

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 (2002)]. 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 (2002)].

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 (2000)], 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

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

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The symmetry operations form a group \tilde{G} of configuration-space operations g_i with the related group G of the function-space operators \tilde{g}_i . Since the multiplication rules

$$g_i g_j = g_k \rightarrow \tilde{g}_i \tilde{g}_j = \tilde{g}_k \quad (2.2.3.5)$$

are preserved, these two groups are isomorphic.

2.2.3.2. Transformation of operators

In a quantum-mechanical treatment of the electronic states in a solid we have the following different entities: points in configuration space, functions defined at these points and (quantum-mechanical) operators acting on these functions. A symmetry operation transforms the points, the functions and the operators in a clearly defined way.

Consider an eigenvalue equation of operator \mathbb{A} (e.g. the Hamiltonian):

$$\mathbb{A}\varphi = a\varphi, \quad (2.2.3.6)$$

where $\varphi(\mathbf{r})$ is a function of \mathbf{r} . When g acts on \mathbf{r} , the function-space operator \tilde{g} acts [according to (2.2.3.4)] on φ yielding ψ :

$$\psi = \tilde{g}\varphi \rightarrow \varphi = \tilde{g}^{-1}\psi. \quad (2.2.3.7)$$

By putting φ from (2.2.3.7) into (2.2.3.6), we obtain

$$\mathbb{A}\tilde{g}^{-1}\psi = a\tilde{g}^{-1}\psi. \quad (2.2.3.8)$$

Multiplication from the left by \tilde{g} yields

$$\tilde{g}\mathbb{A}\tilde{g}^{-1}\psi = a\tilde{g}\tilde{g}^{-1}\psi = a\psi. \quad (2.2.3.9)$$

This defines the transformed operator $\tilde{g}\mathbb{A}\tilde{g}^{-1}$ which acts on the transformed function ψ that is given by the original function φ but at position $g^{-1}\mathbf{r}$.

2.2.3.3. The Seitz operators

The most general space-group operation is of the form $w p$ with the point-group operation p (a rotation, reflection or inversion) followed by a translation w :

$$w p = \{p|\mathbf{w}\}. \quad (2.2.3.10)$$

With the definition

$$\{p|\mathbf{w}\}\mathbf{r} = w p \mathbf{r} = w(p\mathbf{r}) = p\mathbf{r} + \mathbf{w} \quad (2.2.3.11)$$

it is easy to prove the multiplication rule

$$\{p|\mathbf{w}\}\{p'|\mathbf{w}'\} = \{pp'|\mathbf{w} + \mathbf{w}'\} \quad (2.2.3.12)$$

and define the inverse of a Seitz operator as

$$\{p|\mathbf{w}\}^{-1} = \{p^{-1}|-p^{-1}\mathbf{w}\}, \quad (2.2.3.13)$$

which satisfies

$$\{p|\mathbf{w}\}\{p|\mathbf{w}\}^{-1} = \{E|\mathbf{0}\}, \quad (2.2.3.14)$$

where $\{E|\mathbf{0}\}$ does not change anything and thus is the identity of the space group G .

2.2.3.4. The important groups and their first classification

Using the Seitz operators, we can classify the most important groups as we need them at the beginning of this chapter:

(i) the *space group*, which consists of all elements $G = \{\{p|\mathbf{w}\}\}$;
(ii) the *point group* (without any translations) $P = \{\{p|\mathbf{0}\}\}$;
and

(iii) the *lattice translation subgroup* $T = \{\{E|\mathbf{T}\}\}$, which is an invariant subgroup of G , i.e. $T \triangleleft G$. Furthermore T is an Abelian group, i.e. the operation of two translations commute ($t_1 t_2 = t_2 t_1$) (see also Section 1.2.3.1 of the present volume). A useful

consequence of the commutation property is that T can be written as a direct product of the corresponding one-dimensional translations,

$$T = T_x \otimes T_y \otimes T_z. \quad (2.2.3.15)$$

(iv) A *symmorphic* space group contains no fractional translation vectors and thus P is a subgroup of G , i.e. $P \triangleleft G$.

(v) In a *non-symmorphic* space group, however, some p are associated with fractional translation vectors \mathbf{v} . These \mathbf{v} do not belong to the translation lattice but when they are repeated a specific integer number of times they give a vector of the lattice. In this case, $\{p|\mathbf{0}\}$ can not belong to G for all p .

(vi) The *Schrödinger group* is the group S of all operations \tilde{g} that leave the Hamiltonian invariant, i.e. $\tilde{g}\mathbb{H}\tilde{g}^{-1} = \mathbb{H}$ for all $\tilde{g} \in S$. This is equivalent to the statement that \tilde{g} and \mathbb{H} commute: $\tilde{g}\mathbb{H} = \mathbb{H}\tilde{g}$. From this commutator relation we find the degenerate states in the Schrödinger equation, namely that $\tilde{g}\varphi$ and φ are degenerate with the eigenvalue E whenever $\tilde{g} \in S$, as follows from the three equations

$$\mathbb{H}\varphi = E\varphi \quad (2.2.3.16)$$

$$\tilde{g}\mathbb{H}\varphi = E\tilde{g}\varphi \quad (2.2.3.17)$$

$$\mathbb{H}\tilde{g}\varphi = E\tilde{g}\varphi. \quad (2.2.3.18)$$

2.2.4. The Bloch theorem

The electronic structure of an infinite solid looks so complicated that it would seem impossible to calculate it. Two important steps make the problem feasible. One is the *single-particle approach*, in which each electron moves in an average potential $V(\mathbf{r})$ according to a Schrödinger equation,

$$\mathbb{H}\psi(\mathbf{r}) = \left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right\} \psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (2.2.4.1)$$

and has its kinetic energy represented by the first operator. The second important concept is the *translational symmetry*, which leads to Bloch functions. The single-particle aspect will be discussed later (for details see Sections 2.2.9 and 2.2.10).

2.2.4.1. A simple quantum-mechanical derivation

In order to derive the Bloch theorem, we can simplify the problem by considering a one-dimensional case with a lattice constant a . [The generalization to the three-dimensional case can be done easily according to (2.2.3.15).] The one-dimensional Schrödinger equation is

$$\left\{ -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \right\} \psi(x) = E\psi(x), \quad (2.2.4.2)$$

where $V(x)$ is invariant under translations, i.e. $V(x+a) = V(x)$. We define a translation operator t according to (2.2.3.1) for the translation by one lattice constant as

$$t x = x + a \quad (2.2.4.3)$$

and apply its functional counterpart \tilde{t} to the potential, which gives [according to (2.2.3.4)]

$$\tilde{t}V(x) = V(t^{-1}x) = V(x-a) = V(x). \quad (2.2.4.4)$$

The first part in \mathbb{H} corresponds to the kinetic energy operator, which is also invariant under translations. Therefore, since $\tilde{t} \in T$ (the lattice translation subgroup) and $\tilde{t} \in S$ (the Schrödinger group), \tilde{t} commutes with \mathbb{H} , i.e. the commutator vanishes, $[\tilde{t}, \mathbb{H}] = 0$ or $\tilde{t}\mathbb{H} = \mathbb{H}\tilde{t}$. This situation was described above [see (2.2.3.16)–(2.2.3.18)] and leads to the fundamental theorem of quantum mechanics which states that when two operators