Lattice Dynamics and Phonon

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Outline

$$\mathcal{H}(\{\boldsymbol{r}\},\{\boldsymbol{R}\})$$

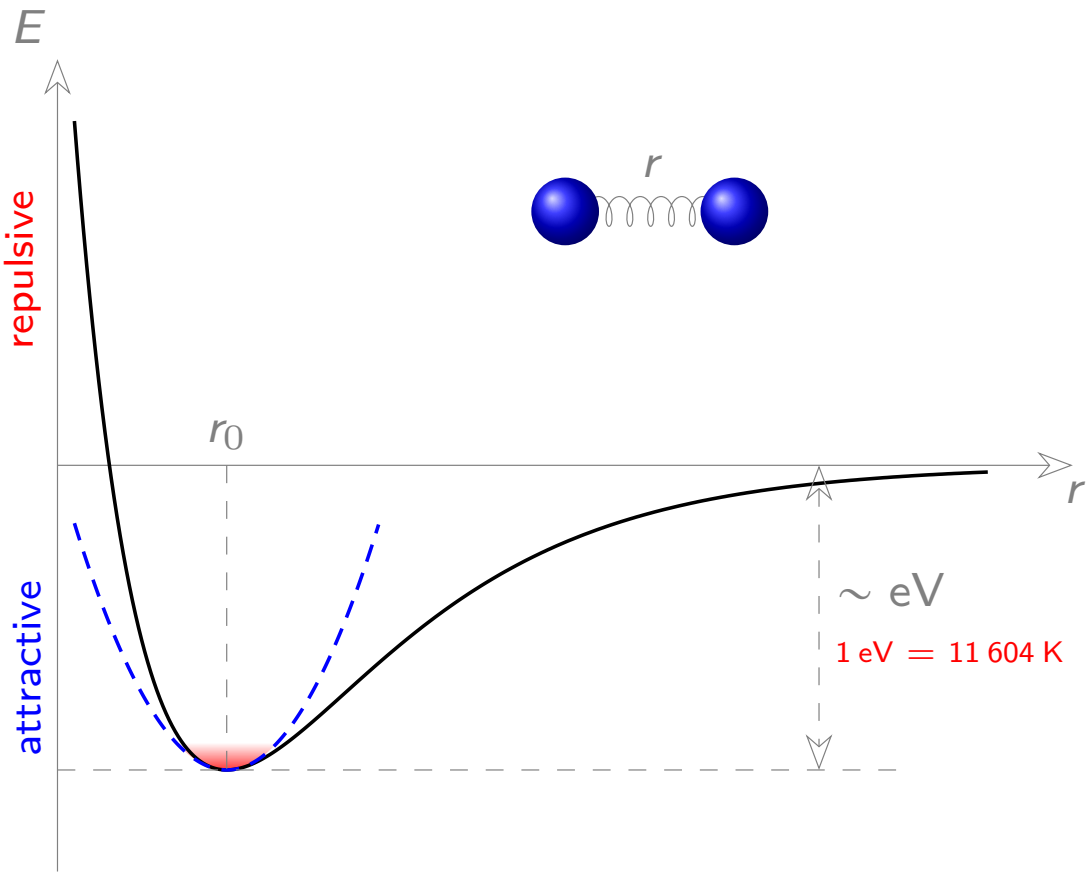
$$\Updownarrow$$

$$\sum_i \frac{\hat{\boldsymbol{p}}_i^2}{2m} + \frac{1}{2}\sum_{i,j}\frac{e^2}{|\boldsymbol{r}_i-\boldsymbol{r}_j|} + \sum_{i,I}\frac{Z_I e^2}{|\boldsymbol{r}_i-\boldsymbol{R}_I|} + \sum_I \frac{\hat{\boldsymbol{P}}_I^2}{2M_I} + \frac{1}{2}\sum_{I,J}\frac{Z_I Z_J e^2}{|\boldsymbol{R}_I-\boldsymbol{R}_J|}$$

$$\Downarrow$$

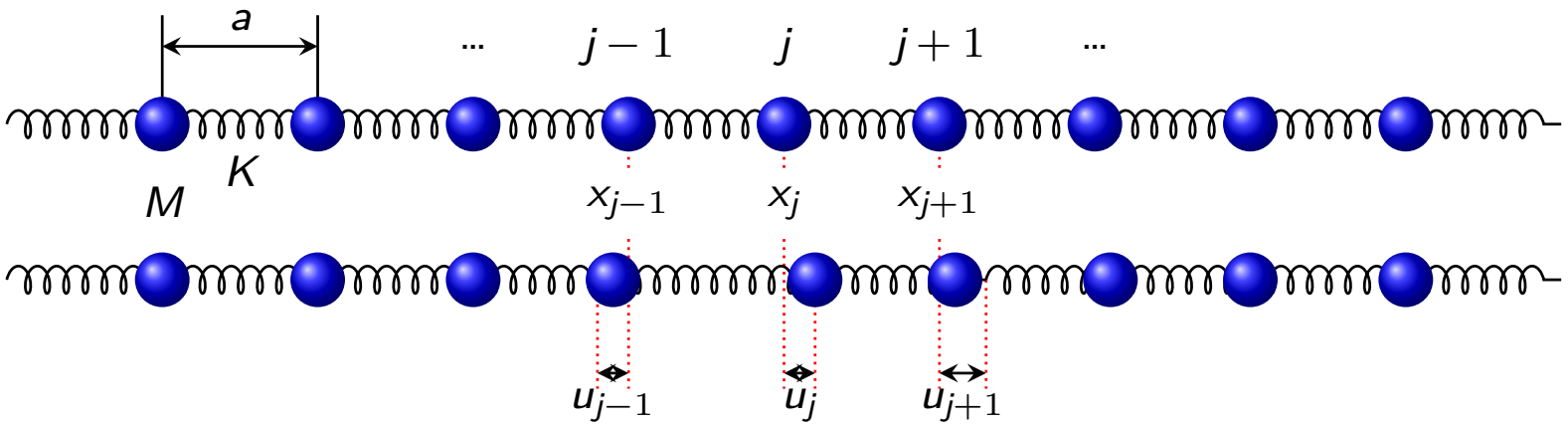
$$i\hbar\frac{\partial}{\partial t}\psi(\{\boldsymbol{r}\},\{\boldsymbol{R}\}) = \mathcal{H}(\{\boldsymbol{r}\},\{\boldsymbol{R}\})\,\psi(\{\boldsymbol{r}\},\{\boldsymbol{R}\})$$

Harmonic Approximation



1D Chain of Atoms — 1 Atom per Unit

A 1D chain of N equally spaced atoms at $R_j(t) = x_j + u_j(t)$



The Newton's Equation

$$M\frac{\mathrm{d}^2 u_j}{\mathrm{d}t^2} = K(u_{j+1} + u_{j-1} - 2u_j) \qquad j = 1, \ldots, N$$

Assume the solution has the form $u_j(t) = \frac{A_q}{\sqrt{M}} e^{i(qx_j - \omega t)}$, then [1]

$$\begin{aligned} \omega^2 &= \frac{K}{M}(2 - e^{iqa} - e^{-iqa}) \\ &= \frac{2K}{M}(1 - \cos qa) \\ \Rightarrow \quad \omega &= \sqrt{\frac{4K}{M}}\left|\sin\frac{qa}{2}\right| \end{aligned}$$

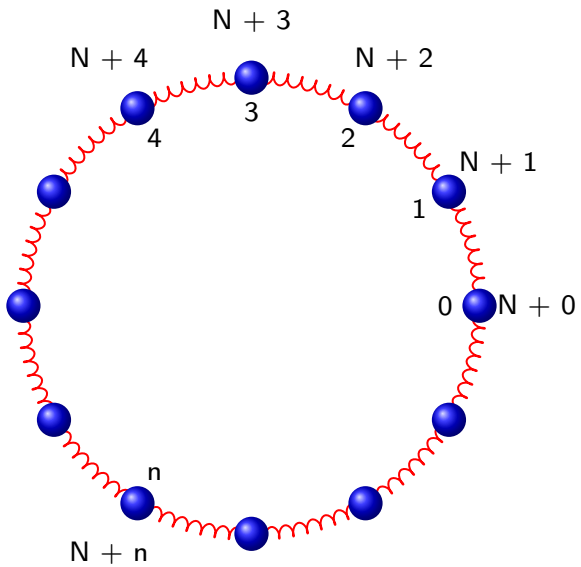
[1] $u_j(t)$ here is complex. In practice, take the real part, i.e. $\mathrm{Re}[u_j(t)]$.

Born–von Karman boundary condition

The Born-von Karman Periodic Boundary Condition:

$$u_n = u_{N+n} \quad \Rightarrow \quad e^{iqx_j} = e^{iqx_{N+j}} \quad \Rightarrow \quad e^{iqNa} = 1$$

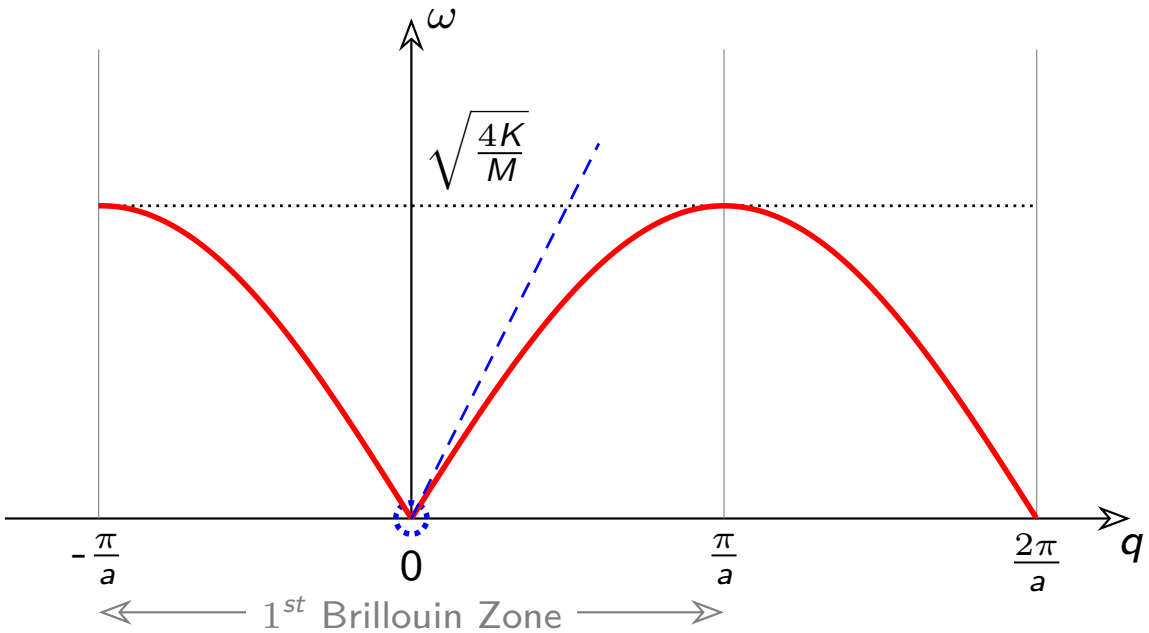
$$\Rightarrow \quad q = \frac{2\pi}{a}\frac{l}{N}; \quad (l = 0, 1, \ldots, N)$$



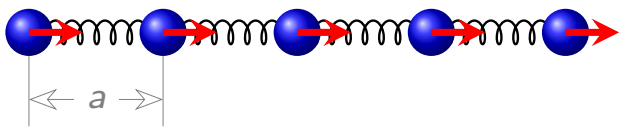
Usually, q is restricted within the first Brillouin Zone

$$-\frac{\pi}{a} \leqslant q \leqslant \frac{\pi}{a}$$

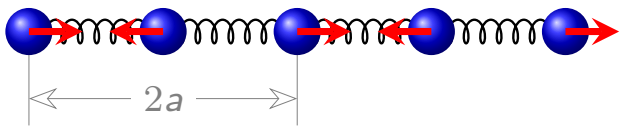
Dispersion and Vibration Pattern

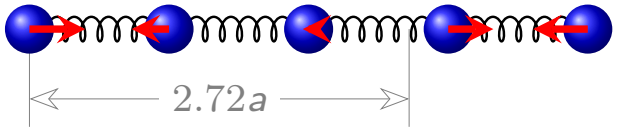


$q = 0$

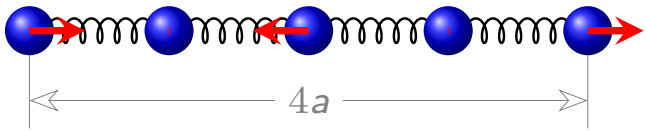


$q = \frac{\pi}{a}$





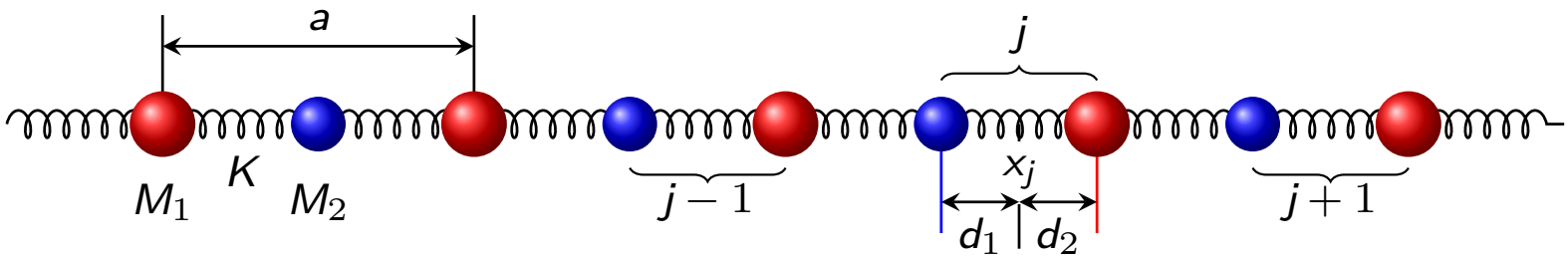
$q = \frac{2.2}{3}\frac{\pi}{a}$



$q = \frac{1}{2}\frac{\pi}{a}$

1D Chain of Atoms — 2 Atoms per Unit

A 1D chain with 2 atoms in each unit: $R_s^j(t) = x_j + d_s + u_s^j(t); \quad s = 1, 2$



The Newton's Equation

$$\begin{aligned} M_1 \frac{\mathrm{d}^2 u_1^j}{\mathrm{d}t^2} &= K(u_2^j + u_2^{j-1} - 2u_1^j) \\ M_2 \frac{\mathrm{d}^2 u_2^j}{\mathrm{d}t^2} &= K(u_1^j + u_1^{j+1} - 2u_2^j) \end{aligned} \quad \Longrightarrow \quad \begin{cases} u_1^j(t) = \dfrac{A_q}{\sqrt{M_1}} e^{i(qx_j - \omega t)} \\ u_2^j(t) = \dfrac{B_q}{\sqrt{M_2}} e^{i(qx_j - \omega t)} \end{cases}$$

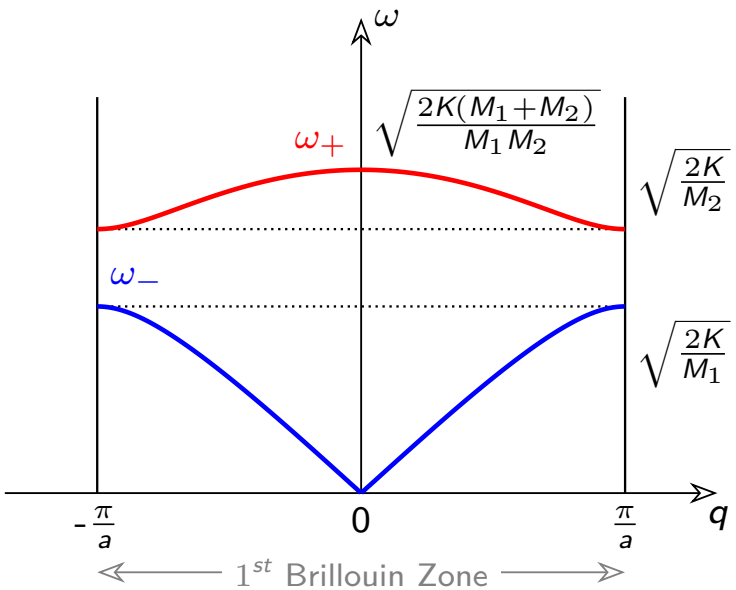
We then have

$$\begin{pmatrix} \frac{2K}{M_1} & \frac{-K}{\sqrt{M_1 M_2}}(1 + e^{-iqa}) \\ \frac{-K}{\sqrt{M_1 M_2}}(1 + e^{iqa}) & \frac{2K}{M_2} \end{pmatrix} \begin{pmatrix} A_q \\ B_q \end{pmatrix} = \omega^2 \begin{pmatrix} A_q \\ B_q \end{pmatrix}$$

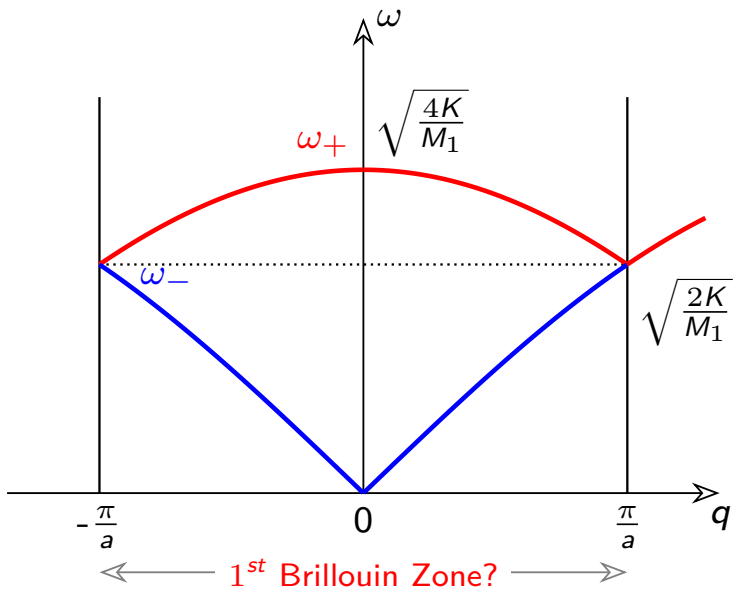
$$\Longrightarrow \quad \omega_{\pm}^2 = \frac{K}{M_1 M_2} \left((M_1 + M_2) \pm \sqrt{M_1^2 + M_2^2 + 2M_1 M_2 \cos qa} \right)$$

Dispersion and Vibration Pattern

$M_1 = 2M_2$

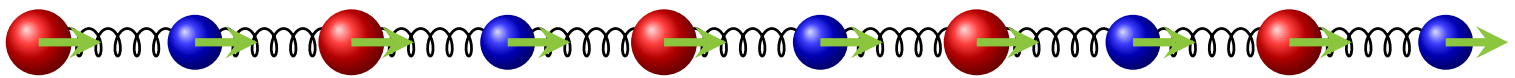


$M_1 = M_2$

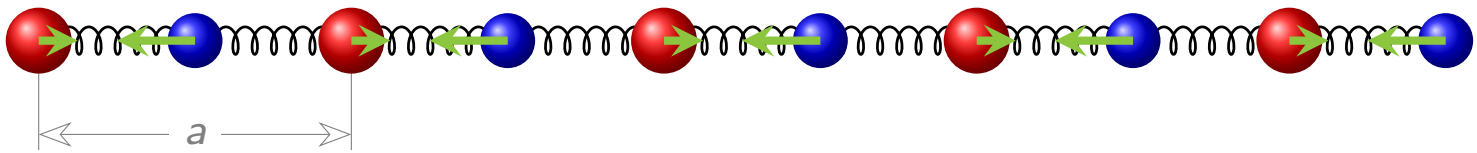


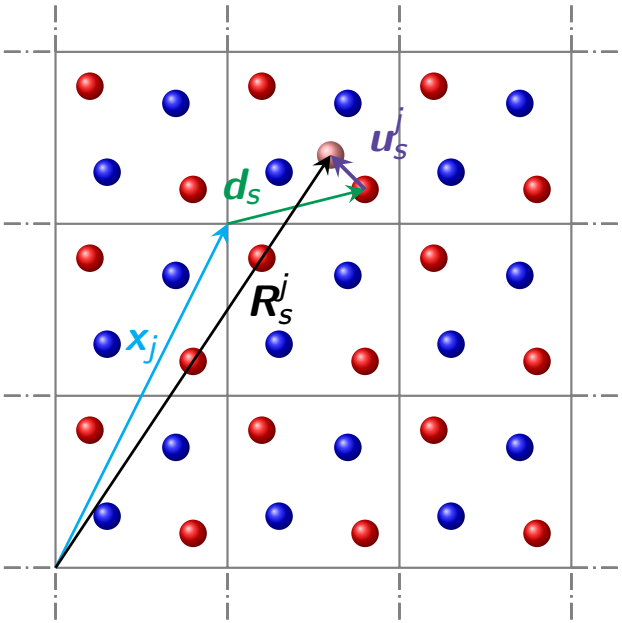
$$\frac{A_q}{B_q} = \left[\frac{K(1+e^{-iqa})}{\sqrt{M_1 M_2}}\right] \Big/ \left[\frac{2K}{M_1} - \omega^2\right]$$

$\omega_-(q=0)$



$\omega_+(q=0)$





- x_j: the position of unit cell j
- d_s: the equilibrum position of the atom s in the cell
- u_s^j: displacement from the equilibrum positon for the atom s in the cell j
- R_s^j: the position of the atom s in the cell j

$$\begin{aligned} R_s^j(t) &= x_j + d_s + u_s^j(t) \\ &= r_s^j + u_s^j(t) \\ R_{s\alpha}^j(t) &= r_{s\alpha}^j + u_{s\alpha}^j(t) \quad (\alpha = x, y, z) \end{aligned}$$

The total energy can be written as

$$E_{\text{tot}}\left(\{R_s^j(t)\}\right) = E_{\text{tot}}^0\left(\{r_s^j\}\right) + \sum_{js\alpha} \frac{\partial E_{\text{tot}}^0}{\partial u_{s\alpha}^j} u_{s\alpha}^j + \frac{1}{2} \sum_{\substack{js\alpha \\ kt\beta}} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} u_{s\alpha}^j u_{t\beta}^k + \dots$$

- The expression is exact if we take all the orders in the expansion.
- All the derivatives are taken at the equilibrium positions $\{r_s^j\}$, i.e. $\frac{\partial E_{\text{tot}}^0}{\partial u_{s\alpha}^j} = 0$.
- Harmonic approximation: truncated at *second* order.

Within the harmonic approximation, the Newton's equation for the atom s in cell j

$$M_s \frac{\mathrm{d}^2 u^j_{s\alpha}(t)}{\mathrm{d}t^2} = -\frac{\partial E_{\mathrm{tot}}}{\partial u^j_{s\alpha}} = -\sum_{kt\beta} \frac{\partial^2 E^0_{\mathrm{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} u^k_{t\beta} = -\sum_{kt\beta} C^{j,k}_{s\alpha,t\beta}\, u^k_{t\beta} \tag{1}$$

The ansatz of the solution

$$u^j_{s\alpha}(t) = \frac{\eta^\sigma_{s\alpha}(\boldsymbol{q})}{\sqrt{M_s}}\, e^{i\boldsymbol{q}\boldsymbol{x}_j}\, e^{-i\omega_\sigma t} \tag{2}$$

Substitute Eq. 2 into Eq. 1

$$\omega^2_\sigma(\boldsymbol{q})\, \eta^\sigma_{s\alpha} = \sum_{t\beta} \left[\sum_k \frac{1}{\sqrt{M_s M_t}} \frac{\partial^2 E^0_{\mathrm{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}}\, e^{i\boldsymbol{q}(\boldsymbol{x}_k - \boldsymbol{x}_j)} \right] \eta^\sigma_{t\beta} = \sum_{t\beta} D_{s\alpha,t\beta}(\boldsymbol{q})\, \eta^\sigma_{t\beta}$$

In matrix form

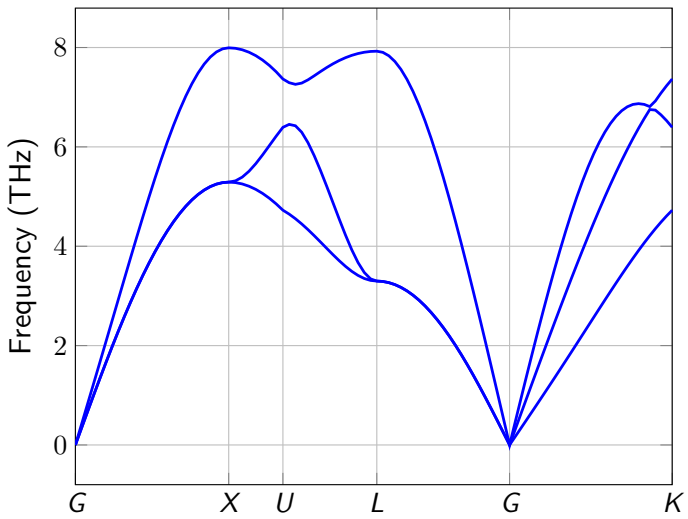
$$\begin{pmatrix} \ddots & & \\ & D_{s\alpha,t\beta}(\boldsymbol{q}) & \\ & & \ddots \end{pmatrix} \begin{pmatrix} \vdots \\ \eta^\sigma_{t\beta}(\boldsymbol{q}) \\ \vdots \end{pmatrix} = \omega^2(\boldsymbol{q}) \begin{pmatrix} \vdots \\ \eta^\sigma_{t\beta}(\boldsymbol{q}) \\ \vdots \end{pmatrix}$$

$3N_a \times 3N_a$ $\quad$ $3N_a$ $\quad$ polarization vector

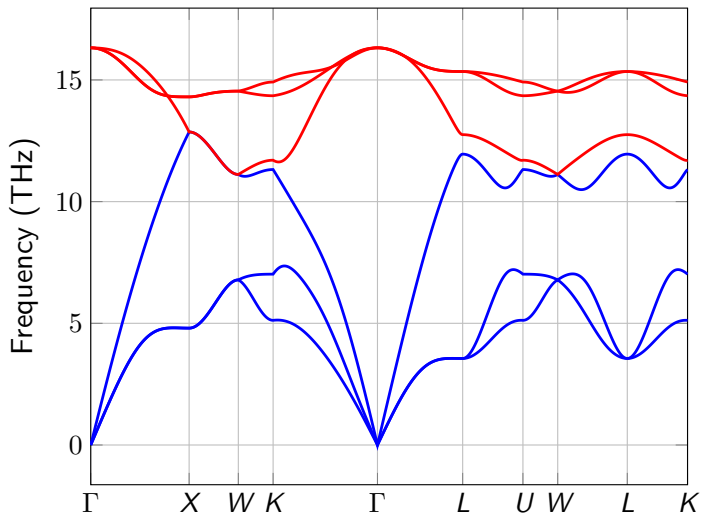
where $\sigma = 1, ..., 3N_a$ and N_a is the number of atoms in the *primitive cell*.

3D Dispersion

Aluminum Dispersion [2]



Silicon Dispersion [3]



- If N_a atoms in the primitive cell, $3N_a$ modes for each $\boldsymbol{q}$.
- At each $\boldsymbol{q}$, 3 acoustic modes, $3N_a - 3$ optical modes.

[2] https://wiki.fysik.dtu.dk/ase/ase/phonons.html

[3] https://github.com/phonopy/phonopy/tree/master/example/Si-CRYSTAL

The Interatomic Force Constants (IFC)

$$\frac{\partial^2 E^0_{\text{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} = C^{j,k}_{s\alpha,t\beta}$$

- Symmetric because partial differentiation is commutative

$$\frac{\partial^2 E^0_{\text{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} = \frac{\partial^2 E^0_{\text{tot}}}{\partial u^k_{t\beta} \partial u^j_{s\alpha}} \quad \Rightarrow \quad C^{j,k}_{s\alpha,t\beta} = C^{k,j}_{t\beta,s\alpha} \tag{3}$$

- Translation invariance, only depend on the difference between j and k

$$\frac{\partial^2 E^0_{\text{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} = \frac{\partial^2 E^0_{\text{tot}}}{\partial u^0_{s\alpha} \partial u^{(k-j)}_{t\beta}} \quad \Rightarrow \quad C^{j,k}_{s\alpha,t\beta} = C^{0,k-j}_{s\alpha,t\beta} \tag{4}$$

- Acoustic Sum Rule (ASR): if we displace the whole solid by an arbitrary uniform displacement, the forces acting on the atoms must be zero.

$$F^j_{s\alpha} = -\sum_{\beta} \left[\sum_{kt} \frac{\partial^2 E^0_{\text{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} \right] \delta_\beta = 0 \quad \Rightarrow \quad \sum_{kt} \frac{\partial^2 E^0_{\text{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} = 0 \tag{5}$$

The Dynamical Matrix

$$D_{s\alpha,t\beta}(\boldsymbol{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_l \frac{\partial^2 E^0_{\text{tot}}}{\partial u^0_{s\alpha} \partial u^l_{t\beta}} e^{i\boldsymbol{q}\boldsymbol{x}_l} = \frac{1}{\sqrt{M_s M_t}} \sum_l C^{0,l}_{s\alpha,t\beta}\, e^{i\boldsymbol{q}\boldsymbol{x}_l}$$

- If we define the distortion pattern $\boldsymbol{u}^l_s(\boldsymbol{q}) = \boldsymbol{v}_s(\boldsymbol{q})\, e^{i\boldsymbol{q}\boldsymbol{x}_l}$

$$D_{s\alpha,t\beta}(\boldsymbol{q}) = \frac{1}{N} \frac{1}{\sqrt{M_s M_t}} \frac{\partial^2 E^0_{\text{tot}}}{\partial v^*_{s\alpha}(\boldsymbol{q}) \partial v_{t\beta}(\boldsymbol{q})}$$

- Dynamical matrix is Hermitian and admit real eigenvalues $\omega^2(\boldsymbol{q})$

$$D_{s\alpha,t\beta}(\boldsymbol{q}) = D^*_{t\beta,s\alpha}(\boldsymbol{q})$$

Proof

$$\begin{aligned} D_{s\alpha,t\beta}(\boldsymbol{q}) &= \frac{1}{\sqrt{M_s M_t}} \sum_l C^{0,l}_{s\alpha,t\beta}\, e^{i\boldsymbol{q}\boldsymbol{x}_l} \\ &= \frac{1}{\sqrt{M_s M_t}} \sum_l C^{l,0}_{s\alpha,t\beta}\, e^{i\boldsymbol{q}\boldsymbol{x}_l} \\ &= \frac{1}{\sqrt{M_s M_t}} \sum_l C^{0,-l}_{t\beta,s\alpha}\, e^{i\boldsymbol{q}\boldsymbol{x}_l} \end{aligned}$$

$$\begin{aligned} D^*_{s\alpha,t\beta}(\boldsymbol{q}) &= \frac{1}{\sqrt{M_s M_t}} \sum_l C^{0,-l}_{t\beta,s\alpha}\, e^{-i\boldsymbol{q}\boldsymbol{x}_l} \\ &= \frac{1}{\sqrt{M_s M_t}} \sum_l C^{0,l}_{t\beta,s\alpha}\, e^{i\boldsymbol{q}\boldsymbol{x}_l} \\ &= D_{t\beta,s\alpha}(\boldsymbol{q}) \end{aligned}$$

Phonon Polarization Vectors

The eigenvectors $\boldsymbol{\eta}^{\sigma}(\boldsymbol{q})$ of the Hermitian matrix $D_{s\alpha,t\beta}(\boldsymbol{q})$ are called the phonon polarization vector.

- The polarization vector is *cell-periodic*.

$$u^{j}_{s\alpha}(t) = \frac{\eta^{\sigma}_{s\alpha}(\boldsymbol{q})}{\sqrt{M_s}}\, e^{i\boldsymbol{q}\boldsymbol{x}_j}\, e^{-i\omega_{\sigma} t}$$

  So the solution is a cell-periodic part multiply by $e^{i\boldsymbol{q}\boldsymbol{x}}$ — Bloch's theorem.

- Orthogonalization relation:

$$\sum_{s\alpha} \eta^{\sigma'*}_{s\alpha}(\boldsymbol{q})\, \eta^{\sigma}_{s\alpha}(\boldsymbol{q}) = \delta_{\sigma\sigma'}; \qquad \sum_{\sigma} \eta^{\sigma*}_{s\alpha}(\boldsymbol{q})\, \eta^{\sigma}_{t\beta}(\boldsymbol{q}) = \delta_{st}\,\delta_{\alpha\beta}$$

- Relation to phonon displacemoment — direction and amplitude of the vibration.

$$\xi^{\sigma}_{s\alpha} = \frac{1}{\sqrt{M_s}}\, \eta^{\sigma}_{s\alpha}(\boldsymbol{q})$$

- At some high-symmetry $\boldsymbol{q}$-path

$$\begin{cases} \boldsymbol{q} \parallel \boldsymbol{\eta}(\boldsymbol{q}) & \text{Longitudinal Wave} \\ \boldsymbol{q} \perp \boldsymbol{\eta}(\boldsymbol{q}) & \text{Transverse Wave} \end{cases}$$

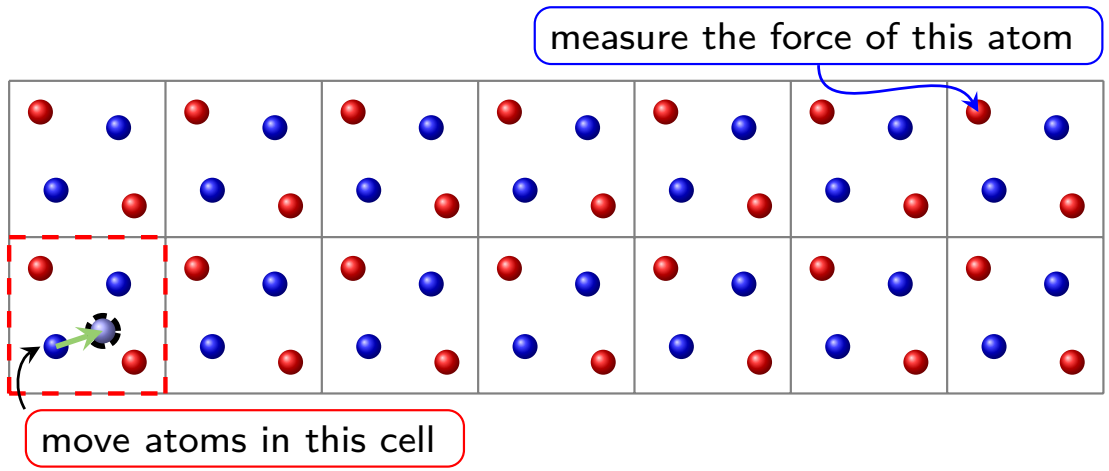
The definition of the dynamical matrix

$$D_{s\alpha,t\beta}(\boldsymbol{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_{l=-\infty}^{\infty} C^{0,l}_{s\alpha,t\beta}\, e^{i\boldsymbol{q}\boldsymbol{x}_l} \approx \frac{1}{\sqrt{M_s M_t}} \sum_{|l|<l_{\text{cut}}} C^{0,l}_{s\alpha,t\beta}\, e^{i\boldsymbol{q}\boldsymbol{x}_l} \tag{6}$$

1. Finite-difference and supercell approach — Frozen phonon method

IFC by finite-difference:

$$\frac{\partial^2 E^0_{\text{tot}}}{\partial u^0_{s\alpha}\partial u^l_{t\beta}} = \frac{\partial F^l_{t\beta}}{\partial u^0_{s\alpha}} \approx \frac{F^l_{t\beta}(\Delta_{s\alpha}) - F^l_{t\beta}(\text{-}\Delta_{s\alpha})}{2\Delta_{s\alpha}}$$

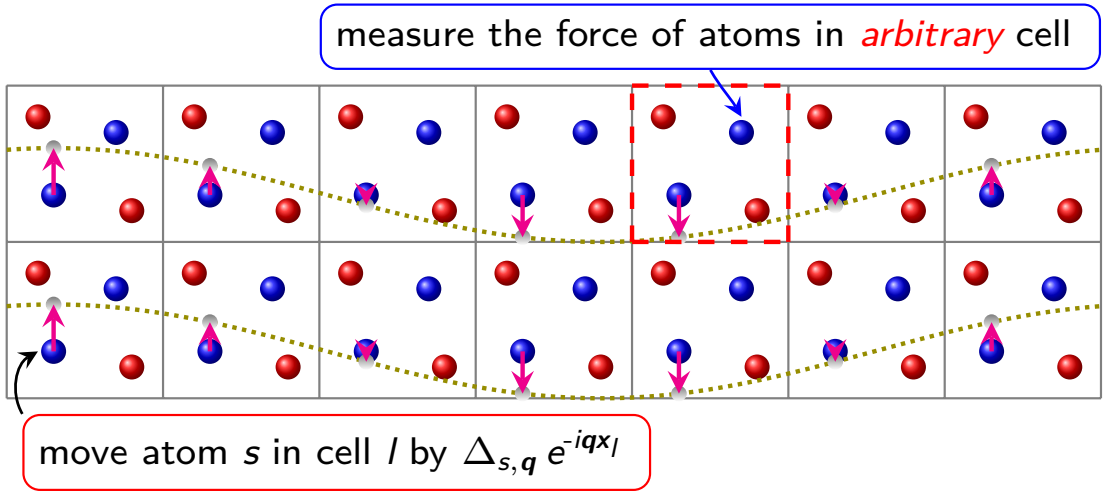


- Supercell must be large enough so that IFC is negligible at the cell boundary.
- Movements done *only* in one primitive cell.
- $3 \times N_a \times 2$ movements, i.e. move by $\pm\Delta$ in $x/y/z$ directions for each atom in the primitive cell.
- Symmetry can be adopted to reduce the number of movements.
- The dynamical matrix can then be obtained at arbitrary $\boldsymbol{q}$ by Eq. 6.

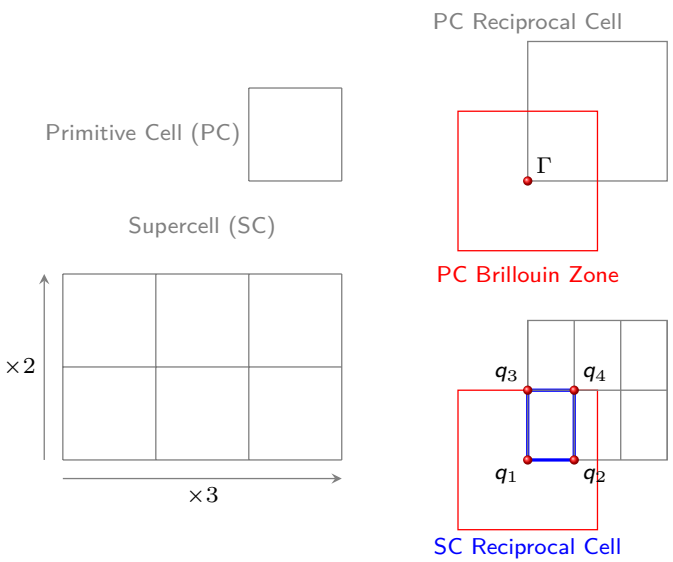
How to Calculate the Dynamical Matrix II

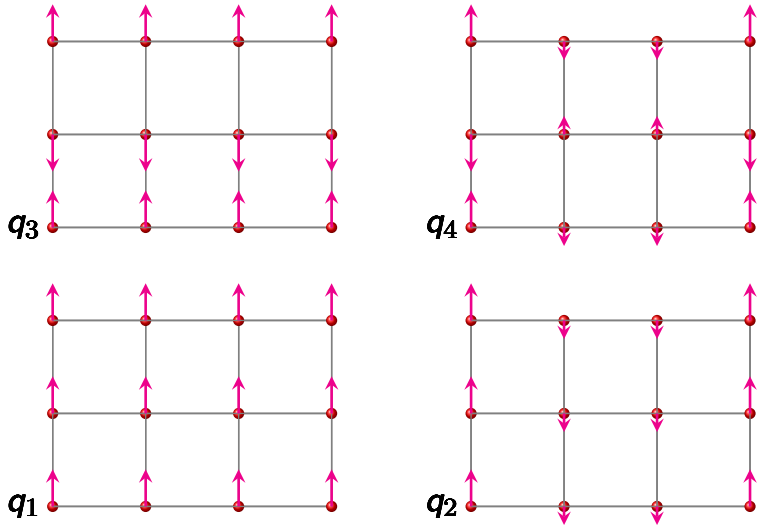
Dynamical matrix:

$$D_{s\alpha,t\beta}(\boldsymbol{q}) \approx \frac{1}{\sqrt{M_s M_t}} \times \frac{F^l_{t\beta}(\Delta_{s,\boldsymbol{q}}) - F^l_{t\beta}(-\Delta_{s,\boldsymbol{q}})}{2\Delta_{s,\boldsymbol{q}}}$$



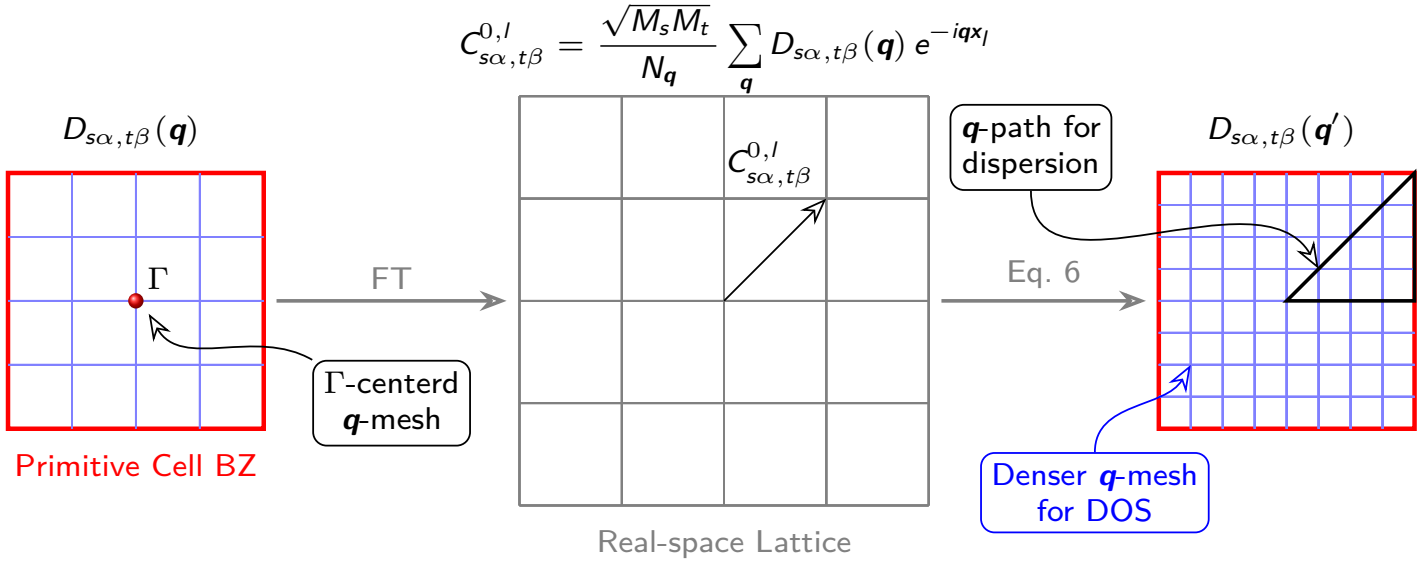
- Can only obtain dynamical matrix at certain $\boldsymbol{q}$.





- $D_{s\alpha,t\beta}(\boldsymbol{q}) \xrightarrow{\text{FT}} C^{0,l}_{s\alpha,t\beta} \xrightarrow{\text{Eq. 6}} D_{s\alpha,t\beta}(\boldsymbol{k})$

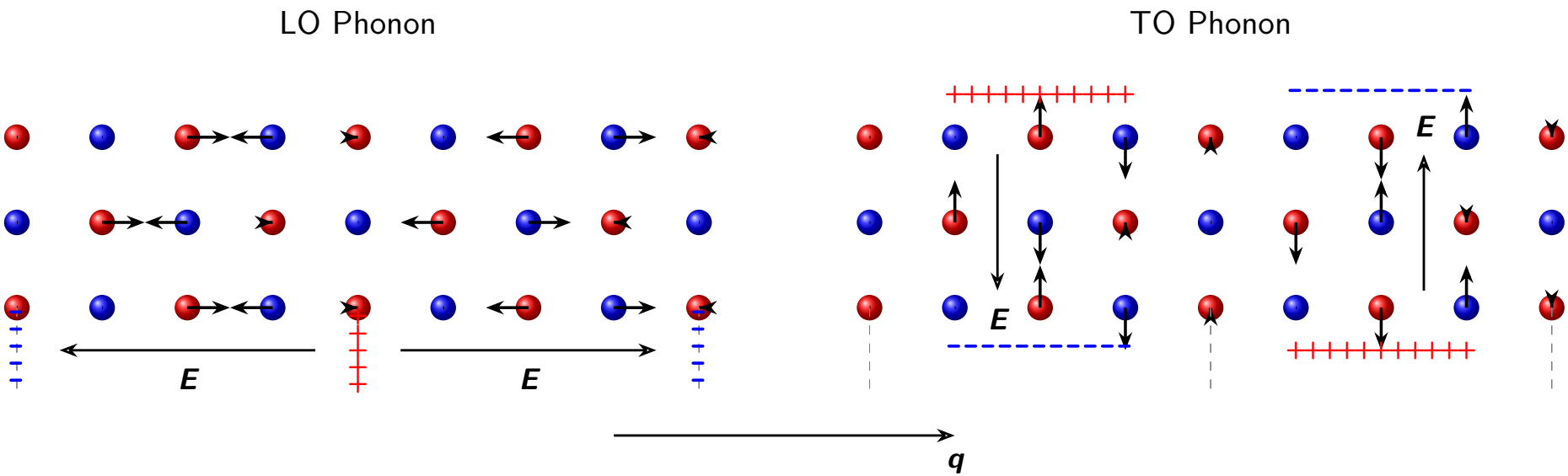
2. Lineare response approach — density functional perturbation theory
   - Can calculate $D_{s\alpha,t\beta}(\boldsymbol{q})$ at *arbitrary* $\boldsymbol{q}$ using a *primitive cell*.
   - $D_{s\alpha,t\beta}(\boldsymbol{q})$ is periodic in reciprocal space: $D_{s\alpha,t\beta}(\boldsymbol{q}+\boldsymbol{G}) = D_{s\alpha,t\beta}(\boldsymbol{q})$



   - In practice, first calculate $D_{s\alpha,t\beta}(\boldsymbol{q})$ with a small $\boldsymbol{q}$-mesh. Then, perform FT to get the IFC in real space. Finally, dynamical matrix at arbitrary $\boldsymbol{q}$ can be obtained.
   - Fails in metal with Kohn anomalies or in polar semiconductors where the dynamical matrix is non-analytic for $\boldsymbol{q} \to 0$.

3. Codes: `Phonopy`, `PHON`, `YPHON`, `PhonTS`, `ShengBTE`, `ALM`, `ALAMODE`, `Quantum Espresso`, `Abinit`, `Siesta` ...

LO-TO Splitting



Long-wavelength limit in polar materials

The dynamical matrix in polar materials can be separated into two parts [4]

$$D_{s\alpha,t\beta}(\boldsymbol{q}\to 0) = D^{\text{an}}_{s\alpha,t\beta}(\boldsymbol{q}=0) + D^{\text{na}}_{s\alpha,t\beta}(\boldsymbol{q}\to 0)$$

where the nonanalytic part is written as

$$D^{\text{na}}_{s\alpha,t\beta}(\boldsymbol{q}\to 0) = \frac{1}{\sqrt{M_s M_t}} \frac{4\pi e^2}{\Omega} \frac{\left(\sum_\gamma q_\gamma Z^{*\gamma\alpha}_s\right)\left(\sum_\mu q_\mu Z^{*\mu\beta}_t\right)}{\sum_{\gamma\mu} q_\gamma \,\epsilon^{\gamma\mu}_\infty\, q_\mu} \tag{7}$$

- Z^*_s is the Born effective charge tensor for atom s

$$Z^{*\alpha\beta}_s = \Omega_0 \frac{\partial \mathcal{P}_\beta}{\partial u_{s\alpha}} = \frac{\partial F_{s\alpha}}{\partial \mathcal{E}_\beta}$$

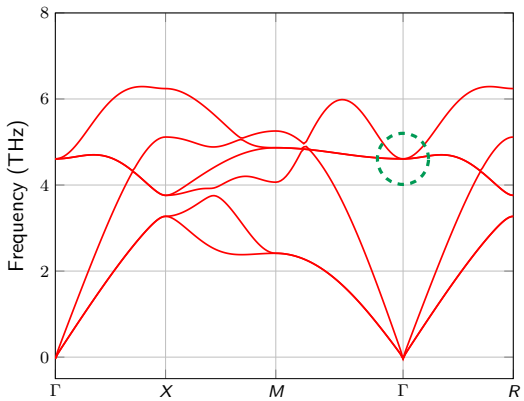
  1. The response of the polarization per unit cell along the direction β induced by a displacement along the direction α of the atoms belonging to the sublattice s, under the condition of a zero electric field.
  2. The force on the atom s along α induced by the macroscopic field along β.
  3. Sum rules: $\sum_s Z^{*\alpha\beta}_s = 0$
  4. The infrared absorption: $I_{\text{IR}}(\omega_\sigma) \propto \sum_{\alpha=1}^{3} \left|\sum_{s\beta} Z^{*\alpha\beta}_s \eta^\sigma_{s\beta}\right|^2$

- ϵ_∞ is the *electronic* dielectric tensor of the crystal, i.e. the static dielectric constant with clamped nuclei.

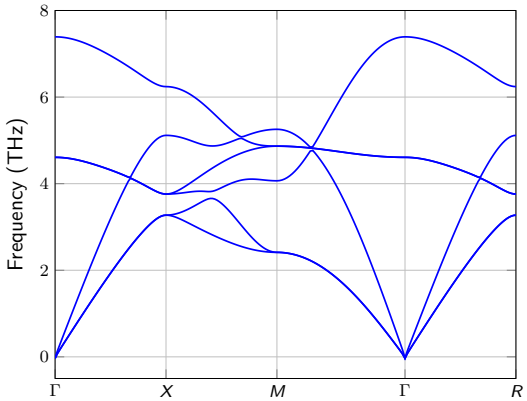
[4] X. Gonze and C. Lee, *Phys. Rev. B* 55, 10355(1997).

Phonon Band Structure with/without NAC

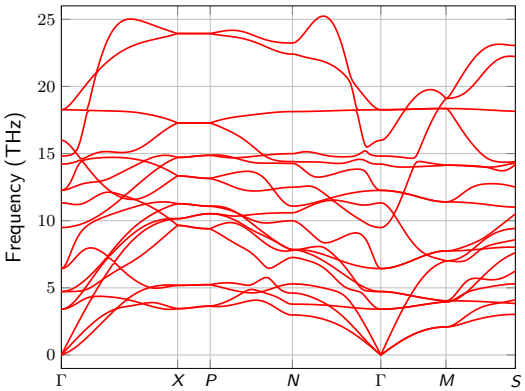
NaCl *WITHOUT* NAC [5]



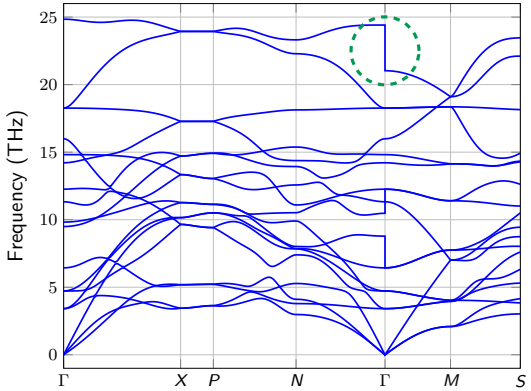
NaCl *WITH* NAC



Anatase TiO_2 *WITHOUT* NAC [6]



Anatase TiO_2 *WITH* NAC

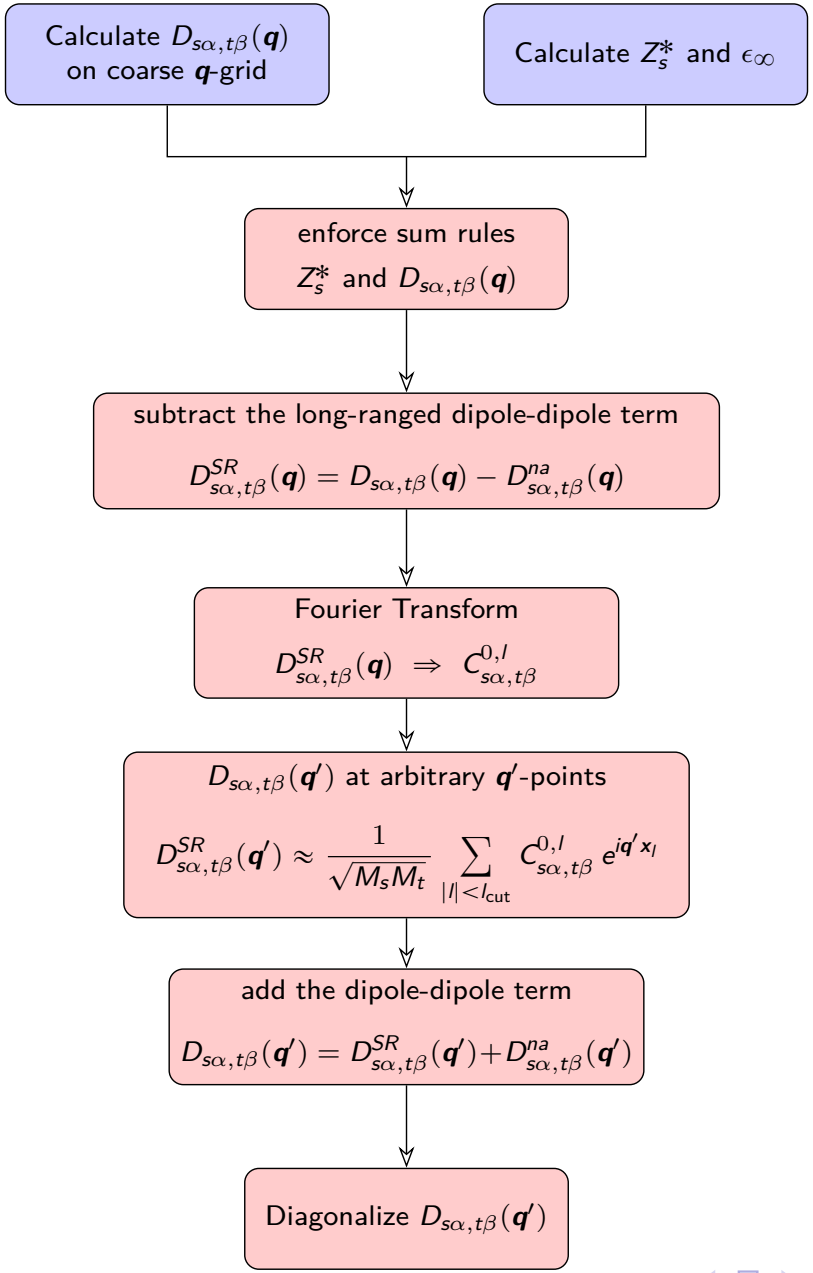


- The limiting value of Eq. 7 may be different for different $\boldsymbol{q} \to 0$ directions, as can be seen in the phonon dispersion of Anatase TiO_2.
- This strange behavior is physical and the frequency of the observed phonons depends on the polarizability in the different directions, with respect to the propagation of the incoming electric field.

[5] https://github.com/phonopy/phonopy/tree/master/example/NaCl

[6] `https://github.com/phonopy/phonopy/tree/master/example/TiO2-anatase`

DFPT Interpolation Scheme for Polar Material



Outline

Within DFT, the total energy is given by

$$E_{\text{tot}} = \sum_{i}^{occ} \langle \psi_i(\boldsymbol{r}) | -\frac{\hbar^2}{2m}\nabla^2 | \psi_i(\boldsymbol{r}) \rangle + \int_V V_{\text{ext}}(\boldsymbol{r})\rho(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} + E_H[\rho] + E_{xc}[\rho] + U_{II}$$

over the entire space

- $V_{\text{ext}}(\boldsymbol{r})$: electron-ion interaction
- U_{II}: ion-ion interaction
- $E_H[\rho]$: electron Hartree energy
- $E_{xc}[\rho]$: exchange-correlation energy
- $\rho(\boldsymbol{r})$: electron density

$$\rho(\boldsymbol{r}) = \sum_{i}^{occ} \psi_i^*(\boldsymbol{r})\psi_i(\boldsymbol{r})$$

The first and second order derivative with respect to external parameter λ, μ

$$\frac{\partial E_{\text{tot}}}{\partial \lambda} = \int_V \frac{\partial V_{\text{ext}}(\boldsymbol{r})}{\partial \lambda}\rho(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} + \frac{\partial U_{II}}{\partial \lambda} \tag{8}$$

$$\begin{aligned}\frac{\partial^2 E_{\text{tot}}}{\partial \lambda \partial \mu} = &\int_V \frac{\partial^2 V_{\text{ext}}(\boldsymbol{r})}{\partial \lambda \partial \mu}\rho(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} + \frac{\partial^2 U_{II}}{\partial \lambda \partial \mu} \\ &+ \int_V \frac{\partial V_{\text{ext}}(\boldsymbol{r})}{\partial \lambda}\frac{\partial \rho(\boldsymbol{r})}{\partial \mu}\,\mathrm{d}\boldsymbol{r}\end{aligned} \tag{9}$$

2-nd derivative requires the extra calculation of the *linear response* of the charge density to the external perturbation!

The Kohn-Sham eqution

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\boldsymbol{r};\mu)\right]\psi_n(\boldsymbol{r}) = \varepsilon_n\psi_n(\boldsymbol{r})$$

$$\rho(\boldsymbol{r}) = \sum_n^{occ} |\psi_n(\boldsymbol{r})|^2$$

$$V_{KS}(\boldsymbol{r}) = V_{ext}(\boldsymbol{r}) + V_H(\boldsymbol{r}) + V_{xc}(\boldsymbol{r})$$

With a small perturbation μ

$$V_{KS}(\boldsymbol{r};\mu) = V_{KS}(\boldsymbol{r};\mu=0) + \mu\frac{\partial V_{KS}(\boldsymbol{r})}{\partial\mu}$$

$$\psi_n(\boldsymbol{r};\mu) = \psi_n(\boldsymbol{r};\mu=0) + \mu\frac{\partial \psi_n(\boldsymbol{r})}{\partial\mu}$$

$$\varepsilon_n(\mu) = \varepsilon_n(\mu=0) + \mu\frac{\partial \varepsilon_n}{\partial\mu}$$

Inserting these equations and keeps only the first-order terms

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\boldsymbol{r}) - \varepsilon_n\right]\frac{\partial\psi_n(\boldsymbol{r})}{\partial\mu} = -\left[\frac{\partial V_{KS}(\boldsymbol{r})}{\partial\mu} - \frac{\partial\varepsilon_n}{\partial\mu}\right]\psi_n(\boldsymbol{r}) \tag{10}$$

where

$$\frac{\partial V_{KS}(\boldsymbol{r})}{\partial\mu} = \frac{\partial V_{ext}(\boldsymbol{r})}{\partial\mu} + \frac{\partial V_H(\boldsymbol{r})}{\partial\mu} + \frac{\partial V_{xc}(\boldsymbol{r})}{\partial\mu} \tag{11}$$

$$\frac{\partial V_H(\boldsymbol{r})}{\partial\mu} = \int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\frac{\partial\rho(\boldsymbol{r}')}{\partial\mu}\,\mathrm{d}\boldsymbol{r}'; \qquad \frac{\partial V_{xc}(\boldsymbol{r})}{\partial\mu} = \int \frac{\mathrm{d}V_{xc}}{\mathrm{d}\rho(\boldsymbol{r}')}\frac{\partial\rho(\boldsymbol{r}')}{\partial\mu}\,\mathrm{d}\boldsymbol{r}' \tag{12}$$

Electron density response to the perturbation

$$\frac{\partial \rho(\boldsymbol{r})}{\partial \mu} = \sum_{n}^{occ} \left[\frac{\partial \psi_n^*(\boldsymbol{r})}{\partial \mu} \psi_n(\boldsymbol{r}) + \psi_n^*(\boldsymbol{r}) \frac{\partial \psi_n(\boldsymbol{r})}{\partial \mu} \right] \tag{13}$$

$$\frac{\partial \psi_n(\boldsymbol{r})}{\partial \mu} = \sum_{m \neq n} \frac{\langle \psi_m | \frac{\partial V_{KS}(\boldsymbol{r})}{\partial \mu} | \psi_n \rangle}{\varepsilon_n - \varepsilon_m} \psi_m(\boldsymbol{r}) \tag{14}$$

Where n is the index for the occupied staets and m runs over all the states.

Define $P_v = \sum_n^{occ} |\psi_n\rangle\langle\psi_n|$ as the projector on the valence bands, then $P_c = \mathbb{1} - P_v$ is the projector on the conduction bands

$$\begin{aligned}
\frac{\partial \rho(\boldsymbol{r})}{\partial \mu} &= \sum_{n}^{occ} \left[P_c \frac{\partial \psi_n^*(\boldsymbol{r})}{\partial \mu} \psi_n(\boldsymbol{r}) + \psi_n^*(\boldsymbol{r}) P_c \frac{\partial \psi_n(\boldsymbol{r})}{\partial \mu} \right] + \sum_{n}^{occ} \left[P_v \frac{\partial \psi_n^*(\boldsymbol{r})}{\partial \mu} \psi_n(\boldsymbol{r}) + \psi_n^*(\boldsymbol{r}) P_v \frac{\partial \psi_n(\boldsymbol{r})}{\partial \mu} \right] \\
&= \sum_{n}^{occ} \left[P_c \frac{\partial \psi_n^*(\boldsymbol{r})}{\partial \mu} \psi_n(\boldsymbol{r}) + \psi_n^*(\boldsymbol{r}) P_c \frac{\partial \psi_n(\boldsymbol{r})}{\partial \mu} \right] + \sum_{mn}^{occ} \psi_m^*(\boldsymbol{r}) \psi_n(\boldsymbol{r}) \left(\langle \frac{\partial \psi_n}{\partial \mu} | \psi_m \rangle + \langle \psi_n | \frac{\partial \psi_m}{\partial \mu} \rangle \right)
\end{aligned}$$

Due the orthonormality of $\psi_n(\boldsymbol{r})$, i.e. $\langle \psi_m | \psi_n \rangle = \delta_{mn}$

$$\frac{\partial \rho(\boldsymbol{r})}{\partial \mu} = \sum_{n}^{occ} \left[P_c \frac{\partial \psi_n^*(\boldsymbol{r})}{\partial \mu} \psi_n(\boldsymbol{r}) + \psi_n^*(\boldsymbol{r}) P_c \frac{\partial \psi_n(\boldsymbol{r})}{\partial \mu} \right] \tag{15}$$

The electron density response depends only on the component of the perturbation that *couples the occupied states with the empty ones.*

Apply P_c on the left and right-hand side of Eq. 10

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\boldsymbol{r}) + \alpha P_v - \varepsilon_n\right] P_c \frac{\partial \psi_n(\boldsymbol{r})}{\partial \mu} = -(\mathbb{1} - P_v)\frac{\partial V_{KS}(\boldsymbol{r})}{\partial \mu}\psi_n(\boldsymbol{r}) \tag{16}$$

where the αP_v is added to make the left-hand-side nonsingular.

$$\frac{\partial V_{KS}(\boldsymbol{r})}{\partial \mu} = \frac{\partial V_{ext}(\boldsymbol{r})}{\partial \mu} + \int \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}\frac{\partial \rho(\boldsymbol{r}')}{\partial \mu}\,\mathrm{d}\boldsymbol{r}' + \int \frac{\mathrm{d}V_{xc}}{\mathrm{d}\rho(\boldsymbol{r}')}\frac{\partial \rho(\boldsymbol{r}')}{\partial \mu}\,\mathrm{d}\boldsymbol{r}' \tag{17}$$

$$\frac{\partial \rho(\boldsymbol{r})}{\partial \mu} = \sum_n^{occ}\left[P_c \frac{\partial \psi_n^*(\boldsymbol{r})}{\partial \mu}\psi_n(\boldsymbol{r}) + \psi_n^*(\boldsymbol{r}) P_c \frac{\partial \psi_n(\boldsymbol{r})}{\partial \mu}\right]$$

Considering the time-reversal symmetry $\psi^*_{n,-\boldsymbol{k}}(\boldsymbol{r}) = \psi_{n,\boldsymbol{k}}(\boldsymbol{r})$

$$\begin{aligned}\frac{\partial \rho(\boldsymbol{r})}{\partial \mu} &= \sum_{n,-\boldsymbol{k}}^{occ} P_c \frac{\partial \psi^*_{n,-\boldsymbol{k}}(\boldsymbol{r})}{\partial \mu}\psi_{n,-\boldsymbol{k}}(\boldsymbol{r}) + \sum_{n,\boldsymbol{k}}^{occ}\psi^*_{n,\boldsymbol{k}}(\boldsymbol{r}) P_c \frac{\partial \psi_{n,\boldsymbol{k}}(\boldsymbol{r})}{\partial \mu} \\ &= 2\sum_{n,\boldsymbol{k}}^{occ}\psi^*_{n,\boldsymbol{k}}(\boldsymbol{r}) P_c \frac{\partial \psi_{n,\boldsymbol{k}}(\boldsymbol{r})}{\partial \mu}\end{aligned} \tag{18}$$

Eq. 16, Eq. 17 and Eq. 18 form a set of self-consistent euqations for the perturbed system.

DFT & DFPT Equations

DFT

$$\rho(\boldsymbol{r}) \rightleftharpoons V_{KS}(\boldsymbol{r})$$

$$V_{KS}(\boldsymbol{r}) = V_{ext}(\boldsymbol{r}) + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,\mathrm{d}\boldsymbol{r}' + V_{xc}(\boldsymbol{r})$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\boldsymbol{r})\right]\psi_n(\boldsymbol{r}) = \varepsilon_n\psi_n(\boldsymbol{r})$$

$$\rho(\boldsymbol{r}) = \sum_n^{occ} \psi_n^*(\boldsymbol{r})\psi_n(\boldsymbol{r})$$

DFPT

$$\frac{\partial\rho(\boldsymbol{r})}{\partial\mu} \rightleftharpoons \frac{\partial V_{KS}(\boldsymbol{r})}{\partial\mu}$$

$$\frac{\partial V_{KS}(\boldsymbol{r})}{\partial\mu} = \frac{\partial V_{ext}(\boldsymbol{r})}{\partial\mu} + \int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\frac{\partial\rho(\boldsymbol{r}')}{\partial\mu}\,\mathrm{d}\boldsymbol{r}' + \int \frac{\mathrm{d}V_{xc}}{\mathrm{d}\rho(\boldsymbol{r}')}\frac{\partial\rho(\boldsymbol{r}')}{\partial\mu}\,\mathrm{d}\boldsymbol{r}'$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\boldsymbol{r}) + \alpha P_v - \varepsilon_n\right] P_c\frac{\partial\psi_n(\boldsymbol{r})}{\partial\mu} = -P_c\frac{\partial V_{KS}(\boldsymbol{r})}{\partial\mu}\psi_n(\boldsymbol{r})$$

$$\frac{\partial\rho(\boldsymbol{r})}{\partial\mu} = 2\sum_n^{occ}\psi_n^*(\boldsymbol{r})P_c\frac{\partial\psi_n(\boldsymbol{r})}{\partial\mu}$$

Add a monochromatic perturbation characterized by generic wavevector $\boldsymbol{q}$ to the periodic potential

$$V_{ext}(\boldsymbol{r}+\boldsymbol{x}_j) = V_{ext}(\boldsymbol{r}); \qquad \Delta V^{\boldsymbol{q}}_{ext}(\boldsymbol{r}+\boldsymbol{x}_j) = e^{i\boldsymbol{q}\cdot\boldsymbol{x}_j}\,\Delta V^{\boldsymbol{q}}_{ext}(\boldsymbol{r})$$

It can be shown that all the linear responses are also characterized by wavevector $\boldsymbol{q}$

$$\Delta V^{\boldsymbol{q}}_{KS}(\boldsymbol{r}+\boldsymbol{x}_j) = e^{i\boldsymbol{q}\cdot\boldsymbol{x}_j}\,\Delta V^{\boldsymbol{q}}_{KS}(\boldsymbol{r})$$

$$\Delta \rho^{\boldsymbol{q}}(\boldsymbol{r}+\boldsymbol{x}_j) = e^{i\boldsymbol{q}\cdot\boldsymbol{x}_j}\,\Delta \rho^{\boldsymbol{q}}(\boldsymbol{r})$$

$$\Delta \psi^{\boldsymbol{q}}_{n,\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{x}_j) = e^{i\boldsymbol{q}\cdot\boldsymbol{x}_j}\,\Delta \psi^{\boldsymbol{q}}_{n,\boldsymbol{k}}(\boldsymbol{r})$$

Let us define the related periodic quantities

$$\Delta V^{\boldsymbol{q}}_{ext}(\boldsymbol{r}) = e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\,\tilde{V}^{\boldsymbol{q}}_{ext}(\boldsymbol{r}); \qquad \tilde{V}^{\boldsymbol{q}}_{ext}(\boldsymbol{r}+\boldsymbol{x}_j) = \tilde{V}^{\boldsymbol{q}}_{ext}(\boldsymbol{r});$$

$$\Delta V^{\boldsymbol{q}}_{KS}(\boldsymbol{r}) = e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\,\tilde{V}^{\boldsymbol{q}}_{KS}(\boldsymbol{r}); \qquad \tilde{V}^{\boldsymbol{q}}_{KS}(\boldsymbol{r}+\boldsymbol{x}_j) = \tilde{V}^{\boldsymbol{q}}_{KS}(\boldsymbol{r});$$

$$\Delta \rho^{\boldsymbol{q}}(\boldsymbol{r}) = e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\,\tilde{\rho}^{\boldsymbol{q}}(\boldsymbol{r}); \qquad \tilde{\rho}^{\boldsymbol{q}}(\boldsymbol{r}+\boldsymbol{x}_j) = \tilde{\rho}^{\boldsymbol{q}}(\boldsymbol{r});$$

$$\psi_{n,\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\,u_{n,\boldsymbol{k}}(\boldsymbol{r}); \qquad u_{n,\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{x}_j) = u_{n,\boldsymbol{k}}(\boldsymbol{r});$$

$$\Delta \psi^{\boldsymbol{q}}_{n,\boldsymbol{k}}(\boldsymbol{r}) = e^{i(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{r}}\,\Delta u^{\boldsymbol{q}}_{n,\boldsymbol{k}}(\boldsymbol{r}); \qquad \Delta u^{\boldsymbol{q}}_{n,\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{x}_j) = \Delta u^{\boldsymbol{q}}_{n,\boldsymbol{k}}(\boldsymbol{r});$$

Substitute into Eq. 16

$$\left[H_{KS}(\boldsymbol{r}) + \alpha P_v - \varepsilon_{n,\boldsymbol{k}}\right] P_c e^{i(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{r}} \frac{\partial u^{\boldsymbol{q}}_{n,\boldsymbol{k}}(\boldsymbol{r})}{\partial\mu} = -P_c e^{i(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{r}} \frac{\partial \tilde{V}^{\boldsymbol{q}}_{KS}(\boldsymbol{r})}{\partial\mu} u_{n,\boldsymbol{k}}(\boldsymbol{r}) \tag{19}$$

Apply the phase $e^{-i(\boldsymbol{k}+\boldsymbol{q})\cdot\boldsymbol{r}}$ to the both sides of Eq. 19

$$\left[H^{\boldsymbol{k}+\boldsymbol{q}}_{KS}(\boldsymbol{r}) + \alpha P^{\boldsymbol{k}+\boldsymbol{q}}_v - \varepsilon_{n,\boldsymbol{k}}\right] P^{\boldsymbol{k}+\boldsymbol{q}}_c \frac{\partial u^{\boldsymbol{q}}_{n,\boldsymbol{k}}(\boldsymbol{r})}{\partial\mu} = -P^{\boldsymbol{k}+\boldsymbol{q}}_c \frac{\partial \tilde{V}^{\boldsymbol{q}}_{KS}(\boldsymbol{r})}{\partial\mu} u_{n,\boldsymbol{k}}(\boldsymbol{r}) \tag{20}$$

where

$$\frac{\partial \tilde{V}_{KS}(\boldsymbol{r})}{\partial\mu} = \frac{\partial \tilde{V}_{ext}(\boldsymbol{r})}{\partial\mu} + \int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} \frac{\partial \tilde{\rho}^{\boldsymbol{q}}(\boldsymbol{r}')}{\partial\mu} \mathrm{d}\boldsymbol{r}' + \int \frac{\mathrm{d}V_{xc}}{\mathrm{d}\rho(\boldsymbol{r}')} \frac{\partial \tilde{\rho}^{\boldsymbol{q}}(\boldsymbol{r}')}{\partial\mu} \mathrm{d}\boldsymbol{r}'$$

$$\frac{\partial \tilde{\rho}^{\boldsymbol{q}}(\boldsymbol{r}')}{\partial\mu} = 2\sum_{n,\boldsymbol{k}}^{occ} u^*_{n,\boldsymbol{k}}(\boldsymbol{r}) P^{\boldsymbol{k}+\boldsymbol{q}}_c \frac{\partial u^{\boldsymbol{q}}_{n,\boldsymbol{k}}(\boldsymbol{r})}{\partial\mu}$$

$$P^{\boldsymbol{k}+\boldsymbol{q}}_v = \sum_{n}^{occ} |u_{n,\boldsymbol{k}+\boldsymbol{q}}\rangle\langle u_{n,\boldsymbol{k}+\boldsymbol{q}}| \,; \quad P^{\boldsymbol{k}+\boldsymbol{q}}_c = \mathbb{1} - P^{\boldsymbol{k}+\boldsymbol{q}}_v$$

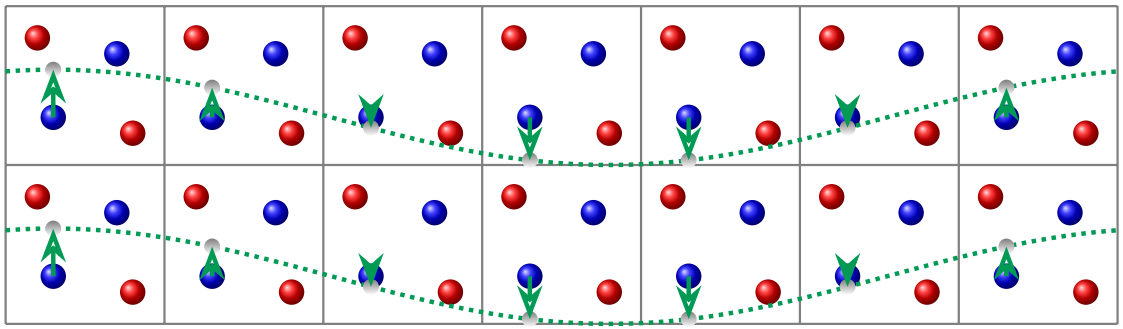
The treatment of perturbations incommensurate with the unperturbed system periodicity is mapped onto the *original periodic system*.

In a solid, the external potential can be expressed as the superposition of atomic potential $v_s(\boldsymbol{r})$

$$V_{ext}(\boldsymbol{r}) = \sum_j \sum_s^{N_a} v_s(\boldsymbol{r} - \boldsymbol{x}_j - \boldsymbol{d}_s - \boldsymbol{u}_s^j)$$

Consider the periodic displacement of the ions of the form

$$u_{s\alpha}^j(\boldsymbol{q}) = \mu_{s\alpha}\, e^{i\boldsymbol{q}\cdot\boldsymbol{x}_j} + \mu_{s\alpha}^*\, e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_j} \qquad (\alpha = x, y, z) \tag{21}$$



$$\frac{\partial V_{ext}^{\boldsymbol{q}}(\boldsymbol{r})}{\partial \mu_{s\alpha}} = -\sum_j e^{i\boldsymbol{q}\cdot\boldsymbol{x}_j} \left.\frac{\partial v_s(\boldsymbol{r} - \boldsymbol{x}_j - \boldsymbol{d}_s)}{\partial r_\alpha}\right|_{u_s^j=0}$$

$$= -e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \sum_j e^{i\boldsymbol{q}\cdot(\boldsymbol{x}_j - \boldsymbol{r})} \left.\frac{\partial v_s(\boldsymbol{r} - \boldsymbol{x}_j - \boldsymbol{d}_s)}{\partial r_\alpha}\right|_{u_s^j=0}$$

The colored quantity has the periodicity of the lattice.

The dynamical matrix

$$D_{s\alpha,t\beta}(\boldsymbol{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_k e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_j} \frac{\partial^2 E^0_{\text{tot}}}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} e^{i\boldsymbol{q}\cdot\boldsymbol{x}_k} = \frac{N}{\sqrt{M_s M_t}} \frac{\partial^2 E^0_{\text{tot}}}{\partial \mu^*_{s\alpha} \partial \mu_{t\beta}}$$

Inserting the equation for the second derivative Eq. 9

$$D_{s\alpha,t\beta}(\boldsymbol{q}) = \frac{N}{\sqrt{M_s M_t}} \int_V \sum_k e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_j} \frac{\partial^2 V^{\boldsymbol{q}}_{ext}(\boldsymbol{r})}{\partial u^j_{s\alpha} \partial u^k_{t\beta}} \rho(\boldsymbol{r})\, e^{i\boldsymbol{q}\cdot\boldsymbol{x}_k}\, \mathrm{d}\boldsymbol{r}$$

$$+ \frac{1}{\sqrt{M_s M_t}} \int_V \sum_k e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_j} \frac{\partial V^{\boldsymbol{q}}_{ext}(\boldsymbol{r})}{\partial u^j_{s\alpha}} \frac{\partial \rho(\boldsymbol{r})}{\partial u^k_{t\beta}} e^{i\boldsymbol{q}\cdot\boldsymbol{x}_k}\, \mathrm{d}\boldsymbol{r}$$

Thank you!