

III.1 Hamiltonian of the lattice and the harmonic approximation

A careful account of the theory of lattice vibrations is given in Cely's monograph. For this reason, we discuss here only some crucial aspects of the theory. We refer the reader to the monograph, where appropriate.

Adiabatic approximation

- Physical insight: Electrons move much faster than the nuclei. They can be assumed to “feel” the current spatial configuration of the nuclei (or ions). The nuclei, on the other hand, can be assumed to feel the average configuration of the electrons.

- Translated into the language of equations.

Hamiltonian function for the system of electrons and nuclei:

$$H = T_e + V_e + V_{e-n} + T_n + V_n. \quad (1)$$

Schrödinger equation:

$$H\Psi = E\Psi, \quad \Psi = \Psi(\mathbf{r}, \mathbf{R}). \quad (2)$$

The adiabatic approximation consists in restricting the space of wavefunctions under consideration to functions of the form

$$\Psi(\mathbf{r}, \mathbf{R}) = \psi_m(\mathbf{r}, \{\mathbf{R}\})\chi(\mathbf{R}), \quad (3)$$

where  $\psi_m$  is an eigenfunction of the electronic hamiltonian  $H_e$ ,

$$H_e(\{\mathbf{R}\}) = T_e + V_e + V_{e-n}(\{\mathbf{R}\}), \quad (4)$$

$$H_e(\{\mathbf{R}\})\psi_m = \epsilon_m\psi_m. \quad (5)$$

The standard variational condition (or, alternatively, insertion of the expression 3 into the Schrödinger equation 2 and neglection of “small terms”) leads to the following equation for the function  $\chi$

$$H_n\chi = E\chi \quad (6)$$

with

$$H_n = T_n + V_n + \epsilon_m(\{\mathbf{R}\}). \quad (7)$$

Usually  $\epsilon_m$  in the preceding equation is replaced with  $\epsilon_{GS}$  (GS ... ground state). It can be easily shown that this description is consistent with the physical picture of electrons responding to the current configuration of the nuclei and the nuclei responding to the average configuration of the electrons.

The problem defined by the hamiltonian 1 has been splitted into two parts: the electronic part characterized by the hamiltonian  $H_e$  of Eq. 4 and that of the nuclei characterized by the hamiltonian  $H_n$  of Eq. 7, the so called hamiltonian of the crystal lattice. The two parts are connected only by the  $\epsilon_m$ -term in Eq. 7 which provides a substantial contribution to the effective potential energy  $W(\mathbf{R})$  of the nuclei defined by

$$W(\mathbf{R}) = V_n(\mathbf{R}) + \epsilon_m(\{\mathbf{R}\}). \quad (8)$$

## Harmonic approximation

Nuclei in a solid move around a certain equilibrium configuration

$$\{\mathbf{R}_{01}, \mathbf{R}_{02}, \dots, \mathbf{R}_{0N}\} \quad (9)$$

corresponding to the global or a local minimum of  $W$ . The potential  $W$  can be expanded into the Taylor series, see Eq. (5.2) in Cely's monograph. The first-order term vanishes because the expansion is about a minimum. In the harmonic approximation only the second order term is retained, the higher order terms neglected. Physical picture: it is assumed that the atomic displacements are so small that they do not bring the system out of the region, where the parabolic approximation to  $W$  is reliable.

### III.2. Classical approach: EQM and the "Bloch theorem" for the crystal lattice

Classical equations of motion (see Cely's monograph for definitions of the symbols):

$$M_J \frac{d^2 u_\alpha(J)}{dt^2} = - \sum_{K=1}^N \sum_{\beta=x}^z A_{\alpha\beta}(J, K) u_\beta(K), \quad (10)$$

where  $\mathbf{u}(J)$  is the displacement vector of the  $J$ -th nucleus,  $\mathbf{R}_J = \mathbf{R}_{0J} + \mathbf{u}(J)$ , and

$$A_{\alpha\beta}(J, K) = \frac{\partial^2 W}{\partial u_\alpha(J) \partial u_\beta(K)} \quad (11)$$

are the so called force constants.

For a crystal lattice, the index  $J$  can be replaced by two indices:  $m$  specifying the position of the unit cell and  $\mu$  specifying the position of the nucleus within the unit cell. It follows from the translation symmetry that

$$A_{\alpha\beta}(m\mu, n\nu) = A_{\alpha\beta}(\mathbf{R}_n - \mathbf{R}_m, \mu\nu), \quad (12)$$

where  $\mathbf{R}_n$  is the vector connecting the origin of the coordinate system with the lattice point labelled as  $n$ . As a consequence, it is possible to find a complete set of solutions of the equations 10 of the form [see Eq. (5.15) in Cely]

$$\mathbf{u}(m\mu, t) = \mathbf{u}_\mu e^{-i\omega t} e^{i\mathbf{q} \cdot \mathbf{R}_m}. \quad (13)$$

This is an analogue of the Bloch theorem. The physical meaning of the wave vector  $\mathbf{q}$  is the following: when going from the unit cell with the lattice vector  $\mathbf{R}_m$  to the unit cell with the vector  $\mathbf{R}_n$  the phase of the atomic displacements changes by  $e^{i\mathbf{q} \cdot (\mathbf{R}_n - \mathbf{R}_m)}$ . By inserting the expression on the right hand side of Eq. 13 into Eq. 10 we obtain [cf. (5.18)]

$$\sum_{\nu, \beta} [B_{\alpha\beta}(\mathbf{q}, \mu\nu) - \omega^2 M_\mu \delta_{\alpha\beta} \delta_{\mu\nu}] u_{\nu\beta} = 0, \quad (14)$$

$\mu, \nu = 1, 2, \dots, s$ , where  $s$  is the number of atoms per unit cell,  $\alpha, \beta = x, y, z$ , and

$$B_{\alpha\beta}(\mathbf{q}, \mu\nu) = \sum_h A_{\alpha\beta}(\mathbf{R}_h, \mu\nu) e^{i\mathbf{q} \cdot \mathbf{R}_h}. \quad (15)$$

The set of equations 14 does not represent a standard eigenvalue problem because of the presence of the factor  $M_\mu$  in the square bracket. An eigenvalue problem can

be obtained, however, by introducing the reduced displacements  $\mathbf{w}_\mu$ ,  $\mu = 1, 2, \dots, s$ , [cf. (5.26)],

$$\mathbf{w}_\mu = \sqrt{M_\mu} \mathbf{u}_\mu \quad (16)$$

and the dynamical matrix  $D_{\alpha\beta}(\mathbf{q}, \mu\nu)$  [cf. (5.27)],

$$D_{\alpha\beta}(\mathbf{q}, \mu\nu) = (M_\mu M_\nu)^{-1/2} B_{\alpha\beta}(\mathbf{q}, \mu\nu). \quad (17)$$

After some arrangements of Eq. 14 we obtain [cf. (5.28)]:

$$\sum_{\nu\beta} [D_{\alpha\beta}(\mathbf{q}, \mu\nu) - \omega^2 \delta_{\alpha,\beta} \delta_{\mu\nu}] w_{\nu\beta} = 0 \text{ or } (D(\mathbf{q}) - \omega^2 I_{3s}) \mathbf{w} = \mathbf{0}, \quad (18)$$

which is already a canonical eigenvalue problem. For any  $\mathbf{q}$  (usually in the first BZ) we obtain a set of eigenvalues

$$\omega_1(\mathbf{q}), \omega_2(\mathbf{q}), \omega_3(\mathbf{q}), \dots, \omega_{3s}(\mathbf{q}) \quad (19)$$

(the corresponding functions of  $\mathbf{q}$  are called the dispersion relations) and the corresponding set of eigenvectors (in the  $3s$ -dimensional space!)

$$\mathbf{w}_1(\mathbf{q}), \mathbf{w}_2(\mathbf{q}), \dots, \mathbf{w}_{3s}(\mathbf{q}). \quad (20)$$

The corresponding normalized eigenvectors

$$\mathbf{e}_1(\mathbf{q}), \mathbf{e}_2(\mathbf{q}), \dots, \mathbf{e}_{3s}(\mathbf{q}) \quad (21)$$

are sometimes also called the polarization vectors. The dynamical matrix satisfies the equation  $D(-\mathbf{q}) = D^*(\mathbf{q})$  and it is therefore always possible to choose a set of polarization vectors such that  $\mathbf{e}_j(-\mathbf{q}) = \mathbf{e}_j^*(\mathbf{q})$ .

Normal coordinates, transformation of the hamiltonian into the form corresponding to a set of harmonic oscillators

Displacement of the  $\mu$ -th atom in the  $m$ -th unit cell in the state, where only one mode (wavevector  $\mathbf{q}$ , phonon branch  $j$ ) is excited:

$$u_{m\mu\alpha} \sim e_{j\mu\alpha}(\mathbf{q}) e^{[i\mathbf{q}\mathbf{R}_m - \omega_j(\mathbf{q})t]}. \quad (22)$$

General solution of the problem: a superposition of terms of the type 22.

Generalized or normal coordinates - see Eq. (5.33) and (5.34).

Hamiltonian in terms of the normal coordinates [cf. (5.37)]:

$$H = \sum_{\mathbf{q} \in BZ} \sum_{j=1}^{3s} \left( \frac{1}{2} P(\mathbf{q}, j) P(-\mathbf{q}, j) + \frac{\omega_j^2(\mathbf{q})}{2} Q(\mathbf{q}, j) Q(-\mathbf{q}, j) \right). \quad (23)$$

New real coordinates  $\Xi(\mathbf{q}, j)$  a  $\Pi(\mathbf{q}, j)$  [cf. (5.41)]:

$$\Xi = \frac{1}{2} [Q(\mathbf{q}, j) + Q(-\mathbf{q}, j)] + \frac{i}{2\omega_j(\mathbf{q})} [P(\mathbf{q}, j) - P(-\mathbf{q}, j)], \quad (24)$$

$$\Pi = \frac{i\omega_j(\mathbf{q})}{2} [-Q(\mathbf{q}, j) + Q(-\mathbf{q}, j)] + \frac{1}{2} [P(\mathbf{q}, j) + P(-\mathbf{q}, j)]. \quad (25)$$

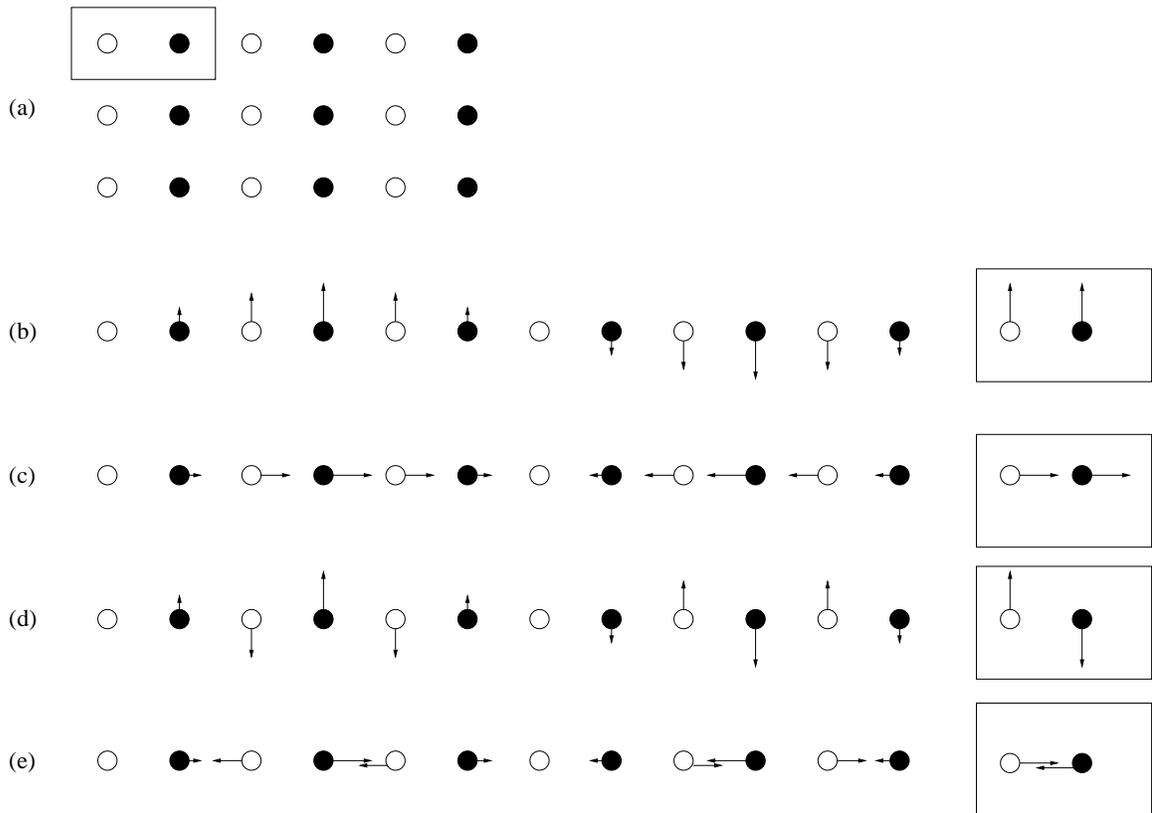
Hamiltonian in terms of  $\Xi$  a  $\Pi$  [cf. (5.42)],

$$H = \sum_{q \in BZ} \sum_{j=1}^{3s} \left( \frac{1}{2} \Pi^2(\mathbf{q}, j) + \frac{\omega_j^2(\mathbf{q})}{2} \Xi^2(\mathbf{q}, j) \right), \quad (26)$$

has precisely the same form as that of a set of independent harmonic oscillators. The quantum-mechanical treatment of the problem leading to the concept of phonons has already been explained earlier when describing excited states of a chain of atoms.

### III.3. Examples of dispersion relations and polarization vectors

- Dispersion relations of some simple materials (Pb,KBr,Ge,NaCl ...) are shown in Kittel; Ashcroft/Mermin; Cely.
- Polarization vectors for a 2D lattice possessing two non-equivalent nuclei per unit cell - a schematic representation.



(a) Crystal structure, the box shows the unit cell; (b) TA-mode; (c) LA-mode; (d) TO-mode; (e) LO-mode. The polarization vectors of the long-wavelength limit are shown in the boxes.

- Polarization vectors for some high-Tc cuprate superconductors - see the file Kova-leva.pdf.