2.2.5. The free-electron (Sommerfeld) model

The free-electron model corresponds to the special case of taking a constant potential in the Schrödinger equation (2.2.4.1). The physical picture relies on the assumption that the (metallic) valence electrons can move freely in the field of the positively charged nuclei and the tightly bound core electrons. Each valence electron moves in a potential which is nearly constant due to the screening of the remaining valence electrons. This situation can be idealized by assuming the potential to be constant [$V(\mathbf{r}) = 0$]. This simple picture represents a crude model for simple metals but has its importance mainly because the corresponding equation can be solved analytically. By rewriting equation (2.2.4.1), we have

$$\nabla^2\psi_{\mathbf{k}}(\mathbf{r}) = -\frac{2mE}{\hbar^2}\psi_{\mathbf{k}}(\mathbf{r}) = -|\mathbf{k}|^2\psi_{\mathbf{k}}(\mathbf{r}), \tag{2.2.5.1}$$

where in the last step the constants are abbreviated (for later convenience) by $|\mathbf{k}|^2$. The solutions of this equation are plane waves (PWs)

$$\psi_{\mathbf{k}}(\mathbf{r}) = C\exp(i\mathbf{k}\cdot\mathbf{r}), \tag{2.2.5.2}$$

where C is a normalization constant which is defined from the integral over one unit cell with volume Ω. The PWs satisfy the Bloch condition and can be written (using the bra–ket notation) as

$$|\mathbf{k}\rangle = \psi_{\mathbf{k}}(\mathbf{r}) = \Omega^{1/2}\exp(i\mathbf{k}\cdot\mathbf{r}). \tag{2.2.5.3}$$

From (2.2.5.1) we see that the corresponding energy (labelled by $\mathbf{k}$) is given by

$$E_{\mathbf{k}} = \frac{\hbar^2}{2m}|\mathbf{k}|^2. \tag{2.2.5.4}$$

In this context it is useful to consider the momentum of the electron, which classically is the vector $\mathbf{p} = m\mathbf{v}$, where m and $\mathbf{v}$ are the mass and velocity, respectively. In quantum mechanics we must replace $\mathbf{p}$ by the corresponding operator $\mathbb{P}$.

$$\mathbb{P}|\mathbf{k}\rangle = \frac{\hbar}{i}\frac{\partial}{\partial\mathbf{r}}|\mathbf{k}\rangle = \frac{\hbar}{i}i\mathbf{k}|\mathbf{k}\rangle = \hbar\mathbf{k}|\mathbf{k}\rangle. \tag{2.2.5.5}$$

Thus a PW is an eigenfunction of the momentum operator with eigenvalue $\hbar\mathbf{k}$. Therefore the $\mathbf{k}$ vector is also called the *momentum* vector. Note that this is strictly true for a vanishing potential but is otherwise only approximately true (referred to as *pseudomomentum*).

Another feature of a PW is that its phase is constant in a plane perpendicular to the vector $\mathbf{k}$ (see Fig. 2.2.5.1). For this purpose, consider a periodic function in space and time,

$$\varphi_{\mathbf{k}}(\mathbf{r}, t) = \exp[i(\mathbf{k}\cdot\mathbf{r} - \omega t)], \tag{2.2.5.6}$$

which has a constant phase factor $\exp(i\omega t)$ within such a plane. We can characterize the spatial part by $\mathbf{r}$ within this plane. Taking the nearest parallel plane (with vector $\mathbf{r}'$) for which the same phase factors occur again but at a distance λ away (with the unit vector $\mathbf{e}$ normal to the plane),

$$\mathbf{r}' = \mathbf{r} + \lambda\mathbf{e} = \mathbf{r} + \lambda\frac{\mathbf{k}}{|\mathbf{k}|}, \tag{2.2.5.7}$$

then $\mathbf{k}\cdot\mathbf{r}'$ must differ from $\mathbf{k}\cdot\mathbf{r}$ by 2π. This is easily obtained from (2.2.5.7) by multiplication with $\mathbf{k}$ leading to

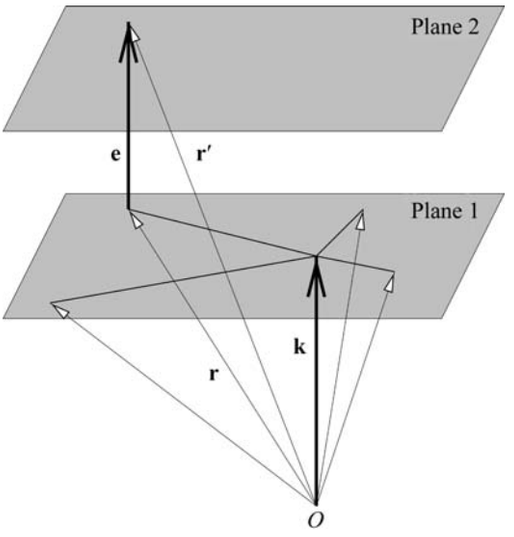

Fig. 2.2.5.1. Plane waves. The wavevector $\mathbf{k}$ and the unit vector $\mathbf{e}$ are normal to the two planes and the vectors $\mathbf{r}$ in plane 1 and $\mathbf{r}'$ in plane 2.

$$\mathbf{k}\cdot\mathbf{r}' = \mathbf{k}\cdot\mathbf{r} + \lambda\frac{|\mathbf{k}|^2}{|\mathbf{k}|} = \mathbf{k}\cdot\mathbf{r} + \lambda|\mathbf{k}| \tag{2.2.5.8}$$

$$\mathbf{k}\cdot\mathbf{r}' - \mathbf{k}\cdot\mathbf{r} = \lambda|\mathbf{k}| = 2\pi \tag{2.2.5.9}$$

$$\lambda = \frac{2\pi}{|\mathbf{k}|} \text{ or } |\mathbf{k}| = \frac{2\pi}{\lambda}. \tag{2.2.5.10}$$

Consequently λ is the wavelength and thus the $\mathbf{k}$ vector is called the *wavevector* or *propagation* vector.

2.2.6. Space-group symmetry

2.2.6.1. *Representations and bases of the space group*

The effect of a space-group operation $\{p|\mathbf{w}\}$ on a Bloch function, labelled by $\mathbf{k}$, is to transform it into a Bloch function that corresponds to a vector $p\mathbf{k}$,

$$\{p|\mathbf{w}\}\psi_{\mathbf{k}} = \psi_{p\mathbf{k}}, \tag{2.2.6.1}$$

which can be proven by using the multiplication rule of Seitz operators (2.2.3.12) and the definition of a Bloch state (2.2.4.17).

A special case is the inversion operator, which leads to

$$\{i|\mathbf{E}\}\psi_{\mathbf{k}} = \psi_{-\mathbf{k}}. \tag{2.2.6.2}$$

The Bloch functions $\psi_{\mathbf{k}}$ and $\psi_{p\mathbf{k}}$, where p is any operation of the point group P, belong to the same basis for a representation of the space group G.

$$\langle\psi_{\mathbf{k}}| = \langle\psi_{p\mathbf{k}}| \text{ for all } p \in P \text{ for all } p\mathbf{k} \in \text{BZ}. \tag{2.2.6.3}$$

The same $p\mathbf{k}$ cannot appear in two different bases, thus the two bases $\psi_{\mathbf{k}}$ and $\psi_{\mathbf{k}'}$ are either identical or have no $\mathbf{k}$ in common.

Irreducible representations of T are labelled by the N distinct $\mathbf{k}$ vectors in the BZ, which separate in disjoint bases of G (with no $\mathbf{k}$ vector in common). If a $\mathbf{k}$ vector falls on the BZ edge, application of the point-group operation p can lead to an equivalent $\mathbf{k}'$ vector that differs from the original by $\mathbf{K}$ (a vector *of* the reciprocal lattice). The set of all mutually inequivalent $\mathbf{k}$ vectors of $p\mathbf{k}$ ($p \in P$) define the *star of the* $\mathbf{k}$ *vector* ($S_{\mathbf{k}}$) (see also Section 1.2.3.3 of the present volume).

The set of all operations that leave a $\mathbf{k}$ vector invariant (or transform it into an equivalent $\mathbf{k} + \mathbf{K}$) forms the *group* $G_{\mathbf{k}}$ of the $\mathbf{k}$ vector. Application of q, an element of $G_{\mathbf{k}}$, to a Bloch function (Section 2.2.8) gives

$$q\psi^j_{\mathbf{k}}(\mathbf{r}) = \psi^{j'}_{\mathbf{k}}(\mathbf{r}) \text{ for } q \in G_{\mathbf{k}}, \tag{2.2.6.4}$$

where the band index j (described below) may change to j'. The Bloch factor stays constant under the operation of q and thus the periodic cell function $u^j_{\mathbf{k}}(\mathbf{r})$ must show this symmetry, namely

$$q u^j_{\mathbf{k}}(\mathbf{r}) = u^{j'}_{\mathbf{k}}(\mathbf{r}) \text{ for } q \in G_{\mathbf{k}}. \quad (2.2.6.5)$$

For example, a p_x-like orbital may be transformed into a p_y-like orbital if the two are degenerate, as in a tetragonal lattice.

A star of $\mathbf{k}$ determines an irreducible basis, provided that the functions of the star are symmetrized with respect to the irreducible representation of the group of $\mathbf{k}$ vectors, which are called *small representations*. The basis functions for the irreducible representations are given according to Seitz (1937) by

$$\langle s\psi^j_{\mathbf{k}}|, \text{ where } s \in S_{\mathbf{k}},$$

written as a row vector $\langle|$ with $j = 1, \ldots, n$, where n is the dimension of the irreducible representation of $S_{\mathbf{k}}$ with the order $|S_{\mathbf{k}}|$. Such a basis consists of $n|S_{\mathbf{k}}|$ functions and forms an $n|S_{\mathbf{k}}|$-dimensional irreducible representation of the space group. The degeneracies of these representations come from the star of $\mathbf{k}$ (not crucial for band calculations except for determining the weight of the $\mathbf{k}$ vector) and the degeneracy from $G_{\mathbf{k}}$. The latter is essential for characterizing the energy bands and using the compatibility relations (Bouckaert *et al.*, 1930; Bradley & Cracknell, 1972).

2.2.6.2. *Energy bands*

Each irreducible representation of the space group, labelled by $\mathbf{k}$, denotes an energy $E^j(\mathbf{k})$, where $\mathbf{k}$ varies quasi-continuously over the BZ and the superscript j numbers the band states. The quantization of $\mathbf{k}$ according to (2.2.4.13) and (2.2.4.15) can be done in arbitrary fine steps by choosing corresponding periodic boundary conditions (see Section 2.2.4.2). Since $\mathbf{k}$ and $\mathbf{k} + \mathbf{K}$ belong to the same Bloch state, the energy is periodic in reciprocal space:

$$E^j(\mathbf{k}) = E^j(\mathbf{k} + \mathbf{K}). \quad (2.2.6.6)$$

Therefore it is sufficient to consider $\mathbf{k}$ vectors within the first BZ. For a given $\mathbf{k}$, two bands will not have the same energy unless there is a multidimensional small representation in the group of $\mathbf{k}$ or the bands belong to different irreducible representations and thus can have an accidental degeneracy. Consequently, this can not occur for a general $\mathbf{k}$ vector (without symmetry).

2.2.7. The k vector and the Brillouin zone

2.2.7.1. *Various aspects of the* k *vector*

The $\mathbf{k}$ vector plays a fundamental role in the electronic structure of a solid. In the above, several interpretations have been given for the $\mathbf{k}$ vector that

(*a*) is given in reciprocal space,

(*b*) can be restricted to the first Brillouin zone,

(*c*) is the quantum number for the electronic states in a solid,

(*d*) is quantized due to the periodic boundary conditions,

(*e*) labels the irreducible representation of the lattice translation subgroup T (see Section 2.2.4.3)

(*f*) is related to the momentum [according to (2.2.5.5)] in the free-electron case and

(*g*) is the propagation vector (wavevector) associated with the plane-wave part of the wavefunction (see Fig. 2.2.5.1).

2.2.7.2. *The Brillouin zone (BZ)*

Starting with one of the 14 Bravais lattices, one can define the reciprocal lattice [according to (2.2.2.4)] by the Wigner–Seitz construction as discussed in Section 2.2.2.2. The advantage of using the BZ instead of the parallelepiped spanned by the three unit vectors is its symmetry. Let us take a simple example first,

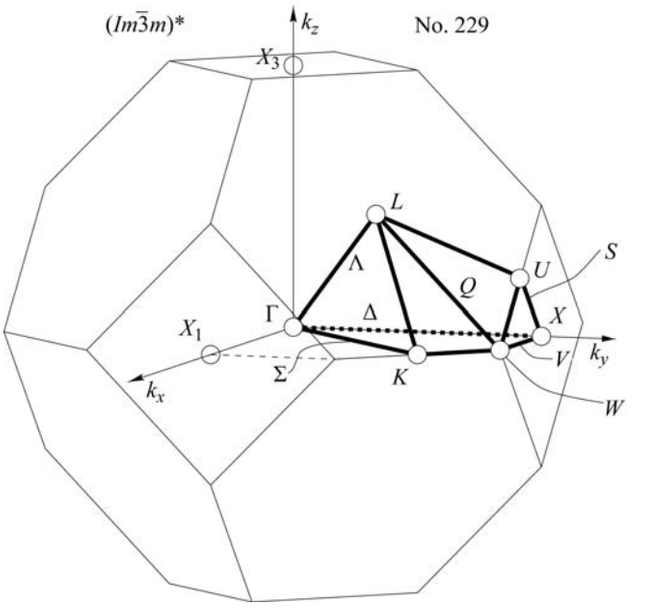

Fig. 2.2.7.1. The Brillouin zone (BZ) and the irreducible wedge of the BZ for the f.c.c. direct lattice. After the corresponding figure from the Bilbao Crystallographic Server (http://www.cryst.ehu.es/). The IBZ for any space group can be obtained by using the option KVEC and specifying the space group (in this case No. 225).

namely an element (say copper) that crystallizes in the face-centred-cubic (f.c.c.) structure. With (2.2.2.4) we easily find that the reciprocal lattice is body-centred-cubic (bcc) and the corresponding BZ is shown in Fig. 2.2.7.1. In this case, f.c.c. Cu has O_h symmetry with 48 symmetry operations $p \in P$ (point group). The energy eigenvalues within a star of $\mathbf{k}$ (*i.e.* $\mathbf{k} \in S_k$) are the same, and therefore it is sufficient to calculate one member in the star. Consequently, it is enough to consider the irreducible wedge of the BZ (called the IBZ). In the present example, this corresponds to 1/48th of the BZ shown in Fig. 2.2.7.1. To count the number of states in the BZ, one counts each $\mathbf{k}$ point in the IBZ with a proper weight w_k to represent the star of this $\mathbf{k}$ vector.

2.2.7.3. *The symmetry of the Brillouin zone*

The BZ is purely constructed from the reciprocal lattice and thus only follows from the translational symmetry (of the 14 Bravais lattices). However, the energy bands $E^j(\mathbf{k})$, with $\mathbf{k}$ lying within the first BZ, possess a symmetry associated with one of the 230 space groups. Therefore one *can not* simply *use* the *geometrical symmetry* of the BZ to find its irreducible wedge, although this is tempting. Since the effort of computing energy eigenvalues increases with the number of $\mathbf{k}$ points, one wishes to restrict such calculations to the basic domain, but the latter can only be found by considering the space group of the corresponding crystal (including the basis with all atomic positions).

One possible procedure for finding the IBZ is the following. First a uniform grid in reciprocal space is generated by dividing the three unit-cell vectors $\mathbf{b}_i$ by an integer number of times. This is easy to do in the parallelepiped, spanned by the three unit-cell vectors, and yields a (more-or-less) uniform grid of $\mathbf{k}$ points. Now one must go through the complete grid of $\mathbf{k}$ points and extract a list of non-equivalent $\mathbf{k}$ points by applying to each $\mathbf{k}$ point in the grid the point-group operations. If a $\mathbf{k}$ point is found that is already in the list, its weight is increased by 1, otherwise it is added to the list. This procedure can easily be programmed and is often used when $\mathbf{k}$ integrations are needed. The disadvantage of this scheme is that the generated $\mathbf{k}$ points in the IBZ are not necessarily in a connected region of the BZ, since one member of the star of $\mathbf{k}$ is chosen arbitrarily, namely the first that is found by going through the complete list.