

2.1. Phonons

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2.1.1. Introduction

Interatomic interactions in crystalline solids not only determine the equilibrium atomic structure but also the possible excitations of the lattice: the motions of atoms, molecules or ions. The investigation of dynamical processes provides us with detailed information about the interatomic forces. Obviously, there are a huge variety of possible collective motions within a solid, which represents a multiparticle system with 10^{23} degrees of freedom. As long as the solid may be described by an equilibrium structure and atomic displacements from the average positions are small compared with interatomic distances, the dynamical behaviour of the lattice is essentially determined by well defined lattice vibrations or phonons. These elementary excitations of a solid are described by eigenvectors and eigenfrequencies reflecting the strength of interatomic interactions. Owing to the symmetry (space group) of the equilibrium structure there are constraints for the individual eigenvectors. In special high-symmetry cases, phonon eigenvectors can even be predicted merely on the basis of group-theoretical considerations.

This chapter is devoted to the implications of lattice symmetry on the form, *i.e.* on the eigenvectors, of lattice vibrations. We restrict ourselves to the consideration of perfect crystals and harmonic vibrations. In addition, some aspects of anharmonicity are discussed in terms of a quasi-harmonic model, yielding the connection between microscopic dynamics and macroscopic thermodynamic quantities such as thermal expansion. However, intrinsic anharmonic effects associated with the interaction of phonons, phonon damping or localized vibrations due to defects, for example, are beyond the scope of this article. In Section 2.1.2 we present the fundamentals of lattice dynamics with special emphasis on the role of the dynamical matrix. Section 2.1.3 deals with the symmetry properties of this matrix along with its eigenvectors and eigenfrequencies. Symmetry-induced degeneracies will be considered in some detail as well as compatibility relations for phonon wavevectors corresponding to points of higher symmetry within the reciprocal space. Finally, the optical selection rules for long wavelength vibrations are presented. Some examples are included in order to illustrate the theoretical results.

For a further discussion of other phenomena associated with lattice vibrations the reader is referred to the monographs of Leibfried (1955), Maradudin *et al.* (1971), Reissland (1973), Srivastava (1990) or Dove (1993).

2.1.2. Fundamentals of lattice dynamics in the harmonic approximation

2.1.2.1. Hamiltonian and equations of motion

In order to reduce the complexity of lattice dynamical considerations, we describe the crystal's periodicity by the smallest unit needed to generate the whole (infinite) lattice by translation, *i.e.* the *primitive cell*. Each individual primitive cell may be characterized by a running index l and a vector \mathbf{r}_l pointing to its origin. Let there be N atoms per cell, the equilibrium positions of which are given by

$$\mathbf{r}_{\kappa l}^o = \mathbf{r}_l + \mathbf{r}_{\kappa}^o \quad \kappa = 1, \dots, N \quad l = 1, 2, \dots, \quad (2.1.2.1)$$

\mathbf{r}_{κ}^o being the vector of the κ th atom with respect to the origin of the primitive cell (see Fig. 2.1.2.1).

The set of vectors $\mathbf{r}_{\kappa l}^o$ describes the structure of the perfect lattice. At a particular time t , however, the κ th atom within the l th primitive cell, denoted by (κl) , may be found at a position $\mathbf{r}_{\kappa l}(t)$ which differs slightly from the equilibrium position, the time-dependent displacement being

$$\mathbf{u}_{\kappa l}(t) = \mathbf{r}_{\kappa l}(t) - \mathbf{r}_{\kappa l}^o = \mathbf{r}_{\kappa l}(t) - \mathbf{r}_l - \mathbf{r}_{\kappa}^o. \quad (2.1.2.2)$$

The potential energy V of the whole crystal depends on the position vectors of all atoms,

$$V = V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{\kappa l}, \dots), \quad (2.1.2.3)$$

and is minimal if all atoms occupy their equilibrium positions. For small displacements, it can be expanded in a Taylor series with respect to $\mathbf{u}_{\kappa l}(t)$:

$$V = V^o + \frac{1}{2} \sum_{\kappa l} \sum_{\kappa' l'} \sum_{\alpha=1}^3 \sum_{\beta=1}^3 u_{\kappa l}^{\alpha}(t) V_{\alpha\beta}(\kappa l, \kappa' l') u_{\kappa' l'}^{\beta}(t) + \dots, \quad (2.1.2.4)$$

where $u_{\kappa l}^{\alpha}(t)$ denotes the Cartesian coordinate of $\mathbf{u}_{\kappa l}(t)$ in direction α . In the *harmonic approximation*, third and higher-order terms are neglected. In order to simplify the formulae, we now drop the time argument, keeping in mind that we are always dealing with dynamical displacements. The expansion coefficients in equation (2.1.2.4) are the partial derivatives of the potential energy with respect to the atomic displacements taken at the equilibrium positions:

$$V_{\alpha\beta}(\kappa l, \kappa' l') = \left. \frac{\partial^2 V}{\partial u_{\kappa l}^{\alpha} \partial u_{\kappa' l'}^{\beta}} \right|_o. \quad (2.1.2.5)$$

Using the matrix notation

$$\mathbf{V}(\kappa l, \kappa' l') = \begin{pmatrix} V_{11}(\kappa l, \kappa' l') & V_{12}(\kappa l, \kappa' l') & V_{13}(\kappa l, \kappa' l') \\ V_{21}(\kappa l, \kappa' l') & V_{22}(\kappa l, \kappa' l') & V_{23}(\kappa l, \kappa' l') \\ V_{31}(\kappa l, \kappa' l') & V_{32}(\kappa l, \kappa' l') & V_{33}(\kappa l, \kappa' l') \end{pmatrix} \quad (2.1.2.6)$$

and dropping the constant V^o , equation (2.1.2.4) reads

$$V = \frac{1}{2} \sum_{\kappa l} \sum_{\kappa' l'} \mathbf{u}_{\kappa l} \mathbf{V}(\kappa l, \kappa' l') \mathbf{u}_{\kappa' l'} + \dots \quad (2.1.2.7)$$

The product $-\mathbf{V}(\kappa l, \kappa' l') \mathbf{u}_{\kappa' l'}$ is just the force $\mathbf{f}(\kappa l)$ acting upon atom (κl) if the atom $(\kappa' l')$ is displaced by $\mathbf{u}_{\kappa' l'}$ (Fig. 2.1.2.2). Hence, the matrix $\mathbf{V}(\kappa l, \kappa' l')$ may be regarded as a *force constant matrix* and its elements $V_{\alpha\beta}(\kappa l, \kappa' l')$ as *force constants*. These parameters may be calculated with the help of specific interaction models such as pair potentials, tensor-force models or more complicated many-body interactions.

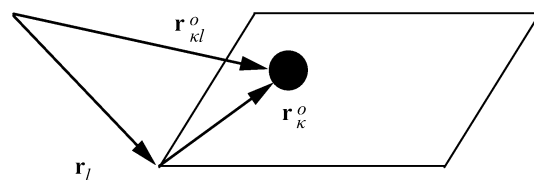


Fig. 2.1.2.1. Definition of position vectors.