

# Chapter 2

## Lattice vibrations

### 2.1 The adiabatic approximation. Hamiltonian for lattice vibrations.

We turn first back to the full Hamiltonian we discussed in the Introduction to these lectures.

$$H = H_{nuc} + H_{el} + H_{el-nuc} , \quad (2.1)$$

where

$$H_{nuc} = \sum_i^N \frac{\mathbf{P}_i^2}{2M_i} + \frac{1}{2} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} , \quad (2.2)$$

$$H_{el} = \sum_i^{ZN} \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{x}_i - \mathbf{x}_j|} , \quad (2.3)$$

$$H_{el-nuc} = - \sum_{i,j} \frac{e^2 Z_j}{|\mathbf{x}_i - \mathbf{R}_j|} . \quad (2.4)$$

As we already said at the beginning, it is in principle a formidable task if we want to solve the eigenvalue problem of (2.1). There is however, a clear distinction of energy scales due to the fact that  $m/M \sim 10^{-3} - 10^{-4}$ , since we know that the mass of a nucleon is approximately 1.800 times larger than that of the electron. This implies that

$$\frac{E_{nuc}^{kin.}}{E_{el}^{kin.}} \ll 1 , \quad (2.5)$$

where by  $E^{kin.}$  we denote the kinetic energy of nuclei and electrons, respectively. This means physically, that since the electrons are much faster than the nuclei, they will be able to accommodate instantaneously to the position of the nuclei, in the time scale that characterizes the motion of the latter. These are the conditions suitable for the *adiabatic approximation*.

We are not going to give the demonstration of the *adiabatic theorem* (see e.g. A. Messiah *Quantum mechanics*, Vol. 2 Sec. 17.2.4 - 17.2.7), but merely use it. For this let us consider a time dependent Hamiltonian, where it changes over a time period  $T$  and we parametrize the time evolution within this period by  $\tau$ , as given below.

$$T = t_1 - t_0, \quad \tau = \frac{t - t_0}{T}, \quad (2.6)$$

In our case we could think of  $H_{el} + H_{el-nuc}$ , where the position of the nuclei will be in general a function of time  $\mathbf{R}_i = \mathbf{R}_i(t)$ , and  $T$  the half-period of oscillation of the nuclei. The adiabatic theorem states that if  $\epsilon_1, \epsilon_2, \dots$  are the eigenvalues of some  $H(\tau)$ , and the following conditions are fulfilled,

$$i) \quad \epsilon_j(\tau) \neq \epsilon_k(\tau) \text{ for } 0 \leq \tau \leq 1 \text{ for all } i \neq k,$$

ii) and the change is such that the time evolution is made in a continuous way,

then, the time evolution operator  $U_T(\tau)$  obtained from the Schrödinger equation

$$i\hbar \frac{d}{d\tau} U_T(\tau) = TH(\tau)U_T(\tau), \quad (2.7)$$

where the Hamiltonian  $H(\tau)$  can be written as

$$H(\tau) = \sum_j \epsilon_j(\tau) P_j(\tau), \quad (2.8)$$

with  $P_j(\tau)$  the projectors to the subspaces, has the following property

$$\lim_{T \rightarrow \infty} U_T(\tau) P_j(0) = P_j(\tau) \lim_{T \rightarrow \infty} U_T(\tau). \quad (2.9)$$

That is, in the limit of an infinitely slow change of  $H$ , we can describe the evolution by considering the instantaneous eigenvalues and eigenvectors of  $H$ .

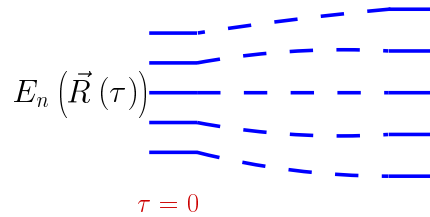


Figure 2.1: Schematic evolution of the eigenvalues in the adiabatic limit.

The application of the adiabatic approximation for the treatment of lattice vibrations is known as the *Born-Oppenheimer approximation*. In this case we need to solve a Schrödinger equation for the electrons as follows

$$(H_{el} + H_{el-nuc}) \psi(\mathbf{x}, \mathbf{R}) = E_{el}(\mathbf{R}) \psi(\mathbf{x}, \mathbf{R}), \quad (2.10)$$

with

$$\begin{aligned}\mathbf{x} &= (\mathbf{x}_1, \dots, \mathbf{x}_{ZN}) , \\ \mathbf{R} &= (\mathbf{R}_1, \dots, \mathbf{r}_N) ,\end{aligned}\tag{2.11}$$

where  $\mathbf{R}$  give the instantaneous positions of the nuclei. Figure 2.1 gives a sketch of the evolution of the eigenvalues for the electrons.

We can now propose an eigenfunction for the whole Hamiltonian (2.1) as a product

$$\Psi(\mathbf{x}, \mathbf{R}) = \psi(\mathbf{x}, \mathbf{R}) \Phi(\mathbf{R}) ,\tag{2.12}$$

such that  $H$  applied on  $\Psi$  gives

$$\begin{aligned}H\Psi &= -\sum_i^N \frac{\hbar^2}{2M_i} \frac{\partial^2}{\partial \mathbf{R}_i^2} \Psi + \frac{1}{2} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} \Psi + E_{el}(\mathbf{R}) \Psi \\ &= \psi(\mathbf{x}, \mathbf{R}) \left\{ -\sum_i^N \frac{\hbar^2}{2M_i} \frac{\partial^2}{\partial \mathbf{R}_i^2} + E_{el} + U_0(\mathbf{R}) \right\} \Phi(\mathbf{R}) \\ &\quad - \underbrace{\sum_i^N \frac{\hbar^2}{2M_i} \left\{ 2 \frac{\partial \Phi}{\partial \mathbf{R}_i} \frac{\partial \psi}{\partial \mathbf{R}_i} + \Phi \frac{\partial^2 \psi}{\partial \mathbf{R}_i^2} \right\}}_{\text{non-adiabatic part}} .\end{aligned}\tag{2.13}$$

Let us first notice, that if we multiply this equation by  $\psi^*(\mathbf{x}, \mathbf{R})$  and integrate over  $\mathbf{x}$ , the first line above gives us an effective Schrödinger equation for the nuclei. After this, we consider the non-adiabatic terms. For the first one we have

$$\int d^3x \psi^* \frac{\partial \psi}{\partial \mathbf{R}_i} = \frac{1}{2} \frac{\partial}{\partial \mathbf{R}_i} \int d^3x \psi^* \psi = 0 ,\tag{2.14}$$

where we used the fact, that without magnetic fields, the wavefunction can be chosen real, and that the total number of electrons cannot be changed by lattice vibrations. For the second non-adiabatic contribution, let us estimate the departure of the nuclei positions from the equilibrium one. For a harmonic oscillator we have  $\delta R \sim M^{-1/4}$ . Hence, the relative amplitude of the oscillation should be

$$\frac{\delta R}{R} \sim \left( \frac{m}{M} \right)^{\frac{1}{4}} \equiv \lambda ,\tag{2.15}$$

where we formed a dimensionless ratio of masses with the only other available mass. The change of the position of the nuclei from their equilibrium position, that we call  $\mathbf{R}^0$ , is

$$\mathbf{R} = \mathbf{R}^0 + \lambda \delta \mathbf{R} .\tag{2.16}$$

This allows us together with (2.10), to carry out a perturbation theory for  $\psi$ , such that

$$\psi(\mathbf{x}, \mathbf{R}) \simeq \psi(\mathbf{x}, \mathbf{R}^0) + \lambda \left. \frac{\partial \psi}{\partial \mathbf{R}} \right|_{\mathbf{R}^0} \delta \mathbf{R} + \frac{1}{2} \lambda^2 \left. \frac{\partial^2 \psi}{\partial \mathbf{R}^2} \right|_{\mathbf{R}^0} \delta \mathbf{R}^2, \quad (2.17)$$

showing that

$$\frac{\partial^2 \psi}{\partial \mathbf{R}_i^2} \sim \lambda^2. \quad (2.18)$$

Then,

$$\begin{aligned} \frac{\hbar^2}{2M} \int d^3x \psi^* \frac{\partial^2 \psi}{\partial \mathbf{R}_i^2} &\simeq \lambda^2 \frac{\hbar^2}{2M} \int d^3x \psi^* \frac{\partial^2 \psi}{\partial \mathbf{R}_i^{02}} \\ &\simeq \lambda^6 \frac{\hbar^2}{2m} \int d^3x \psi^* \frac{\partial^2 \psi}{\partial \mathbf{x}^2} \\ &= \lambda^6 E_{el}^{\text{kin.}}, \end{aligned} \quad (2.19)$$

where in going from the first to the second line, we assumed the worst case that the electrons are tightly bound to the nuclei, i.e.  $\psi(\mathbf{x}, \mathbf{R}) = \psi(\mathbf{x} - \mathbf{R})$ . Since  $E_{el}^{\text{kin.}} \sim \lambda^{-4} E_{nuc}^{\text{kin.}}$ , and  $\lambda \sim 0.1$ , we can neglect this term also.

Neglecting the non-adiabatic terms, the *lattice dynamics* is described by the following Schrödinger equation:

$$\left[ \sum_i^N \frac{\mathbf{P}_i^2}{2M_i} + E_{el}(\mathbf{R}) + U_0(\mathbf{R}) \right] \Phi(\mathbf{R}) = E \Phi(\mathbf{R}). \quad (2.20)$$

The determination of the potential

$$U(\mathbf{R}) \equiv E_{el}(\mathbf{R}) + U_0(\mathbf{R}) \quad (2.21)$$

is still a rather demanding task. On the one hand, we should be able to deal with the long-range Coulomb potential in  $U_0(\mathbf{R})$ , but on the other hand, we know (we will see this in detail later) that the long-range part will be screened by the electrons (think about Gauß' law). Furthermore, although it is nowadays possible to calculate at least the ground state for the electrons given the positions of the atoms in the frame of the *density functional theory*, that inspite of the approximations involved in the actual calculations works surprisingly accurately, the determination of  $E_{el}$  is even within that approximation rather demanding if it has to be carried out for many nuclei positions  $\mathbf{R}_i$ . We therefore, discuss general features of  $U(\mathbf{R})$  in the next section, that will give us the main features that characterize *harmonic oscillations* of nuclei in crystals.

## 2.2 Hamiltonian for the harmonic lattice. The dynamical matrix

We start here with a potential  $U(\mathbf{R})$  for the nuclei (or for the ions, in the case that the electrons are tightly bound to the nuclei, like in the case of ionic crystals, e.g. NaCl). Since we assume that  $U(\mathbf{R})$  describes some solid, there should be an equilibrium position for the ions, that we call  $\mathbf{R}_i^0$ . They correspond to the minimum of the potential, i.e.

$$\nabla_{\mathbf{R}_i} U(\mathbf{R}) \Big|_{\mathbf{R}_i = \mathbf{R}_i^0} = 0. \quad (2.22)$$

This means that if we restrict ourselves to small deviations from the equilibrium position, the potential  $U(\mathbf{R})$  can be expanded around the equilibrium position as follows:

$$U(\mathbf{R}) = U(\mathbf{R}^0) + \frac{1}{2} \sum_{\substack{i,j \\ \alpha,\beta}} D_{\alpha\beta}(\mathbf{R}_i^0, \mathbf{R}_j^0) (\mathbf{R}_i - \mathbf{R}_i^0)_\alpha (\mathbf{R}_j - \mathbf{R}_j^0)_\beta + \text{higher orders}, \quad (2.23)$$

where  $\alpha, \beta = x, y, z$ , and

$$D_{\alpha\beta}(\mathbf{R}_i^0, \mathbf{R}_j^0) = \frac{\partial^2 U}{\partial \mathbf{R}_{i\alpha} \partial \mathbf{R}_{j\beta}} \Big|_{\mathbf{R}^0}. \quad (2.24)$$

If higher orders are neglected, one has the *harmonic approximation*. Let us denote the small deviations from the equilibrium position

$$u_{i\alpha} \equiv (\mathbf{R}_i - \mathbf{R}_i^0)_\alpha, \quad (2.25)$$

and we finally arrive at the *Hamiltonian of the harmonic lattice*:

$$H_h = \sum_i^N \frac{\mathbf{P}_i^2}{2M_i} + \frac{1}{2} \sum_{\substack{i,j \\ \alpha,\beta}} D_{\alpha\beta}(\mathbf{R}_i^0, \mathbf{R}_j^0) u_{i\alpha} u_{j\beta}. \quad (2.26)$$

This is nothing else than a set of coupled harmonic oscillators, where the coordinates and momenta fulfill the canonical commutation relations

$$[u_{i\alpha}, P_{j\beta}] = i\hbar \delta_{ij} \delta_{\alpha\beta}. \quad (2.27)$$

In order to obtain the eigenmodes of the coupled harmonic oscillators above, we discuss next, the symmetry properties of  $D_{\alpha\beta}$ .

### 2.2.1 Symmetry properties of the dynamical matrix

We discuss first the symmetry properties of  $D_{\alpha\beta}(\mathbf{R}_i^0, \mathbf{R}_j^0)$ .

1.  $D_{\alpha\beta}(\mathbf{R}_i^0, \mathbf{R}_j^0) = D_{\beta\alpha}(\mathbf{R}_j^0, \mathbf{R}_i^0)$ . This results from (2.24), that is,  $D_{\alpha\beta}$  is a second derivative.
2. Since the system is periodic,  $D_{\alpha\beta}(\mathbf{R}_i^0, \mathbf{R}_j^0) = D_{\alpha\beta}(\mathbf{R}_i^0 + \mathbf{R}_\ell^0, \mathbf{R}_j^0 + \mathbf{R}_\ell^0) \forall \mathbf{R}_\ell^0$ . This implies  $D_{\alpha\beta}(\mathbf{R}_i^0, \mathbf{R}_j^0) = D_{\alpha\beta}(\mathbf{R}_i^0 - \mathbf{R}_j^0)$
3.  $D_{\alpha\beta}(\mathbf{R}_i^0 - \mathbf{R}_j^0) = D_{\alpha\beta}(\mathbf{R}_j^0 - \mathbf{R}_i^0)$  due to inversion symmetry.
4. Let us consider a small deviation from the equilibrium position that is the same for all the atoms. In this case we have

$$\sum_{\substack{i,j \\ \alpha,\beta}} D_{\alpha\beta}(\mathbf{R}_i^0 - \mathbf{R}_j^0) u_{i\alpha} u_{j\beta} = N \sum_{\alpha,\beta} u_{\alpha} u_{\beta} \sum_i D_{\alpha\beta}(\mathbf{R}_i^0 - \mathbf{R}_j^0) = 0, \quad (2.28)$$

since a rigid translation of the lattice cannot change the potential energy ( $\mathbf{R}$ ). Therefore,  $D_{\alpha\beta}$  fulfills the following sum rule

$$\sum_i D_{\alpha\beta}(\mathbf{R}_i^0 - \mathbf{R}_j^0) = 0. \quad (2.29)$$

The result of point 2 implies that we can Fourier transform  $D_{\alpha\beta}$  as follows

$$D_{\alpha\beta}(\mathbf{q}) = \sum_i D_{\alpha\beta}(\mathbf{R}_i^0) \exp(i\mathbf{q} \cdot \mathbf{R}_i^0), \quad (2.30)$$

where we used periodic boundary conditions.  $D_{\alpha\beta}(\mathbf{q})$  is called the *dynamical matrix*.

Using the symmetry properties discussed in the points 1-4 above, we can also obtain the symmetry properties of the dynamical matrix.

- i) From point 3 (inversion symmetry), we have  $D_{\alpha\beta}(\mathbf{q}) = D_{\alpha\beta}(-\mathbf{q})$ .
- ii) From points 1 and 2 we have  $D_{\beta\alpha}(-\mathbf{q}) = D_{\alpha\beta}(\mathbf{q})$ .
- iii) Since  $D_{\alpha\beta}(\mathbf{R}_i^0)$  is real,  $D_{\alpha\beta}^*(\mathbf{q}) = D_{\alpha\beta}(-\mathbf{q})$ .

After having iii), we can use ii), and we finally have

$$D_{\alpha\beta}^*(\mathbf{q}) = D_{\beta\alpha}(\mathbf{q}), \quad (2.31)$$

i.e. the dynamical matrix is hermitian, and hence, it can be diagonalized, and the eigenvalues are real.

### 2.2.2 Normal modes of the harmonic lattice

Once we have seen that the dynamical matrix can be rendered diagonal, we look for a solution of the harmonic Hamiltonian (2.26). If we have translational invariance, by e.g. setting all masses equal, it is better to go over to Fourier space:

$$\begin{aligned} \mathbf{u}_{\mathbf{q}} &= \frac{1}{\sqrt{N}} \sum_i \mathbf{u}_i \exp(i\mathbf{q} \cdot \mathbf{R}_i) , \\ \mathbf{P}_{\mathbf{q}} &= \frac{1}{\sqrt{N}} \sum_i \mathbf{P}_i \exp(i\mathbf{q} \cdot \mathbf{R}_i) , \end{aligned} \quad (2.32)$$

such that for the kinetic and potential parts of the Hamiltonian (2.26) we have

i) Kinetic part

$$\begin{aligned} \sum_i^N \frac{\mathbf{P}_i^2}{2M} &= \frac{1}{2M N} \sum_{\mathbf{q}, \mathbf{q}'} \mathbf{P}_{\mathbf{q}} \cdot \mathbf{P}_{\mathbf{q}'} \underbrace{\sum_i \exp[-i(\mathbf{q} + \mathbf{q}') \cdot \mathbf{R}_i]}_{N \delta_{\mathbf{q}, -\mathbf{q}'}} \\ &= \frac{1}{2M} \sum_{\mathbf{q}} \mathbf{P}_{\mathbf{q}} \cdot \mathbf{P}_{-\mathbf{q}} . \end{aligned} \quad (2.33)$$

ii) Potential part

$$\frac{1}{2} \sum_{\substack{i,j \\ \alpha,\beta}} D_{\alpha\beta}(\mathbf{R}_i^0, \mathbf{R}_j^0) u_{i\alpha} u_{j\beta} = \frac{1}{2} \sum_{\mathbf{q}} u_{-\mathbf{q},\alpha} D_{\alpha\beta}(\mathbf{q}) u_{\mathbf{q},\beta} . \quad (2.34)$$

Putting both parts together, we finally have

$$H_h = \sum_{\mathbf{q}} \left[ \frac{1}{2M} \mathbf{P}_{\mathbf{q}} \cdot \mathbf{P}_{-\mathbf{q}} + \frac{1}{2} \sum_{\alpha,\beta} u_{-\mathbf{q},\alpha} D_{\alpha\beta}(\mathbf{q}) u_{\mathbf{q},\beta} \right] . \quad (2.35)$$

Next we make use of the fact that the dynamical matrix can be diagonalized. This means, it fulfills an equation of the form

$$\sum_{\beta} D_{\alpha\beta}(\mathbf{q}) e_{\nu\beta}(\mathbf{q}) = D_{\nu}(\mathbf{q}) e_{\nu\alpha}(\mathbf{q}) , \quad (2.36)$$

where  $D_{\nu}(\mathbf{q})$ ,  $\nu = 1, 2, 3$ , are the eigenvalues and  $e_{\nu\alpha}(\mathbf{q})$  the eigenvectors. The eigenvectors fulfill the conditions of orthonormality and completeness

$$\begin{aligned} \mathbf{e}_{\nu} \cdot \mathbf{e}_{\mu} &= \delta_{\nu\mu} , \\ \sum_{\nu} e_{\nu\alpha} e_{\nu\beta} &= \delta_{\alpha\beta} . \end{aligned} \quad (2.37)$$

Once we have the eigenvectors, we can expand both  $\mathbf{u}_{\mathbf{q}}$  and  $\mathbf{P}_{\mathbf{q}}$  in terms of the eigenvectors, leading to the following definitions

$$\begin{aligned} u_{\mathbf{q}}^{\nu} &= \mathbf{u}_{\mathbf{q}} \cdot \mathbf{e}_{\nu}(\mathbf{q}) , \\ P_{\mathbf{q}}^{\nu} &= \mathbf{P}_{\mathbf{q}} \cdot \mathbf{e}_{\nu}(\mathbf{q}) . \end{aligned} \quad (2.38)$$

With these definitions, we can translate the harmonic Hamiltonian (2.35) in a form that is diagonal with respect to the eigenmodes of the dynamical matrix. In order to see this, we consider again the kinetic and potential parts separately.

i) Kinetic part

$$\begin{aligned} \mathbf{P}_{\mathbf{q}} \cdot \mathbf{P}_{-\mathbf{q}} &= \sum_{\alpha} P_{\mathbf{q}}^{\alpha} P_{-\mathbf{q}}^{\alpha} \\ &= \sum_{\substack{\alpha, \beta \\ \nu}} P_{\mathbf{q}}^{\alpha} e_{\nu\alpha} e_{\nu\beta} P_{-\mathbf{q}}^{\beta} = \sum_{\nu} P_{\mathbf{q}}^{\nu} P_{-\mathbf{q}}^{\nu} . \end{aligned} \quad (2.39)$$

ii) Potential part

$$\begin{aligned} \sum_{\alpha, \beta} u_{-\mathbf{q}, \alpha} D_{\alpha\beta}(\mathbf{q}) u_{\mathbf{q}, \beta} &= \sum_{\substack{\alpha, \beta, \gamma, \delta \\ \nu, \mu}} u_{-\mathbf{q}, \alpha} e_{\nu\alpha} e_{\nu\gamma} \underbrace{D_{\gamma\delta}(\mathbf{q})}_{e_{\nu\gamma} D_{\mu}(\mathbf{q}) e_{\mu\gamma}} e_{\mu\delta} e_{\mu\beta} u_{\mathbf{q}, \beta} \\ &= \sum_{\nu} u_{-\mathbf{q}}^{\nu} D_{\nu}(\mathbf{q}) u_{\mathbf{q}}^{\nu} . \end{aligned} \quad (2.40)$$

With the help of the manipulations above, we have

$$H_h = \sum_{\mathbf{q}} \sum_{\nu=1}^3 \left[ \frac{P_{\mathbf{q}}^{\nu} P_{-\mathbf{q}}^{\nu}}{2M} + \frac{1}{2} M \omega_{\nu}^2(\mathbf{q}) u_{-\mathbf{q}}^{\nu} u_{\mathbf{q}}^{\nu} \right] , \quad (2.41)$$

where

$$\omega_{\nu}(\mathbf{q}) = \sqrt{\frac{D_{\nu}(\mathbf{q})}{M}} . \quad (2.42)$$

Equation (2.41) clearly shows that we have a collection of harmonic oscillators with frequencies  $\omega_{\nu}(\mathbf{q})$ .

As we already know from lectures on quantum mechanics, it is possible to introduce creation and annihilation operators, such that we have a very explicit diagonal form for the Hamiltonian. With such a transformation we introduce the elements of second quantization, where we have a space of states characterized by occupation numbers (Fock-space). The relationship between creation/annihilation operators and position/momentum operators is

$$\begin{aligned} b_{\nu\mathbf{q}} &= \sqrt{\frac{M\omega_{\nu}(\mathbf{q})}{2\hbar}} \left[ u_{\mathbf{q}}^{\nu} + \frac{i}{M\omega_{\nu}(\mathbf{q})} P_{\mathbf{q}}^{\nu} \right] , \\ b_{\nu\mathbf{q}}^{\dagger} &= \sqrt{\frac{M\omega_{\nu}(\mathbf{q})}{2\hbar}} \left[ u_{-\mathbf{q}}^{\nu} - \frac{i}{M\omega_{\nu}(\mathbf{q})} P_{-\mathbf{q}}^{\nu} \right] . \end{aligned} \quad (2.43)$$

These operators satisfy the canonical commutation relations for *bosons*, namely

$$\begin{aligned} [b_{\nu\mathbf{q}}, b_{\mu\mathbf{q}'}^{\dagger}] &= \delta_{\nu\nu'} \delta_{\mathbf{q}\mathbf{q}'} \\ [b_{\nu\mathbf{q}}, b_{\mu\mathbf{q}'}] &= [b_{\nu\mathbf{q}}^{\dagger}, b_{\mu\mathbf{q}'}^{\dagger}] = 0 . \end{aligned} \quad (2.44)$$



Furthermore, we can define an occupation number operator  $b_{\nu\mathbf{q}}^\dagger b_{\nu\mathbf{q}} = \hat{n}_{\nu\mathbf{q}}$  that counts the number of excitations for a given state:

$$\hat{n}_{\nu\mathbf{q}} | n_{\nu\mathbf{q}} \rangle = n_{\nu\mathbf{q}} | n_{\nu\mathbf{q}} \rangle . \quad (2.45)$$

As a consequence of the commutation relations (2.44), it can be shown that

$$\begin{aligned} b_{\nu\mathbf{q}} | n_{\nu\mathbf{q}} \rangle &= \sqrt{n_{\nu\mathbf{q}}} | n_{\nu\mathbf{q}} - 1 \rangle , \\ b_{\nu\mathbf{q}}^\dagger | n_{\nu\mathbf{q}} \rangle &= \sqrt{n_{\nu\mathbf{q}} + 1} | n_{\nu\mathbf{q}} + 1 \rangle , \end{aligned} \quad (2.46)$$

and hence the name annihilation and creation operators. By annihilating bosons on a given state, a state without bosons can be reached where

$$b_{\nu\mathbf{q}} | 0 \rangle = 0 . \quad (2.47)$$

This state is called the *vacuum*.

By expressing the Hamiltonian (2.41) with the creation and annihilation operators, we have finally

$$H_h = \sum_{\mathbf{q}} \sum_{\nu=1}^3 \hbar\omega_{\nu}(\mathbf{q}) \left( b_{\nu\mathbf{q}}^\dagger b_{\nu\mathbf{q}} + \frac{1}{2} \right) , \quad (2.48)$$

where  $b_{\nu\mathbf{q}}^\dagger, b_{\nu\mathbf{q}}$  create/annihilate a *phonon* with wavevector  $\mathbf{q}$  on the branch  $\nu$ . The ground state of the system is the vacuum, with a zero-point energy

$$E_0 = \frac{1}{2} \sum_{\mathbf{q}, \nu} \hbar\omega_{\nu}(\mathbf{q}) . \quad (2.49)$$

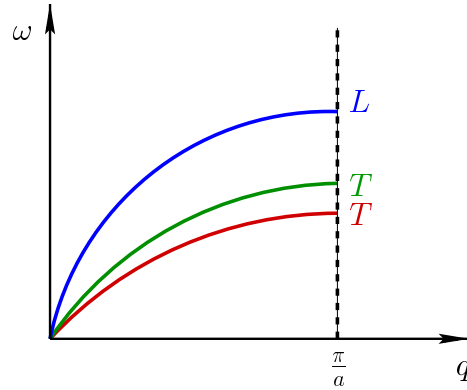


Figure 2.2: Phonon dispersion in a Bravais lattice. L denotes the longitudinal mode, whereas T the two transverse modes.

The branches correspond to the fact that we had a system with one atom per unit cell (the one we obtained by choosing  $M_i = M$ ), such that three degrees of freedom were present per site, and hence, the same number of modes appears per

$q$ -point. Given the wavevector  $\mathbf{q}$  for the phonon, there is one mode *longitudinal mode* (L in Fig. 2.2) polarized parallel to  $\mathbf{q}$  and two *transverse modes* (T in Fig. 2.2) polarized perpendicular to  $\mathbf{q}$ . As we discussed it before, we need only to plot the dispersion inside the first Brillouin zone, since in this case, it contains all the physical information.

## 2.3 Density of states, internal energy, and specific heat.

After obtaining the *phonon spectrum* in the harmonic approximation, we discuss an important concept when dealing with spectra, namely the density of states. We denote it by  $g(\omega)$ , and

$g(\omega) d\omega$ : number of phonon-modes/ unit volume in the interval  $[\omega, \omega + d\omega]$ .

It can be calculated in the following way:

$$\begin{aligned} g(\omega) &= \frac{1}{V} \sum_{\mathbf{q}} \sum_{\nu=1}^3 \delta[\omega - \omega_{\nu}(\mathbf{q})] \\ &= \frac{1}{(2\pi)^3} \int_{BZ} d^3q \sum_{\nu=1}^3 \delta[\omega - \omega_{\nu}(\mathbf{q})] . \end{aligned} \quad (2.50)$$

We can then easily see, that the density of states fulfills a *sum rule*, i.e. an exact relationship that in general appears when summing some physical quantity over its argument.

$$\begin{aligned} \int_{-\infty}^{\infty} g(\omega) d\omega &= \frac{1}{V} \sum_{\mathbf{q}} \sum_{\nu=1}^3 \\ &= 3 \frac{N}{V} = 3 \cdot n , \end{aligned} \quad (2.51)$$

where we denote with  $n$  the particle density, in this case the nuclei density. A very simple model to describe phonons is the *Debye model*, where it is assumed that all phonon branches have a linear dispersion up to a maximal cutoff wavevector  $q_D$ . The material is assumed completely isotropic, such that all the states should be contained inside a sphere with radius

$$\frac{4\pi}{3} q_D^3 = \frac{(2\pi)^3}{V} N , \quad (2.52)$$

such that we can determine the cutoff wavevector as

$$q_D = 2\pi \left( \frac{3n}{4\pi} \right) . \quad (2.53)$$

We can now calculate the form of the density of states within the Debye model.

$$\begin{aligned}
g_D(\omega) &= \frac{3}{(2\pi)^3} \int_{q < q_D} d^3q \delta(\omega - cq) \\
&= \frac{3}{2\pi^2} \int_0^{q_D} q^2 dq \delta(\omega - cq) \\
&= \begin{cases} \frac{1}{2\pi^2} \frac{\omega^2}{c^3} & \omega < \omega_D \equiv q_D c : \text{ Debye energy} \\ 0 & \omega > \omega_D \end{cases} \quad (2.54)
\end{aligned}$$

Once the density of states was obtained, we can calculate several physical quantities. One of them is the *internal energy*

$$\begin{aligned}
U &= \int_0^\infty d\omega g(\omega) \hbar\omega \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \\
&\xrightarrow{T \rightarrow 0} \int_0^{\omega_D} d\omega \omega^2 \hbar\omega \exp\left(-\frac{\hbar\omega}{k_B T}\right) \sim T^4. \quad (2.55)
\end{aligned}$$

From this we can obtain the temperature dependence of the *specific heat*:

$$c_V = \frac{1}{V} \frac{\partial U}{\partial T} \xrightarrow{T \rightarrow 0} \frac{12\pi^4}{5} nk_B \left(\frac{T}{\theta_D}\right)^3, \quad (2.56)$$

where we have assumed that the Debye model applies, and we defined

$$\theta_D = \frac{\hbar\omega_D}{k_B}, \quad (2.57)$$

the *Debye temperature*. On the other hand, for very high temperatures, we obtain the well known classical result by *Dulong - Petit*, i.e.

$$T \rightarrow \infty \quad c_V = 3nk_B. \quad (2.58)$$

## 2.4 Lattice with basis

Here we consider the effect on the spectrum of having  $F > 1$  atoms per elementary cell. The deviation from the equilibrium position will in general be denoted by  $u_{i\alpha}^\rho$ , with  $\rho = 1, \dots, F$ , i.e. it describes the deviation of the  $\rho$ -th atom in the elementary cell  $i$  in the direction  $\alpha$ . In the same way, we have to generalize the dynamical matrix, or its Fourier transformed in real space. In particular, the harmonic potential energy is described by

$$U_{\text{harmonic}}(\mathbf{R}) = \frac{1}{2} \sum_{\substack{i,j \\ \alpha,\beta \\ \rho,\rho'}} D_{\alpha\beta}^{\rho\rho'}(\mathbf{R}_i^0, \mathbf{R}_j^0) u_{i\alpha}^\rho u_{j\beta}^{\rho'}, \quad (2.59)$$

whereas the kinetic energy is simply generalized by

$$T_{\text{kinetic}} = \sum_{i,\rho}^N \frac{\mathbf{P}_i^{\rho 2}}{2M_\rho}. \quad (2.60)$$

From the discussion above, it is clear that now the dynamical matrix is a  $3F \times 3F$  dimensional matrix, and hence, after diagonalization, there will be  $3F$  eigenmodes per each value of the wavevector  $\mathbf{q}$ . From them, 3 will be acoustical modes and the rest constitute  $3F - 3$  optical modes.

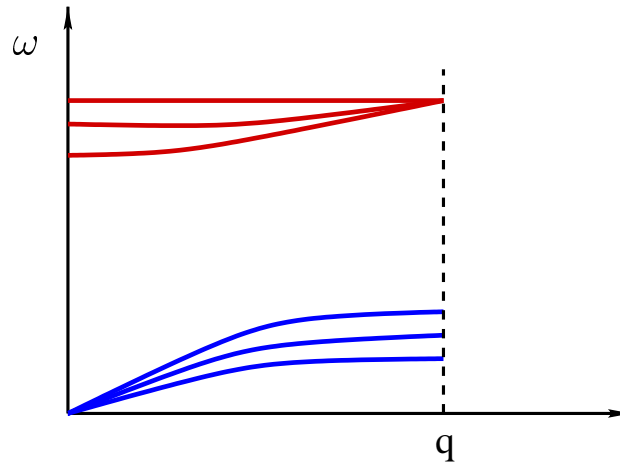


Figure 2.3: Example for the phonon dispersion in a solid with 2 atoms per elementary cell.