

# Lattice Dynamics and Phonon

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## 1 Lattice Dynamics

- 1D Atomic Chain
- 3D lattice
- How to calculate the dynamical matrix

## 2 Density functional perturbation theory

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

$$\parallel$$

$$\sum_i \frac{\hat{\mathbf{p}}_i^2}{2m} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$+$$

$$\sum_{i,l} \frac{Z_l e^2}{|\mathbf{r}_i - \mathbf{R}_l|}$$

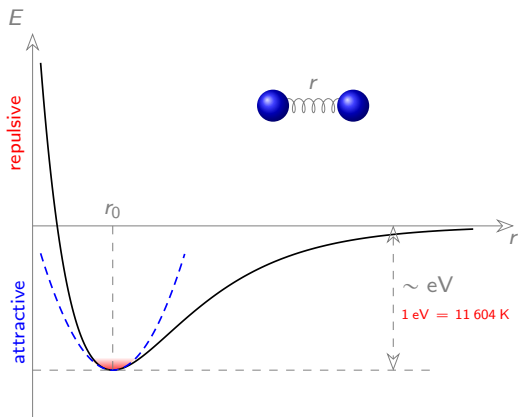
$$+$$

$$\sum_l \frac{\hat{\mathbf{p}}_l^2}{2M_l} + \frac{1}{2} \sum_{l,j} \frac{Z_l Z_j e^2}{|\mathbf{R}_l - \mathbf{R}_j|}$$

$$\Downarrow$$

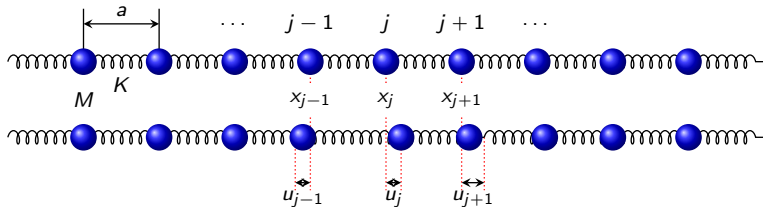
$$i\hbar \frac{\partial}{\partial t} \psi(\{\mathbf{r}\}, \{\mathbf{R}\}) = \mathcal{H}(\{\mathbf{r}\}, \{\mathbf{R}\}) \psi(\{\mathbf{r}\}, \{\mathbf{R}\})$$

# 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

$$M \frac{d^2 u_j}{dt^2} = K(u_{j+1} + u_{j-1} - 2u_j) \quad j = 1, \dots, N$$

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

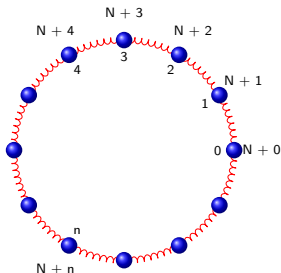
$$\begin{aligned} \omega^2 &= \frac{K}{M} (2 - e^{iqa} - e^{-iqa}) \\ &= \frac{2K}{M} (1 - \cos qa) \\ \Rightarrow \quad \omega &= \sqrt{\frac{4K}{M}} \left| \sin \frac{qa}{2} \right| \end{aligned}$$

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

The Born-von Karman Periodic Boundary Condition:

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

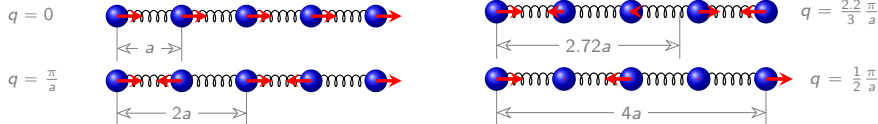
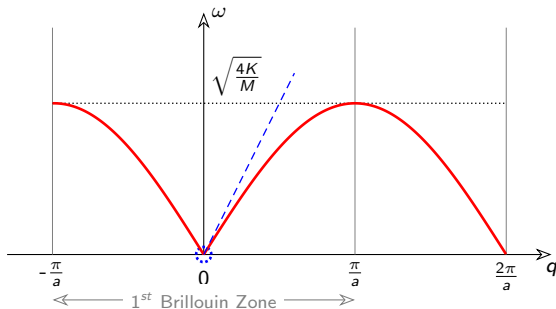
$$\Rightarrow q = \frac{2\pi}{a} \frac{l}{N}; \quad (l = 0, 1, \dots, N)$$



Usually,  $q$  is restricted within the first Brillouin Zone

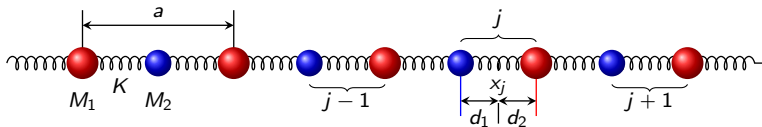
$$-\frac{\pi}{a} \leq q \leq \frac{\pi}{a}$$

# Dispersion and Vibration Pattern



# 1D Chain of Atoms — 2 Atoms per Unit

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



The Newton's Equation

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

We then have

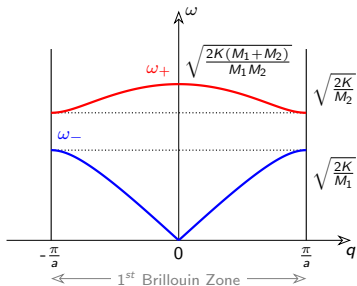
$$\begin{pmatrix} \frac{2K}{M_1} & \frac{-K}{\sqrt{M_1 M_2}} (1 + e^{-iqa}) \\ \frac{-K}{\sqrt{M_1 M_2}} (1 + e^{iqa}) & \frac{2K}{M_2} \end{pmatrix} \begin{pmatrix} A_q \\ B_q \end{pmatrix} = \omega^2 \begin{pmatrix} A_q \\ B_q \end{pmatrix}$$

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

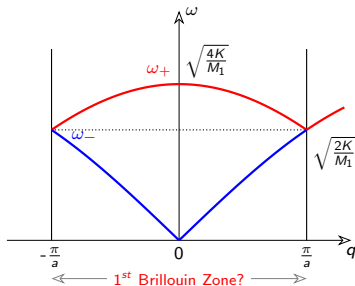


# Dispersion and Vibration Pattern

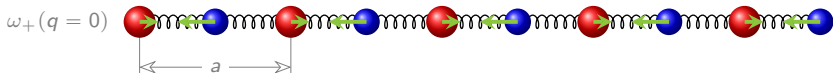
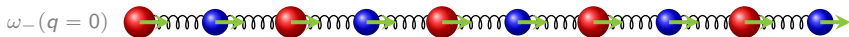
$$M_1 = 2M_2$$

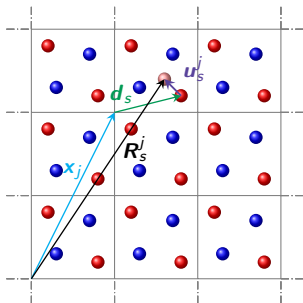


$$M_1 = M_2$$



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





- $\mathbf{x}_j$ : the position of unit cell  $j$
- $\mathbf{d}_s$ : the equilibrium position of the atom  $s$  in the cell
- $\mathbf{u}_s^j$ : displacement from the equilibrium position for the atom  $s$  in the cell  $j$
- $\mathbf{R}_s^j$ : the position of the atom  $s$  in the cell  $j$

$$\begin{aligned}\mathbf{R}_s^j(t) &= \mathbf{x}_j + \mathbf{d}_s + \mathbf{u}_s^j(t) \\ &= \mathbf{r}_s^j + \mathbf{u}_s^j(t)\end{aligned}$$

$$R_{s\alpha}^j(t) = r_{s\alpha}^j + u_{s\alpha}^j(t) \quad (\alpha = x, y, z)$$

The total energy can be written as

$$E_{\text{tot}}(\{\mathbf{R}_s^j(t)\}) = E_{\text{tot}}^0(\{\mathbf{r}_s^j\}) + \sum_{js\alpha} \frac{\partial E_{\text{tot}}^0}{\partial u_{s\alpha}^j} u_{s\alpha}^j + \frac{1}{2} \sum_{js\alpha} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} u_{s\alpha}^j u_{t\beta}^k + \dots$$

- The expression is exact if we take all the orders in the expansion.
- All the derivatives are taken at the equilibrium positions  $\{\mathbf{r}_s^j\}$ , 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  $j$

$$M_s \frac{d^2 u_{s\alpha}^j(t)}{dt^2} = - \frac{\partial E_{\text{tot}}}{\partial u_{s\alpha}^j} = - \sum_{kt\beta} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} u_{t\beta}^k = - \sum_{kt\beta} C_{s\alpha,t\beta}^{j,k} u_{t\beta}^k \quad (1)$$

The ansatz of the solution

$$u_{s\alpha}^j(t) = \frac{\eta_{s\alpha}^\sigma(\mathbf{q})}{\sqrt{M_s}} e^{i\mathbf{q}\cdot\mathbf{x}_j} e^{-i\omega_\sigma t} \quad (2)$$

Substitute Eq. 2 into Eq. 1

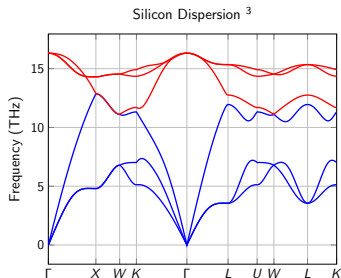
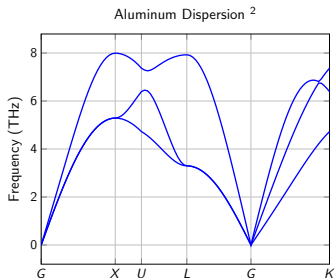
$$\omega_\sigma^2(\mathbf{q}) \eta_{s\alpha}^\sigma = \sum_{t\beta} \left[ \sum_k \frac{1}{\sqrt{M_s M_t}} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} e^{i\mathbf{q}(\mathbf{x}_k - \mathbf{x}_j)} \right] \eta_{t\beta}^\sigma = \sum_{t\beta} D_{s\alpha,t\beta}(\mathbf{q}) \eta_{t\beta}^\sigma$$

In matrix form

$$\begin{pmatrix} \ddots & & \\ & D_{s\alpha,t\beta}(\mathbf{q}) & \\ & & \ddots \end{pmatrix}_{3N_a \times 3N_a} \begin{pmatrix} \vdots \\ \eta_{t\beta}^\sigma(\mathbf{q}) \\ \vdots \end{pmatrix}_{3N_a} = \omega^2(\mathbf{q}) \begin{pmatrix} \vdots \\ \eta_{t\beta}^\sigma(\mathbf{q}) \\ \vdots \end{pmatrix}_{\text{polarization vector}}$$

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

# 3D Dispersion



- If  $N_a$  atoms in the primitive cell,  $3N_a$  modes for each  $\mathbf{q}$ .

- At each  $\mathbf{q}$ , 3 acoustic modes,  $3N_a - 3$  optical modes.

<sup>2</sup> <https://wiki.fysik.dtu.dk/ase/ase/phonons.html>

<sup>3</sup> <https://github.com/phonopy/phonopy/tree/master/example/Si-CRYSTAL>

## The Interatomic Force Constants (IFC)

$$\frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} = C_{s\alpha, t\beta}^{j,k}$$

- Symmetric because partial differentiation is commutative

$$\frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} = \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{t\beta}^k \partial u_{s\alpha}^j} \Rightarrow C_{s\alpha, t\beta}^{j,k} = C_{t\beta, s\alpha}^{k,j} \quad (3)$$

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

$$\frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} = \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^0 \partial u_{t\beta}^{(k-j)}} \Rightarrow C_{s\alpha, t\beta}^{j,k} = C_{s\alpha, t\beta}^{0, k-j} \quad (4)$$

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

$$F_{s\alpha}^j = - \sum_{\beta} \left[ \sum_{kt} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} \right] \delta_{\beta} = 0 \Rightarrow \sum_{kt} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} = 0 \quad (5)$$

## The Dynamical Matrix

$$D_{s\alpha,t\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_l \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^0 \partial u_{t\beta}^l} e^{i\mathbf{q}\mathbf{x}_l} = \frac{1}{\sqrt{M_s M_t}} \sum_l C_{s\alpha,t\beta}^{0,l} e^{i\mathbf{q}\mathbf{x}_l}$$

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

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

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

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

## PROOF

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

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

- The polarization vector is *cell-periodic*.

$$u_{s\alpha}^j(t) = \frac{\eta_{s\alpha}^\sigma(\mathbf{q})}{\sqrt{M_s}} e^{i\mathbf{q}\cdot\mathbf{r}_j} e^{-i\omega_\sigma t}$$

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

- Orthogonalization relation:

$$\sum_{s\alpha} \eta_{s\alpha}^{\sigma'}(\mathbf{q}) \eta_{s\alpha}^\sigma(\mathbf{q}) = \delta_{\sigma\sigma'}; \quad \sum_{\sigma} \eta_{s\alpha}^{\sigma*}(\mathbf{q}) \eta_{t\beta}^\sigma(\mathbf{q}) = \delta_{st} \delta_{\alpha\beta}$$

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

$$\xi_{s\alpha}^\sigma = \frac{1}{\sqrt{M_s}} \eta_{s\alpha}^\sigma(\mathbf{q})$$

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

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

# How to Calculate the Dynamical Matrix I

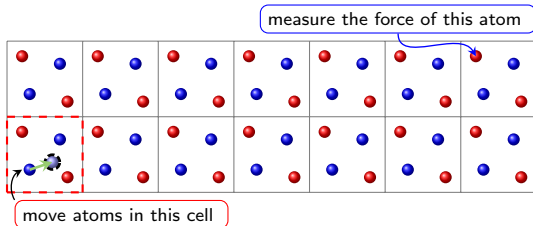
The definition of the dynamical matrix

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

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

IFC by finite-difference:

$$\frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^0 \partial u_{t\beta}^l} = \frac{\partial F_{t\beta}^l}{\partial u_{s\alpha}^0}$$
$$\approx \frac{F_{t\beta}^l(\Delta_{s\alpha}) - F_{t\beta}^l(-\Delta_{s\alpha})}{2\Delta_{s\alpha}}$$



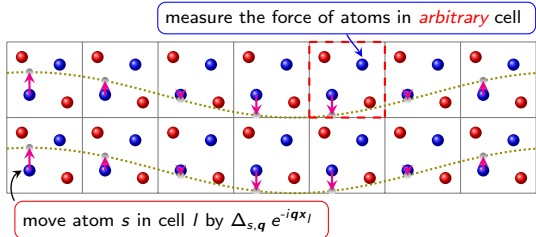
- Supercell must be large enough so that IFC is negligible at the cell boundary.
- Movements done **only** in one primitive cell.
- $3 \times N_a \times 2$  movements, i.e. move by  $\pm \Delta$  in x/y/z directions for each atom in the primitive cell.
- Symmetry can be adopted to reduce the number of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



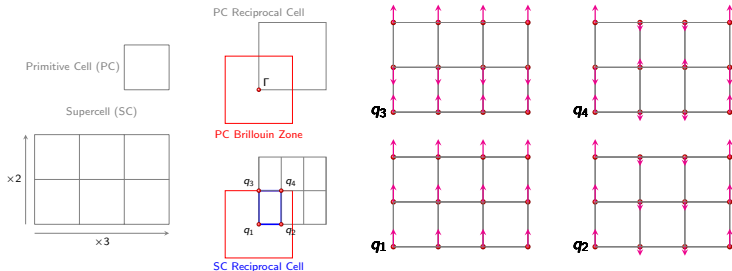
# How to Calculate the Dynamical Matrix II

Dynamical matrix:

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



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

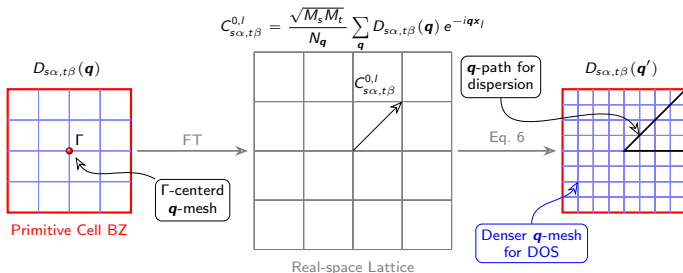


$$D_{s\alpha,t\beta}(\mathbf{q}) \xrightarrow{\text{FT}} C_{s\alpha,t\beta}^{0,l} \xrightarrow{\text{Eq. 6}} D_{s\alpha,t\beta}(\mathbf{k})$$

# How to Calculate the Dynamical Matrix III

## ② Linear response approach — density functional perturbation theory

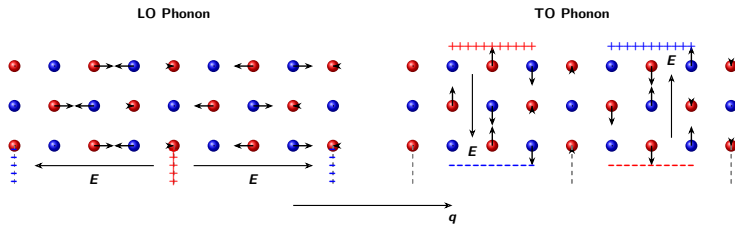
- Can calculate  $D_{s\alpha,t\beta}(\mathbf{q})$  at **arbitrary**  $\mathbf{q}$  using a **primitive cell**.
- $D_{s\alpha,t\beta}(\mathbf{q})$  is periodic in reciprocal space:  $D_{s\alpha,t\beta}(\mathbf{q} + \mathbf{G}) = D_{s\alpha,t\beta}(\mathbf{q})$



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

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

# LO-TO Splitting



The dynamical matrix in polar materials can be separated into two parts <sup>4</sup>

$$D_{s\alpha,t\beta}(\mathbf{q} \rightarrow 0) = D_{s\alpha,t\beta}^{\text{an}}(\mathbf{q} = 0) + D_{s\alpha,t\beta}^{\text{na}}(\mathbf{q} \rightarrow 0)$$

where the nonanalytic part is written as

$$D_{s\alpha,t\beta}^{\text{na}}(\mathbf{q} \rightarrow 0) = \frac{1}{\sqrt{M_s M_t}} \frac{4\pi e^2}{\Omega} \frac{\left( \sum_{\gamma} q_{\gamma} Z_s^{*\gamma\alpha} \right) \left( \sum_{\mu} q_{\mu} Z_t^{*\mu\beta} \right)}{\sum_{\gamma\mu} q_{\gamma} \epsilon_{\infty}^{\gamma\mu} q_{\mu}} \quad (7)$$

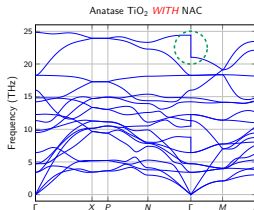
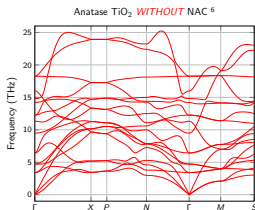
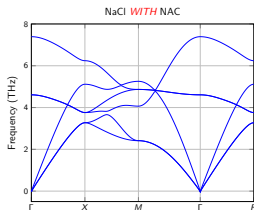
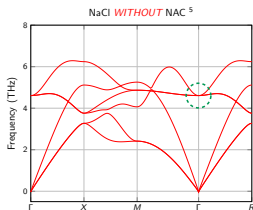
- $Z_s^*$  is the Born effective charge tensor for atom  $s$

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

- 1 The response of the polarization per unit cell along the direction  $\beta$  induced by a displacement along the direction  $\alpha$  of the atoms belonging to the sublattice  $s$ , under the condition of a zero electric field.
  - 2 The force on the atom  $s$  along  $\alpha$  induced by the macroscopic field along  $\beta$ .
  - 3 Sum rules:  $\sum_s Z_s^{*\alpha\beta} = 0$
  - 4 The infrared absorption:  $I_{\text{IR}}(\omega_{\sigma}) \propto \sum_{\alpha=1}^3 \left| \sum_{s\beta} Z_s^{*\alpha\beta} \eta_{s\beta}^{\sigma} \right|^2$
- $\epsilon_{\infty}$  is the **electronic** dielectric tensor of the crystal, i.e. the static dielectric constant with clamped nuclei.

<sup>4</sup>X. Gonze and C. Lee, *Phys. Rev. B* 55, 10355(1997).

# Phonon Band Structure with/without NAC

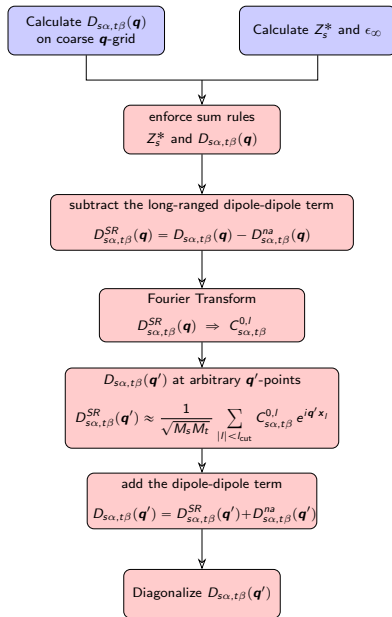


- The limiting value of Eq. 7 may be different for different  $\mathbf{q} \rightarrow 0$  directions, as can be seen in the phonon dispersion of Anatase TiO<sub>2</sub>.
- This strange behavior is physical and the frequency of the observed phonons depends on the polarizability in the different directions, with respect to the propagation of the incoming electric field.

<sup>5</sup><https://github.com/phonopy/phonopy/tree/master/example/NaCl>

<sup>6</sup><https://github.com/phonopy/phonopy/tree/master/example/TiO2-anatase>

# DFPT Interpolation Scheme for Polar Material




- 1 Lattice Dynamics
  - 1D Atomic Chain
  - 3D lattice
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- 2 Density functional perturbation theory

# First and Second-order Derivatives of the Total Energy

Within DFT, the total energy is given by

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

over the entire space 

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

- $\rho(\mathbf{r})$ : electron density

$$\rho(\mathbf{r}) = \sum_i^{\text{occ}} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$$

The first and second order derivative with respect to external parameter  $\lambda, \mu$

$$\frac{\partial E_{\text{tot}}}{\partial \lambda} = \int_V \frac{\partial V_{\text{ext}}(\mathbf{r})}{\partial \lambda} \rho(\mathbf{r}) d\mathbf{r} + \frac{\partial U_{II}}{\partial \lambda} \quad (8)$$

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

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



## The Kohn-Sham equation

With a small perturbation  $\mu$

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

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

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

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

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

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

Inserting these equations and keeps only the first-order terms

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

where

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

$$\frac{\partial V_H(\mathbf{r})}{\partial \mu} = \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial \rho(\mathbf{r}')}{\partial \mu} d\mathbf{r}'; \quad \frac{\partial V_{xc}(\mathbf{r})}{\partial \mu} = \int \frac{dV_{xc}}{d\rho(\mathbf{r}')} \frac{\partial \rho(\mathbf{r}')}{\partial \mu} d\mathbf{r}' \quad (12)$$

## Electron density response to the perturbation

$$\frac{\partial \rho(\mathbf{r})}{\partial \mu} = \sum_n^{\text{occ}} \left[ \frac{\partial \psi_n^*(\mathbf{r})}{\partial \mu} \psi_n(\mathbf{r}) + \psi_n^*(\mathbf{r}) \frac{\partial \psi_n(\mathbf{r})}{\partial \mu} \right] \quad (13)$$

$$\frac{\partial \psi_n(\mathbf{r})}{\partial \mu} = \sum_{m \neq n} \frac{\langle \psi_m | \frac{\partial V_{KS}(\mathbf{r})}{\partial \mu} | \psi_n \rangle}{\epsilon_n - \epsilon_m} \psi_m(\mathbf{r}) \quad (14)$$

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

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

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

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

$$\frac{\partial \rho(\mathbf{r})}{\partial \mu} = \sum_n^{\text{occ}} \left[ P_c \frac{\partial \psi_n^*(\mathbf{r})}{\partial \mu} \psi_n(\mathbf{r}) + \psi_n^*(\mathbf{r}) P_c \frac{\partial \psi_n(\mathbf{r})}{\partial \mu} \right] \quad (15)$$

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

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

where the  $\alpha P_v$  is added to make the left-hand-side nonsingular.

$$\frac{\partial V_{KS}(\mathbf{r})}{\partial \mu} = \frac{\partial V_{ext}(\mathbf{r})}{\partial \mu} + \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial \rho(\mathbf{r}')}{\partial \mu} d\mathbf{r}' + \int \frac{dV_{xc}}{d\rho(\mathbf{r}')} \frac{\partial \rho(\mathbf{r}')}{\partial \mu} d\mathbf{r}' \quad (17)$$

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

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

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

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

## DFT

$$\rho(\mathbf{r}) \Rightarrow V_{KS}(\mathbf{r})$$

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

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

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

## DFPT

$$\frac{\partial \rho(\mathbf{r})}{\partial \mu} \Rightarrow \frac{\partial V_{KS}(\mathbf{r})}{\partial \mu}$$

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

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

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

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

$$V_{\text{ext}}(\mathbf{r} + \mathbf{x}_j) = V_{\text{ext}}(\mathbf{r}); \quad \Delta V_{\text{ext}}^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = e^{i\mathbf{q} \cdot \mathbf{x}_j} \Delta V_{\text{ext}}^{\mathbf{q}}(\mathbf{r})$$

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

$$\Delta V_{\text{KS}}^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = e^{i\mathbf{q} \cdot \mathbf{x}_j} \Delta V_{\text{KS}}^{\mathbf{q}}(\mathbf{r})$$

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

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

Let us define the related periodic quantities

$$\Delta V_{\text{ext}}^{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q} \cdot \mathbf{r}} \tilde{V}_{\text{ext}}^{\mathbf{q}}(\mathbf{r});$$

$$\tilde{V}_{\text{ext}}^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = \tilde{V}_{\text{ext}}^{\mathbf{q}}(\mathbf{r});$$

$$\Delta V_{\text{KS}}^{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q} \cdot \mathbf{r}} \tilde{V}_{\text{KS}}^{\mathbf{q}}(\mathbf{r});$$

$$\tilde{V}_{\text{KS}}^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = \tilde{V}_{\text{KS}}^{\mathbf{q}}(\mathbf{r});$$

$$\Delta \rho^{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q} \cdot \mathbf{r}} \tilde{\rho}^{\mathbf{q}}(\mathbf{r});$$

$$\tilde{\rho}^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = \tilde{\rho}^{\mathbf{q}}(\mathbf{r});$$

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

$$u_{n,\mathbf{k}}(\mathbf{r} + \mathbf{x}_j) = u_{n,\mathbf{k}}(\mathbf{r});$$

$$\Delta \psi_{n,\mathbf{k}}^{\mathbf{q}}(\mathbf{r}) = e^{i(\mathbf{k} + \mathbf{q}) \cdot \mathbf{r}} \Delta u_{n,\mathbf{k}}^{\mathbf{q}}(\mathbf{r});$$

$$\Delta u_{n,\mathbf{k}}^{\mathbf{q}}(\mathbf{r} + \mathbf{x}_j) = \Delta u_{n,\mathbf{k}}^{\mathbf{q}}(\mathbf{r});$$

Substitute into Eq. 16

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

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

$$\left[ H_{KS}^{\mathbf{k}+\mathbf{q}}(\mathbf{r}) + \alpha P_v^{\mathbf{k}+\mathbf{q}} - \varepsilon_{n,k} \right] P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial u_{n,k}^{\mathbf{q}}(\mathbf{r})}{\partial \mu} = -P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial \tilde{V}_{KS}^{\mathbf{q}}(\mathbf{r})}{\partial \mu} u_{n,k}(\mathbf{r}) \quad (20)$$

where

$$\begin{aligned} \frac{\partial \tilde{V}_{KS}(\mathbf{r})}{\partial \mu} &= \frac{\partial \tilde{V}_{\text{ext}}(\mathbf{r})}{\partial \mu} + \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial \tilde{\rho}^{\mathbf{q}}(\mathbf{r}')}{\partial \mu} d\mathbf{r}' + \int \frac{dV_{\text{xc}}}{d\rho(\mathbf{r}')} \frac{\partial \tilde{\rho}^{\mathbf{q}}(\mathbf{r}')}{\partial \mu} d\mathbf{r}' \\ \frac{\partial \tilde{\rho}^{\mathbf{q}}(\mathbf{r}')}{\partial \mu} &= 2 \sum_{n,k}^{\text{occ}} u_{n,k}^*(\mathbf{r}) P_c^{\mathbf{k}+\mathbf{q}} \frac{\partial u_{n,k}^{\mathbf{q}}(\mathbf{r})}{\partial \mu} \\ P_v^{\mathbf{k}+\mathbf{q}} &= \sum_n^{\text{occ}} |u_{n,\mathbf{k}+\mathbf{q}}\rangle \langle u_{n,\mathbf{k}+\mathbf{q}}|; \quad P_c^{\mathbf{k}+\mathbf{q}} = \mathbb{1} - P_v^{\mathbf{k}+\mathbf{q}} \end{aligned}$$

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

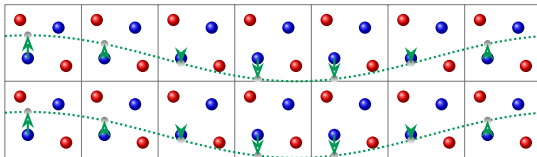
# Periodic Displacement of Ions — Phonon Perturbation I

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

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

Consider the periodic displacement of the ions of the form

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



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

The **colored quantity** has the periodicity of the lattice.

The dynamical matrix

$$D_{s\alpha,t\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_t}} \sum_k e^{-i\mathbf{q} \cdot \mathbf{x}_j} \frac{\partial^2 E_{\text{tot}}^0}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} e^{i\mathbf{q} \cdot \mathbf{x}_k} = \frac{N}{\sqrt{M_s M_t}} \frac{\partial^2 E_{\text{tot}}^0}{\partial \mu_{s\alpha}^* \partial \mu_{t\beta}}$$

Inserting the equation for the second derivative Eq. 9

$$D_{s\alpha,t\beta}(\mathbf{q}) = \frac{N}{\sqrt{M_s M_t}} \int_V \sum_k e^{-i\mathbf{q} \cdot \mathbf{x}_j} \frac{\partial^2 V_{\text{ext}}^{\mathbf{q}}(\mathbf{r})}{\partial u_{s\alpha}^j \partial u_{t\beta}^k} \rho(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{x}_k} d\mathbf{r} \\ + \frac{1}{\sqrt{M_s M_t}} \int_V \sum_k e^{-i\mathbf{q} \cdot \mathbf{x}_j} \frac{\partial V_{\text{ext}}^{\mathbf{q}}(\mathbf{r})}{\partial u_{s\alpha}^j} \frac{\partial \rho(\mathbf{r})}{\partial u_{t\beta}^k} e^{i\mathbf{q} \cdot \mathbf{x}_k} d\mathbf{r}$$



Thank you!