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

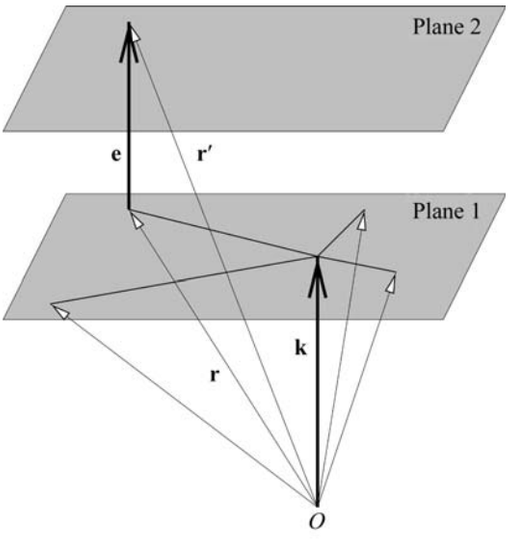

Fig. 2.2.5.1. Plane waves. The wavevector $\mathbf{k}$ and the unit vector $\mathbf{e}$ are normal to the two planes and the vectors $\mathbf{r}$ in plane 1 and $\mathbf{r}'$ in plane 2.

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

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

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

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

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