It turns out that every BZ has the same volume, given by:

$$V_{\mathrm{BZ}} = |\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)| = \frac{(2\pi)^3}{|\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|} = \frac{(2\pi)^3}{V_{\mathrm{PUC}}} \tag{2.33}$$

which is explicitly shown for the example of the 2D square lattice below. By comparing the result of Eq. (2.33) with Eq. (2.28), we conclude that in each BZ there are N distinct values of $\mathbf{k}$, where N is the total number of PUCs in the crystal. This is a very useful observation: if there are n electrons in the PUC (that is, nN electrons in the crystal), then we need exactly $nN/2$ different $\psi_{\mathbf{k}}^{(n)}(\mathbf{r})$ states to accommodate them, taking into account spin degeneracy (two electrons with opposite spins can coexist in state $\psi_{\mathbf{k}}^{(n)}(\mathbf{r})$). Since the first BZ contains N distinct values of $\mathbf{k}$, it can accommodate up to $2N$ electrons. Similarly, each subsequent BZ can accommodate $2N$ electrons because it has the same volume in reciprocal space. For n electrons per unit cell, we need to fill completely the states that occupy a volume in $\mathbf{k}$-space equivalent to $n/2$ BZs. Which states will be filled is determined by their energy: in order to minimize the total energy of the system, the lowest-energy states must be occupied first. The Fermi level is defined as the value of the energy below which all single-particle states are occupied.

Example 2.1 Brillouin zones of a 2D square lattice

For a concrete example of these ideas, let us consider a square lattice with lattice constant a. The explicit construction of the first three BZs for this case, by bisecting the corresponding reciprocal space vectors, is shown in Fig. 2.6. The reconstructed version of the first six Brillouin zones, obtained by displacing the different parts by reciprocal space vectors, is shown in Fig. 2.7, which proves by construction that each BZ has the same volume.

To demonstrate the filling of the BZs, we consider that there is one atom per primitive unit cell in this model. We shall assume that this atom has Z electrons so that there are Z/a^2 electrons per unit cell, that is, a total of NZ electrons in the crystal of volume Na^2, where N is the number of unit cells. We shall also assume, for simplicity, that states are equally occupied in all directions of $\mathbf{k}$ for the same value of $|\mathbf{k}|$, up to the highest value needed to accommodate all the electrons, which we defined as the Fermi momentum k_{F} (this is actually equivalent to assuming free-electron bands, a model discussed in Chapter 1). Therefore, the Fermi momentum can be obtained by integrating over all $\mathbf{k}$-vectors until we have enough states to accommodate all the electrons. Taking into account a factor of 2 for spin, the total number of states we need in reciprocal space to accommodate all the electrons of the crystal is given by:

$$\sum_{\mathbf{k},|\mathbf{k}|<k_{\mathrm{F}}} 2 \to \frac{2}{(2\pi)^2}(Na^2)\int_{|\mathbf{k}|<k_{\mathrm{F}}} \mathrm{d}\mathbf{k} = NZ \Rightarrow \frac{2}{(2\pi)^2}\int_{|\mathbf{k}|<k_{\mathrm{F}}} \mathrm{d}\mathbf{k} = \frac{Z}{a^2} \tag{2.34}$$

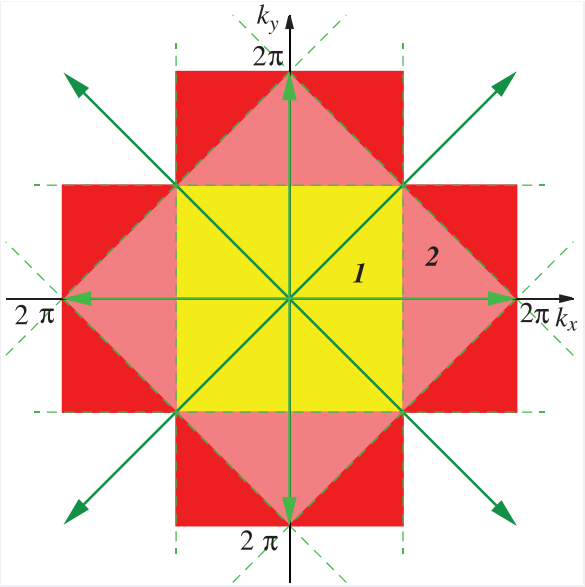

Fig. 2.6

Illustration of the construction of Brillouin zones in a 2D crystal with $\mathbf{a}_1 = \hat{\mathbf{x}}, \mathbf{a}_2 = \hat{\mathbf{y}}$. The first two sets of reciprocal lattice vectors, $\mathbf{G} = \pm 2\pi\,\hat{\mathbf{x}}, \pm 2\pi\hat{\mathbf{y}}$, light-green arrows, and $\mathbf{G} = 2\pi(\pm\hat{\mathbf{x}} \pm \hat{\mathbf{y}})$, dark-green arrows, are shown, along with the Bragg planes that bisect them, as dashed lines of the same color as the arrows. The first BZ, shown in yellow and labeled 1, is the central square; the second BZ, shown in pink and labeled 2, is composed of the four triangles around the central square; the third BZ, shown in red and labeled 3, is composed of the eight smaller triangles around the second BZ.

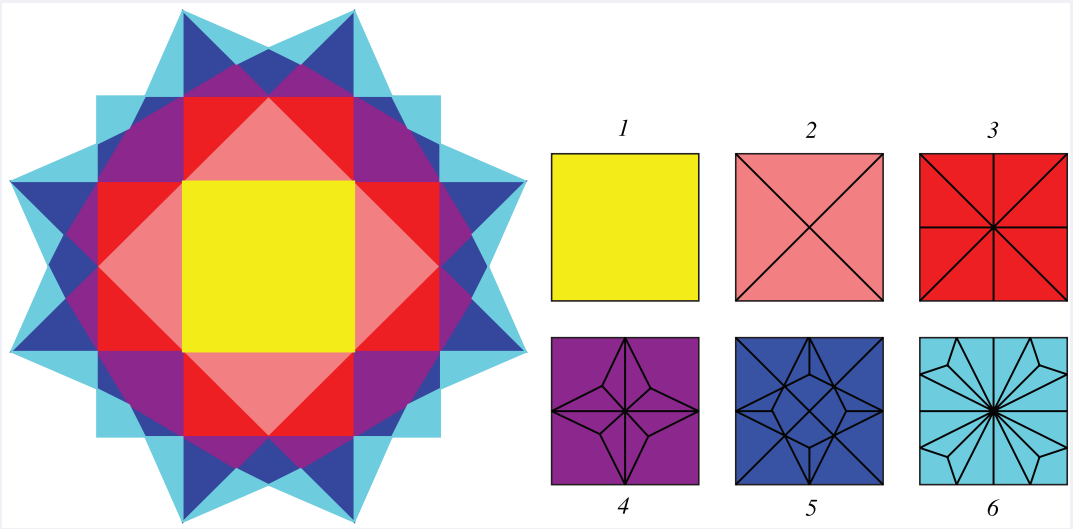

Fig. 2.7

The first six Brillouin zones of the 2D square lattice, coded in color, and their reconstructed version through translations by reciprocal lattice vectors, showing explicitly that they have exactly the same volume.

where we have used $\mathrm{d}\mathbf{k} = (2\pi)^2/(Na^2)$ for the 2D square lattice, by analogy to the general result for the 3D lattice $\mathrm{d}\mathbf{k} = (2\pi)^3/(NV_{\mathrm{PUC}})$, see Eq. (2.27). Using spherical coordinates for the integration over $\mathbf{k}$, we obtain:

$$\frac{2}{(2\pi)^2} 2\pi \int_0^{k_\mathrm{F}} k\,\mathrm{d}k = \frac{1}{2\pi} k_\mathrm{F}^2 = \frac{Z}{a^2} \Rightarrow k_\mathrm{F} = \left(\frac{2\pi}{a}\right)\left(\frac{Z}{2\pi}\right)^{1/2} \tag{2.35}$$

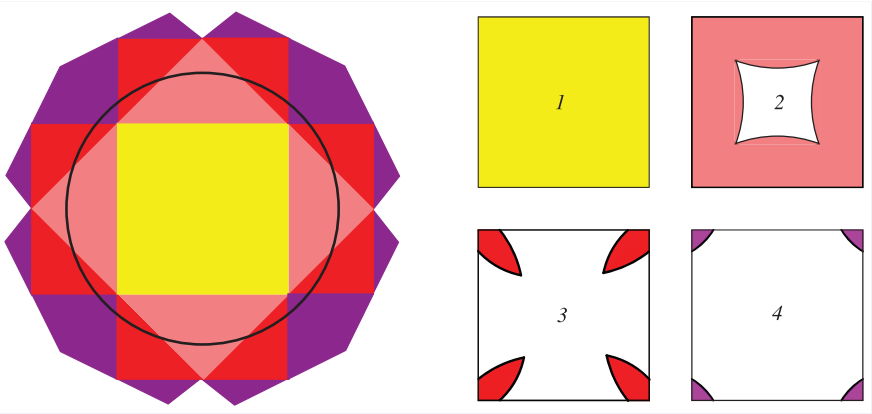

Fig. 2.8 The shape of occupied portions of the various Brillouin zones for the 2D square lattice with $Z = 4$ electrons per unit cell. The black circle represents the Fermi surface: this corresponds to the first BZ being full, the second BZ having a large hole at the center, and the third and fourth BZs with electron pockets at the corners.

and from this we can obtain the Fermi energy ϵ_F:

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m_e} = \frac{\hbar^2}{2m_e}\left(\frac{2\pi}{a}\right)^2 \frac{Z}{2\pi} \tag{2.36}$$

The value of k_F determines the so-called "Fermi surface" in reciprocal space, which contains all the occupied states for the electrons; the Fermi surface in the present case is a sphere in **k**-space.

This Fermi sphere corresponds to a certain number of BZs with all states occupied by electrons, and a certain number of partially occupied BZs with interestingly shaped regions for the occupied portions. The number of full BZs and the shapes of occupied regions in partially filled BZs depend on k_F through Z; an example for $Z = 4$ is shown in Fig. 2.8. In this case, the first BZ is fully occupied, the second BZ is mostly occupied but has some empty portion (missing electrons or "holes") at the center, the third BZ has small sections near the corners which are occupied (called "electron pockets"), and the fourth BZ has even smaller electron pockets at the corners.

2.2.3 Periodicity in Reciprocal Space

The usefulness of BZs is that they play an analogous role in reciprocal space as the PUCs do in real space. We saw above that due to crystal periodicity, we only need to solve the single-particle equations inside the PUC. We also saw that values of **k** are equivalent if one adds to them any vector **G**. Thus, we only need to solve the single-particle equations for values of **k** within the first BZ, or within any single BZ: points in other BZs are related by **G** vectors, which make them equivalent. To prove this, suppose we have calculated the complete set of wavefunctions at some value of **k**, given by the usual expression:

$$\psi_{\mathbf{k}}^{(n)}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \sum_{\mathbf{G}'} \alpha_{\mathbf{k}}^{(n)}(\mathbf{G}') e^{i\mathbf{G}'\cdot\mathbf{r}} \Rightarrow \hat{\mathcal{H}}^{sp}\psi_{\mathbf{k}}^{(n)}(\mathbf{r}) = \epsilon_{\mathbf{k}}^{(n)}\psi_{\mathbf{k}}^{(n)}(\mathbf{r}) \tag{2.37}$$