$\underline{\underline{D}}$ is diagonalized by an orthogonal transformation

$$\underline{\underline{C}} \cdot \underline{\underline{D}}\, \underline{\underline{C}}^T = \underline{\underline{\Omega}} = \begin{pmatrix} \omega_1^2 & & 0 \\ & \ddots & \\ 0 & & \omega_{Nd}^2 \end{pmatrix} \qquad (3.6)$$

such that $\underline{\underline{C}}\,\underline{\underline{C}}^T = \underline{\underline{C}}^T \underline{\underline{C}} = \mathbb{1}$. By the variable transformation

$$\underline{p} = \underline{\underline{C}}\, \underline{\tilde{p}} \quad , \quad \underline{u} = \underline{\underline{C}}\, \underline{\tilde{u}} \qquad (3.7)$$

one obtain a new set of canonically conjugated variables in which the ions hamilton function reads

$$H_{harm} = \frac{1}{2}\left(\underline{\bar{p}}^t \cdot \underline{\bar{p}} + \underline{\bar{u}}^t \cdot \underline{\underline{\Omega}} \cdot \underline{\bar{u}} \right) = \frac{1}{2} \sum_{i=1}^{Nd} \left(\bar{p}_i^2 + \omega_i^2 \bar{u}_i^2 \right) \qquad (3.8)$$

That is, the Hamilton function of a set of independent harmonic oscillators with frequencies ω_i and normal coordinate $\bar{u}_i = \sum_{\alpha\ell} \frac{1}{\sqrt{M_\alpha}} C_{i,\alpha\ell}\, u_{\alpha\ell}$

- <u>Quantum analysis</u>

Equations (3.3) – (3.8) admit a quantum interpretation since, after verifying the canonical commutation relations:

$$\left[\hat{R}_{\alpha\ell}, \hat{p}_{\beta m} \right] = i\hbar\, \delta_{\ell m}\, \delta_{\alpha\beta} \qquad (3.9)$$

easily obtained since $\hat{p}_{\beta m} = -i\hbar \frac{\partial}{\partial R_{\beta m}}$, we also obtain

$$\left[\hat{u}_{\alpha\ell}, \hat{p}_{\beta m} \right] = i\hbar\, \delta_{\ell m}\, \delta_{\alpha\beta} \qquad (3.10)$$

being $\hat{u}_{\alpha\ell} = \hat{R}_{\alpha\ell} - R_{\alpha\ell}^0$. Analogously, the commutation relations are fulfilled by the operators associated to the normal coordinates

$$[\hat{u}_i, \hat{p}_j] = i\hbar\delta_{ij} \qquad (3.11)$$

proof:

The commutator is a bilinear operation, thus:

$$[\hat{u}_i, \hat{p}_j] = \sum_{\substack{\alpha l \\ \beta m}} \sqrt{\frac{M_\beta}{M_\alpha}}\, c_{i,\alpha l}\, c_{j,\beta m} \overbrace{[\hat{u}_{\alpha l}, \hat{p}_{\beta m}]}^{i\hbar\delta_{\alpha\beta}\delta_{lm}} =$$

$$= i\hbar \sum_{\alpha l} \sqrt{\frac{M_\alpha}{M_\alpha}}\, c_{i,\alpha l}\, c^{T}_{\alpha l,j} = i\hbar\delta_{ij} \quad \blacksquare$$

One can thus conveniently introduce the set of ladder operators:

$$\begin{cases} \hat{b}_j = \sqrt{\frac{\omega_j}{2\hbar}}\,\hat{u}_j + i\sqrt{\frac{1}{2\hbar\omega_j}}\,\hat{p}_j \\ \hat{b}_j^{+} = \sqrt{\frac{\omega_j}{2\hbar}}\,\hat{u}_j - i\sqrt{\frac{1}{2\hbar\omega_j}}\,\hat{p}_j \end{cases} , \quad \begin{cases} \hat{u}_j = \sqrt{\frac{\hbar}{2\omega_j}}\left(\hat{b}_j + \hat{b}_j^{+}\right) \\ \hat{p}_j = -i\sqrt{\frac{\hbar\omega_j}{2}}\left(\hat{b}_j - \hat{b}_j^{+}\right) \end{cases} \qquad (3.12)$$

which satisfy the (bosonic) commutation relations (verify)

$$[\hat{b}_j, \hat{b}_k^{+}] = \delta_{jk}\,, \quad [\hat{b}_j, \hat{b}_k] = 0 \qquad (3.13)$$

The harmonic approximation of the Hamilton operator in (1.10a) can thus be written as:

$$\hat{H}_{harm} = \sum_{j=1}^{Nd} \hbar\omega_j \left(\hat{b}_j^{+}\hat{b}_j + \frac{1}{2}\right) \qquad (3.14)$$

proof

$$H_{harm} = \frac{1}{2}\sum_{i=1}^{Nd}\left(\hat{p}_i^2 + \omega_i^2\hat{u}_i^2\right) \overset{(3.12)}{=} \frac{1}{2}\sum_{i=1}^{Nd} -1\,\frac{\hbar\omega_j}{2}\left(\hat{b}_j - \hat{b}_j^{+}\right)^2 + \frac{\hbar\omega_j}{2}\left(\hat{b}_j + \hat{b}_j^{+}\right)^2$$

$$= \frac{1}{2}\sum_{i=1}^{Nd}\hbar\omega_j\left[-\hat{b}_j^2 - \hat{b}_j^{+2} + 2\hat{b}_j\hat{b}_j^{+} + 2\hat{b}_j^{+}\hat{b}_j + \hat{b}_j^2 + \hat{b}_j^{+2}\right] \overset{(3.13)}{=}$$

$$= \frac{1}{2}\sum_{i=1}^{Nd}\hbar\omega_j\left[2\hat{b}_j^{+}\hat{b}_j + 1\right] = \sum_{j=1}^{Nd}\hbar\omega_j\left(\hat{b}_j^{+}\hat{b}_j + \frac{1}{2}\right)$$

$\blacksquare$

The spectrum of a quantum harmonic oscillator is evenly spaced thus one can naturally associate to the quantum of excitation the notion of particle. The eigenstates and eigenvalues of (3.14) read:

$$E_{\{n_j\}} = \sum_{j=1}^{Nd} \hbar\omega_j \left(n_j + \frac{1}{2} \right) \qquad (3.15)$$

$$|\{n_j\}\rangle = \prod_j \frac{(b_j^+)^{n_j}}{\sqrt{n_j!}} |0\rangle$$

and $|0\rangle$ is defined by the Nd relations $b_j|0\rangle = 0$ and the normalization condition $\langle 0|0\rangle = 1$.

3.2 Acoustic and optical phonons in 3D

Now we specialize the discussion of the section 3.1 to the case of a crystal structure, to obtain the dispersion relation of the phonons.

1) (Still generic) The effective potential $V_{eff}(\{\vec{R}_{a\tau}\})$ shows a "continuous" translational invariance: i.e by displacing ALL ionic positions by the <u>same</u> vector $\vec{v}$ the eigenvalue $\varepsilon_{el,k}$ of the electronic problem does NOT change. See eq. (1.3).

proof
- $\hat{V}_{ii}$ is obviously invariant
- We operate a translation of $\vec{v}$ of all electronic positions $\vec{r}_j$

  => $\hat{V}_{ei}$ is the same as before ions and electron translation
  $\hat{V}_{ee}$ is invariant
  $\hat{T}_{el}$ is invariant

■

Consequently we can write:

$$V_{eff} = V_{eff}(\{\vec{R}_{a\tau} - \vec{R}_{a\tau'}\}) \qquad (3.16)$$

where with $\{\vec{R}_{a\tau} - \vec{R}_{a\tau'}\}$ we indicate all possible differences of position vectors in the crystal.

We define the displacement from the equilibrium position:

$$u_{\alpha\tau n} = R_{\alpha\tau n} - R^0_{\alpha n} - \tau_n$$

$\alpha = 1 \dots N_{cell}$
$\tau = 1 \dots r$ (basis size)
$n = x, y, z$

The classical equation of motion for $u_{\alpha\tau n}$ in the harmonic approx. read

$$M_\tau \ddot{u}_{\alpha\tau n} = -\frac{\partial^2 V_{eff}}{\partial u_{\alpha\tau n}} = -\sum_{\alpha'\tau'n'} \Phi_{\alpha\tau n, \alpha'\tau'n'} u_{\alpha'\tau'n'} \qquad (3.17)$$

where

$$\Phi_{\alpha\tau n, \alpha'\tau'n'} = \frac{1}{2} \frac{\partial^2 V_{eff}}{\partial R_{\alpha\tau n} \partial R_{\alpha'\tau'n'}} \Bigg|_{\{\vec{R}_{\alpha\tau}\} = \{\vec{R}^0_\alpha + \vec{\tau}\}} \qquad (3.18)$$

2) The symmetric and positive definite force constant matrix Φ obeys the sum rule:

$$\sum_{\alpha'\tau'} \Phi_{\alpha\tau n, \alpha'\tau'n'} = 0 \qquad \forall\, n, n' \in \{x, y, z\} \qquad (3.19)$$

proof:
The force in the direction n experienced by the atom $|\alpha, \tau\rangle$ is given by

$$F_{\alpha\tau n} = \sum_{\alpha'\tau'n'} \Phi_{\alpha\tau n, \alpha'\tau'n'} u_{\alpha'\tau'n'}$$

If all atoms are displaced by $\vec{u}$ in the same direction by the same constant $\Rightarrow F_{\alpha\tau n} = 0 = \sum_{\alpha'\tau'n'} \Phi_{\alpha\tau n, \alpha'\tau'n'} u_{n'}$. The sum over n' can be omitted since the result does not depend on the special choice of $\vec{u}$.

3) Due to the periodicity of the crystal structure in equilibrium, we can write:

$$\Phi_{\alpha\tau n, \alpha'\tau'n'} = \Phi_{\tau n, \tau'n'}\left(\vec{R}^0_\alpha - \vec{R}^0_{\alpha'}\right) \qquad (3.20)$$

In other terms, the constant force matrix cannot depend on the peculiar points of the Bravais lattice with respect of which it is calculated, but only on the distance between the two points.

If one makes the Ansatz:

$$u_{\alpha\tau n}(t) = \frac{1}{\sqrt{M_\tau}} \nu_{\alpha\tau n} e^{-i\omega t} \qquad (3.21)$$

in (3.17) one obtains

$$\omega^2 \nu_{\alpha\tau n} = \sum_{\alpha'\tau'n'} \Delta_{\tau n,\tau' n'} \left(\vec{R}_\alpha^{\,0} - \vec{R}_{\alpha'}^{\,0}\right) \nu_{\alpha'\tau'n'} \qquad (3.22)$$

where $\underline{\underline{\Delta}} = \frac{1}{\sqrt{M_\tau M_{\tau'}}} \Phi$ is a matrix of dimension $N_{cell}\,rd \times N_{cell}\,rd$.

Since ω^2 and $\underline{\underline{\Delta}}$ are invariant under translation of a vector in the Bravais lattice, the function $\nu_{\alpha\tau n}$ has the Bloch form:

$$\nu_{\alpha\tau n}(\vec{q}) = \frac{1}{\sqrt{N_{cell}}} W_{\tau n}(\vec{q}) e^{i\vec{q}\vec{R}_\alpha^{\,0}} \qquad (3.23)$$

$W_{\tau n}$ is playing the role played by the Bloch factor for the electronic wave function. Since $\nu_{\alpha\tau n}$ is defined only for discrete α => $W_{\tau n}$ is indep. of α. By substitution of (3.23) in (3.22)

$$\omega^2 W_{\tau n} = \sum_{\alpha'\tau'n'} \frac{1}{\sqrt{N_{cell}}} \Delta_{\tau n,\tau' n'} \left(\vec{R}_\alpha^{\,0} - \vec{R}_{\alpha'}^{\,0}\right) e^{-i\vec{q}\left(\vec{R}_\alpha^{\,0} - \vec{R}_{\alpha'}^{\,0}\right)} W_{\tau' n'}$$

or, by redefinition of the sum over α',

$$\omega^2 W_{\tau n} = \sum_{\tau' n'} \frac{1}{\sqrt{N_{cell}}} \sum_{\vec{R}\in BL} \Delta_{\tau n,\tau' n'}(\vec{R})\, e^{-i\vec{q}\cdot\vec{R}}\, W_{\tau' n'} \qquad (3.24)$$

If we introduce the Fourier transform of the dynamical matrix

$$\tilde{\Delta}_{\tau n,\tau' n'}(\vec{q}) = \frac{1}{\sqrt{N_{cell}}} \sum_{\vec{R}\in BL} \Delta_{\tau n,\tau' n'}(\vec{R})\, e^{-i\vec{q}\cdot\vec{R}} \qquad (3.25)$$

One obtains the eigenvalue problem:

$$\sum_{\tau',n'} \tilde{D}_{n\tau,n'\tau'}(\vec{q})\, w_{n'\tau'} = \omega^2 w_{n\tau} \qquad (3.26)$$

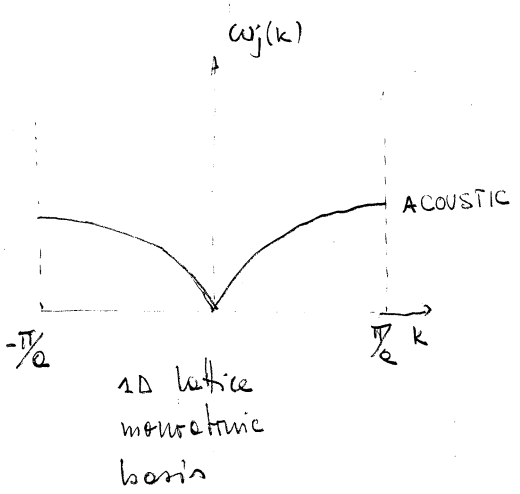
with $\tilde{\tilde{D}}(\vec{q})$ of dimension $dr \times dr$. Notice that once again $\vec{q} \in 1BZ$ since solutions with $\vec{q}' \notin 1BZ$ are indistinguishable from the associated one with $\vec{q} = \vec{q}' + \vec{G}$ where $\vec{G} \in RL$. If we call $\omega_j(\vec{q})$ the square root of the eigenvalue of (3.26) and $e^{(j)}_{n\tau}$ the corresponding eigenvector, we can write the special solutions of (3.17) as:

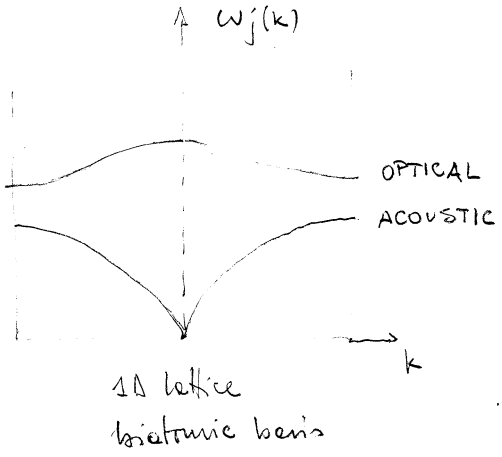
$$\vec{u}_{\alpha\tau}(t;\vec{q},j) = \frac{1}{\sqrt{M_\tau N_{cell}}} \vec{e}_\tau(\vec{q},j) e^{i(\vec{q}\vec{R}^0_\alpha - \omega_j(\vec{q})t)} \qquad (3.27)$$

where $\vec{e}_\tau(\vec{q},j)$ is obtained by combining into a regular d-dimensional vector the $e^{(j)}_{n\tau}$ component relative to the basis atom τ. Moreover $\vec{e}_\tau(\vec{q},j)$ is called polarization vector. $\omega_j(\vec{q})$ represents the dispersion relation of the normal mode branch j, defined as the electronic band structure on the 1BZ.

Let us now consider the phonons close to the Γ point. In general, out of the dr branches of the phonon dispersion d vanish at the Γ point and have a linear dispersion relation in the long wave length limit ACOUSTIC PHONONS, the other $(r-1)d$ start instead with a finite frequency at the Γ point (OPTICAL PHONONS)

Example:





Proof of the existence of d acoustic branches

Consider the special displacement of the crystal atoms in which ALL atoms in a unit cell move in the same direction and with equal displacement $\vec{u}_\alpha$ (independent from the basis index τ). Let's assume that eigenmodes of this type exist:

$$M_\tau \omega_j^2(\vec{q})\, u_n\, e^{i\vec{q}\cdot\vec{R}_\alpha} = \sum_{\alpha'\tau'} \Phi_{\alpha\tau n,\alpha'\tau' n}\, u_n\, e^{i\vec{q}\cdot\vec{R}_{\alpha'}} \qquad (3.28)$$

follows from (3.17). Now we expand both sides of (3.28) for small moments $\vec{q}$ and obtain

$$M_\tau \left(\omega_j(0) + \nabla_{\vec{q}}\,\omega_j(\vec{q})\big|_{\vec{q}=0}\cdot\vec{q} + \dots\right)^2 = \sum_{\vec{R}\in BL}\sum_{\tau'} \Phi_{\tau n,\tau' n}(\vec{R}) \left(1 - i\vec{q}\cdot\vec{R} - \frac{1}{2}(\vec{q}\vec{R})^2 + \dots\right) \qquad (3.29)$$

We compare order by order in $\vec{q}$:

- 0^{th} order in $\vec{q}$

$$M_\tau \omega_j^2(0) = \sum_{\vec{R}}\sum_{\tau'} \Phi_{\tau n,\tau' n}(\vec{R}) = 0 \qquad (3.19)$$

For these special branches j $\lim_{\vec{q}\to 0} \omega_j(\vec{q}) = 0$.

- 1^{st} order in $\vec{q}$

$$M_\tau\, 2\,\omega_j(0)\left(\nabla_{\vec{q}}\,\omega_j(\vec{q})\big|_{\vec{q}=0}\cdot\vec{q}\right) = \sum_{\vec{R}\tau'} \Phi_{\tau n,\tau' n}(\vec{R})\,(-i\vec{q}\cdot\vec{R})$$

The LHS vanishes due to $\omega_j(0)=0$ => we obtain a new symmetry relation for the force constant matix Φ:

$$\sum_{\vec{R}\tau'} \Phi_{\tau n,\tau' n}(\vec{R})\,\vec{R} = 0 \qquad (3.30)$$

- 2nd order in $\vec{q}$

$$M_\tau \left(\nabla_{\vec{q}}\, \omega_j(\vec{q})\big|_{\vec{q}=0} \cdot \vec{q} \right)^2 = -\frac{1}{2} \sum_{\vec{R}\tau'} \Phi_{\tau n, \tau' n}(\vec{R}) \left(\vec{R}\cdot\vec{q}\right)^2$$

In general this term does not vanish. One can thus write, in general

$$\omega_j^2(\vec{q}) = \sum_{mm'} C_{mm'} q_m q_{m'} \qquad m, m' = x, y, z \text{ in } 3D$$

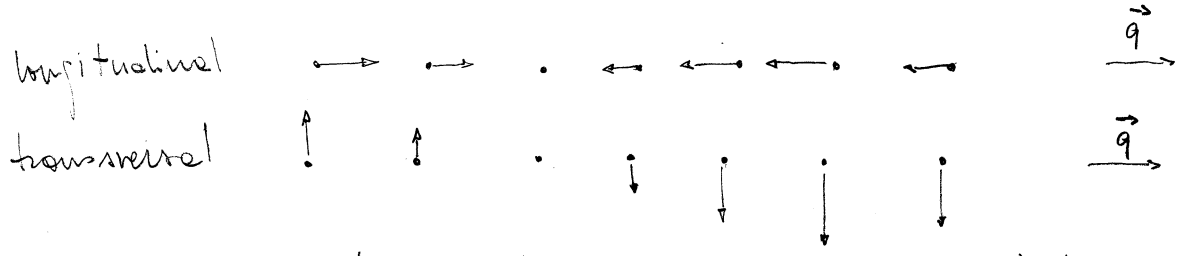
for small $|\vec{q}|$ and the eigenvalues of $\underline{\underline{C}}$ will give the coefficients of the linear dispersion of the d acoustic modes.

There is a further classification of the phonon branches in 1D

LONGITUDINAL: the displacement of all ions is parallel to $\vec{q}$

TRANSVERSAL: the displacement of all ions is perpendicular to $\vec{q}$

Example: 1D chain with 3D motion



Notice that the classification in terms of longitudinal and transverse is not possible for every momentum of the BZ, but only along particular symmetry directions.