5.1 Bloch’s Theorem

We have learned that atoms in a crystal are arranged in a Bravais lattice. This arrangement gives rise to a periodic potential that has the full symmetry of the Bravais lattice to the electrons in the solid.

Qualitatively, a typical crystalline potential may have the form shown in Fig. 5.1, resembling individual atomic potential at the atomic site, but flattening off in the region between adjacent ions. It turns out irrespective of the details of the crystalline potential, the mere fact that the potential is periodic enables many important conclusions to be drawn.

Let’s continue to consider the independent electron picture. Then the Schrödinger equation for a single electron in a periodic potential, \( U(\mathbf{r}) \), is:

\[
H\psi = \left(-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r})\right)\psi = E\psi
\]  

The resulting electron eigenstates can be shown to have the following important properties according to Bloch’s Theorem:

\[
\psi_{nk}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{nk}(\mathbf{r})
\]

where

\[
u_{nk}(\mathbf{r} + \mathbf{R}) = u_{nk}(\mathbf{r})
\]

for all \( \mathbf{R} \) in the Bravais lattice. With eqns. 5.2 and 5.3, an alternative form of Bloch’s Theorem is:

\[
\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi(\mathbf{r})
\]
Proof:

Define the translation operator $T_{\vec{R}}$ that will translate the system by a Bravais vector, $\vec{R}$, in real space:

$$T_{\vec{R}} \psi(\vec{r}) = \psi(\vec{r} + \vec{R})$$  \hspace{1cm} (5.5)

We show that $[T_{\vec{R}}, H] = 0$:

$$T_{\vec{R}} H \psi(\vec{r}) = H(\vec{r} + \vec{R}) \psi(\vec{r} + \vec{R}) = H(\vec{r}) T_{\vec{R}} \psi(\vec{r})$$  
$$\Rightarrow [T_{\vec{R}}, H] = 0$$  \hspace{1cm} (5.6)

If $T_{\vec{R}}$ commutes with $H$, $T_{\vec{R}}$ and $H$ may have simultaneous eigenstates:

i.e.

$$T_{\vec{R}} \psi(\vec{r}) = C_{\vec{R}} \psi(\vec{r})$$  \hspace{1cm} (5.7)

$$H \psi(\vec{r}) = E \psi(\vec{r})$$  \hspace{1cm} (5.8)

where $\psi(\vec{r})$ is the simultaneous eigenfunction of $H$ with eigenvalue $E$, and of $T_{\vec{R}}$ with eigenvalue $C_{\vec{R}}$. Consider:

$$T_{\vec{R}} T_{\vec{R}} \psi(\vec{r}) = C_{\vec{R}} C_{\vec{R}} \psi(\vec{r})$$  \hspace{1cm} (5.9)

But we also have:

$$T_{\vec{R}} T_{\vec{R}} \psi(\vec{r}) = T_{\vec{R} + \vec{R}} \psi(\vec{r}) = C_{\vec{R} + \vec{R}} \psi(\vec{r})$$

Hence,

$$C_{\vec{R} + \vec{R}} = C_{\vec{R}} C_{\vec{R}}$$  \hspace{1cm} (5.10)

Since $\psi(\vec{r})$ is an electron wavefunction, $|\psi(\vec{r})|^2$ has the physical meaning of electron density. Due to the symmetry of the potential $U(\vec{r})$, we should have:

$$|\psi(\vec{r})|^2 = |\psi(\vec{r} + \vec{R})|^2$$  \hspace{1cm} (5.11)

But $\psi(\vec{r} + \vec{R}) = T_{\vec{R}} \psi(\vec{r}) = C_{\vec{R}} \psi(\vec{r})$. Eqn. 5.11 implies:

$$|C_{\vec{R}}|^2 = 1$$  \hspace{1cm} (5.12)

We may therefore define:

$$C_{\vec{R}} = e^{2\pi i \alpha_i}$$  \hspace{1cm} (5.13)

to be the translational eigenvalues for the translation through the primitive vector, $\vec{a}_i$. Here, $\alpha_i$ is in general a real number.

Since $\vec{R}$ is a Bravais lattice vector, we can write:

$$\vec{R} = n_i \vec{a}_i;$$

where $n_i$ are integers.

(For the R.H.S., it is understood that it is a sum over the index $i$.)

$$\therefore C_{\vec{R}} = C_{n_1 \vec{a}_1} = \prod_{i=1}^{3} (C_{\vec{a}_i})^{n_i} = e^{2\pi i n \cdot \vec{R}}$$  \hspace{1cm} (5.14)

$$\therefore \text{eqn. 5.10}$$
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Now define a wavevector, $\vec{k} = \mathbf{z} \cdot \vec{b}_i$, where $\vec{b}_i$ are the primitive reciprocal lattice vectors.

Clearly, $\vec{k} \cdot \vec{R} = x_i n_j \vec{a}_j \cdot \vec{b}_i = x_i n_j (2\pi \delta_{ij}) = 2\pi x_i n_j$.

Hence, we can rewrite eqn. 5.14 as:

$$C_R = e^{i\vec{k} \cdot \vec{R}}$$ (5.16)

Now, $T \Phi(\vec{r}) = \Phi(\vec{r} + \vec{R}) = C_R \Phi(\vec{r})$

Hence

$$\Phi(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \Phi(\vec{r})$$

In the above proof, we seem to have arbitrarily introduced the wavevector $\vec{k}$ in eqn. 5.15. The allowed values of $\vec{k}$ can in fact be determined by using the Born-Von Karman boundary condition. It is fundamentally the same as the periodic boundary condition we have introduced earlier for the Sommerfeld theory with a cubic system. With a Bravais lattice, it is more convenient to work with a volume that commensurates with a primitive cell of the underlying lattice. We therefore generalize the periodic boundary condition to:

$$\Phi(\vec{r} + N_i \vec{a}_i) = \Phi(\vec{r}) \quad i = 1, 2, 3$$ (5.17)

where $N_i$ is the number of primitive cells counted along the direction of $\vec{a}_i$. One should note that we have the liberty to define the boundary condition because with $N_i$ being very large ($\sim 10^6$), the choice of the boundary condition cannot affect the physical properties of the solid. Applying Bloch’s theorem to the boundary condition eqn. 5.17:

$$\Phi(\vec{r} + N_i \vec{a}_i) = e^{iN_i \vec{k} \cdot \vec{a}_i} \Phi(\vec{r}) = \Phi(\vec{r}) \quad i = 1, 2, 3$$ (5.18)

This result demands that:

$$e^{iN_i \vec{k} \cdot \vec{a}_i} = 1, \quad i = 1, 2, 3$$

When $\vec{k}$ has the form of eqn. 5.15, we have

$$e^{i2\pi N_i x_i} = 1,$$ (5.19)

Hence

$$x_i = \frac{m_i}{N_i}, \quad m_i \text{ integral.} \quad (5.20)$$

Therefore, the general form of the Bloch wavevector is:

$$\vec{k} = \sum_{i=1}^{3} \frac{m_i}{N_i} \vec{b}_i \quad m_i \text{ integral.}$$ (5.21)

From eqn. 5.21, the volume $\Delta^3k$ of $k$-space per allowed value of $\vec{k}$ is just:

$$\Delta^3k = \frac{\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)}{N_1} = \frac{1}{N} \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)$$ (5.22)

$$N = N_1 N_2 N_3 = \text{total number of primitive cells in the crystal.}$$
Recall that \( b_1 \cdot (b_2 \times b_3) \) is the volume of a reciprocal lattice primitive cell. For a cubic lattice, one readily see that Eqn. 5.22 gives
\[
\Delta^3 \mathbf{k} = (2\pi)^3/V,
\]
(5.23)
where \( V \) is the volume of the specimen. One can show that this result in fact applies to any crystalline structures.

To gain further insight, we examine another proof of the Bloch’s Theorem. We start with the observation that we can always expand any function obeying the Born-von Karman boundary condition (eqn. 5.17) in the set of all plane waves that satisfy the same boundary condition. This means that the expansion comprises terms with wavevectors equal to the allowed Bloch wavevectors:
\[
\psi(\mathbf{r}) = \sum_k c_k e^{i\mathbf{k} \cdot \mathbf{r}}.
\]
(5.24)

Because \( U(\mathbf{r}) \) is periodic in the Bravais lattice, its plane wave expansion (i.e. Fourier expansion) will only contain components with wavevectors that are the reciprocal wavevectors.
\[
U(\mathbf{r}) = \sum_G U_G \exp(i\mathbf{G} \cdot \mathbf{r})
\]
(5.25)

Obviously, for \( U(\mathbf{r}) \) to be real,
\[
U_G = U_{-G}^*
\]
(5.26)

Substitute eqns. 5.24 and 5.25 in each term of the Schrödinger equation (eqn. 5.1):
\[
\frac{p^2}{2m} \psi = -\frac{\hbar^2}{2m} \nabla^2 \psi = \sum_k \frac{\hbar^2}{2m} k^2 c_k e^{i\mathbf{k} \cdot \mathbf{r}}.
\]

\[
U \psi = (\sum_G U_G e^{i\mathbf{G} \cdot \mathbf{r}})(\sum_k c_k e^{i\mathbf{k} \cdot \mathbf{r}}) = \sum_{k,G} U_G c_k e^{i(k+\mathbf{G}) \cdot \mathbf{r}}
\]

Put \( \mathbf{k}' = \mathbf{k} + \mathbf{G} \) then replace \( \mathbf{k}' \) by \( \mathbf{k} \),
\[
U \psi = \sum_{k,G} U_G c_{\mathbf{k}'-\mathbf{G}} e^{i\mathbf{k} \cdot \mathbf{r}}
\]
(5.27)

The Schrödinger equation becomes:
\[
\sum_k \left\{ \left( \frac{\hbar^2}{2m} k^2 - \varepsilon \right) c_k + \sum_G U_G c_{\mathbf{k}'-\mathbf{G}} \right\} e^{i\mathbf{k} \cdot \mathbf{r}} = 0
\]
(5.28)

Or,
\[
\left( \frac{\hbar^2}{2m} k^2 - \varepsilon \right) c_k + \sum_G U_G c_{\mathbf{k}'-\mathbf{G}} = 0
\]
(5.29)

It is convenient to limit the wavevectors \( \mathbf{k} \) in eqn. (5.29) to those lying in the first Brillouin zone (BZ). We can do so by writing \( \mathbf{k} = \mathbf{q} - \mathbf{G} \), where \( \mathbf{q} \) lies in the first BZ.
\[
\left( \frac{\hbar^2}{2m} (\mathbf{q} - \mathbf{G})^2 - \varepsilon \right) c_{\mathbf{q}-\mathbf{G}} + \sum_G U_G c_{\mathbf{q}-\mathbf{G}} = 0
\]
Next, replace $q$ by $k$, and $G'$ by $G' - G$:

$$
\frac{\hbar^2}{2m}(\bar{k} - \bar{G})^2 - \epsilon) c_{\bar{k} - \bar{G}} + \sum_{G'} U_{\bar{G}' - \bar{G}} c_{\bar{k} - \bar{G}'} = 0 ,
$$

(5.30)

where $k$ lies in the first BZ. Equation (5.29) represents a set of equations relating $c_k$ with the other coefficients $c_{k-G}$, $c_{k-G'}$, ..., corresponding to wavevectors differing from $k$ by a reciprocal lattice vector. It may help to write eqn. (5.30) in a matrix form:

$$
\begin{pmatrix}
\frac{\hbar^2}{2m}(\bar{k} + \bar{G})^2 - \epsilon + U_0 & U_{\bar{G}_1 + \bar{G}_2} & U_{\bar{G}_2} & U_{\bar{G}_1 + \bar{G}_2} & U_{\bar{G}_2} \\
U_{\bar{G}_1 - \bar{G}_2} & \frac{\hbar^2}{2m}(\bar{k} + \bar{G})^2 - \epsilon + U_0 & U_{\bar{G}_2} & U_{\bar{G}_1 + \bar{G}_2} & U_{\bar{G}_2} \\
U_{\bar{G}_2} & U_{\bar{G}_1} & \frac{\hbar^2}{2m}(\bar{k} + \bar{G})^2 - \epsilon + U_0 & U_{\bar{G}_2} & U_{\bar{G}_1 + \bar{G}_2} \\
U_{-(\bar{G}_1 + \bar{G}_2)} & U_{\bar{G}_2} & U_{\bar{G}_1} & \frac{\hbar^2}{2m}(\bar{k} + \bar{G})^2 - \epsilon + U_0 & U_{\bar{G}_1 + \bar{G}_2} \\
U_{\bar{G}_2} & U_{-(\bar{G}_1 + \bar{G}_2)} & U_{\bar{G}_1} & U_{-(\bar{G}_1 + \bar{G}_2)} & \frac{\hbar^2}{2m}(\bar{k} + \bar{G})^2 - \epsilon + U_0 \\
\end{pmatrix}
\begin{pmatrix}
c_{\bar{k} + \bar{G}_1} \\
c_{\bar{k} + \bar{G}_2} \\
c_{\bar{k}} \\
c_{\bar{k} - \bar{G}_1} \\
c_{\bar{k} - \bar{G}_2} \\
\end{pmatrix} = 0
$$

(5.31)

The matrix equation (5.31) provides an explicit form for the eigenvalue problem with the plane wave states, $e^{ikr}$, $e^{i(k-G)r}$, etc. constituting the working basis. Notice that there are $N$ different values of $k$ in the first BZ and so there are $N$ different problems being expressed by eqn. (5.31), where $N$ is the number of primitive unit cells in the specimen.

Given the above scheme, in which all the wavevectors are reduced to the ones lying in the first BZ, any wavevectors $k'$ differing from $k$ by a reciprocal lattice vector, i.e., $k' = k + G$, would end in the same eigenvalue problem as that found for $k$. Therefore, $\epsilon(k)$ is periodic in $k$.

One may also perceive that there are many eigenvalue solutions $\epsilon_k$ to eq. (5.30) or (5.31) for each $k$. We may thus label the eigenvalues $\epsilon_k$ by a “band index”, $n$, analogous to the quantum number used to label the energies of a particle confined in a box. For a given $n$, the set of $\epsilon_k$ or $\epsilon(k)$ constitutes an energy band.
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The solutions to each of the problems with a given $k$ and $n$ would give eigenfunctions that are linear combinations of the basis functions, $e^{i(k-G)r}$ and the corresponding eigenvalues, $\epsilon$. Explicitly, we may write

$$\Psi_{nk}(r) = \sum_G c_{k-G} e^{i(k-G)r} = e^{ikr} \sum_G c_{k-G} e^{-iG\cdot r} = e^{ikr} u_{nk}(r),$$

where $u_{nk}(r) = \sum_G c_{k-G} e^{-iG\cdot r}$, which clearly fulfills the condition, $u_{nk}(r + R) = u_{nk}(r)$. This proves the Bloch’s Theorem.

5.2 Some Consequential New Concepts

5.2.1 Crystal Momentum

For free electrons (for which $U(r) = 0$ in the Hamiltonian), the electron wavefunctions, $\psi_{nk}(r)$, are simultaneous eigenstates of the momentum operator, $\hat{p} = -i\hbar \nabla$, with $\hbar \vec{k}$ being the momentum eigenvalue. But for Bloch electrons, their wavefunctions (which are of the form shown in eqn. (5.2)) are in general NOT eigenstates of $p$ since

$$-i\hbar \nabla \psi_{nk}(\vec{r}) = -i\hbar \nabla (e^{i\vec{k}\cdot \vec{r}} u_{nk}(\vec{r})) = \hbar \vec{k} \psi_{nk}(\vec{r}) + (e^{i\vec{k}\cdot \vec{r}})(-i\hbar)\nabla u_{nk}(\vec{r}).$$

Nevertheless, $\hbar \vec{k}$ is in many ways a natural extension of $p$ for electrons in a periodic potential, which you would appreciate later. It has therefore been called the crystal momentum to emphasize this similarity, but it should always be borne in mind that it is not the electron momentum.

Note that since $\Psi_k(r) = \sum_G c_{k-G} e^{i(k-G)r}$, the probability of any scattering event where a $k$ state is scattered into a $k'$ state would involve the integral of $\Psi_k^*(r)\Psi_k(r) \sim \sum_G c_{k-G} e^{i(k-G-k')r}$. This leads to the selection rule: $k' = k - G$.

5.2.2 Energy Bands

As pointed out above, there are many eigenvalue solutions $\epsilon_k$ to eqn. (5.30) for each $k$ that we may label by a “band index”, $n$. And the set of $\epsilon(k)$ for a given $n$ constitutes an energy band.

In addition, $\epsilon_k$ is periodic in units of a BZ. It is customary to represent all $\epsilon_k$ in the first BZ by translating those “outside pieces” through a suitable reciprocal lattice vector back into the first BZ. Such presentation scheme is called the reduced zone scheme. An example is shown immediately below. We shall discuss the other common schemes later.
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Example 1: Find the low-lying free-electron (\(U = 0\)) energy bands, \(\varepsilon(k)\), in the [100] direction of a simple cubic lattice with lattice constant \(a\).

\[
\varepsilon(k - G) = \left(\frac{\hbar^2}{2m}\right)(k_x - G_x)^2 + G_y^2 + G_z^2
\]

<table>
<thead>
<tr>
<th>(G)</th>
<th>(\varepsilon(000)/\left(\frac{\hbar^2}{2m}\right))</th>
<th>(\varepsilon(k,00))</th>
<th>Band index, (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>000</td>
<td>0</td>
<td>(k_x^2)</td>
<td>1</td>
</tr>
<tr>
<td>100, -100</td>
<td>((2\pi/a)^2)</td>
<td>((k_x + 2\pi/a)^2)</td>
<td>2, 3</td>
</tr>
<tr>
<td>010, 0-10, 001, 00-1</td>
<td>((2\pi/a)^2)</td>
<td>(k_x^2 + (2\pi/a)^2)</td>
<td>4, 5, 6, 7</td>
</tr>
<tr>
<td>110, 101, 1-10, 10-1</td>
<td>((2\pi/a)^2)</td>
<td>((k_x + 2\pi/a)^2 + (2\pi/a)^2)</td>
<td>8, 9, 10, 11</td>
</tr>
<tr>
<td>-110, -101, -1-10, -10-1</td>
<td>((2\pi/a)^2)</td>
<td>((k_x - 2\pi/a)^2 + (2\pi/a)^2)</td>
<td>12, 13, 14, 15</td>
</tr>
<tr>
<td>011, 0-11, 011, 0-1-1</td>
<td>((2\pi/a)^2)</td>
<td>(k_x^2 + 2(2\pi/a)^2)</td>
<td>16, 17, 18, 19</td>
</tr>
</tbody>
</table>

5.2.3 Mean Velocity

The mean velocity of an electron with a non-plane-wave wavefunction is determined by its group velocity:

\[
v_n(\vec{k}) = \frac{1}{\hbar} \nabla \varepsilon_n(\vec{k}) \tag{5.39}
\]

This result is remarkable. It asserts that electrons in a periodic potential can forever maintain a constant mean velocity that depends on which stationary eigenstates the electrons are in despite of the strong interactions they have with the positive ions of the lattice, as accounted for by \(V(r)\).

5.3 Density of States and van Hove Singularity

In Chapter 2 (pp. 6-7), we have derived the expression for the density of states, \(g(\varepsilon)\) for Sommerfeld’s free electron model, and used it to obtain the average energy and heat capacity of the electronic system. The algebra can be extended in a straightforward manner to the present problem of electrons in a periodic potential. Like before, the average value of a quantity \(Q\) that is a function of \(n\) and \(k\) (or \(\varepsilon\)) is given by:

\[
Q = 2\sum_{n,k} Q_n(\vec{k}) \tag{5.40}
\]

An intensive quantity \(q\) can be defined from \(Q\):
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\[ q = \lim_{V \to \infty} \frac{Q}{V} = 2 \sum_n \int \frac{d^3 \vec{k}}{(2\pi)^3} Q_n(\vec{k}) \tag{5.41} \]

We can re-write eqn. 5.41 as:

\[ q = \int d\varepsilon g(\varepsilon)Q(\varepsilon) \tag{5.42} \]

if

\[ g(\varepsilon) = \sum_n g_n^\varepsilon(\varepsilon) = \sum_n \int \frac{d^3 \vec{k}}{4\pi^3} \delta(\varepsilon_n(\vec{k}) - \varepsilon), \tag{5.43} \]

where the integral is over a primitive cell. Clearly, \( g_n(\varepsilon) d\varepsilon \) is the number of allowed states of the \( n \)th band, lying within the shell in \( \mathbf{k} \)-space enclosed by the energy surfaces \( \varepsilon_n = \varepsilon \) and \( \varepsilon_n = \varepsilon + d\varepsilon \). From eqn. (5.43), we can write,

\[ g_n(\varepsilon) = \int_{s_n(\varepsilon)} \frac{dS_n(\vec{k})}{4\pi^3} \delta k_{\perp}(\vec{k}) \delta(\varepsilon - \varepsilon_n(\vec{k})), \tag{5.44} \]

where \( dS_n(\vec{k}) \) is the surface area element of the energy surfaces at point \( \mathbf{k} \) (see Fig. 5.2) and \( \delta k_{\perp}(\vec{k}) \) is the local distance between the two energy surfaces \( \varepsilon_n = \varepsilon \) and \( \varepsilon_n = \varepsilon + d\varepsilon \) at point \( \mathbf{k} \) (such that \( d\varepsilon = \nabla_\varepsilon \varepsilon_n(\vec{k}) \cdot d\vec{k} = |\nabla_\varepsilon \varepsilon_n(\vec{k})| \delta k_{\perp}(\vec{k}) \)). By substituting

\[ \delta k_{\perp}(\vec{k}) = \frac{d\varepsilon}{|\nabla_\varepsilon \varepsilon_n(\vec{k})|} \]

in eqn. (5.44) and integrating over \( d\varepsilon \), one obtains

\[ g_n(\varepsilon) = \int_{s_n(\varepsilon)} \frac{dS_n(\vec{k})}{4\pi^3} \frac{1}{|\nabla_\varepsilon \varepsilon_n(\vec{k})|}. \tag{5.55} \]

At points where \( \nabla \varepsilon_n(\mathbf{k}) \) vanishes (i.e. maximum or minimum, whether local or global, of the energy band in \( \mathbf{k} \)-space), the integrand of eqn. (5.55) diverges although in three dimensions the integral of \( g_n(\varepsilon) \) remains finite. Nevertheless, the local slope of the density of states, \( d\varepsilon g_n/d\varepsilon \), may still diverge. Such divergence is called van Hove
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singularity. Since \( \frac{dg_\nu}{d\epsilon_{\nu}} \) enters into all terms except the first one in the Sommerfeld expansion (eqn. 2.44), van Hove singularities at the Fermi surface may lead to anomalies in some thermodynamic quantities at low temperatures.

5.4 **Electrons in a Weak Periodic Potential – A Simple Example**

We shall examine the application of the Bloch’s theorem to the simple case of a weak periodic potential. At first sight, this may appear to be a purely academic problem. But in reality, this model provides good approximation to metals of groups I to IV (i.e. those that only have s and p electrons outside the noble gas configuration.) There are two reasons for this *Nearly-Free Electron* behavior:

(1) Due to the Pauli’s exclusion principle, the conduction electrons are excluded by the core electrons and hence cannot go very near to the positive ion where the potential is strong.

(2) In the regions where conduction electrons are allowed, their mere existence helps screen out the electrical potential of the positive ions (see A&M Ch. 17), making the potential much shorter range than 1/r.

In the presence of a periodic potential, eqn. (5.30) applies and says that

\[
\psi_{\mathbf{k}}(\mathbf{\mathcal{r}}) = \sum_{\mathbf{G}} c_{\mathbf{k} - \mathbf{G}} e^{i(\mathbf{k} - \mathbf{G}) \cdot \mathbf{\mathcal{r}}},
\]

and

\[
\left( \frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{G})^2 - \epsilon \right) c_{\mathbf{k} - \mathbf{G}} + \sum_{\mathbf{G}'} U_{\mathbf{G}'} c_{\mathbf{k} - \mathbf{G}'} c_{\mathbf{k} - \mathbf{G}'} = 0
\]

With a weak potential, we may treat the problem as a small perturbation to the (unperturbed) free electron problem that has eigenvalue and eigenfunction:

\[
\epsilon = \epsilon^0_{\mathbf{k}} = \frac{\hbar^2}{2m} (\mathbf{k})^2, \quad \text{and} \quad \psi^0_{\mathbf{k}}(\mathbf{r}) \propto e^{i\mathbf{k} \cdot \mathbf{r}}
\]

By using the perturbation theory and assuming \( U_{\mathbf{G}} << \epsilon^0_{\mathbf{k}} \), we have:

\[
\epsilon - \epsilon^0_{\mathbf{k}} = U_0 + \sum_{\mathbf{G} \neq 0} \frac{|U_{\mathbf{G}}|^2}{\epsilon^0_{\mathbf{k}} - \epsilon^0_{\mathbf{k} - \mathbf{G}}} + O(U^3).
\]

Eqn. (5.59) is valid only if \( \epsilon^0_{\mathbf{k}} \neq \epsilon^0_{\mathbf{k} - \mathbf{G}} \). In the case where there is a reciprocal lattice vector \( \mathbf{G} \) such that the states \( \mathbf{k} \) and \( \mathbf{k} - \mathbf{G} \) are degenerate, we must diagonalize the part of the Hamiltonian that couples these degenerate states. Below we show that degeneracy always occurs at the Brillouin zone boundary:

**Proof:** Recall that any wavevector \( \mathbf{k} \) on the Brillouin zone boundary satisfies:
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\[ \mathbf{k} \cdot \mathbf{G} = \frac{\mathbf{G}^2}{2} \]  
(5.60)

Hence,  
\[ \varepsilon^0_{k \cdot \mathbf{G}} = \frac{(\mathbf{k} - \mathbf{G})^2}{2m} = \frac{(\mathbf{k}^2 + \mathbf{G}^2 - 2\mathbf{k} \cdot \mathbf{G})}{2m} = \frac{\mathbf{k}^2}{2m} = \varepsilon^0_k \]  
(5.61)

Suppose there are only two degenerate states, such that  
\[ \varepsilon^0_k = \varepsilon^0_{k \cdot \mathbf{G}} + O(U) \]
and  
\[ |\varepsilon^0_k - \varepsilon^0_{k \cdot \mathbf{G}}| >> U \quad \text{if} \quad \mathbf{G} \neq \mathbf{G}' \]

Then only those terms in (5.59) involving the coefficients \( c_k \) and \( c_{k \cdot \mathbf{G}} \) dominate.

\[ (\varepsilon - \varepsilon^0_k) c_k - U c_{k \cdot \mathbf{G}} = 0 \]  
(5.62)

\[ -U c_{k \cdot \mathbf{G}} + (\varepsilon - \varepsilon^0_{k \cdot \mathbf{G}}) c_k = 0 \]  
(5.63)

These equations will have consistent solutions only if

\[ \begin{vmatrix} \varepsilon - \varepsilon^0_k & -U \cr -U & \varepsilon - \varepsilon^0_{k \cdot \mathbf{G}} \end{vmatrix} = 0 \]  
(5.64)

\[ \left( \varepsilon^0_{k \cdot \mathbf{G}} - \varepsilon \right) \left( \varepsilon^0_{k \cdot \mathbf{G}} - \varepsilon \right) - 1U^2 \left| \varepsilon \right|^2 = 0 \quad \text{\( U^2 = U^* \) if \( U \) is real} \]

\[ \varepsilon^2 - (\varepsilon^0_{k \cdot \mathbf{G}} + \varepsilon^0_{k \cdot \mathbf{G}}) \varepsilon + \varepsilon^0_{k \cdot \mathbf{G}} \varepsilon^0_{k \cdot \mathbf{G}} - U^2 = 0 \]

\[ \varepsilon = \frac{\varepsilon^0_{k \cdot \mathbf{G}} \pm \left( \varepsilon^0_{k \cdot \mathbf{G}} - \varepsilon^0_{k \cdot \mathbf{G}} \right)^2 + 4U^2}{2} \]

(5.65)

At the Brillouin zone boundary where \( \varepsilon^0_{k \cdot \mathbf{G}} = \varepsilon^0_k - \mathbf{G} \),

\[ \varepsilon = \varepsilon_{\pm} = \varepsilon^0_{k \cdot \mathbf{G}} \pm 1U^2 \]

(5.66)

Subs. eqn. 5.66 into eqn. 5.62 and 5.63:

\[ \left\{ \begin{array}{ll} \pm \left| U^2 \right| C_{\mathbf{G}} - U^2 c_{k \cdot \mathbf{G}} = 0 \\ -U^2 c_{k \cdot \mathbf{G}} \pm \left| U^2 \right| C_{\mathbf{G}} = 0 \end{array} \right. \quad \text{for} \quad \varepsilon = \varepsilon_{\pm} \]

(5.67)

We consider the case where \( U(r) \) is attractive such that \( U_G < 0 \). Equation (5.67) becomes:
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Note that \( \frac{d\epsilon}{dk} \) along the direction of \( G \) is zero at the BZ boundary. That means \( \nabla_k \epsilon \cdot k \) at the BZ boundary \( k = G/2 \) is zero, or \( \nabla_k \epsilon \) is perpendicular to \( G \) there.

Let's now consider a 2-dimensional rectangular lattice, where \( a_y = a' < a_x = a \) as shown at right. The energy contour for \( \epsilon = A(\hbar^2/2m)(\pi/a)^2 \), where \( 1 < A < (a/a')^2 \), is shown in the left panel of Fig. 5.4 below. The right panel shows the energy dispersion \( \epsilon(k) \) along the [10] direction. (Figure credit: NPO).

As the derivation of eqn. (5.66) is general, the effect of a small perturbation from a weak periodic potential, \( U(r) \), is to produce a splitting in \( \epsilon(k) \) at a Brillouin zone boundary. For a BZ boundary at \( G/2 \), the amount of splitting is \( 2|U_G| \) (see Fig. 5.4). Hence, if any particular \( U_G \) vanishes due to the structure of the Bravais lattice, energy curves \( \epsilon(k) \) crossing the BZ boundary along \( G \) will not suffer any splitting.
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Fig. 5.4. The two arrows drawn at the BZ boundary indicates the direction of the electron velocity at the respective points on the BZ boundary.

Fig. 5.5. Perspective sketch of the energy $\varepsilon_k$ vs. $k_x$ and $k_y$. The intersection of $\varepsilon_k$ with the Bragg planes $k_x = \pm \pi/a$ results in energy gaps and slight flaring of the energy surface. The unperturbed surface (paraboloid) is shown by the faint curve. At the Bragg planes, the group velocity $v_g \sim \nabla \varepsilon_k$ is parallel to the Bragg planes. The energy gaps lead to discontinuities of the energy surface. The contour in the left panel of Fig. 3 is the projection of a horizontal section of the surface on the $k_x-k_y$ plane. The dispersion curve in the right panel of Fig. 3 is a vertical section of the energy surface at the plane $k_y=0$.

Figure credit: NPO
Other zone schemes (z.s.): We have discussed the reduced z.s. There are also other common z.s. such as the extended z.s. and repeated z.s. The figure below illustrates how various z.s. are constructed and related.

The physical motivation for the extended zone scheme is that, when an electron in an applied E or B field reaches a Bragg plane (at k, say), an Umklap scattering process takes it to \( k - G \). If we strictly restrict our view to the first BZ (i.e., the reduced z.s.), the U scattering causes a large discontinuity in the electron trajectory in the k space. But in the repeated z.s., the trajectory continues smoothly into the next replica as shown at right in the extended z.s. for the 2D rectangular lattice discussed above. The advantage of working in the repeated z.s. becomes apparent when we consider the equation of motion in the next chapter.
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**Quasi-1-D behavior:** In the above example, the Bragg planes normal to \( b_x \) are brought close together by the assumption \( a_x \gg a_y \). If \( \varepsilon_F \) lies within the gap between the side pockets in the 2\(^{\text{nd}}\) BZ, all the occupied states are in the first BZ, leaving the 2\(^{\text{nd}}\) BZ unoccupied. In the repeated z.s., the Fermi surface (FS) consists of two sinusoidal curves (Fig. 5.7). Because the group velocities on the FS (arrows) are predominantly parallel to \( k_y \), the conductivity along the y-axis is much larger than that along the x-axis. By simply arranging for the ions to be closer along the y-axis, we attain quasi-1D electronic behavior even though the starting SE is fully isotropic. Such FS are found in the organic conductor (TMTSF)\(_2\)PF\(_6\), a member of the Bechgaard Salts.

**5.4 Fermi Surface**

As in the Sommerfeld theory, the electron ground state (i.e the \( T = 0 \) state) of the Bloch electrons is obtained by progressively filling the lowest available (i.e. unoccupied) energy level until all the electrons are filled. With this procedure, two kinds of configurations may result: (1) The uppermost populated energy band \( n \) is completely filled. (2) The uppermost populated energy band \( n \) is partially filled. Since each energy level \( \varepsilon_n(k) \) can accommodate two electrons (each of spin \(+1/2\) or \(-1/2\)), and there are \( N \) \( k \)-states in each band (where \( N \) is the number of primitive unit cells), an energy band can accommodate up to \( 2N \) electrons. Therefore, a completely filled uppermost band can occur only if the number of electrons per primitive cell is even. If configuration (1) occurs, there will be an energy gap between the highest occupied band (the *valence band*) and the lowest
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unoccupied band (the conduction band). A large energy gap (such as several eV), that is much bigger than \( k_B T_{\text{room}} \) results in the solid behaving like an insulator. On the other hand, a small energy gap (\(< \sim 1 \text{ eV}\)) results in the behavior of an intrinsic semiconductor. In case (2) where the uppermost populated energy band is partially filled, a constant energy surface in \( k \)-space can be defined whereat the energy equals that of the highest energy level occupied. This surface serves as the Fermi surface of the Bloch electrons. Note that in the case where the uppermost band is completely filled, such definition of the Fermi surface as the dividing surface between occupied and unoccupied states become ill-defined since it can be anywhere within the energy gap. In this case, the chemical potential is often employed to define the Fermi level, which can be shown, for intrinsic semiconductors, to be near the middle of the band gap.

5.4.1 Fermi Surface in the Extended and Reduced Zone Scheme

For metals with valence > 1, the Fermi surface often lies outside the 1st BZ, and intercepts several other BZ’s of higher order. Below we shall discuss how the different “pieces” of the Fermi surface within each BZ of the same (higher) order can be reconstructed back into the 1st BZ. In essence, the procedure reconstructs the Fermi surface in the reduced zone scheme. We shall discuss how presenting the Fermi surface in various zone schemes may give better insight to the energy band structure, and transport properties of the metal.

We first discuss how the higher order BZ’s are defined. Like the 1st BZ, they are also defined by first drawing perpendicular bisectors to the lines joining any two points in the reciprocal lattice. The \( n \)th BZ is the region containing points that can be reached from the origin by crossing \((n - 1)\) perpendicular bisectors, but no fewer. Fig. 5.8 illustrates how this definition applies to a 2D square lattice.

As one can see, the boundary of the \( n \)th BZ gets progressively more complex as \( n \) increases. Nonetheless, various pieces of a BZ of order \( n \) can be reconstructed into the 1st BZ through translations by a set of suitably chosen reciprocal lattice vectors. Figs. 5.9 - 5.13 show examples of how a Fermi surface may be reconstructed for various lattices.
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Fig. 5.9 (Kittel) Brillouin zones of a square lattice in two dimensions. The circle shown is a surface of constant energy for free electrons; it will be the Fermi surface for some particular value of the electron concentration. The total area of the filled region in $k$ space depends only on electron concentration and is independent of the interaction of electrons with the lattice. The shape of the Fermi surface depends on lattice interaction, and the shape will not be an exact circle in actual lattice. The labels within the sections of the second and third zones refer to Fig. 5.8.

Fig. 5.10 (Kittel) Mapping of the first, second, and third Brillouin zones in the reduced zone scheme. Sections of the second zone in Fig. 5.7 are put together into a square by translation through appropriate reciprocal lattice vector. A different $G$ is needed for each piece of a zone.

Fig. 5.11 (Kittel) The free electron Fermi surface of Fig. 5.7, as viewed in the reduced zone scheme. Shaded areas represent occupied electron states. Parts of the Fermi surface fall in the second, third, and fourth zones. The fourth zone is not shown. The first zone is entirely occupied.
**5.4.2 Hole Pockets (based on NPO)**

Consider the square lattice and assume that we have a population of $2N$ electrons (two valence electrons per ion) to occupy the $1^{\text{st}}$ and $2^{\text{nd}}$ BZ as shown in Fig. 5.8. If $U(r)$ is absent, the (unperturbed) Fermi surface is a circle whose area $A$ equals that of the $1^{\text{st}}$ BZ ($A$ contains $N_k$ states). This is plotted as a faint circle in the left panel of Fig. 5.14 (credit to NPO). The perturbed FS (bold arcs) shows discontinuities reflecting the energy gap at each intersection with Bragg planes. As shown, occupied states spill into the $2^{\text{nd}}$ BZ while an equal number of unoccupied states remain at the corners of the $1^{\text{st}}$ BZ. By translating the triangular segments by some $\mathbf{G}$, we may rearrange the $2^{\text{nd}}$ BZ patches so
that the FS re-assemble into two elliptical volumes (upper right panel). Because the group velocities point outwards, the lowest energy state in the 2nd BZ is at the center of each elliptical volume. Similarly, we may rearrange the patches in the 1st BZ to get a nominally circular FS in the 1st BZ. In this pocket, the group velocity points inwards, indicating that the \( k \) state with the highest energy within the 1st BZ is at the center of the hold pocket. The volume encloses an “air bubble” of unoccupied states trapped in the 1st BZ.

In the excitation picture, we focus on the small pockets in the 2nd BZ and the vacant states in the 1st BZ, and ignore the remaining \( \sim N \) occupied \( k \) states. We identify each unoccupied state \( k \) in the bubble as a hole excitation, whose properties we shall discuss shortly.

At the start, we had a population of \( 2N \) potentially itinerant electrons. However, because the unperturbed FS embraces almost the entire 1st BZ, most of these electrons are actually precluded from responding to an applied E and/or H field by Pauli’s Exclusion Principle. What remain are a small electron minority occupying states in the 2nd BZ and an equal no. of vacant states in the 1st BZ.

Fig. 5.14 (Left figure) The Fermi Surface (bold lines) in the 2D lattice assuming each ion contributes 2 itinerant electrons, in the extended zone scheme. At the intersection with a Bragg plane, the FS folds in to meet the plane perpendicularly (the unperturbed FS is the faint circle). (Right upper figure) The two elliptical electron Fermi Surfaces in the 2nd BZ in the repeated zone scheme, obtained by translating triangular patches of the left figure by an appropriate \( G \). The lower figure shows the single hole pocket in the 1st BZ. Arrows indicate the group velocity \( \mathbf{v}_g \sim \nabla \epsilon_k \).