

LATTICE DYNAMICS

(A) CRYSTAL HAMILTONIAN

• For an assembly of atoms, the classical energy equals the sum of the following contributions:

- Kinetic energy of the nuclei
- potential energy of the nuclei in one another's electrostatic field
- Kinetic energy of the electrons
- Potential energy of the electrons in the field of the nuclei
- potential energy of the electrons in one another's field

• Therefore, the crystal Hamiltonian is represented as:

$$H = \underbrace{\sum_l \frac{p_l^2}{2M_l}}_{H_L} + \sum_l \sum_{m \neq l} U(\vec{R}_l - \vec{R}_m) + \underbrace{\sum_i \frac{p_i^2}{2m} + \sum_i \sum_l V(\vec{r}_i - \vec{R}_l)}_{H_e} + \sum_i \sum_j \frac{e^2/4\pi\epsilon_0}{|\vec{r}_i - \vec{r}_j|} \quad (1)$$

Lattice Hamiltonian

Electronic part

In (1),
 $U(\vec{R}_l - \vec{R}_m) \rightarrow$ interionic potential
 $V(\vec{r}_i - \vec{R}_l) \rightarrow$ electron-ion interaction

• The time-independent Schrödinger equation:

$$H \Xi = E \Xi \quad (2)$$

determines the stationary energies of the system.

(B) ADIABATIC APPROXIMATION

• Since the mass of an ion is at least a factor of 10^3 larger than that of an electron, the electrons can be regarded as instantaneously adjusting their motion to that of the ions. With this in mind, one can write:

$$\Xi = \Psi(\vec{r}, \vec{R}) \Phi(\vec{R}) \quad (3)$$

where:

$\Phi(\vec{R}) \rightarrow$ wavefunction for all ions

$\Psi(\vec{r}, \vec{R}) \rightarrow$ total electronic wavefunction that is instantaneously dependent on the ionic position

- Using this representation for Ξ , the TISE becomes:

$$H_L \Psi(\vec{r}, \vec{R}) \Phi(\vec{R}) + H_e \Psi(\vec{r}, \vec{R}) \Phi(\vec{R}) = E \Psi(\vec{r}, \vec{R}) \Phi(\vec{R})$$

or alternatively:

$$\Psi(\vec{r}, \vec{R}) H_L \Phi(\vec{R}) + \Phi(\vec{R}) H_e \Psi(\vec{r}, \vec{R}) + H' \Psi(\vec{r}, \vec{R}) \Phi(\vec{R}) = E \Psi(\vec{r}, \vec{R}) \Phi(\vec{R}) \quad (4)$$

where:

$$H_L = \sum_l \frac{p_l^2}{2M_l} + \sum_l \sum_{m \neq l} U(\vec{R}_l - \vec{R}_m)$$

$$H_e = \sum_i \frac{p_i^2}{2m} + \sum_i \sum_l V(\vec{r}_i - \vec{R}_l) + \sum_i \sum_j \frac{e^2/4\pi\epsilon_0}{|\vec{r}_i - \vec{r}_j|}$$

and:

$$H' \Psi(\vec{r}, \vec{R}) \Phi(\vec{R}) = H_L \Psi(\vec{r}, \vec{R}) \Phi(\vec{R}) - \Psi(\vec{r}, \vec{R}) H_L \Phi(\vec{R})$$

- The adiabatic approximation consists of neglecting the terms involving H' . In this case, equation (4) can be separated into purely ionic equation:

$$H_L \Phi(\vec{R}) = E_L \Phi(\vec{R}) \quad (5a)$$

and a purely electronic equation:

$$H_e \Psi(\vec{r}, \vec{R}) = \left[\sum_i \frac{p_i^2}{2m} + \sum_i \sum_l V(\vec{r}_i - \vec{R}_l) + \underbrace{\sum_i \sum_j \frac{e^2/4\pi\epsilon_0}{|\vec{r}_i - \vec{r}_j|}}_{V_{ee}} \right] \Psi(\vec{r}, \vec{R}) = E_e \Psi(\vec{r}, \vec{R}) \quad (5b)$$

- The goal of the rest of this section is twofold:

(a) We will introduce the concept of phonons (lattice vibrations) by finding the solutions to (5a) for the case when the ions do not move far from their equilibrium positions. In this case, we will show that the ionic motion can be regarded as simple harmonic.

(b) When solving (5b) for the case when $V_{ee} = 0$ and the ions are at their equilibrium positions, we introduced the concept of Bloch functions. When the ions are at motion, the Hamiltonian H_e (for $V_{ee} = 0$) can be represented as:

$$\hat{H}_{ei} = \underbrace{\frac{p_i^2}{2m} + \sum_l V(\vec{r}_i - \vec{R}_{l0})}_{\text{Bloch functions}} + \underbrace{H_{ep}}_{\text{electron-phonon interaction}} \quad (6)$$

In (6), index i refers to the i -th independent electron.

(C) Equations of motion of a lattice

- In deriving the equations of motion of a lattice, one assumes that the atoms do not move far from their equilibrium positions. In this case, their motion can be regarded as simple harmonic.
- If we consider a crystal that is specified by a set of direct lattice vectors \vec{X}_i that locate each cell of the crystal, then the position of an atom belonging to the i -th unit cell is given by:

$$\vec{R}_{i\alpha} = \vec{X}_i + \vec{d}_\alpha \quad (7)$$

where \vec{d}_α are a set of basis vectors that specify the position of that atom within the unit cell.

- If the atoms are in motion, each of them will be displaced by an amount $\vec{u}_{i\alpha}$ (the d -th rectangular coordinate of $\vec{u}_{i\alpha}$ is denoted by $u_{d,i\alpha}$). The mass of the atom α is M_α .
- The total kinetic energy of the lattice is:

$$T_L = \sum_{d,i,\alpha} M_\alpha \left(\frac{du_{d,i\alpha}}{dt} \right)^2 \quad (8)$$

degree of freedom \uparrow cell number \uparrow atom # within unit cell ($\alpha=1,2,\dots,r$)

- The total potential energy of the ions is U_L and is a function of the atomic positions. When the atoms are displaced from their equilibrium positions, U_L will be different from its equilibrium value. This difference may be expressed as a Taylor series in the atomic displacements, i.e.

$$U_L = U_{L0} + \sum_{d,i,\alpha} \frac{\partial U_L}{\partial u_{d,i\alpha}} \Big|_0 u_{d,i\alpha} + \frac{1}{2} \sum_{d,i,\alpha} \sum_{\beta,j,\gamma} \underbrace{\frac{\partial^2 U_L}{\partial u_{d,i\alpha} \partial u_{\beta,j\gamma}}}_{\Phi_{d\beta,i\alpha,j\gamma}} u_{d,i\alpha} u_{\beta,j\gamma} + \dots \quad (9)$$

This term represents the negative of the net force on the atom. Now, if the atom is at its equilibrium position, this term must vanish.

- The equations of motion of the lattice are then easily found to be:

$$M_\alpha \frac{d^2 u_{d,i\alpha}}{dt^2} = - \frac{\partial U_L}{\partial u_{d,i\alpha}} = - \sum_{\beta,j,\gamma} \underbrace{\Phi_{d\beta,i\alpha,j\gamma}}_{\text{tensor force constant}} u_{\beta,j\gamma} \quad (10)$$

This is a rather complicated problem in 3D.

(1) 1D Monoatomic lattice



- Let U_n describe the displacement of the n -th atom from equilibrium
- If the nearest neighbor force is linear in the displacement, the equation of motion for the n -th atom is:

$$m \frac{d^2 U_n}{dt^2} = F_n = \beta(U_{n+1} - U_n) - \beta(U_n - U_{n-1}) \quad (11)$$

- We look for a periodic solution of this equation of the form:

$$U_n = A e^{i(\omega t - qna)} \quad (12)$$

Substituting this into the equation of motion leads to:

$$-m\omega^2 A e^{i(\omega t - qna)} = \beta A e^{i\omega t} \left[e^{-iq(n+1)a} - e^{-iqna} \right] - \beta A e^{i\omega t} \left[e^{-iqna} - e^{-iq(n-1)a} \right]$$

$$\text{or: } -m\omega^2 = \beta e^{iqna} \left[e^{-iq(n+1)a} - e^{-iqna} \right] - \beta e^{iqna} \left[e^{-iqna} - e^{-iq(n-1)a} \right]$$

$$-m\omega^2 = \beta (e^{-iqa} - 1) - \beta (1 - e^{iqa})$$

$$= -\beta (1 - e^{iqa} - e^{-iqa} + 1)$$

$$= -\beta [2 - 2\cos(qa)] = -2\beta [1 - \cos(qa)] = -4\beta \sin^2\left(\frac{qa}{2}\right)$$

Therefore:

$$m\omega^2 = 4\beta \sin^2\left(\frac{qa}{2}\right) \Rightarrow \omega(q) = 2\sqrt{\frac{\beta}{m}} \left| \sin\left(\frac{qa}{2}\right) \right| \quad (13)$$

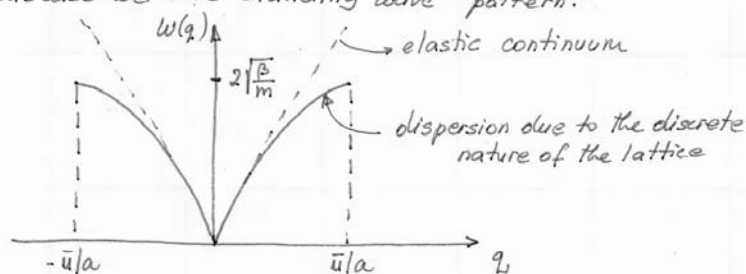
- The dispersion relation $\omega(q)$ given in (13) is not a linear function of q . For values of $q = 2\pi/\lambda \ll \pi/a$ ($\lambda \gg 2a$), we get the linear dispersion and in this case the wavelength is much larger than $2 \times$ interatomic spacing. For this case:

$$\omega(q) \approx 2\sqrt{\frac{\beta}{m}} \frac{qa}{2} \approx a\sqrt{\frac{\beta}{m}} q = v_s q \quad (v_s = \text{sound velocity})$$

- The group velocity (velocity with which we have energy transfer) is:

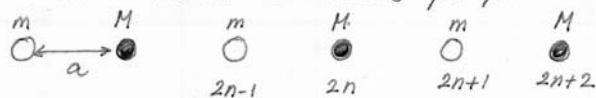
$$v_{gr} = \frac{d\omega}{dq} = 2\sqrt{\frac{\beta}{m}} \frac{a}{2} \cos\left(\frac{qa}{2}\right) = \sqrt{\frac{\beta}{m}} a \cos\left(\frac{qa}{2}\right)$$

The group velocity is zero when $\frac{qa}{2} = \pm \frac{\pi}{2}$, i.e. $q = \pm \frac{\pi}{a}$.
 In this case we have standing wave pattern.



(2) 1D Lattice with 2 atoms per primitive basis

The phonon dispersion relation shows new features in crystals with two or more atoms per primitive basis.



Under the assumption that each atom only interacts with the nearest neighbor atoms and that force (spring constants) are identical between nearest neighbors, the equations of motion for atoms $2n$ and $(2n+1)$ are:

$$\begin{cases} M \frac{d^2 u_{2n}}{dt^2} = \beta (u_{2n+1} - u_{2n}) - \beta (u_{2n} - u_{2n-1}) \\ m \frac{d^2 u_{2n+1}}{dt^2} = \beta (u_{2n+2} - u_{2n+1}) - \beta (u_{2n+1} - u_{2n}) \end{cases} \quad (14)$$

We now look for solutions of the form:

$$\begin{aligned} u_{2n} &= A e^{i[\omega t - 2nqa]} \\ u_{2n+1} &= B e^{i[\omega t - (2n+1)qa]} \end{aligned} \quad (15)$$

In this case:

$$\frac{u_{2n+2}}{u_{2n}} = \frac{A e^{i[\omega t - (2n+2)qa]}}{A e^{i[\omega t - 2nqa]}} = e^{-i2qa}$$

$$\frac{u_{2n-1}}{u_{2n+1}} = \frac{B e^{i[\omega t - (2n-1)qa]}}{B e^{i[\omega t - (2n+1)qa]}} = \frac{1}{e^{-i2qa}} = e^{i2qa}$$

Substituting these results into the corresponding equations of motion leads to:

$$\begin{cases} -M\omega^2 U_{2n} = \beta (U_{2n+1} - U_{2n}) - \beta (U_{2n} - e^{i2qa} U_{2n+1}) \\ -m\omega^2 U_{2n+1} = \beta (U_{2n} e^{-i2qa} - U_{2n+1}) - \beta (U_{2n+1} - U_{2n}) \end{cases}$$

Reorganizing slightly these equations gives:

$$(2\beta - M\omega^2) U_{2n} = \beta U_{2n+1} (1 + e^{i2qa})$$

$$(2\beta - m\omega^2) U_{2n+1} = \beta U_{2n} (e^{-i2qa} + 1)$$

In matrix notation:

$$\underbrace{\begin{bmatrix} 2\beta - M\omega^2 & -\beta(1 + e^{i2qa}) \\ -\beta(1 + e^{-i2qa}) & 2\beta - m\omega^2 \end{bmatrix}}_A \begin{bmatrix} U_{2n} \\ U_{2n+1} \end{bmatrix} = 0$$

The ~~only~~ non-trivial solutions are obtained when $\det(A) = 0$, i.e.

$$(2\beta - M\omega^2)(2\beta - m\omega^2) - \beta^2 (1 + e^{i2qa})(1 + e^{-i2qa}) = 0$$

$$4\beta^2 - 2\beta(M\omega^2 + m\omega^2) + Mm\omega^4 - \beta^2 (1 + e^{i2qa} + e^{-i2qa} + 1) = 0$$

$$Mm\omega^4 - 2\beta(M+m)\omega^2 + 4\beta^2 - 4\beta^2 \cos^2(qa) = 0$$

$2 + 2\cos(2qa) = 2 \cdot 2\cos^2(qa)$

$$\omega^4 - 2\beta \frac{M+m}{Mm} \omega^2 + \frac{4\beta^2}{mM} \sin^2(qa) = 0$$

The solutions of this equation are of the form:

$$\omega_{\pm}^2 = \beta \frac{M+m}{Mm} \pm \frac{1}{2} \sqrt{\left(2\beta \frac{M+m}{Mm}\right)^2 - 16\beta^2 \frac{\sin^2(qa)}{mM}}$$

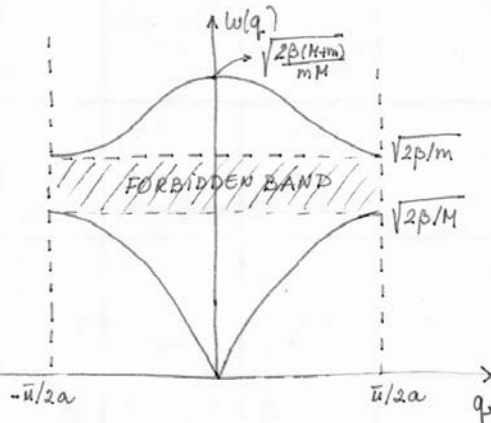
$$= \beta \frac{M+m}{Mm} \pm \beta \sqrt{\left(\frac{M+m}{mM}\right)^2 - 4 \frac{\sin^2(qa)}{mM}}$$

$$= \beta \left(\frac{M+m}{mM}\right) \left[1 \pm \sqrt{1 - \frac{4mM}{(m+M)^2} \sin^2(qa)} \right]$$

These two solutions result in two branches of the ω vs. q dispersion relation.

optical branch: $\omega_+^2 = \beta \frac{m+M}{Mm} \left[1 + \sqrt{1 - \frac{4mM}{(m+M)^2} \sin^2(qa)} \right]$

acoustic branch: $\omega_-^2 = \beta \frac{m+M}{Mm} \left[1 - \sqrt{1 - \frac{4mM}{(m+M)^2} \sin^2(qa)} \right]$



optical branch:



acoustic branch



If one looks for solutions in the gap at the boundary for ω real, the wavevector will be complex, which implies that the wave is damped in space.

optical modes of vibration in ionic crystals can be excited by electric field that tends to move the atoms in the opposite direction.

• 3D crystals

- The results presented for 1D monatomic and 1D diatomic lattice suggest that one branch of the spectrum occurs for each atom per unit cell.

- one can generalize the above, that for each degree of freedom one expects to find additional number of equivalent spectral branches. For example, in 3D with P atoms per unit cell, one has:

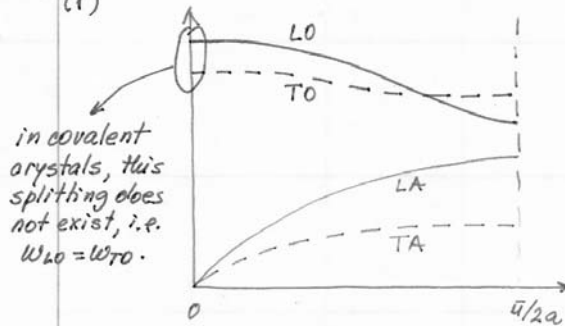
$3P \rightarrow$ total # of spectral branches

$3 \rightarrow$ acoustic branches (1 longitudinal + 2 transverse)

$3P - 3 \rightarrow$ optical branches $(P-1)$ -longitudinal + $(2P-2)$ -transverse

Discussion on the acoustic and optical modes of vibration:

(1)



- Splitting at $q=0$ of the LO and the TO modes arises because of the charge transfer and slight ionicity of the bonds.
- Splitting at $q=\bar{u}/2a$ occurs because of the difference of the masses.

(2) Let us now consider the vibration of the two atoms in a 1D lattice with two atoms per unit cell, for which:

$$\frac{u_{2n+1}}{u_{2n}} = \frac{2\beta - M\omega^2}{1 + \exp(i2qa)}$$

$$\omega_{\pm}^2 = \beta \frac{M+m}{mM} \left[1 \pm \sqrt{1 - \frac{4mM}{(m+M)^2} \sin^2(qa)} \right]$$

We consider two limiting cases:

Case (a): $q \rightarrow 0$ (Zone center)

$$\omega_{\pm}^2 = \beta \frac{M+m}{mM} [1 \pm 1] \Rightarrow \omega_+^2 = 2\beta \frac{M+m}{mM}; \omega_-^2 = 0$$

$$\rightarrow \text{for } \omega = \omega_+ \text{ we have: } \frac{u_{2n+1}}{u_{2n}} = \sqrt{2} \beta \frac{1 - M \frac{M+m}{mM}}{2} = \beta \frac{m-M-m}{m} = -\beta \frac{M}{m}$$

The neighboring atoms with masses m and M are displaced in the opposite direction and the amount of displacement of each atom is inversely proportional to its mass.

$$\rightarrow \text{for } \omega = \omega_- \text{ we have: } \frac{u_{2n+1}}{u_{2n}} = \frac{2\beta}{2} = \beta = \text{const.}$$

All atoms are displaced along the same direction and by the same amount.

(Case (b): $q \rightarrow \bar{u}/2a$ (Zone boundary))

At the zone boundary, we have that: $\sin(qa) = \sin\left(\frac{\bar{u}}{2a}a\right) = \sin\left(\frac{\bar{u}}{2}\right) = 1$, which gives us:

$$\omega_{\pm}^2 = \beta \frac{M+m}{mM} \left[1 \pm \sqrt{1 - \frac{4mM}{(M+m)^2}} \right] = \beta \frac{M+m}{mM} \left[1 \pm \frac{M-m}{M+m} \right]$$

→ For $\omega^2 = \omega_+^2 = \beta \frac{M+m}{Mm} \left[1 + \frac{M-m}{M+m} \right] = \beta \frac{M+m}{Mm} \frac{M+m+M-m}{M+m}$
 $= \beta \frac{2M}{Mm} = 2\beta/m$,

The relative displacement of neighboring atoms is:

$$\frac{u_{2n+1}}{u_{2n}} = \frac{2\beta - M \cdot 2\beta \frac{1}{m}}{1 + \exp(i2a \frac{\bar{u}}{2a})} = 2\beta \frac{1 - \frac{M}{m}}{1 + e^{i\bar{u}}} \rightarrow -\infty$$



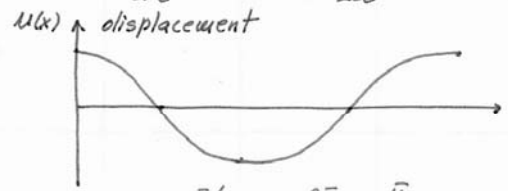
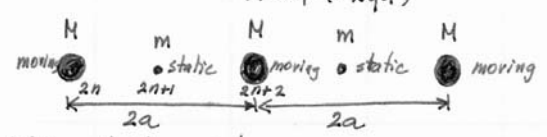
⇒ The above result can be understood in the following way:

- (1) Because $u_{2n+1}/u_{2n} \rightarrow -\infty$, It means that the atoms with mass (m) are vibrating and the atoms with mass (M) are static.
- (2) Since $u_{2n+1}/u_{2n-1} = e^{-i2qa} = -1$, alternating atoms with mass (m) move in the opposite direction.

→ For $\omega^2 = \omega_-^2 = \beta \frac{M+m}{Mm} \left[1 - \frac{M-m}{M+m} \right] = \beta \frac{M+m}{Mm} \frac{M+m-M+m}{M+m} = \frac{2\beta m}{Mm} = \frac{2\beta}{M}$

In this case, the relative displacement of neighboring atoms is:

$$\frac{u_{2n+1}}{u_{2n}} = \frac{2\beta - M \cdot 2\beta \frac{1}{M}}{1 + \exp(i2qa)} = 2\beta \cdot 0 \Rightarrow \frac{u_{2n}}{u_{2n+1}} = \frac{1 + e^{i2qa}}{2\beta \cdot 0} \rightarrow +\infty \text{ if } q = \frac{\bar{u}}{2a} - \epsilon \text{ (}\epsilon \rightarrow 0\text{)}$$



$$q = \bar{u}/2a = \frac{2\bar{u}}{\lambda} = \frac{\bar{u}}{2a} \Rightarrow \lambda = 4a$$

- (1) Now the sublattice of atoms with mass (m) is static and the sublattice of atoms with mass (M) is moving. Since $M > m$, the frequency of this mode is smaller.

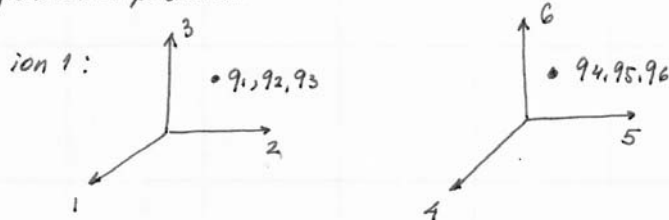
- (2) The displacement of neighboring atoms is

$$\frac{u_{2n+2}}{u_{2n}} = -1$$

but this still represents acoustic mode but with $\lambda = 4a$ (see figure)

(D) Quantum model of Lattice vibrations

- One can employ the method of normal coordinates to reduce the problem of the lattice vibrations to a solvable one. Let the position of the n -th ion in the crystal be described by giving the Cartesian coordinates of each ion that refer to its equilibrium position:



If there are n ions in the crystal:

$$T = \sum_{i=1}^{3n} \frac{1}{2} M_i \dot{q}_i^2 \quad \text{kinetic energy}$$

The potential energy depends upon the mutual position of the ions, and therefore upon the coordinates q_i : $V(q_1, q_2, \dots, q_{3n})$

- If we restrict ourselves to a discussion of small vibrations, we can expand V as a Taylor series in powers of the q 's:

$$V(q_1, q_2, \dots, q_{3n}) = V_0 + \sum_i \left(\frac{\partial V}{\partial q_i} \right)_0 dq_i + \frac{1}{2} \sum_{i,j} b_{ij} dq_i dq_j$$

$$= V_0 + \sum_i \left(\frac{\partial V}{\partial q_i} \right)_0 dq_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 dq_i dq_j$$

$\left(\frac{\partial V}{\partial q_i} \right)_0 = 0$ (gives constant value)
 negative of the net force on the ion which must be zero in equilibrium.
 derivatives evaluated when the ions are at their equilibrium position

Therefore:

$$V(q_1, q_2, \dots, q_{3n}) = V_0 + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 dq_i dq_j \quad (17)$$

- The Lagrangian equations in this case have the form:

$$\frac{d}{dt} \frac{\partial T}{\partial \dot{q}_k} + \frac{\partial V}{\partial q_k} = 0 \quad [L = T - V = T(q_k) - V(q_k)]$$

which gives:

$$m_k \ddot{q}_k + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 \left[\underbrace{\frac{\partial q_i}{\partial q_k}}_{\delta_{ik}} dq_j + dq_i \underbrace{\frac{\partial q_j}{\partial q_k}}_{\delta_{jk}} \right] = 0$$

$$m_k \ddot{q}_k + \frac{1}{2} \sum_j b_{kj} dq_j + \frac{1}{2} \sum_j b_{ik} dq_j = 0$$

$$m_k \ddot{q}_k + \sum_j b_{jk} dq_j = 0 \quad (18)$$

If $b_{ik} = \delta_{ik}$ we get: $m_k \ddot{q}_k + b_{kk} dq_k = 0$

• If we now introduce $q_k = q_k^0 + u_k$, where u_k is the displacement, we get:

$$m_k \frac{d^2 u_k}{dt^2} + \sum_j b_{kj} u_j = 0 \quad (19)$$

This equation was used in connection with monoatomic and diatomic lattices where $b_{kj} = \beta$ was the spring constant and nearest-neighbor interactions were only allowed.

• To obtain quantum description of the vibrations of a 1D monoatomic chain of N atoms, we start with the total Hamiltonian of this system:

$$H = \frac{1}{2} \sum_i \left[\frac{p_i^2}{m} + \beta (u_{i+1} - u_i)^2 \right] \quad (20)$$

where $p_i = \partial L / \partial \dot{q}_i = \frac{\partial L}{\partial \dot{u}_i} = m \dot{q}_i = m \dot{u}_i$ is the canonical momentum. The theory is quantized with the condition:

$$[u_r, p_s] = i \hbar \delta_{rs}$$

• We want to find the eigenfrequencies and eigenvectors of (20). To achieve this goal, we expand the displacement of atom r in terms of phonon coordinates, i.e.

$$\begin{aligned} u_r &= \frac{1}{\sqrt{N}} \sum_n Q_{kn} e^{i \vec{k}_n \cdot \vec{r}_r} = \frac{1}{\sqrt{N}} \sum_n Q_{kn} e^{i \frac{2\pi}{Na} n r a} \\ &= \frac{1}{\sqrt{N}} \sum_n e^{i \frac{2\pi}{N} n r} Q_{kn} = \frac{1}{\sqrt{N}} \sum_k Q_k e^{i k r} \end{aligned}$$

, r here is integer
 $k = \frac{2\pi}{N} n$

This discrete set of allowed values for k is obtained from the periodic boundary condition, i.e. $u_{r+N} = u_r$, which gives:

$$U_{r+N} = \frac{1}{\sqrt{N}} \sum_k Q_k e^{ik(r+N)} = \frac{1}{\sqrt{N}} \sum_k Q_k e^{ikr}$$

which is satisfied only when: $e^{ikN} = e^{i2\pi n}$, which gives:

$$k_n = \frac{2\pi n}{N}$$

The sum over all k 's is:

$$\begin{aligned} \sum_k e^{ikr} &= \sum_{n=1}^N e^{i \frac{2\pi n r}{N}} = \frac{1 - e^{i2\pi r}}{1 - e^{i2\pi r/N}} \\ &= \frac{e^{i\pi r} (e^{i\pi r} - e^{-i\pi r})}{e^{i\pi r/N} (e^{i\pi r/N} - e^{-i\pi r/N})} = e^{i\pi r(1-\frac{1}{N})} \frac{\sin(\pi r)}{\sin(\frac{\pi r}{N})} = N \delta_{r,0} \end{aligned}$$

- Since the displacement must be Hermitian, we must have that:

$$U_r^\dagger = U_r \Rightarrow \frac{1}{\sqrt{N}} \sum_k Q_k^\dagger e^{-ikr} = \frac{1}{\sqrt{N}} \sum_k Q_k e^{ikr}$$

This leads to:

$$Q_k = Q_{-k}^\dagger$$

where Q_k^\dagger is the hermitian adjoint operator to Q_k .

- The next task is to determine the momentum coordinate P_k that is canonical to Q_k . This can be achieved by making coordinate transformation in the lagrangian:

$$\begin{aligned} \sum_r (\dot{U}_r)^2 &= \left(\frac{1}{\sqrt{N}}\right)^2 \sum_r \sum_k \dot{Q}_k e^{ikr} \sum_{k'} \dot{Q}_{k'} e^{ik'r} \\ &= \sum_k \sum_{k'} \dot{Q}_k \dot{Q}_{k'} \underbrace{\frac{1}{N} \sum_r e^{i(k+k')r}}_{\delta_{k+k',0}} = \sum_k \dot{Q}_k \dot{Q}_{-k} \end{aligned}$$

Therefore:

$$T = \sum_r \frac{1}{2} m (\dot{U}_r)^2 = \frac{1}{2} m \sum_k \dot{Q}_k \dot{Q}_{-k} \quad \text{kinetic term}$$

For the potential energy term, we get:

$$\sum_r (U_{r+1} - U_r)^2 = \frac{1}{N} \sum_r \sum_k Q_k e^{ikr} (e^{ik} - 1) \sum_{k'} Q_{k'} e^{ik'r} (e^{ik'} - 1)$$

$$= \sum_K \sum_{K'} Q_K Q_{K'} (e^{iK} - 1)(e^{iK'} - 1) \underbrace{\frac{1}{N} \sum_r e^{i(K+K')r}}_{\delta_{K+K',0}}$$

$$= \sum_K Q_K Q_{-K} (e^{iK} - 1)(e^{-iK} - 1) = 2 \sum_K Q_K Q_{-K} (1 - \cos k)$$

Therefore, the Lagrangian is:

$$L = T - V = \sum_K \frac{1}{2} m \dot{Q}_K \dot{Q}_{-K} + \frac{1}{2} \beta \cdot 2 \sum_K Q_K Q_{-K} (1 - \cos k)$$

The canonical momentum is:

$$P_K = \frac{\partial L}{\partial \dot{Q}_K} = \frac{1}{2} m \dot{Q}_{-K} \Rightarrow \dot{Q}_K = P_{-K} / m$$

• With these new coordinates, the Hamiltonian becomes

$$H = \sum_K P_K \dot{Q}_K - L = \sum_K \frac{P_K P_{-K}}{m} - \frac{1}{2} \sum_K m \frac{P_{-K}}{m} \frac{P_K}{m} + \beta \sum_K Q_K Q_{-K} (1 - \cos k)$$

$$H = \sum_K \frac{P_K P_{-K}}{2m} + \beta \sum_K Q_K Q_{-K} (1 - \cos k)$$

$$\boxed{H = \sum_K \frac{P_K P_{-K}}{2m} + \sum_K \frac{1}{2} m \omega_K^2 Q_K Q_{-K}} \quad (21)$$

where: $\frac{1}{2} m \omega_K^2 = \beta (1 - \cos k) \Rightarrow \omega_K = \sqrt{\frac{2\beta}{m} (1 - \cos k)}$

• It can be shown that:

$$P_K = m \dot{Q}_{-K} = \frac{m}{\sqrt{N}} \sum_s \dot{u}_s e^{iKs}$$

$$P_r = \frac{1}{\sqrt{N}} \sum_K P_K e^{-iKr}$$

$$[Q_K, P_{K'}] = i\hbar \delta_{K,K'}$$

• The Hamiltonian given in (21) is not quite in a form of a set of harmonic oscillators because of the mixture of terms k and $-k$.

If one tries the linear transformation:

$$a_{\mathbf{k}}^{\dagger} = \sqrt{\frac{m\omega_{\mathbf{k}}}{2\hbar}} \left(Q_{-\mathbf{k}} - i \frac{P_{\mathbf{k}}}{m\omega_{\mathbf{k}}} \right)$$

$$a_{\mathbf{k}} = \sqrt{\frac{m\omega_{\mathbf{k}}}{2\hbar}} \left(Q_{\mathbf{k}} + i \frac{P_{-\mathbf{k}}}{m\omega_{\mathbf{k}}} \right)$$

we get:

$$\begin{aligned} \hbar\omega_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} &= \hbar\omega_{\mathbf{k}} \frac{m\omega_{\mathbf{k}}}{2\hbar} \left(Q_{-\mathbf{k}} - i \frac{P_{\mathbf{k}}}{m\omega_{\mathbf{k}}} \right) \left(Q_{\mathbf{k}} + i \frac{P_{-\mathbf{k}}}{m\omega_{\mathbf{k}}} \right) \\ &= \frac{1}{2} m\omega_{\mathbf{k}}^2 \left(Q_{-\mathbf{k}} Q_{\mathbf{k}} + i \frac{Q_{-\mathbf{k}} P_{-\mathbf{k}}}{m\omega_{\mathbf{k}}} - i \frac{P_{\mathbf{k}} Q_{\mathbf{k}}}{m\omega_{\mathbf{k}}} + \frac{P_{\mathbf{k}} P_{-\mathbf{k}}}{m^2 \omega_{\mathbf{k}}^2} \right) \\ &= \frac{1}{2} m\omega_{\mathbf{k}}^2 Q_{-\mathbf{k}} Q_{\mathbf{k}} + \frac{1}{2} m\omega_{\mathbf{k}}^2 \frac{1}{m^2 \omega_{\mathbf{k}}^2} P_{\mathbf{k}} P_{-\mathbf{k}} + \\ &\quad + \frac{i}{m\omega_{\mathbf{k}}} (Q_{-\mathbf{k}} P_{-\mathbf{k}} - P_{\mathbf{k}} Q_{\mathbf{k}}) \frac{m\omega_{\mathbf{k}}^2}{2} \\ &= \frac{P_{\mathbf{k}} P_{-\mathbf{k}}}{2m} + \frac{1}{2} m\omega_{\mathbf{k}}^2 Q_{\mathbf{k}} Q_{-\mathbf{k}} + \frac{i}{\hbar\omega_{\mathbf{k}}} \underbrace{(Q_{-\mathbf{k}} P_{-\mathbf{k}} - P_{\mathbf{k}} Q_{\mathbf{k}})}_{i\hbar} \frac{\hbar\omega_{\mathbf{k}}}{2} \\ &= \frac{P_{\mathbf{k}} P_{-\mathbf{k}}}{2m} + \frac{1}{2} m\omega_{\mathbf{k}}^2 Q_{\mathbf{k}} Q_{-\mathbf{k}} - \frac{\hbar\omega_{\mathbf{k}}}{2} \end{aligned}$$

Thus, the Hamiltonian of the lattice vibrations may be written in the form:

$$H = \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} \left(a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \frac{1}{2} \right) \quad \text{where } \omega_{\mathbf{k}} = \sqrt{\frac{2\beta}{m} (1 - \cos k)} \quad (2)$$

and this is essentially a Hamiltonian for a collection of harmonic oscillators of frequency $\omega_{\mathbf{k}}$. Therefore, the total wavefunction of the system is

$$\Phi = \prod_{\mathbf{k}} |Q_{\mathbf{k}} N_{\mathbf{k}}\rangle$$

where $Q_{\mathbf{k}}$ is the amplitude of the oscillator \mathbf{k} and $N_{\mathbf{k}}$ is the number of phonons in that mode with energy $E_{\mathbf{k}}$.

- We can also express Q_k 's in terms of the creation and annihilation operators :

$$Q_k = \sqrt{\frac{\hbar}{2m\omega_k}} (a_k + a_k^\dagger) \quad \text{where } U_r = \frac{1}{\sqrt{N}} \sum_k Q_k e^{ikr}$$

$$P_k = i \sqrt{\frac{m\omega_k \hbar}{2}} (a_k^\dagger - a_k)$$

- To understand what phonons are, we consider a single mode with amplitude Q_k , i.e.

$$U_r = \frac{Q_k}{\sqrt{N}} \cos(kr - \omega_k t)$$

The kinetic energy is:

$$T = \frac{1}{2} m (U_r)^2 = \frac{1}{2} \frac{m}{N} Q_k^2 \omega_k^2 \sin^2(kr - \omega_k t)$$

Since the total energy is:

$$E_k = (n_k + 1/2) \hbar \omega_k \approx n_k \hbar \omega_k$$

we have :

$$\frac{1}{2} \frac{m}{N} |Q_k|^2 \omega_k^2 = n_k \hbar \omega_k$$

or the amplitude of the mode is:

$$|Q_k| = \sqrt{\frac{2n_k \hbar \omega_k N}{m \omega_k^2}} \sim \sqrt{n_k}$$

- Therefore, the vibrational energy of the oscillator k is quantized in units $\hbar \omega_k$. We can also visualize this as an energy level in which we can put n -phonons.
- The greater the number of phonons in a given vibrational mode, the greater the energy of the vibrations, and hence the greater the amplitude of the vibrations.
- Since all of the ions move with the same frequency and same phase (the amplitudes are not the same), these vibrational modes are called NORMAL MODES OF VIBRATION of the system.

→ The number of phonons in a given mode is given by:

$$n(\omega_k) = n_k = \frac{1}{e^{\hbar\omega_k/k_B T} - 1} \quad (\text{Bose-Einstein})$$

→ One can generalize these results for 3D crystals, in which case the displacement of a mode \vec{q} with polarization ν is given by:

$$\vec{u}_{\vec{q},\nu}(\vec{R},t) = \sqrt{\frac{\hbar}{2MN\omega_q}} \vec{e}_{\vec{q},\nu} \left[a_{\vec{q},\nu} e^{i(\vec{q}\cdot\vec{R} - \omega_q t)} + a_{\vec{q},\nu}^{\dagger} e^{-i(\vec{q}\cdot\vec{R} - \omega_q t)} \right]$$

where: \vec{R} → position of a unit cell
 $\vec{e}_{\vec{q},\nu}$ → polarization vector: $\vec{e}_{\vec{q},\nu} \parallel \vec{q}$ (longitudinal modes)
 $\vec{e}_{\vec{q},\nu} \perp \vec{q}$ (transverse modes)

→ For acoustic waves, $\vec{u}_{\vec{q},\nu}(\vec{R},t)$ represents the displacement of the unit cell and for optical waves it refers to the relative displacement of the two atoms within the unit cell.

→ The linear dependence of the electron-phonon interaction on strain (either acoustic or optical) means that it is also linearly dependent on the normal coordinates of the simple harmonic oscillators. This, as shown in the next section, has the well known consequence that a given mode may change its phonon occupancy by unity.

(E) MATRIX ELEMENT FOR SCATTERING BETWEEN Ψ_i AND Ψ_f

→ In general, the wavefunction Ψ_i of the initial state can be written as a product of the one-electron wavefunction (Bloch function) $\Psi_{n\vec{k}}(\vec{r})$ and a harmonic oscillators wavefunction:

$$\Psi_i = \Psi_{n\vec{k}}(\vec{r}) \Phi_i = \Psi_{n\vec{k}}(\vec{r}) \prod_{\vec{q}, b_i} |Q_{\vec{q}, b_i}, n_{\vec{q}, b_i}\rangle$$

→ The final state wavefunction also consists of a product of a Bloch function and oscillator functions product, i.e.

$$\Psi_f = \Psi_{n'\vec{k}'}(\vec{r}) \Phi_f = \Psi_{n'\vec{k}'}(\vec{r}) \prod_{\vec{q}, b_j} |Q_{\vec{q}, b_j}, n_{\vec{q}, b_j}\rangle$$

where: n, n' → band index
 b_i, b_j → phonon branch

→ Let H_{ep} be the electron-phonon interaction. Since H_{ep} depends linearly on U_{qv} , that means that it depends linearly on Q_{qv} . therefore, when describing the electron-phonon interaction, one needs to evaluate matrix elements of the form:

$$M_{fi} = \sum_{q,r} \langle \Psi_f | U_{qv}(\vec{R}, t) H_{qv}(\vec{r}) | \Psi_i \rangle$$

↑ ion displacement at location \vec{R} in the crystal
 ↑ electronic component of the electron-phonon interaction

→ Substituting the expressions for $U_{qv}(\vec{R}, t)$ and Ψ_i and Ψ_f leads to:

$$M_{fi} = \sum_{q,r} \frac{1}{V} \int d\vec{r} U_{n'k'}^* e^{-i\vec{r}' \cdot \vec{r}} H_{qv}(\vec{r}) U_{nk} e^{i\vec{r} \cdot \vec{r}}$$

$$\cdot \prod_{q;b_i} \prod_{q;b_j} \sqrt{\frac{\hbar}{2MN\omega_{qv}}} \langle Q_{q;b_j} n_{q;b_j} | \hat{a}_{qv} e^{i\vec{q} \cdot \vec{R}} + \hat{a}_{qv}^\dagger e^{-i\vec{q} \cdot \vec{R}} | Q_{q;b_i} n_{q;b_i} \rangle$$

• The integration over the phonon coordinates leads to the condition that $q=q_i=q_f$ and $r=b_i=b_j$, which leaves only one term in the double product. Since the number of phonons in a given mode of lattice vibrations is not necessarily conserved, we have that, in general,

$$\langle n_{qv}' | \hat{a}_{qv} e^{i\vec{q} \cdot \vec{R}} + \hat{a}_{qv}^\dagger e^{-i\vec{q} \cdot \vec{R}} | n_{qv} \rangle$$

$$= e^{i\vec{q} \cdot \vec{R}} \langle n_{qv}' | \hat{a}_{qv} | n_{qv} \rangle + e^{-i\vec{q} \cdot \vec{R}} \langle n_{qv}' | \hat{a}_{qv}^\dagger | n_{qv} \rangle$$

$$= e^{i\vec{q} \cdot \vec{R}} \sqrt{n_{qv}} \delta_{n_{qv}', n_{qv}-1} + e^{-i\vec{q} \cdot \vec{R}} \sqrt{n_{qv}+1} \delta_{n_{qv}', n_{qv}+1}$$

of phonons in final state
of phonons in initial state

$n_{qv}' = n_{qv} - 1$

of phonons in final state is smaller than # of phonons in initial state, which means that electron has absorbed a phonon

ABSORPTION

$n_{qv}' = n_{qv} + 1$

Electron has emitted a phonon since # of phonons in the final state is larger by one

EMISSION

- After the integration over the phonon coordinates, the expression for M_{fi} simplifies to:

$$M_{fi} = \sum_{q\nu} \left[\frac{(n_{q\nu})^{1/2}}{(n_{q\nu}+1)^{1/2}} \right] \sqrt{\frac{\hbar}{2MN\omega_{q\nu}}} \frac{1}{V} \int d\vec{r} U_{n'k'}^* e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} H_{q\nu}(\vec{r}) e^{\pm i\vec{q}\cdot\vec{R}} U_{nk}$$

Because of the periodic properties of the Bloch function and of the interaction, the integral over the crystal can be factored into an integral over a unit cell, ~~unit cell~~ and a sum over all unit cells. This is achieved by using:

$$\vec{r} = \vec{R} + \vec{r}'$$

\vec{R} ← Lattice vector (location of unit cell)
 \vec{r}' ← vector within the unit cell

Therefore:

$$\begin{aligned} & \frac{1}{V} \int d\vec{r} U_{n'k'}^*(\vec{r}) e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} H_{q\nu}(\vec{r}) e^{\pm i\vec{q}\cdot\vec{R}} U_{nk}(\vec{r}) \\ &= \frac{1}{V} \sum_{\vec{R}} \int_{\Omega} d\vec{r}' U_{n'k'}^*(\vec{r}'+\vec{R}) e^{i(\vec{k}-\vec{k}')\cdot(\vec{r}'+\vec{R})} e^{\pm i\vec{q}\cdot\vec{R}} H_{q\nu}(\vec{r}'+\vec{R}) U_{nk}(\vec{r}'+\vec{R}) \\ &= \frac{1}{V} \sum_{\vec{R}} e^{i(\vec{k}-\vec{k}'\pm\vec{q})\cdot\vec{R}} \int_{\Omega} d\vec{r}' U_{n'k'}^*(\vec{r}') e^{i(\vec{k}-\vec{k}')\cdot\vec{r}'} H_{q\nu}(\vec{r}') U_{nk}(\vec{r}') \\ & \quad N \delta_{\vec{k}\pm\vec{q}-\vec{k}', \vec{G}} ; \text{ where } \vec{G} \text{ is a vector in the reciprocal lattice space} \\ &= \frac{N}{V} \delta_{\vec{k}\pm\vec{q}-\vec{k}', \vec{G}} \int_{\Omega} d\vec{r}' U_{n'k'}^*(\vec{r}') e^{i(\vec{k}-\vec{k}')\cdot\vec{r}'} H_{q\nu}(\vec{r}') U_{nk}(\vec{r}') \\ &= \delta_{\vec{k}\pm\vec{q}-\vec{k}', \vec{G}} \frac{1}{\Omega} \int_{\Omega} d\vec{r}' U_{n'k'}^*(\vec{r}') e^{i(\vec{k}-\vec{k}')\cdot\vec{r}'} H_{q\nu}(\vec{r}') U_{nk}(\vec{r}') \\ & \quad C_{q\nu} I_{nn'}(\vec{k}, \vec{k}') ; I_{nn'}(\vec{k}, \vec{k}') = \int_{\Omega} \psi_{n'k'}^*(\vec{r}) \psi_{nk}(\vec{r}) d\vec{r} \\ & \quad C_{q\nu} I_{nn'}(\vec{k}, \vec{k}') = \int_{\Omega} d\vec{r} \psi_{n'k'}^*(\vec{r}) H_{q\nu}(\vec{r}) \psi_{nk}(\vec{r}) \end{aligned}$$

→ To summarize:

$$M_{fi} = (n_{qv} + \frac{1}{2} \mp \frac{1}{2})^{1/2} \sqrt{\frac{\hbar}{2MN\omega_q}} C_{qv} \text{Inn}'(\vec{k}, \vec{k}') \delta_{\vec{k} \pm \vec{q} - \vec{k}', \vec{G}}$$

where:

$$C_{qv} = \frac{\int d\vec{r} \Psi_{n'k'}^*(\vec{r}) H_{qv}(\vec{r}) \Psi_{nk}(\vec{r})}{\int d\vec{r} \Psi_{n'k'}^*(\vec{r}) \Psi_{nk}(\vec{r})} = \frac{\int d\vec{r} \Psi_{n'k'}^*(\vec{r}) H_{qv}(\vec{r}) \Psi_{nk}(\vec{r})}{\text{Inn}'(\vec{k}, \vec{k}')}$$

and $H_{qv}(\vec{r})$ is the electronic part of the electron-phonon interaction, that does not depend upon the lattice coordinate and refers to a given mode.

→ Important remarks:

- (1) The δ -function in the expression for M_{fi} involves the reciprocal lattice vector \vec{G} . Depending upon the value of \vec{G} , the scattering processes can be separated into:

$\vec{G} = 0 \rightarrow$ NORMAL process

$\vec{G} \neq 0 \rightarrow$ UMKLAPP process, in which a reciprocal lattice vector is needed to satisfy the momentum conservation requirement.

- (2) The integral $C_{qv} \text{Inn}'(\vec{k}, \vec{k}')$ provides a final selection rule depending on the type of $H_{qv}(\vec{r})$ and the symmetries of the Bloch functions. For the polar, optical and piezoelectric interactions the macroscopic fields produced are essentially long-range fields (Coulomb-type interactions) that vary slowly over the unit cell. The integral is zero unless the Bloch functions belong to the same valley. Both intra-valley and inter-valley are allowed for deformation potential interaction.
- (3) In a single lattice scattering event only one mode is involved, that can affect the transition for a given initial and final electronic states.
- (4) To summarize, ignoring the non-parabolicity of the bands, i.e. assuming that $I(\vec{k}, \vec{k}') = 1$ (for intravalley transition), the results of this section can be summarized as follows:

$$|M_{fi}|^2 = \frac{\hbar}{2MN\omega_{qv}} C_{qv}^2 (n_{qv} + \frac{1}{2} \mp \frac{1}{2}) \delta_{\vec{k} \pm \vec{q} - \vec{k}', \vec{G}} \quad ; \quad MN = \rho V$$

where the top sign refers to absorption and the bottom to emission. The coupling constant C_{qv} , in general, depends upon the magnitude of q . For acoustic mode, the mass M is the total mass of the unit cell, whereas for optical modes, the mass $M = (1/M_1 + 1/M_2)^{-1}$ is the reduced mass.