

# Phonons and Electron-Phonon Couplings

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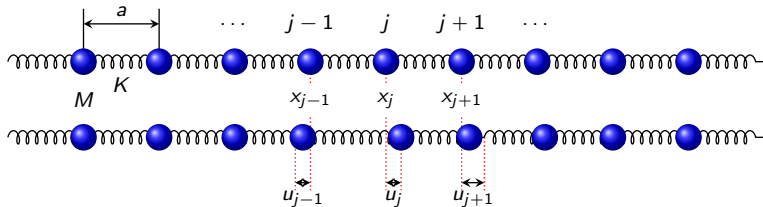
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## 1 Lattice Dynamics

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

# 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

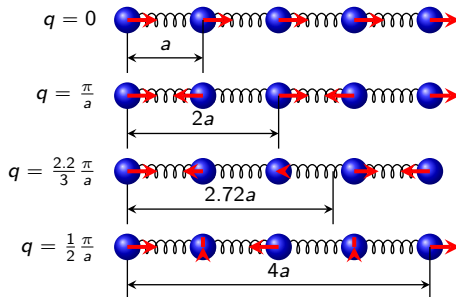
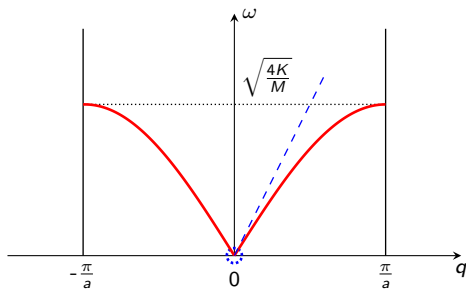
$$M \frac{d^2 u_j}{dt^2} = K(u_{j+1} + u_{j-1} - 2u_j) \quad j = 1, \dots, N$$

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

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

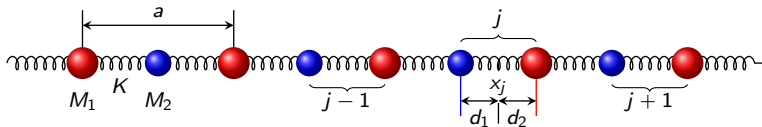
<sup>1</sup> $u_j(t)$  here is complex. In practice, take the real part, i.e.  $\text{Re}[u_j(t)]$ .

# 1D Chain of Atoms



# 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

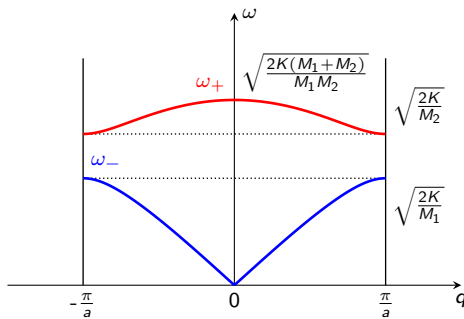
$$\begin{aligned} M_1 \frac{d^2 u_1^j}{dt^2} &= K(u_2^j + u_2^{j-1} - 2u_1^j) \\ M_2 \frac{d^2 u_2^j}{dt^2} &= K(u_1^j + u_1^{j+1} - 2u_2^j) \end{aligned} \quad \Rightarrow \quad \begin{cases} u_1^j(t) = \frac{A_q}{\sqrt{M_1}} e^{i(qx_j - \omega t)} \\ u_2^j(t) = \frac{B_q}{\sqrt{M_2}} e^{i(qx_j - \omega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

We then have

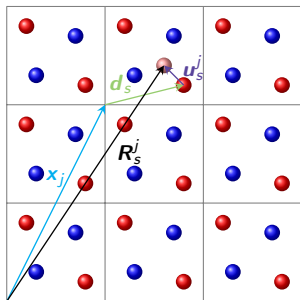
$$\begin{pmatrix} \frac{2K}{M_1} & \frac{-K}{\sqrt{M_1 M_2}} (1 + e^{-iqa}) \\ \frac{-K}{\sqrt{M_1 M_2}} (1 + e^{iqa}) & \frac{2K}{M_2} \end{pmatrix} \begin{pmatrix} A_q \\ B_q \end{pmatrix} = \omega^2 \begin{pmatrix} A_q \\ B_q \end{pmatrix}$$

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

# 1D Chain of Atoms



# 3D Lattice



- $\mathbf{x}_j$ : 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

$$\begin{pmatrix} \ddots & & \\ & D_{s\alpha,t\beta}(\mathbf{q}) & \\ & & \ddots \end{pmatrix} \begin{pmatrix} \vdots \\ \eta_{t\beta}^\sigma(\mathbf{q}) \\ \vdots \end{pmatrix} = \omega^2(\mathbf{q}) \begin{pmatrix} \vdots \\ \eta_{t\beta}^\sigma(\mathbf{q}) \\ \vdots \end{pmatrix}$$

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

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



## 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

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

## PROOF

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

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

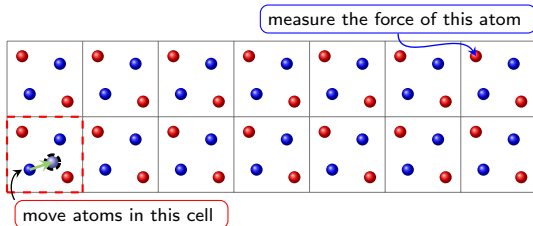
The definition of the dynamical matrix

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

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

IFC by finite-difference:

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

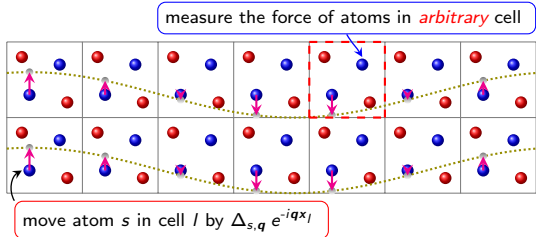


- Supercell must be large enough so that IFC is negligible at the cell boundary.
- Movements done **only** in one primitive cell.
- $3 \times N_a \times 2$  movements, i.e. move by  $\pm \Delta$  in x/y/z directions for each atom in the primitive cell.
- Symmetry can be adopted to reduce the number of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

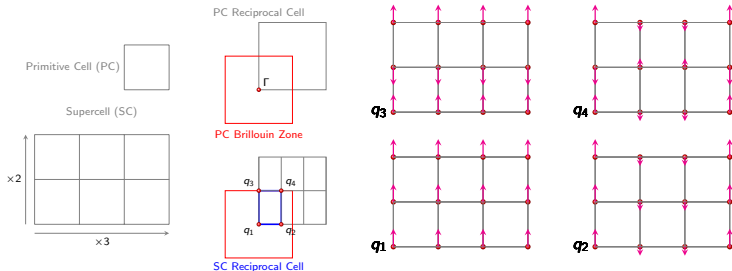
# How to Calculate the Dynamical Matrix II

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  $\mathbf{q}$ .

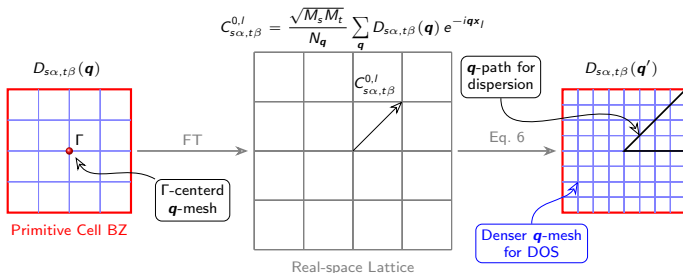


$$D_{s\alpha,t\beta}(\mathbf{q}) \xrightarrow{\text{FT}} C_{s\alpha,t\beta}^{0,l} \xrightarrow{\text{Eq. 6}} D_{s\alpha,t\beta}(\mathbf{k})$$

# 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 ...

The dynamical matrix in polar materials can be separated into two parts <sup>2</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  $\beta$ .
- $\epsilon_{\infty}$  is the **electronic** dielectric tensor of the crystal, i.e. the static dielectric constant with clamped nuclei.

<sup>2</sup>X. Gonze and C. Lee, *Phys. Rev. B* 55, 10355(1997).

Thank you!