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

$$g_i g_j = g_k \rightarrow \widetilde{g}_i \widetilde{g}_j = \widetilde{g}_k \tag{2.2.3.5}$$

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):

$$\mathbb{A}\varphi = a\varphi, \tag{2.2.3.6}$$

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

$$\psi = \widetilde{g}\varphi \rightarrow \varphi = \widetilde{g}^{-1}\psi. \tag{2.2.3.7}$$

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

$$\mathbb{A}\widetilde{g}^{-1}\psi = a\widetilde{g}^{-1}\psi. \tag{2.2.3.8}$$

Multiplication from the left by $\widetilde{g}$ yields

$$\widetilde{g}\mathbb{A}\widetilde{g}^{-1}\psi = a\widetilde{g}\widetilde{g}^{-1}\psi = a\psi. \tag{2.2.3.9}$$

This defines the transformed operator $\widetilde{g}\mathbb{A}\widetilde{g}^{-1}$ 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 wp with the point-group operation p (a rotation, reflection or inversion) *followed* by a translation w:

$$wp = \{p|\mathbf{w}\}. \tag{2.2.3.10}$$

With the definition

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

it is easy to prove the multiplication rule

$$\{p|\mathbf{w}\}\{p'|\mathbf{w}'\} = \{pp'|p\mathbf{w}' + \mathbf{w}\} \tag{2.2.3.12}$$

and define the inverse of a Seitz operator as

$$\{p|\mathbf{w}\}^{-1} = \{p^{-1}|-p^{-1}\mathbf{w}\}, \tag{2.2.3.13}$$

which satisfies

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

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,

$$T = T_x \otimes T_y \otimes T_z. \tag{2.2.3.15}$$

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

$$\mathbb{H}\varphi = E\varphi \tag{2.2.3.16}$$

$$\widetilde{g}\mathbb{H}\varphi = E\widetilde{g}\varphi \tag{2.2.3.17}$$

$$\mathbb{H}\widetilde{g}\varphi = E\widetilde{g}\varphi. \tag{2.2.3.18}$$

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,

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

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

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

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

$$tx = x + a \tag{2.2.4.3}$$

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

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

The first part in $\mathbb{H}$ corresponds to the kinetic energy operator, which is also invariant under translations. Therefore, since $\widetilde{t} \in T$ (the lattice translation subgroup) and $\widetilde{t} \in S$ (the Schrödinger group), $\widetilde{t}$ commutes with $\mathbb{H}$, *i.e.* the commutator vanishes, $[\widetilde{t}, \mathbb{H}] = 0$ or $\widetilde{t}\mathbb{H} = \mathbb{H}\widetilde{t}$. 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

commute the eigenvectors of the first must also be eigenvectors of the second. Consequently we have

$$\mathbb{H}\psi(x) = E\psi(x) \tag{2.2.4.5}$$

$$\widetilde{t}\psi(x) = \mu\psi(x), \tag{2.2.4.6}$$

where μ is the eigenvalue corresponding to the translation by the lattice constant a. The second equation can be written explicitly as

$$\widetilde{t}\psi(x) = \psi(t^{-1}x) = \psi(x-a) = \mu\psi(x) \tag{2.2.4.7}$$

and tells us how the wavefunction changes from one unit cell to the neighbouring unit cell. Notice that the electron density must be translationally invariant and thus it follows

$$\text{from } \psi^*(x-a)\psi(x-a) = \psi^*(x)\psi(x) \text{ that } \mu^*\mu = 1, \tag{2.2.4.8}$$

which is a necessary (but not sufficient) condition for defining μ.

2.2.4.2. *Periodic boundary conditions*

We can expect the bulk properties of a crystal to be insensitive to the surface and also to the boundary conditions imposed, which we therefore may choose to be of the most convenient form. Symmetry operations are covering transformations and thus we have an *infinite* number of translations in T, which is most inconvenient. A way of avoiding this is provided by periodic boundary conditions (*Born–von Karman*). In the present one-dimensional case this means that the wavefunction $\psi(x)$ becomes periodic in a domain $L = Na$ (with integer N number of lattice constants a), *i.e.*

$$\psi(x+Na) = \psi(x+L) = \psi(x). \tag{2.2.4.9}$$

According to our operator notation (2.2.4.6), we have the following situation when the translation t is applied n times:

$$\widetilde{t}^n\psi(x) = \psi(x-na) = \mu^n\psi(x). \tag{2.2.4.10}$$

It follows immediately from the periodic boundary condition (2.2.4.9) that

$$\mu^N = 1 \tag{2.2.4.11}$$

with the obvious solution

$$\mu = \exp[2\pi i(n/N)] \quad \text{with} \quad n = 0 \pm 1, \pm 2, \ldots. \tag{2.2.4.12}$$

Here it is convenient to introduce a notation

$$k = \frac{2\pi}{a}\frac{n}{N} \tag{2.2.4.13}$$

so that we can write $\mu = \exp(ika)$. Note that k is quantized due to the periodic boundary conditions according to (2.2.4.13). Summarizing, we have the Bloch condition (for the one-dimensional case):

$$\psi(x+a) = \exp(ika)\psi(x), \tag{2.2.4.14}$$

i.e. when we change x by one lattice constant a the wavefunction at x is multiplied by a phase factor $\exp(ika)$. At the moment (2.2.4.13) suggests the use of k as label for the wavefunction $\psi_k(x)$.

Generalization to three dimensions leads to the exponential $\exp(i\mathbf{kT})$ with

$$\sum_{i=1}^{3} k_i n_i = \mathbf{k}\cdot\mathbf{T} \quad \text{using (2.2.2.6) and (2.2.2.1)} \tag{2.2.4.15}$$

and thus to the Bloch condition

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{T}) = \exp(i\mathbf{kT})\psi_{\mathbf{k}}(\mathbf{r}), \tag{2.2.4.16}$$

or written in terms of the translational operator $\{E|\mathbf{T}\}$ [see (2.2.3.15)]

$$\{E|\mathbf{T}\}\psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r}-\mathbf{T}) = \exp(-i\mathbf{kT})\psi_{\mathbf{k}}(\mathbf{r}). \tag{2.2.4.17}$$

The eigenfunctions that satisfy (2.2.4.17) are called Bloch functions and have the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{kr})u_{\mathbf{k}}(\mathbf{r}), \tag{2.2.4.18}$$

where $u_{\mathbf{k}}(\mathbf{r})$ is a periodic function in the lattice,

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{T}) \quad \text{for all } \mathbf{T}, \tag{2.2.4.19}$$

and $\mathbf{k}$ is a vector in the reciprocal lattice [see (2.2.2.6)] that plays the role of the quantum number in solids. The $\mathbf{k}$ vector can be chosen in the first BZ, because any $\mathbf{k}'$ that differs from $\mathbf{k}$ by just a lattice vector $\mathbf{K}$ of the reciprocal lattice has the same Bloch factor and the corresponding wavefunction $\psi_{\mathbf{k}+\mathbf{K}}(\mathbf{r})$ satisfies the Bloch condition again, since

$$\exp[i(\mathbf{k}+\mathbf{K})\mathbf{T}] = \exp(i\mathbf{kT})\exp(i\mathbf{KT}) = \exp(i\mathbf{kT}), \tag{2.2.4.20}$$

where the factor $\exp(i\mathbf{KT})$ is unity according to (2.2.2.7). Since these two functions, $\psi_{\mathbf{k}+\mathbf{K}}(\mathbf{r})$ and $\psi_{\mathbf{k}}(\mathbf{r})$, belong to the same Bloch factor $\exp(i\mathbf{kT})$ they are equivalent. A physical interpretation of the Bloch states will be given in Section 2.2.8.

2.2.4.3. *A simple group-theoretical approach*

Let us repeat a few fundamental definitions of group theory: For any symmetry operation $g_i \in G$, the product gg_ig^{-1} can always be formed for any $g \in G$ and defines the conjugate element of g_i by g. Given any operation g_i, its class $C(g_i)$ is defined as the set of all its conjugates under all operations $g \in G$. What we need here is an important property of classes, namely that no two classes have any element in common so that any group can be considered as a sum of classes.

Assuming periodic boundary conditions with N_1, N_2, N_3 number of primitive cells along the axes $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, respectively, a lump of crystal with $N = N_1N_2N_3$ unit cells is studied. The translation subgroup T contains the general translation operators $\mathbf{T}$, which [using (2.2.3.15)] can be written as

$$\{E|\mathbf{T}\} = \{E|n_1\mathbf{a}_1\}\{E|n_2\mathbf{a}_2\}\{E|n_3\mathbf{a}_3\}, \tag{2.2.4.21}$$

where each factor belongs to one of the three axes. Since T is commutative (Abelian), each operation of T is its own class and thus the number of classes equals its order, namely N. From the general theorem that the squares of the dimensions of all irreducible representations of a group must equal the order of the group, it follows immediately that all N irreducible representations of T must be one-dimensional (see also Section 1.2.3.2 of the present volume). Taking the subgroup along the $\mathbf{a}_1$ axis, we must have N_1 different irreducible representations, which we label (for later convenience) by k_1 and denote as

$${}_{k_1}\widehat{T}\{E|n_1\mathbf{a}_1\}. \tag{2.2.4.22}$$

These representations are one-dimensional matrices, *i.e.* numbers, and must be exponentials, often chosen of the form $\exp(-2\pi ik_1n_1)$. The constant k_1 must be related to the corresponding label of the irreducible representation. In the three-dimensional case, we have the corresponding representation

$${}_{k_1k_2k_3}\widehat{T}\{E|\mathbf{T}\} = \exp[-2\pi i(k_1n_1 + k_2n_2 + k_3n_3)] = \exp(-i\mathbf{k}\cdot\mathbf{T}), \tag{2.2.4.23}$$

where we have used the definitions (2.2.2.6) and (2.2.2.1). Within the present derivation, the vector $\mathbf{k}$ corresponds to the label of the irreducible representation of the lattice translation subgroup.