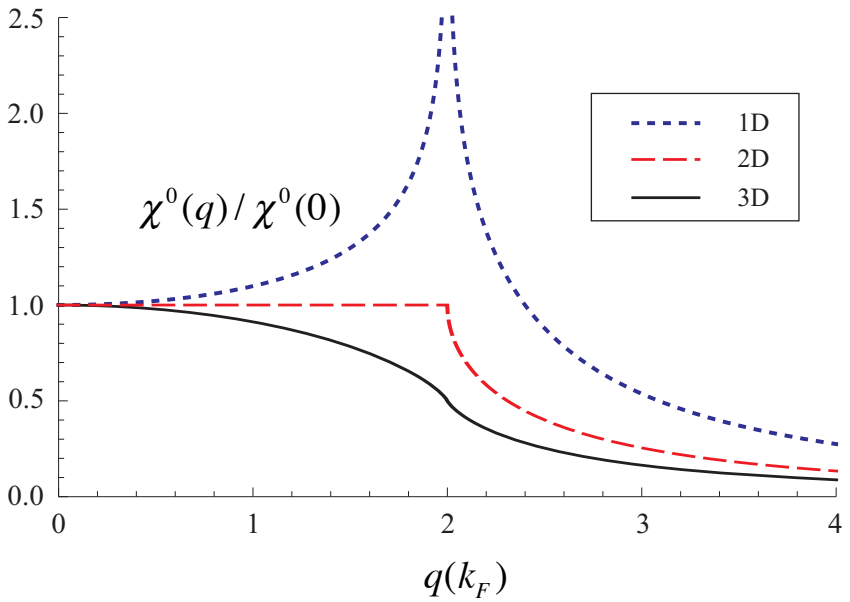
- Let's assume the free electron gas model, where $\phi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{\Omega}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ are simple plane waves and $E_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m}$
- In this case $\chi^0 = \chi$
- The Fourier transform of the non-interacting response function is analytic in 3D, 2D, and 1D: the Lindhard function
- In this approch the contribution to the dispersive part of the force constants coming from the electron-ion iteraction will give a following contribution to the phonon frequency

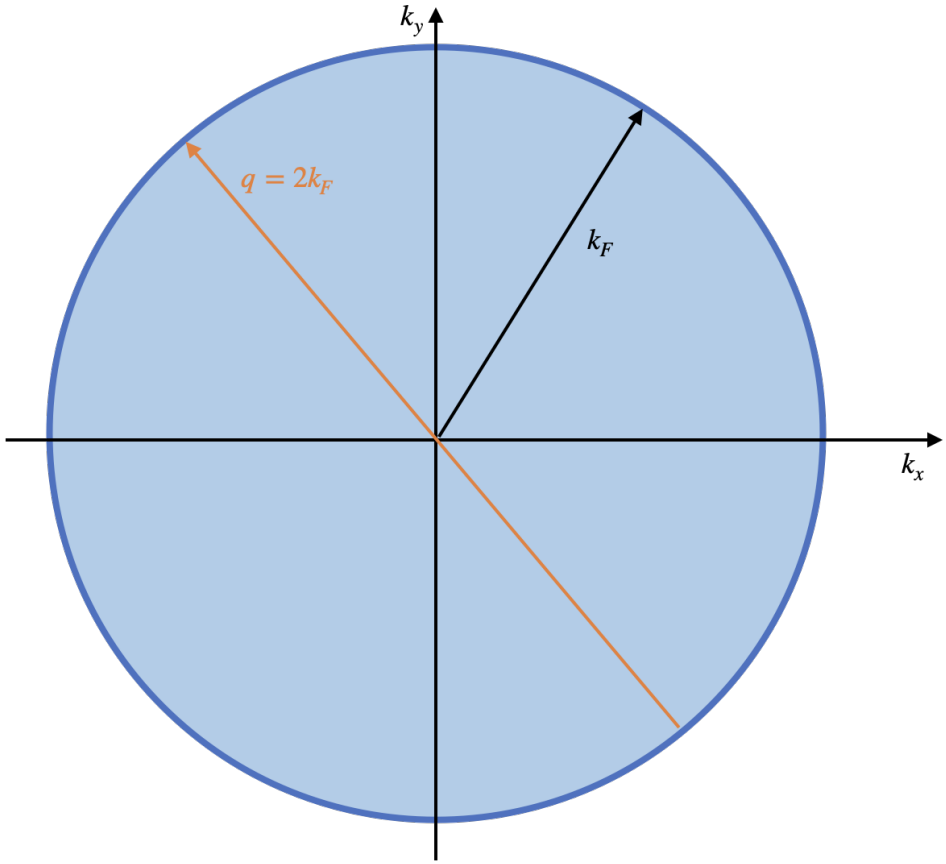
$$\omega_{ei}^2(\boldsymbol{q}) \sim v_c(\boldsymbol{q})^2 \chi(\mathbf{q}) q^2$$

  where $v_c(\boldsymbol{q})$ is the Fourier transformed Coulomb potential
- The analytical dependence on $\boldsymbol{q}$ of the response fuction will determine the phonon dispersion
- Electrons affect phonons

Linear response theory and dimensionality

- $\chi^0(\boldsymbol{q})$ is pathological at $q = 2k_F$
- The pathologies are larger for 1D than for 2D, and for 2D than for 3D
- The pathologies are associated to the Fermi surface nesting

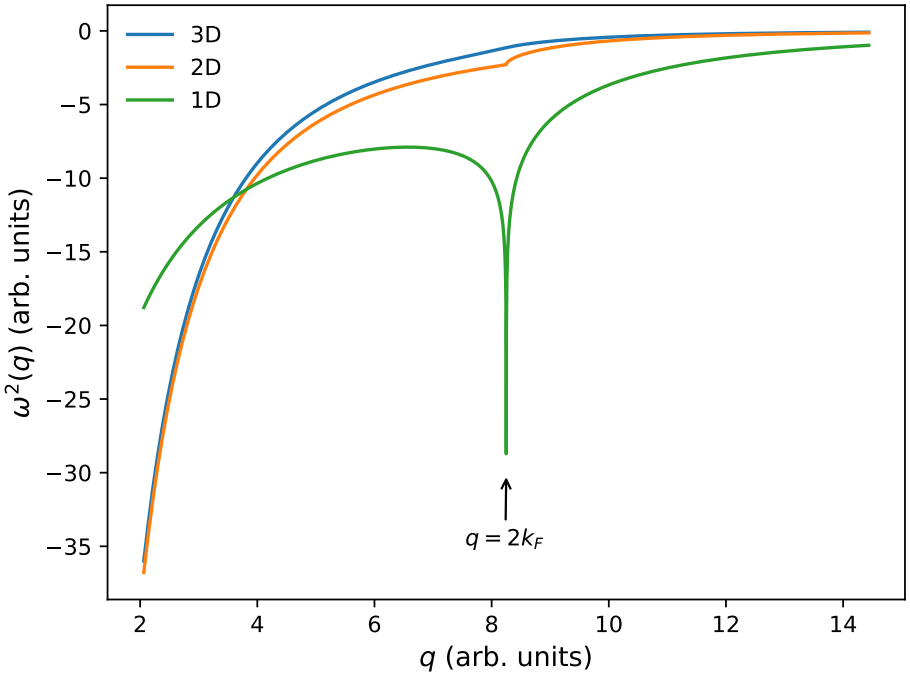




Fermi surface of the 2D free electron gas

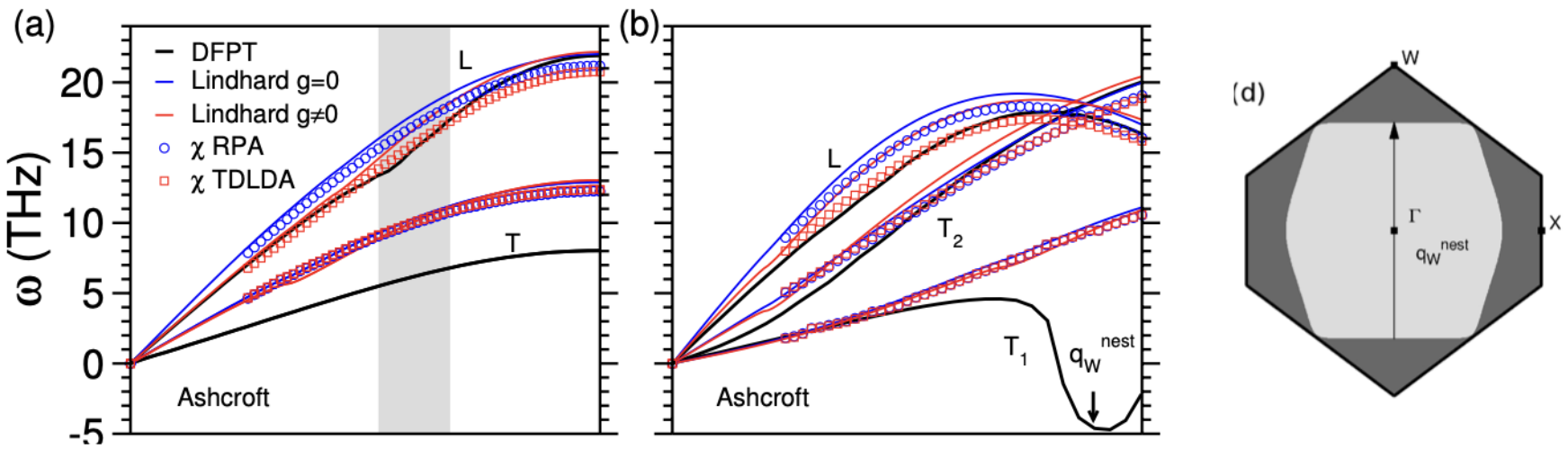
Linear response theory and dimensionality

- $\omega^2_{ei}(\boldsymbol{q})$ is consequently pathological at $q = 2k_F$ yielding to phonon softening
- the softening is very pronounced for 1D, less for 2D, and barely appreciable for 3D
- Dimensionality plays a crucial role in phonon instabilities



Have you ever heard of nesting and phonon instabilities?

Have you ever heard of nesting and phonon instabilities?



DFPT

Density functional perturbation theory (DFPT)

- A more efficient (and equivalent) approach than calculating the response function is offered by DFPT
- In order to get the derivative of the density, a first order change due to atomic displacements is assumed in the KS states, the KS Hamiltonian, and the energy

$$\begin{aligned} |\psi_{n\boldsymbol{k}}\rangle &\rightarrow |\psi_{n\boldsymbol{k}}\rangle + |\delta\psi_{n\boldsymbol{k}}\rangle \\ H_{KS} &\rightarrow H_{KS} + \delta V_{KS} \\ E_{n\boldsymbol{k}} &\rightarrow E_{n\boldsymbol{k}} + \delta E_{n\boldsymbol{k}} \end{aligned}$$

- The linearized KS equation reads

$$(\delta V_{KS} - \delta E_{n\boldsymbol{k}})|\psi_{n\boldsymbol{k}}\rangle = -(H_{KS} - E_{n\boldsymbol{k}})|\delta\psi_{n\boldsymbol{k}}\rangle$$

- This is called the Sternheimer equation

- Terms in the Sternherimer equation

$$(\delta V_{KS} - \delta E_{n\boldsymbol{k}})|\psi_{n\boldsymbol{k}}\rangle = -(H_{KS} - E_{n\boldsymbol{k}})|\delta\psi_{n\boldsymbol{k}}\rangle$$

  are

$$\begin{aligned}
\delta V_{KS}(\boldsymbol{r}) &= \delta V_{e-i}(\boldsymbol{r}) + \int d\boldsymbol{r}' \left[\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} + f^{xc}(\boldsymbol{r},\boldsymbol{r}')\right] \delta n(\boldsymbol{r}') \\
\delta n(\boldsymbol{r}) &= \sum_{n\boldsymbol{k}} [\delta\psi^*_{n\boldsymbol{k}}(\boldsymbol{r})\psi_{n\boldsymbol{k}}(\boldsymbol{r}) + \psi^*_{n\boldsymbol{k}}(\boldsymbol{r})\delta\psi_{n\boldsymbol{k}}(\boldsymbol{r})]
\end{aligned}$$

  where $f^{xc}(\boldsymbol{r},\boldsymbol{r}') = \frac{\delta V_{xc}(\boldsymbol{r})}{\delta n(\boldsymbol{r}')}$

- These three equations can be solved self-consistently
- At the end of the self-consistent loop the change of the density can be calculated due to the displacement of ions and, thus, the force constants

DFPT

- The advantage of this method is that we can take a first order change given by any particular μ mode at any $\boldsymbol{q}$

$$(\delta_{\mu\boldsymbol{q}} V_{KS} - \delta_{\mu\boldsymbol{q}} E_{n\boldsymbol{k}})|\psi_{n\boldsymbol{k}}\rangle = -(H_{KS} - E_{n\boldsymbol{k}})|\delta_{\mu\boldsymbol{q}}\psi_{n\boldsymbol{k}}\rangle$$

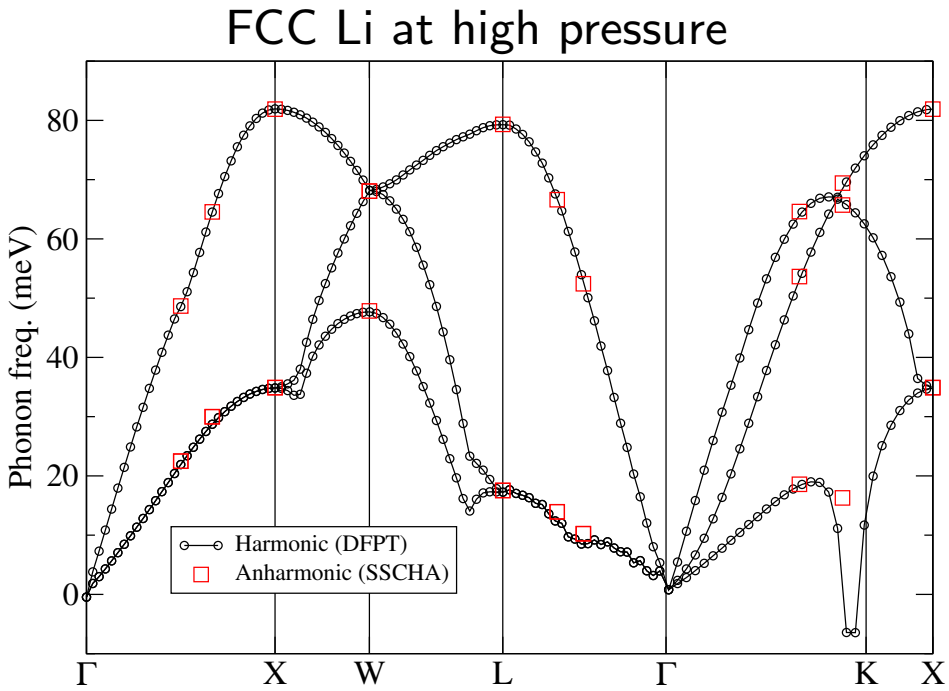
- This will give the density change due to the mode $\mu\boldsymbol{q}$, which can be used to construct the contribution of this mode to the dynamical matrix at $\boldsymbol{q}$
- In order to build the full $D(\boldsymbol{q})$ it is sufficient to repeat the self-consistent calculation for all the irreps of the little co-group of $\boldsymbol{q}$ present in the crystal
- Due to translational invariance states will be coupled with $\boldsymbol{k}$ and $\boldsymbol{k}+\boldsymbol{q}$, thus the perturbed KS state will be $|\delta_{\mu\boldsymbol{q}}\psi_{n\boldsymbol{k}+\boldsymbol{q}}\rangle$
- In practice this means that the DFPT self-consistent loop requires to calculate the bands in $\boldsymbol{k}+\boldsymbol{q}$

Baroni et al., RMP 73, 515 (2001)

DFPT

Pros:

- The calculation can be performed at any $\boldsymbol{q}$ without the need of a supercell
- Implemented in several DFT codes



What is the step that we have to take in a finite displacement approach to match the DFPT result?

Effective charges and the LO-TO splitting

- In polar semiconductors or insulators the long range character of the Coulomb interaction gives rise to a macroscopic electric field for the longitudinal optic phonons in the long wavelength ($\boldsymbol{q} \to 0$) limit
- Let's take a cubic crystal with two atoms per unit cell. The most general quadratic energy that we can write is

$$E(\boldsymbol{u}, \boldsymbol{E}) = \frac{1}{2} M \omega_0^2 u^2 - \frac{\Omega}{8\pi N} \epsilon_\infty \boldsymbol{E}^2 - eZ^* \boldsymbol{u} \cdot \boldsymbol{E}$$

  where ϵ_∞ is the electronic dielectric constant in the static limit, Z^* are the so-called Born effective charges, $\boldsymbol{E}$ is the electric field, and M is the reduced mass
- The forces and the electrical induction vectors D_a are then

$$\begin{aligned} f_a &= -\frac{\partial E}{\partial u_a} = -M\omega_0^2 u_a + eZ^* E_a \\ D_a &= -\frac{4\pi N}{\Omega} \frac{\partial E}{\partial E_a} = \frac{4\pi N}{\Omega} eZ^* u_a + \epsilon_\infty E_a \end{aligned}$$

Effective charges and the LO-TO splitting

- The Maxwell equations in the absence of external charges give

$$\begin{aligned} \boldsymbol{\nabla} \times \boldsymbol{E} &\sim i\boldsymbol{q} \times \boldsymbol{E} = 0 \\ \boldsymbol{\nabla} \cdot \boldsymbol{D} &\sim i\boldsymbol{q} \cdot \boldsymbol{D} = 0 \end{aligned}$$

- For the transverse optical (TO) mode ($\boldsymbol{q} \perp \boldsymbol{E}$) $\boldsymbol{E} = 0$ and, thus,

$$\omega_T = \omega_0$$

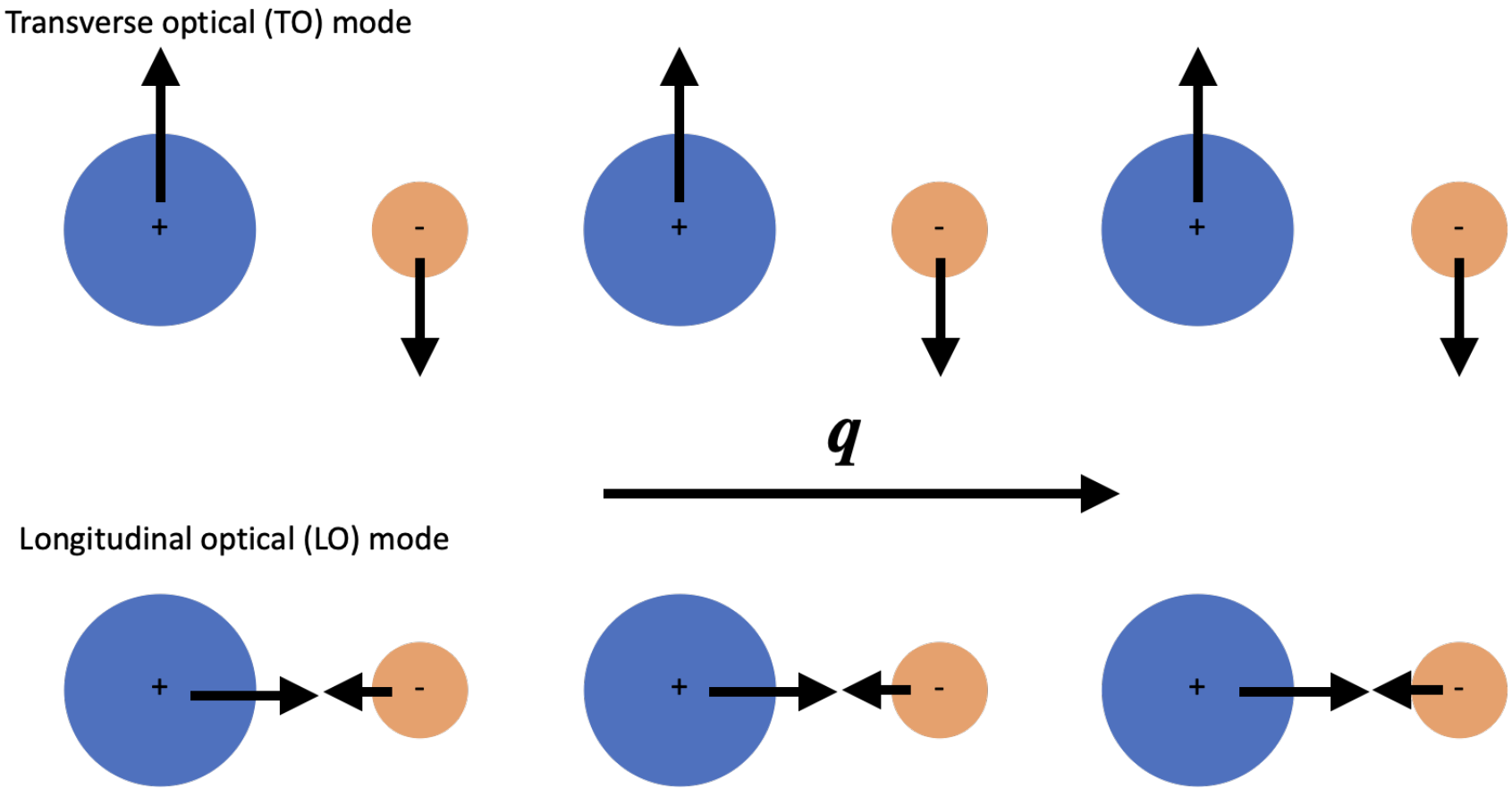
- For the longitudinal optical (LO) mode ($\boldsymbol{q} \parallel \boldsymbol{E}$) $\boldsymbol{D} = 0$ and, thus,

$$\omega_L = \sqrt{\omega_0 + 4\pi e^2 Z^{*2} \epsilon_\infty MN/\Omega}$$

- The TO mode has a higher frequency than the LO mode, the LO-TO splitting
- The magnitude of the LO-TO splitting depends on the effective charges on the ions and the $\omega \to 0$ limit of the electronid dielectric function, ϵ_∞

Effective charges and the LO-TO splitting

- The LO creates a dipole at linear order in u, the TO no, so there is an extra electrostatic term form the LO
- This problem occurs only at Γ and gives a non-analytic correction to the dynamical matrix



Effective charges and the LO-TO splitting

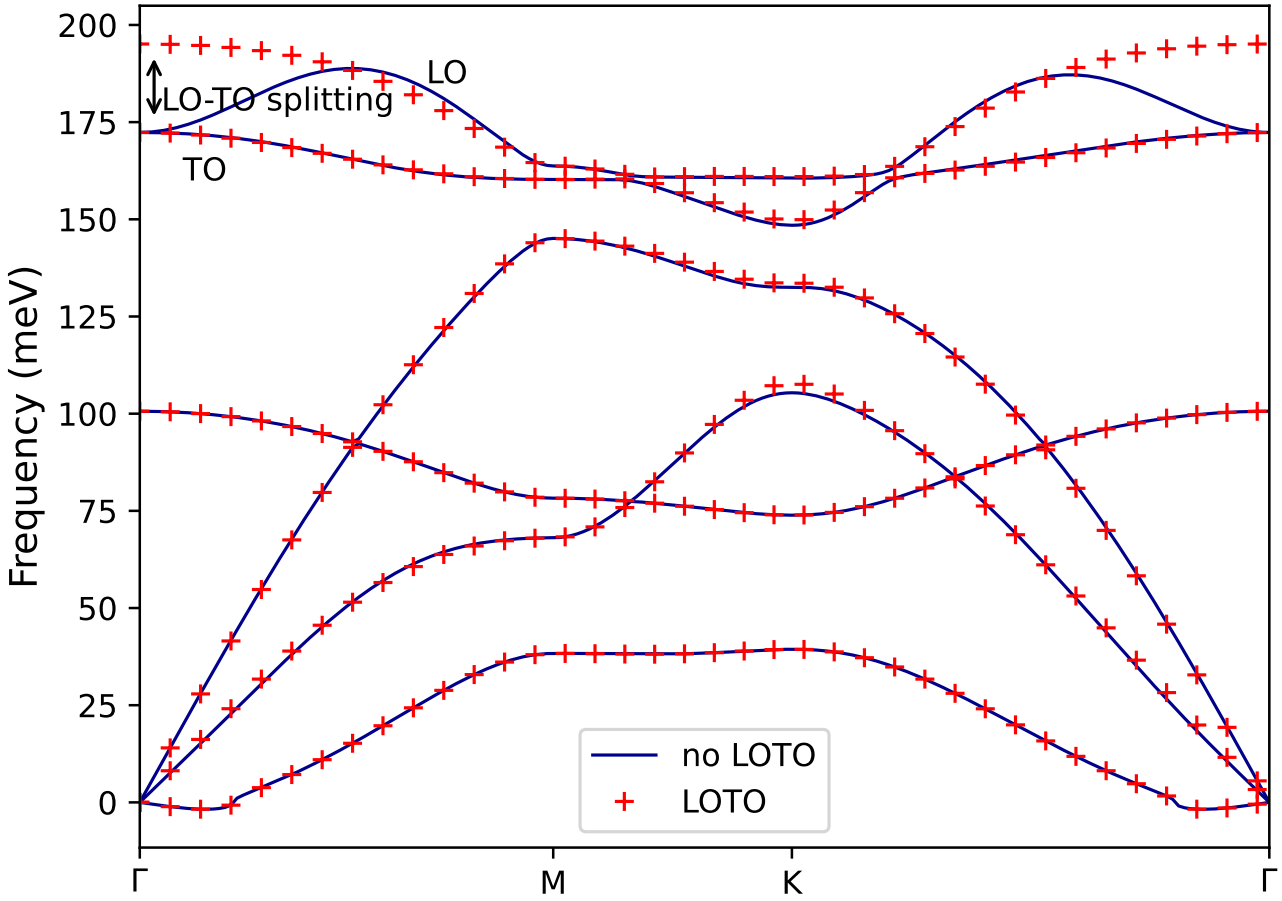
- The general procedure to calculate the force constants at Γ for a polar material is to calculate the analytic dynamical matrix from DFPT and add the non-analytic part to it

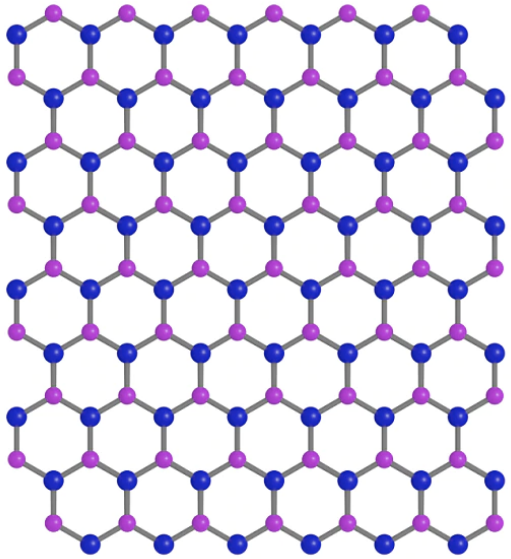
$$\begin{aligned} {}^{(2)}\phi_{ab}(\boldsymbol{q}=0) &= {}^{an}{}^{(2)}\phi_{ab}(\boldsymbol{q}=0) + {}^{non-an}{}^{(2)}\phi_{ab}(\boldsymbol{q}=0) \\ {}^{non-an}{}^{(2)}{}^{\alpha\beta}\phi_{st}(\boldsymbol{q}=0) &= \frac{4\pi N}{\Omega} e^2 \frac{(\boldsymbol{q}\cdot\boldsymbol{Z^*}_s)^\alpha (\boldsymbol{q}\cdot\boldsymbol{Z^*}_t)^\beta}{\boldsymbol{q}\cdot\boldsymbol{\epsilon}_\infty\cdot\boldsymbol{q}} \end{aligned}$$

- Note that the non-analytic correction depends on the direction of $\boldsymbol{q}$
- The effective charge tensor $Z_s^{*\alpha\beta}$ and the static limit of the electronic dielectric function $\epsilon_\infty^{\alpha\beta}$ can be obtained from DFPT once the derivatives of the KS states with respect to displacements are known

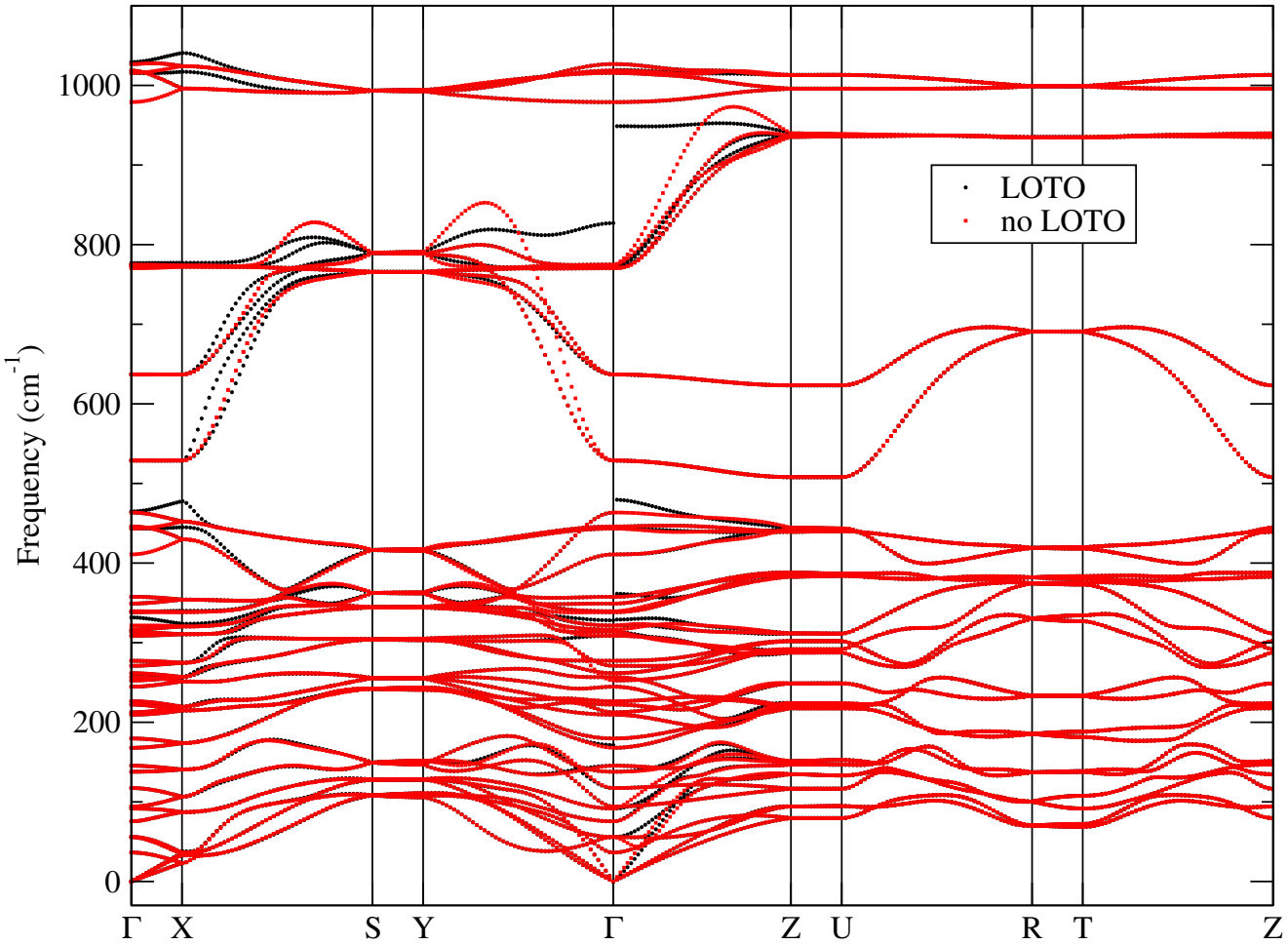
Baroni et al., RMP 73, 515 (2001)
Giannozzi et al., PRB 43, 7231 (1991)
Gonze et al., PRB 55, 10355 (1997)

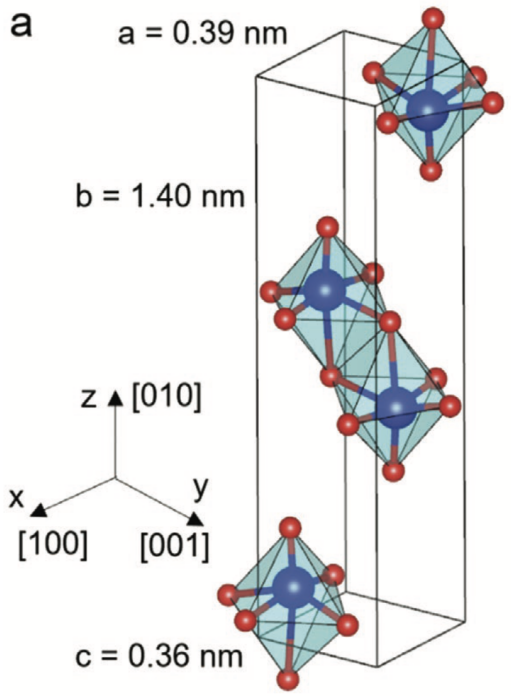
LO-TO splitting in hexagonal BN monolayer





The LO-TO splitting is direction dependent





Procedure to obtain phonon spectra in finite displacement methods

- In finite displacements methods once the force constants are known for a supercell the force constants at any $\boldsymbol{q}$ point are obtained by Fourier interpolation

$$\overset{(2)}{\phi}_{ab}(\boldsymbol{q}) = \frac{1}{N_{sc}} \sum_{\boldsymbol{T}_{sc}} \overset{(2)}{\phi}_{ab}(\boldsymbol{T}_{sc}) e^{i\boldsymbol{q}\cdot\boldsymbol{T}_{sc}},$$

  Here N_{sc} is the supercell size and the sum extends to the N_{sc} lattice vectors in the supercell

- Then, the phonon frequencies at any $\boldsymbol{q}$ point can later be extracted diagonalizing the interpolated dynamical matrix

$$\sum_b D_{ab}(\boldsymbol{q}) e^b_\mu(\boldsymbol{q}) = \sum_b \frac{\overset{(2)}{\phi}_{ab}(\boldsymbol{q})}{\sqrt{M_a M_b}} e^b_\mu(\boldsymbol{q}) = \omega^2_\mu(\boldsymbol{q}) e^a_\mu(\boldsymbol{q})$$

- This procedure may gives the exact frequencies at $\boldsymbol{q}$ points commmensurate with the supercell
- For other $\boldsymbol{q}$ points the interpolation may not lead to good phononfrequencies

Procedure to obtain phonon spectra in DFPT

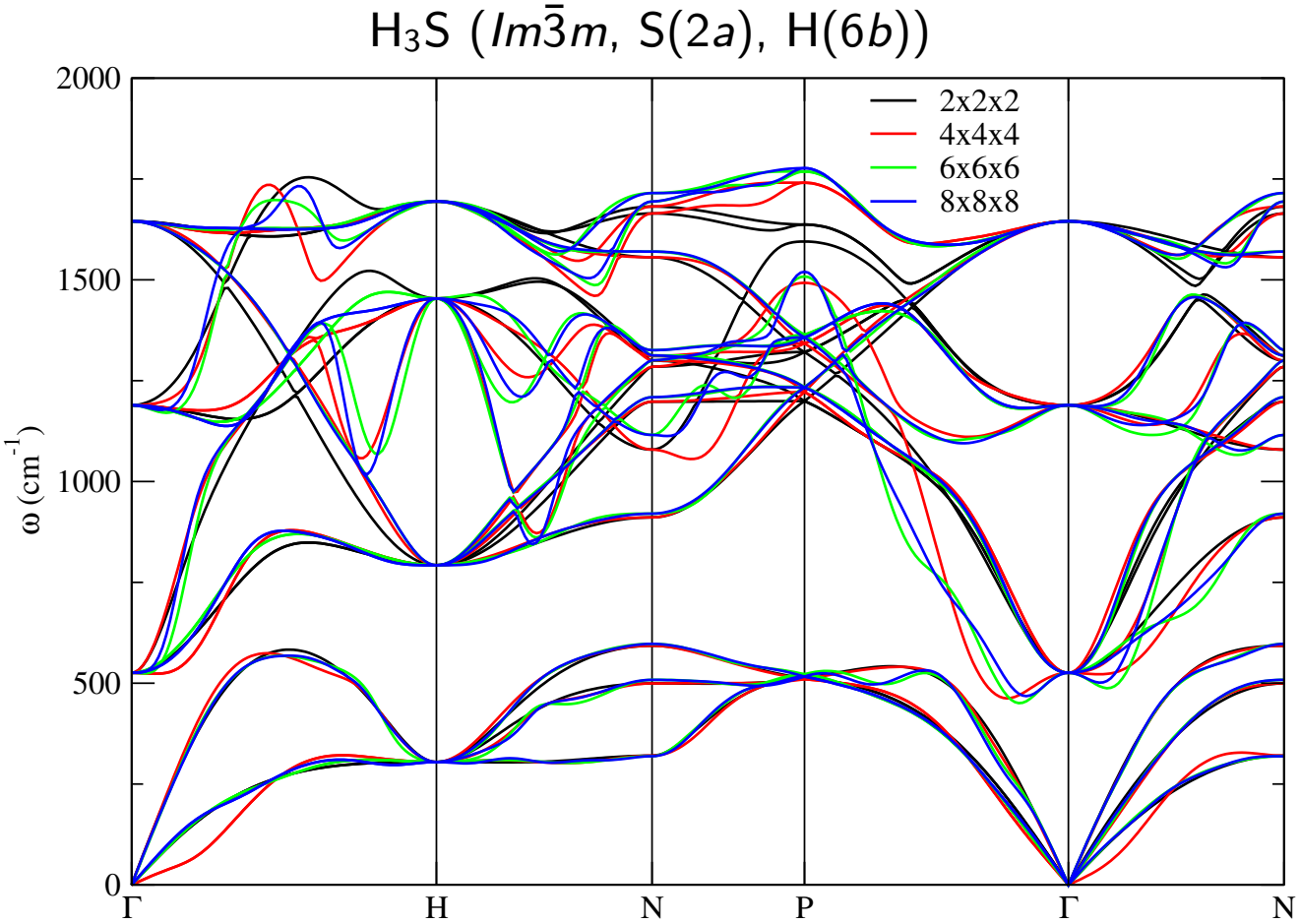
- Even if in principle the phonon spectra can be calculated point by point in DFPT, doing so can be CPU expensive, and a Fourier interpolation method is usually followed
- Calculate with DFPT the dynamical matrices in a regular $n_1 \times n_2 \times n_3$ grid of the first BZ
- Build the force-constants by Fourier transform in the commensurate $n_1 \times n_2 \times n_3$ supercell

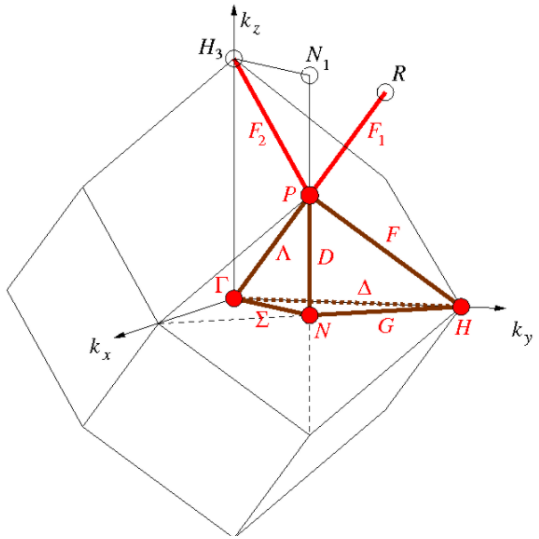
$$\overset{(2)}{\phi}_{ab}(\boldsymbol{T}_{sc}) = \frac{1}{N_{sc}} \sum_{\boldsymbol{q} \in grid} \overset{(2)}{\phi}_{ab}(\boldsymbol{q}) e^{-i\boldsymbol{q}\cdot\boldsymbol{T}_{sc}}$$

- Once the force constants are built we can proceed as in the finite displacements case and obtain the dynamical matrix at a $\boldsymbol{q}$ point that was not originally in the grid

$$D_{ab}(\boldsymbol{q}) = \sum_{\boldsymbol{T}_{sc}} \frac{\overset{(2)}{\phi}_{ab}(\boldsymbol{T}_{sc})}{\sqrt{M_{s_1} M_{s_2}}} e^{i\boldsymbol{q}\cdot\boldsymbol{T}_{sc}},$$

Convergence with respect to the $\boldsymbol{q}$ point grid or supercell





- Phonon frequencies for the $\boldsymbol{q}$ points present in all the grids coincide: Γ, H, N

Exercises

1. Show that the dipole created by the TO mode has no linear term on the displacement and thus does not create any dipole
2. Show that the number of $\boldsymbol{q}$ points commensurate with a given supercell is exactly the size of the supercell