

2.2. Electrons

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2.2.1. Introduction

The electronic structure of a solid, characterized by its energy band structure, is the fundamental quantity that determines the ground state of the solid and a series of excitations involving electronic states. In this chapter, we first summarize several basic concepts in order to establish the notation used here and to repeat essential theorems from group theory and solid-state physics that provide definitions which we need in this context. Next the quantum-mechanical treatment, especially density functional theory, is described and the commonly used methods of band theory are outlined. One scheme is presented explicitly so that concepts in connection with energy bands can be explained. The electric field gradient is discussed to illustrate a tensorial quantity and a few examples illustrate the topics of this chapter.

2.2.2. The lattice

2.2.2.1. The direct lattice and the Wigner–Seitz cell

The three unit-cell vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 define the parallelepiped of the unit cell. We define

(i) a translation vector *of* the lattice (upper case) as a primitive vector (integral linear combination) of all translations

$$\mathbf{T}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \text{ with } n_i \text{ integer,} \quad (2.2.2.1)$$

(ii) but a vector *in* the lattice (lower case) as

$$\mathbf{r} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3 \text{ with } x_i \text{ real.} \quad (2.2.2.2)$$

From the seven possible crystal systems one arrives at the 14 possible space lattices, based on both primitive and non-primitive (body-centred, face-centred and base-centred) cells, called the *Bravais lattices* [see Chapter 9.1 of *International Tables for Crystallography*, Volume A (2005)]. Instead of describing these cells as parallelepipeds, we can find several types of polyhedra with which we can fill space by translation. A very important type of space filling is obtained by the *Dirichlet construction*. Each lattice point is connected to its nearest neighbours and the corresponding bisecting (perpendicular) planes will delimit a region of space which is called the *Dirichlet region*, the *Wigner–Seitz cell* or the *Voronoi cell*. This cell is uniquely defined and has additional symmetry properties.

When we add a basis to the lattice (*i.e.* the atomic positions in the unit cell) we arrive at the well known 230 space groups [see Part 3 of *International Tables for Crystallography*, Volume A (2005)].

2.2.2.2. The reciprocal lattice and the Brillouin zone

Owing to the translational symmetry of a crystal, it is convenient to define a reciprocal lattice, which plays a dominating role in describing electrons in a solid. The three unit vectors of the reciprocal lattice \mathbf{b}_i are given according to the standard definition by

$$\mathbf{a}_i\mathbf{b}_j = 2\pi\delta_{ij}, \quad (2.2.2.3)$$

where the factor 2π is commonly used in solid-state physics in order to simplify many expressions. Strictly speaking (in terms of mathematics) this factor should not be included [see Section 1.1.2.4 of the present volume and Chapter 1.1 of *International*

Tables for Crystallography, Volume B (2001)], since the (complete) reciprocity is lost, *i.e.* the reciprocal lattice of the reciprocal lattice is no longer the direct lattice.

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \text{ and cyclic permutations.} \quad (2.2.2.4)$$

In analogy to the direct lattice we define

(i) a vector *of* the reciprocal lattice (upper case) as

$$\mathbf{K}_m = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3 \text{ with } m_i \text{ integer;} \quad (2.2.2.5)$$

(ii) a vector *in* the lattice (lower case) as

$$\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3 \text{ with } k_i \text{ real.} \quad (2.2.2.6)$$

From (2.2.2.5) and (2.2.2.1) it follows immediately that

$$\mathbf{T}_n\mathbf{K}_m = 2\pi N \text{ with } N \text{ an integer.} \quad (2.2.2.7)$$

A construction identical to the Wigner–Seitz cell delimits in reciprocal space a cell conventionally known as the *first Brillouin zone* (BZ), which is very important in the band theory of solids. There are 14 first Brillouin zones according to the 14 Bravais lattices.

2.2.3. Symmetry operators

The concepts of symmetry operations in connection with a quantum-mechanical treatment of the electronic states are essential for an understanding of the electronic structure. In this context the reader is referred, for example, to the book by Altmann (1994).

For the definition of symmetry operators we use in the whole of this chapter the *active picture*, which has become the standard in solid-state physics. This means that the whole configuration space is rotated, reflected or translated, while the coordinate axes are kept fixed.

A translation is given by

$$\mathbf{r}' = \mathbf{r} + \mathbf{T} \quad (2.2.3.1)$$

$$t\mathbf{r} = \mathbf{r} + \mathbf{T}, \quad (2.2.3.2)$$

where t on the left-hand side corresponds to a symmetry (configuration-space) operator.

2.2.3.1. Transformation of functions

Often we are interested in a function (*e.g.* a wavefunction) $f(\mathbf{r})$ and wish to know how it transforms under the configuration operator g which acts on \mathbf{r} . For this purpose it is useful to introduce a function-space operator \tilde{g} which defines how to modify the function in the transformed configuration space so that it agrees with the original function $f(\mathbf{r})$ at the original coordinate \mathbf{r} :

$$\tilde{g}f(g\mathbf{r}) = f(\mathbf{r}). \quad (2.2.3.3)$$

This must be valid for all points \mathbf{r} and thus also for $g^{-1}\mathbf{r}$, leading to the alternative formulation

$$\tilde{g}f(\mathbf{r}) = f(g^{-1}\mathbf{r}). \quad (2.2.3.4)$$