spectrum of electron eigenstates in the crystal (known as the band structure). The electron density n, which is actually *not* very well defined in the Drude model, becomes a well-defined quantity that is either the density of electrons in the so-called conduction band, or the density of holes in the so-called valence band. And even the universal constant e requires re-interpretation in the latter case; the holes behave like positively charged particles. While such a sign change does not affect the Drude formula because it involves e^2, the Hall resistivity *is* sensitive to this sign change, as discussed above. Perhaps most fundamentally, the correct quantum-mechanical theory is capable of predicting when a crystal is actually an *insulator* (which many materials are) that has zero conductivity at $T = 0$. This corresponds to having $n = 0$ in the Drude formula, but the Drude theory is not able to explain when and why this happens.

We now start our development of this quantum-mechanical theory of electron motion in a periodic crystal.

Exercise 7.3. Assume the probability that an electron experiences a collision between time t and $t + dt$ is dt/τ. (i) Let t_c be the time between two subsequent collisions. Show that the probability distribution function for t_c is $p(t_c) = (1/\tau)e^{-t_c/\tau}$. (ii) Calculate $\langle t_c \rangle$ and $\langle t_c^2 \rangle$. (iii) Let n be the number of collisions experienced by the electron in a time interval of length t (say, between t' and $t' + t$). Show that the probability distribution for n is the Poisson distribution $P(n) = e^{-\overline{n}}\overline{n}^n/n!$, where $\overline{n}$ is its average. Find the value of $\overline{n}$.

7.2 Independent Electron Model

We will be interested in solving the Schrödinger equation for electrons in a condensed matter system with some fixed set of positions of the nuclei. In particular, when the system is in the crystalline state the nuclei are located on lattice sites $\{\vec{R}_I\}$. Neglecting for the moment the spin degree of freedom of the electrons, the Schrödinger equation for the nth eigenfunction is

$$\mathcal{H}\Phi_n(\vec{r}_1, \ldots, \vec{r}_N) = E_n \Phi_n(\vec{r}_1, \ldots, \vec{r}_N), \tag{7.25}$$

where the Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{N} \left(\frac{-\hbar^2 \nabla_i^2}{2m_e} - \sum_I \frac{e^2 Z}{|\vec{r}_i - \vec{R}_I|} \right) + \frac{1}{2} \sum_{i \neq j}^{N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}. \tag{7.26}$$

The presence of the (last) electron–electron Coulomb interaction term couples the degrees of freedom of different electrons and makes this many-body Schrödinger equation difficult to solve. Fortunately, it is frequently (but not always!) a good approximation to replace $\mathcal{H}$ by an effective independent-particle Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} H_i = \sum_{i=1}^{N} \left(\frac{-\hbar^2 \nabla_i^2}{2m_e} + v_{\text{eff}}(\vec{r}_i) \right). \tag{7.27}$$

There are (at least) two different approaches leading to effective independent-particle Hamiltonians of this form. We will discuss these approaches and their limitations in Chapter 15. It is clear that $v_{\text{eff}}(\vec{r})$ is some sort of effective potential which includes the interaction of an electron with the nuclei and represents in some average way the interaction of an electron with all other electrons. The most naive approximation to a condensed matter system is one where $v_{\text{eff}}(\vec{r})$ is replaced by a constant, which we can take to be the zero of energy. This leaves us with the so-called free-electron-gas model. In this model the single-particle states are plane waves, which can be labeled by a wave vector,

$$\langle \vec{r}\,|\vec{k}\rangle = \frac{1}{\sqrt{L^3}} \exp{(i\vec{k}\cdot\vec{r})}, \tag{7.28}$$

where L^3 is the normalization volume. These plane waves have eigenenergy

$$\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m_{\mathrm{e}}} \tag{7.29}$$

and are eigenstates of the velocity operator

$$\vec{V} = \frac{d\vec{r}}{dt} = \frac{i}{\hbar}[H,\vec{r}] = \frac{i}{2m_{\mathrm{e}}\hbar}[\vec{p}\cdot\vec{p},\vec{r}] = \frac{i}{m_{\mathrm{e}}\hbar}\vec{p}(-i\hbar) = \frac{\vec{p}}{m_{\mathrm{e}}} = \frac{-i\hbar\nabla}{m_{\mathrm{e}}} \tag{7.30}$$

with eigenvalue $\hbar\vec{k}/m_{\mathrm{e}}$. Because the velocity is a constant of motion, the electrical resistance is strictly zero, since a current does not decay in the free-electron model.

The next-simplest model (and one which we will now study extensively), sometimes called the independent-particle model, uses

$$v_{\mathrm{eff}}(\vec{r}) = V(\vec{r}), \tag{7.31}$$

where V is a periodic potential with the symmetries of the crystalline lattice:

$$V(\vec{r}+\vec{R}_j) = V(\vec{r}), \tag{7.32}$$

where $\vec{R}_j$ is a lattice vector of the crystal. Amazingly, as we will see shortly, one is able to make many concrete statements about the electronic structure that are based on this symmetry property *alone*, without additional information on the detailed form of $V(\vec{r})$. Recall that in Drude's classical model it was scattering from the periodic potential that produced a very short mean free path (on the order of the lattice spacing) and hence was responsible for the finite electrical resistance. We now need to learn how to solve this problem quantum mechanically. We will find from a powerful result known as **Bloch's theorem** that quantum coherence makes the mean free path infinite. Hence the electrical resistance is actually zero in this model for metals with perfectly ordered crystalline lattices. In the end, we will find that Drude's transport formulas are still very useful, provided that we compute the scattering time τ (due to impurities or phonons which disturb the perfect crystalline order) quantum mechanically rather than classically.

7.3 Bloch's Theorem

Bloch's theorem is a powerful tool in the study of *independent* electrons moving in a periodic potential. It is of such importance that electrons moving in a periodic potential are often referred to as "Bloch electrons." We learned in our study of elastic X-ray and neutron scattering that the periodicity of the structure enforces a conservation law,

$$\Delta\vec{k} = \vec{G}, \tag{7.33}$$

where $\Delta\vec{k}$ is the change of wave vector of the probe particle and $\vec{G}$ is an element of the reciprocal lattice. We frequently treat X-ray and neutron scattering in the Born approximation, but we cannot do this for low-energy electrons because the potential is too strong. There is a lot of multiple scattering and, as we shall see, a special sort of coherence develops, which effectively gives the electrons an infinite mean free path in a perfect crystal, a situation which is quite impossible classically.

Let us begin by finding the solutions to the Schrödinger equation for a single particle in a periodic potential with Hamiltonian

$$H = \frac{\vec{p}^{\,2}}{2m} + V(\vec{r}). \tag{7.34}$$

Now $V(\vec{r}\,)$ (and hence H) has the translation symmetry of the lattice:

$$V(\vec{r}+\vec{a}_j) = V(\vec{r}), \tag{7.35}$$

where $\vec{a}_j$ is one of the primitive vectors of the lattice. For example, V might be a sum of atomic potentials

$$V(\vec{r}\,) = \sum_{\{\vec{R}_j\}} v(\vec{r}-\vec{R}_j), \tag{7.36}$$

where $\vec{R}_j$ is a lattice site. In general (because of chemical bonding and other effects), v will *not* be identical to the free-atom potential; this is just an example that has the right translation symmetry.

We would like to take advantage of the lattice translation symmetry, Eq. (7.35), in the solution of H. Let us start with the simplest possible case, $V(\vec{r}\,) =$ constant. In this case H is invariant under *any* translation. Formally, this is the consequence of the fact that in this case

$$[H, T_{\vec{l}}\,] = 0 \tag{7.37}$$

for any vector $\vec{l}$, where

$$T_{\vec{l}} = e^{i\vec{p}\cdot\vec{l}/\hbar} \tag{7.38}$$

is the (unitary) translation operator (see Exercise 7.4) that translates the system by $\vec{l}$. This can be seen from how $T_{\vec{l}}$ transforms a wave function,

$$T_{\vec{l}}\,\psi(\vec{r}\,) = \psi(\vec{r}+\vec{l}), \tag{7.39}$$

and how it transforms an operator,

$$T_{\vec{l}} F(\vec{r}, \vec{p}) T_{\vec{l}}^{\dagger} = T_{\vec{l}} F(\vec{r}, \vec{p}) T_{-\vec{l}} = F(\vec{r}+\vec{l}, \vec{p}). \tag{7.40}$$

Exercise 7.4. Prove Eq. (7.39) by expanding the exponential in $T_{\vec{l}}$ in a power series and comparing the Taylor-series expansion of the RHS of (7.39).

Since $\vec{l}$ is arbitrary in Eq. (7.37), we must have

$$[H, \vec{p}\,] = 0, \tag{7.41}$$

namely H commutes with *every* component of $\vec{p}$, which are the *generators* of translation. Because different components of $\vec{p}$ commute with each other, eigenstates of H may be *chosen* to be eigenstates of $\vec{p}$, which are plane waves. They are also eigenstates of any $T_{\vec{l}}$, which also commute among themselves.

Box 7.2. Symmetries in Quantum Mechanics

A quantum system is said to have a certain symmetry (translation, rotation, spatial inversion, particle–hole, gauge, time-reversal, etc.) if carrying out the symmetry operation leaves the Hamiltonian H invariant. Most symmetry operations (time-reversal being one exception, see Section 7.8) are effected via unitary transformations obeying $UHU^{\dagger} = H$. Just because the Hamiltonian is left invariant by the transformation does *not* mean that its eigenstates are invariant. For example, the free-particle Hamiltonian is invariant under translation by an arbitrary distance, but its plane-wave eigenstates are *not*. Under translation $\vec{r} \to \vec{r}+\vec{a}$, the wave function gets multiplied by a phase,

$$e^{i\vec{k}\cdot\vec{r}} \to e^{i\vec{k}\cdot\vec{a}} e^{i\vec{k}\cdot\vec{r}}. \tag{7.42}$$

This is a characteristic feature of symmetries in quantum mechanics. As another example, consider reflection (spatial inversion) symmetry $PxP^\dagger = -x$ in a 1D problem. Because $P^2 = I$, $PP^\dagger = I$ implies $P^\dagger = P$. If the potential has even parity, $PV(x)P = V(x)$, then $[H, P] = 0$, and H and P can be simultaneously diagonalized. Because $P^2 = I$, the simultaneous eigenstates must obey $P|\psi\rangle = \pm|\psi\rangle$. Thus we see in the case of this discrete symmetry that the phase in the factor multiplying the transformed wave function can only be 0 or π.

The group theory of symmetries in quantum mechanics is a vast topic and the reader is referred to the many existing books devoted specifically to the topic. See, for example, Ref. [32].

When $V(\vec{r}\,)$ is not a constant, we no longer have Eq. (7.41), and Eq. (7.37) is not true for general $\vec{l}$. However, with Eq. (7.35) we have

$$[H, T_j] = 0, \tag{7.43}$$

where

$$T_j = T_{\vec{a}_j} \tag{7.44}$$

is one of the primitive translation operators. Furthermore, the translation operators all commute with each other:[7] $[T_j, T_k] = 0$ for all j, k. Hence H and $\{T_j\}$ can all be simultaneously diagonalized. That is, we can choose our energy eigenstates ψ to be eigenstates of $\{T_j\}$:

$$\begin{aligned} T_j\,\psi &= \lambda_j \psi; \\ \psi(\vec{r} + \vec{a}_j) &= \lambda_j \psi(\vec{r}\,); \\ \psi(\vec{r} + n\vec{a}_j) &= T_j^n \psi = \lambda_j^n \psi. \end{aligned} \tag{7.45}$$

If we now invoke periodic boundary conditions

$$\psi(\vec{r} + M\vec{a}_j) = \psi(\vec{r}\,), \tag{7.46}$$

where M is a large integer, then we must have

$$\lambda_j^M = 1. \tag{7.47}$$

This means that

$$\lambda_j = e^{i\vec{k}\cdot\vec{a}_j}, \tag{7.48}$$

where $\vec{k}$ is one of the usual wave vectors allowed in a periodic system,

$$\vec{k} = \frac{\vec{G}}{M}, \tag{7.49}$$

and $\vec{G}$ is a member of the reciprocal lattice. The reader should verify that Eq. (7.47) is satisfied.

It follows that the most general solution of the periodic Schrödinger equation is

$$\psi_{\vec{k}}(\vec{r}\,) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}\,), \tag{7.50}$$

where $u_{\vec{k}}(\vec{r}\,)$ is a periodic function having the translation symmetry of the lattice:

$$u_{\vec{k}}(\vec{r} + \vec{a}_j) = u_{\vec{k}}(\vec{r}\,), \qquad j = 1, 2, 3. \tag{7.51}$$

It is straightforward to see that Eq. (7.50) is the most general form consistent with Eqs. (7.45) and (7.48). This is known as **Bloch's theorem**.

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[7] Complications arise if a magnetic field is present and the appropriately generalized *magnetic* translation operators do not necessarily commute. This will be discussed in Chapter 12.

The simplest example we could have is the case

$$u_{\vec{k}}(\vec{r}\,) = 1; \tag{7.52}$$

$$\psi_{\vec{k}}(\vec{r}\,) = e^{i\vec{k}\cdot\vec{r}}. \tag{7.53}$$

This, of course, is the answer for the case $V = \text{constant}$. This "empty lattice" model is often a useful check on one's calculations.

For the more general case, we can draw on our experience from Chapter 3 in writing functions with the periodicity of the lattice using the reciprocal lattice vectors:

$$u_{\vec{k}}(\vec{r}\,) = \sum_{\{\vec{G}\}} a_{\vec{G}}(\vec{k}\,)e^{i\vec{G}\cdot\vec{r}}. \tag{7.54}$$

Thus Bloch's theorem tells us that the general solution is of the form

$$\psi_{\vec{k}}(\vec{r}\,) = \sum_{\{\vec{G}\}} a_{\vec{G}}(\vec{k}\,)e^{i(\vec{k}+\vec{G})\cdot\vec{r}}. \tag{7.55}$$

This should look familiar from our earlier discussion of conservation of crystal momentum, and it is clear that $\hbar\vec{k}$, being a good quantum number and thus a conserved quantity, is the electron's *crystal* momentum. The electron originally at $\vec{k}$ keeps getting scattered so that its momentum is uncertain modulo the $\vec{G}$ vectors. As with X-ray photons or neutrons propagating in a crystal, it is tempting to view $\hbar\vec{k}$ as the electron momentum, but it is *not*, as the above argument makes clear. However, it turns out that we can often ignore the distinction between momentum and crystal momentum, as we shall see later. In particular, as we will discuss in Chapter 8, it is possible to make wave packets out of Bloch waves, and their group velocity is given by the usual expression (see Section 7.3.3 for the derivation)

$$\vec{v}_{\vec{k}} = \frac{1}{\hbar}\nabla_{\vec{k}}\epsilon(\vec{k}\,). \tag{7.56}$$

These packets travel coherently through the lattice and, if there is no disorder, the mean free path will be infinite. This is in stark contrast to the results of the classical Drude picture, where the electrons scatter chaotically off each of the ions and have a very short mean free path.

Without loss of generality, we can restrict the wave vector $\vec{k}$ to the first Brillouin zone. To see this, write

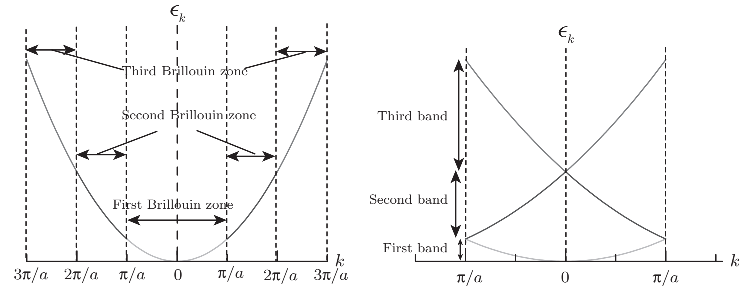
$$\psi_{\vec{k}}(\vec{r}\,) = \sum_{\{\vec{G}\}} b_{\vec{G}}(\vec{k}\,)e^{i(\vec{k}+\vec{G}\,'+\vec{G})\cdot\vec{r}}, \tag{7.57}$$

where $b_{\vec{G}}(\vec{k}\,) \equiv a_{\vec{G}+\vec{G}\,'}(\vec{k}\,)$. Now we can always choose $\vec{G}\,'$ so that $\vec{k}\,' \equiv \vec{k} + \vec{G}\,'$ lies in the first Brillouin zone. Thus we can always write the wave functions in the form

$$\psi_{n\vec{k}\,'}(\vec{r}\,) = e^{i\vec{k}\,'\cdot\vec{r}}u_{n\vec{k}\,'}(\vec{r}\,), \tag{7.58}$$

where $\vec{k}\,'$ is restricted to the first Brillouin zone, and use the integer label n, known as the band index, to make up for this restriction.

It turns out that Eq. (7.58) is the most general form for the eigenfunctions of a periodic potential. It tells us that the energy eigenstates are labeled by a lattice wave vector $\vec{k}$ defined within the first Brillouin zone, and an integer-valued band index n. The situation is similar to that for the eigenstates of a central potential, which are labeled by three integer-valued quantum numbers, nlm. There the presence of the angular momentum quantum numbers l and m is guaranteed by *rotation* symmetry, similarly to how the $\vec{k}$ quantum number here is guaranteed by the lattice translation symmetry; these quantum numbers dictate which representation of the symmetry group the eigenstate(s) form. However, these symmetry quantum numbers do not uniquely determine the state (except in very special



(a) (b)

Figure 7.1 Electron dispersion of a 1D empty lattice, in the extended-zone scheme (a) and in the reduced-zone scheme (b).

cases); in general one needs an additional energy quantum number n. (In atoms n is known as the "principal" quantum number. In solids it is the band index.) Eigenstates that differ *only* in n have the same symmetry properties, but different energies.

As an illustrative example, let us consider a 1D empty lattice model. We assume a lattice constant a, but take the periodic potential to vanish. The eigenfunctions are, of course,

$$\psi_k(x) = e^{ikx}, \tag{7.59}$$

with eigenvalue $\epsilon_k \equiv \hbar^2 k^2/2m$. Unlike the case of phonons, it is meaningful for electron de Broglie waves to have wave vectors outside the first Brillouin zone. In the so-called "extended zone" scheme we simply plot the energy in the usual way, as shown in Fig. 7.1(a).

In the so-called "reduced-zone" scheme we map all wave vectors back into the first Brillouin zone by shifting them by integer multiples of $G_1 = 2\pi/a$, resulting in the energy-band diagram shown in Fig. 7.1(b). The energies of the various bands are given by:

$$\epsilon_{0k} = \frac{\hbar^2}{2m}k^2; \tag{7.60}$$

$$\epsilon_{1k} = \frac{\hbar^2}{2m}\left[k - \mathrm{sgn}(k)G_1\right]^2; \tag{7.61}$$

$$\epsilon_{nk} = \frac{\hbar^2}{2m}\left[k - \mathrm{sgn}(k)nG_1\right]^2. \tag{7.62}$$

Except for the fact that there are an infinite number of bands, this empty lattice band structure is reminiscent of the phonon dispersion curves we studied for the uniform lattice, where we chose an artificially doubled unit cell which hid some of the translation symmetry. (Recall Fig. 5.4.) In both cases there are degeneracies between different bands at the zone boundary or zone center because of the extra translation symmetry. We saw for the phonons that, if this symmetry is removed by choosing alternating masses and/or spring constants, the degeneracy is lifted. We will see shortly that, if the electrons see a periodic potential rather than an empty lattice, their degeneracies are also lifted.

Knowing the general form of the solution for Bloch waves from Eq. (7.58) and using

$$\vec{p}\,\psi_{n\vec{k}} = e^{i\vec{k}\cdot\vec{r}}\left(\vec{p} + \hbar\vec{k}\right)u_{n\vec{k}}, \tag{7.63}$$

the Schrödinger equation can be rewritten as

$$h_{\vec{k}}u_{n\vec{k}}(\vec{r}\,) = \epsilon_{n\vec{k}}u_{n\vec{k}}(\vec{r}\,), \tag{7.64}$$

where

$$h_{\vec{k}} \equiv \frac{1}{2m}\left(\vec{p} + \hbar\vec{k}\right)^2 + V(\vec{r}\,). \tag{7.65}$$

Now notice that the equation need only be solved within a single unit cell because of the periodicity of $u_{n\vec{k}}$. This vast simplification makes clear the true power of Bloch's theorem. We know on general grounds that for a given $\vec{k}$ the solutions will be *discrete* (labeled by n) because of the finite size of the unit cell. We have essentially reduced the problem to a particle in a box.[8]

Let us return to our 1D empty-lattice example. The Schrödinger equation reduces to

$$\frac{1}{2m}(p + \hbar k)^2 u_{nk}(x) = \epsilon_{nk} u_{nk}(x), \tag{7.66}$$

with periodic boundary condition

$$u_{nk}\left(-\frac{a}{2}\right) = u_{nk}\left(+\frac{a}{2}\right); \qquad u'_{nk}\left(-\frac{a}{2}\right) = u'_{nk}\left(+\frac{a}{2}\right). \tag{7.67}$$

Choosing

$$u_{nk}(x) = \sqrt{\frac{1}{a}}e^{-inG_1 \operatorname{sgn}(k) x} \tag{7.68}$$

satisfies the boundary condition and recovers our previous result. Note that the normalization corresponds to that of a unit cell. The factor $\operatorname{sgn}(k)$ is included purely for later convenience.

Let us now do a non-empty lattice. Consider the case of a weak periodic potential of the form

$$V(x) = v\cos(G_1 x) = \frac{v}{2}(e^{iG_1 x} + e^{-iG_1 x}). \tag{7.69}$$

Clearly this potential can scatter an electron at wave vector k to $k \pm G_1$. Of particular interest is the zone-boundary case $k_\pm = \pm\frac{1}{2}G_1$. The states ψ_{k_+} and ψ_{k_-} are degenerate but mixed by this perturbation:

$$\langle \psi_{k_+}|V|\psi_{k_-}\rangle = \frac{v}{2}. \tag{7.70}$$

States with $k = \pm\frac{3}{2}G_1$ are also mixed in, but they are far away in energy so we can ignore them if v is sufficiently small.

In the reduced-zone scheme

$$\psi_{k_+} = \psi_{n=0,k=+\frac{G_1}{2}}, \tag{7.71}$$

$$\psi_{k_-} = \psi_{n=1,k=+\frac{G_1}{2}}, \tag{7.72}$$

so the mixing is between states at the *same* k (note that ks that differ by G_1 are *equivalent*) but in *different* bands. Within degenerate perturbation theory we need to diagonalize the Hamiltonian in the degenerate subspace:

$$\begin{aligned}&\begin{pmatrix} \left\langle n=0, k=\frac{G_1}{2}|H|n=0, k=\frac{G_1}{2}\right\rangle & \left\langle n=0, k=\frac{G_1}{2}|H|n=1, k=\frac{G_1}{2}\right\rangle \\ \left\langle n=1, k=\frac{G_1}{2}|H|n=0, k=\frac{G_1}{2}\right\rangle & \left\langle n=1, k=\frac{G_1}{2}|H|n=1, k=\frac{G_1}{2}\right\rangle \end{pmatrix} \\ &= \begin{pmatrix} \hbar^2 G_1^2/8m & v/2 \\ v/2 & \hbar^2 G_1^2/8m \end{pmatrix}. \end{aligned} \tag{7.73}$$

---

[8] This simplification is analogous to reducing a 3D Schrödinger equation to a 1D Schrödinger equation by using the rotation symmetry of a spherical potential.

This has eigenvalues $\epsilon_{\pm} = \hbar^2 G_1^2/8m \pm v/2$ corresponding to eigenvectors

$$\chi_{\pm} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}. \tag{7.74}$$

This means that the states are

$$|\psi_{\pm}\rangle = \frac{1}{\sqrt{2}} \left\{ \left| n = 0, k = \frac{G_1}{2} \right\rangle \pm \left| n = 1, k = \frac{G_1}{2} \right\rangle \right\}, \tag{7.75}$$

which yields (properly normalized in a unit cell)

$$\psi_+(x) = \sqrt{\frac{2}{a}} \cos\left(\frac{G_1 x}{2}\right), \tag{7.76}$$

$$\psi_-(x) = i \sqrt{\frac{2}{a}} \sin\left(\frac{G_1 x}{2}\right). \tag{7.77}$$

These are, of course, standing waves. As shown in Fig. 7.2, the antinodes of ψ_+ are at the peaks of the potential (if $v > 0$), and so the eigenvalue is positive. The antinodes of ψ_- are in the valleys, and so it has the lower energy. In the language of chemistry, we can think of these as "anti-bonding" and "bonding" orbitals (more on this later).

As a result of the lifting of the degeneracy, the band structure looks like that shown in Fig. 7.3. To explore this further, let us examine the energy levels slightly away from the zone boundary at

$$k = \frac{1}{2} G_1 - \delta k. \tag{7.78}$$

The unperturbed states are no longer exactly degenerate, but they are still close together, so it is appropriate to continue to use degenerate perturbation theory. The subspace Hamiltonian is now

$$h = \begin{pmatrix} (\hbar^2/2m)\,(G_1/2 - \delta k)^2 & v/2 \\ v/2 & (\hbar^2/2m)\,(-G_1/2 - \delta k)^2 \end{pmatrix}. \tag{7.79}$$

Diagonalization of this gives the energy dispersion of bands $n = 0$ and $n = 1$ near the zone boundary, as shown in Fig. 7.3.

The band gaps produced by the lattice potential can have a profound impact on the transport properties of a material. If the chemical potential lies in a band gap [i.e. all states in bands below the gap (known as valence bands) are filled at zero temperature and states in bands above the gap (known as conduction bands) are empty], then the system is an insulator at $T = 0$. The Pauli principle requires

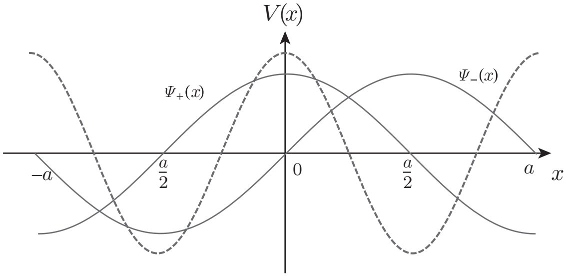


Figure 7.2 Degenerate perturbation solutions of wave functions with the wave vector at the zone boundary (ψ_+ and ψ_-, solid lines), in the presence of a cosine potential (dashed line).

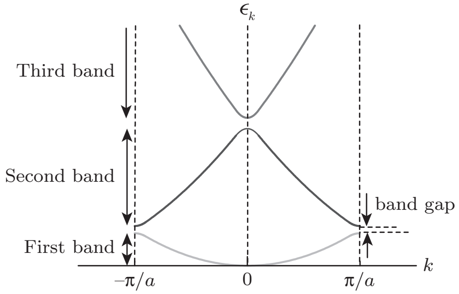


Figure 7.3 Band structure in the presence of a weak 1D periodic potential.

that an electron can absorb energy only by moving across the gap. Infinitesimal electric fields (at low frequencies) cannot accomplish this, and the system is effectively inert.[9]

As a result of these considerations, we are naturally led to ask how many electrons it takes to fill all the states in a band. In one dimension, we have (ignoring spin)

$$N_{\text{states}} = \int_{-\frac{G_1}{2}}^{+\frac{G_1}{2}} \left(\frac{L}{2\pi}\right) dk = \frac{L}{2\pi}\frac{2\pi}{a} = \frac{L}{a} = N_{\text{cells}}. \tag{7.80}$$

Thus the number of states in a single band is equal to the number of unit cells. In general dimensions

$$N_{\text{states}} = \left(\frac{L}{2\pi}\right)^d \int_{\text{BZ}} d^d\vec{k} = N_{\text{cells}}, \tag{7.81}$$

since the volume of the Brillouin zone is $(2\pi)^d/|\omega|$, where $|\omega|$ is the volume of the real-space unit cell. Thus the **density of states** is one per cell per band per spin.

Recall that the number of phonon states per polarization mode is also N_{cells}. The total number of modes (including polarizations) is, however, finite: d times the number of atoms per unit cell. We again emphasize that the electrons have an infinite number of bands going up to arbitrarily large energies.

In a Bravais lattice (one atom/cell) and taking into account the two spin states for electrons, it takes $2N_{\text{cells}} = 2N_{\text{atoms}}$ electrons to fill a band. Thus we have the following prediction of the independent-electron model: odd valence elements that form Bravais lattices are metals, because in this case one expects the highest band populated by electrons to be *half-filled*. The alkali element atoms all have odd valence and are all good metals. By the same argument, one would expect even-valence elements that form Bravais lattices to be insulators. Si, Ge, and C (diamond form) all satisfy this rule.[10] But there are many exceptions to this expectation, due to overlaps in band dispersions as illustrated in Fig. 7.4. In portions of the Brillouin zone the states in the nth band are actually higher in energy than states (in another part of the zone) in the $(n+1)$th band. As a result, electrons are transferred from band n to band $n+1$, leaving two partially filled bands. Zn is divalent, but is a good metal because of large interband transfer of electrons. Other examples of good metals formed by divalent elements include alkaline earth metals, formed by elements on the second column of the periodic table. When the band overlap is small, resulting in a low density of charge carriers, the system is known as a **semimetal**, and Bi is a good example of that.

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[9] We emphasize that all of this is still assuming the independent-electron model.

[10] In fact these elements do *not* form Bravais lattices. It is a straightforward exercise to show that the conclusion that these even-valence elements are insulators remains valid, regardless of the actual lattice structure.

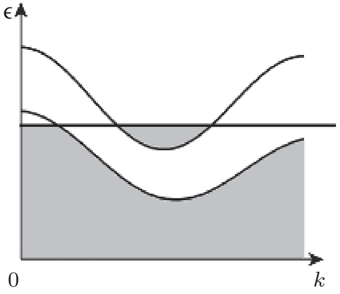

Figure 7.4 Schematic band structure of a semimetal, in which band dispersions overlap in energy, and the Fermi energy crosses more than one band. Shaded regions represent states fully occupied by electrons at zero temperature. The lower band has a small "hole pocket" that is unoccupied and the upper band has a small "electron pocket" that is occupied.

Box 7.3. Floquet Theory of Driven Systems

(N.B. $\hbar = 1$ in this discussion.)

We have learned from Bloch's theorem that the solution of the Schrödinger equation for electrons moving in a crystal is vastly simplified by recognizing the discrete translation symmetry of the spatially periodic crystal potential. **Floquet's theorem** gives an analogous result for Hamiltonians that are periodic in *time*. For example, periodic external magnetic field drives are frequently applied to quantum spin systems (see Chapter 17), and periodic laser fields and microwave fields are frequently applied to cold atoms in optical lattices (see Section 7.10). The purpose of these drives is to induce novel effective Hamiltonians (without excessively heating up the system). These effective Hamiltonians have the advantage that they are tunable *in situ* (by changing the drives), and they can place the system into different non-trivial topological phases of the types described in Chapter 13. For example, periodic drives have been successfully used to create strong pseudomagnetic fields seen by cold atoms in optical lattices, even though the atoms are charge neutral!

Suppose that a time-dependent Hamiltonian is invariant under discrete time translation by "distance" T

$$H(t+T) = H(t). \tag{7.82}$$

Then, by analogy with the quasi-momentum k in Bloch's theorem, we can define a quasi-energy ω such that the state evolution obeys

$$|\Psi(t+T)\rangle = e^{-i\omega T}|\Psi(t)\rangle, \quad |\Psi(t)\rangle = e^{-i\omega t}|u_{\omega,n}(t)\rangle, \tag{7.83}$$

where $-\pi/T \le \omega \le \pi/T$ lives in the first "Brillouin zone," and the periodic part of the state $|u_{\omega,n}(t)\rangle = |u_{\omega,n}(t+T)\rangle$ carries the quasi-energy label and a "band index," n, in analogy with Eq. (7.58).

Just as Bloch's theorem tells us that momentum is conserved modulo reciprocal lattice vectors $\vec{G}$, Floquet's theorem tells us that energy is conserved modulo $\Omega = 2\pi/T$. For the case of a single, sinusoidal driving term in the Hamiltonian, Ω is its frequency and the energy non-conservation comes from absorbing and emitting quanta of the drive frequency. For the case of multiple drive frequencies (which are rationally related), the "unit cell size," T, is determined by the shortest interval at which all the drives are back in phase with each other (after being in phase at some arbitrary time zero).

Another good example of a semimetal is graphene, where there are *no* overlapping bands at the Fermi energy, but the valence and conduction band are *degenerate* at special points in the Brillouin zone, as a result of which there is *no* band gap. We discuss the band structure of graphene in Section 7.5.

> **Exercise 7.5.** Consider an empty lattice ($V = 0$) in 2D, but pretend we have a square lattice with lattice constant a. Find the energy range over which the first and second bands overlap.

7.3.1 Band Gaps and Bragg Reflection

We have seen from our study of a periodic potential in 1D that scattering between two degenerate states can create a band gap. Let us now consider the general case in arbitrary dimension with a (weak) periodic potential,

$$V(\vec{r}\,) = \sum_{\{\vec{G}\}} V_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}. \tag{7.84}$$

This potential can scatter an electron from $\vec{k}$ to $(\vec{k} + \vec{G})$. These two unperturbed states will be degenerate, provided that

$$\frac{\hbar^2}{2m_e}|\vec{k}|^2 = \frac{\hbar^2}{2m_e}|\vec{k} + \vec{G}|^2. \tag{7.85}$$

This, however, is identical to the Laue condition for X-ray diffraction,

$$|\vec{k}| = |\vec{k} + \vec{G}|. \tag{7.86}$$

Hence we can use the Ewald construction just as before, and whenever $\vec{k}$ satisfies the Laue condition we can expect a band gap[11] (within the simple degenerate perturbation theory approximation we have been using).

Consider the wave vectors shown in Fig. 7.5. The dashed line is a Bragg plane which is the perpendicular bisector of $\vec{G}$. Any point on this plane defines a pair of vectors which satisfy the Laue condition. Hence we expect that a contour map of the energy-band dispersion $\epsilon_n(\vec{k}\,)$ in the extended-zone scheme to qualitatively resemble that shown in Fig. 7.6. The iso-energy contours bulge out toward the Bragg planes because the potential energy is negative in that region (for the $n = 0$ band) and must be compensated for by larger kinetic energy. The discontinuities at the Bragg planes are the origin of the band gaps. It is possible to prove that lines of constant energy intersect the Bragg planes at right angles, as the following construction will show.

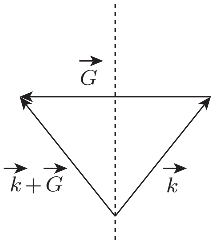

Figure 7.5 Illustration of the Laue condition, applied here to the scattering of electrons by the lattice potential.

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[11] This is even true for the propagation of X-rays in crystals, although the band gaps are typically very small. This is the subject of the so-called "dynamical diffraction theory." See Section 7.9 for related discussion.

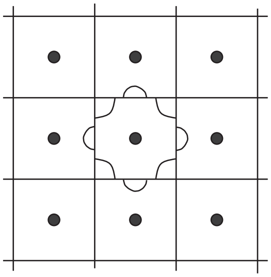


Figure 7.6 Equal-energy contours of Bloch bands, in the extended-zone scheme. The lines meet the Bragg planes at right angles and are generically discontinuous there.

In degenerate perturbation theory the wave function is of the form

$$\psi_{\vec{k}} = ae^{i\vec{k}\cdot\vec{r}} + be^{i(\vec{k}+\vec{G})\cdot\vec{r}}. \tag{7.87}$$

The 2 × 2 matrix form of the Schrödinger equation is

$$h\begin{pmatrix} a \\ b \end{pmatrix} = E\begin{pmatrix} a \\ b \end{pmatrix}, \tag{7.88}$$

where

$$h \equiv \begin{pmatrix} \epsilon_{\vec{k}} & V_{\vec{G}}^* \\ V_{\vec{G}} & \epsilon_{\vec{k}+\vec{G}} \end{pmatrix}. \tag{7.89}$$

The two eigenvalues are

$$E_{\pm} = \epsilon_{+} \pm \sqrt{\epsilon_{-}^2 + |V_{\vec{G}}|^2}, \tag{7.90}$$

where

$$\epsilon_{\pm} \equiv \frac{1}{2}(\epsilon_{\vec{k}} \pm \epsilon_{\vec{k}+\vec{G}}). \tag{7.91}$$

The gradient of the energy eigenvalue is

$$\nabla_{\vec{k}} E_{\pm} = \nabla_{\vec{k}}\epsilon_{+} \pm \left(\nabla_{\vec{k}}\epsilon_{-}\right) \frac{\epsilon_{-}}{\sqrt{\epsilon_{-}^2 + |V_{\vec{G}}|^2}}. \tag{7.92}$$

Using $\nabla_{\vec{k}}\,\epsilon_{+} = (\hbar^2/m_{\mathrm{e}})\left(\vec{k} + \frac{1}{2}\vec{G}\right)$ and the fact that $\epsilon_{-} = 0$ on the Bragg plane, we obtain

$$\nabla_{\vec{k}} E_{\pm} = \frac{\hbar^2}{m_{\mathrm{e}}}\left(\vec{k} + \frac{1}{2}\vec{G}\right). \tag{7.93}$$

As can be seen from Fig. 7.5, this gradient vector lies in the Bragg plane and hence has no component perpendicular to it. The constant-energy lines must therefore meet the plane at right angles.

7.3.2 Van Hove Singularities

The periodic potential distorts the energy dispersion away from its free-electron value. It is true on quite general grounds that these distortions inevitably lead to singularities in the electronic density of states known as **van Hove singularities**. We know that we can label all the states by $(\vec{k}, n)$, where $\vec{k}$ lies in the first Brillouin zone. We will find it convenient, however, to let $\vec{k}$ run outside the first zone. A 1D example is shown in Fig. 7.7. Then we can label the (redundant) solutions in such a way that $\epsilon_{n\vec{k}}$ is a smooth periodic bounded function in reciprocal space. It must therefore be the case that $\epsilon_{n\vec{k}}$ has smooth local maxima and minima within the first zone at which $\nabla_{\vec{k}}\epsilon_{n\vec{k}} = \vec{0}$. This topological fact

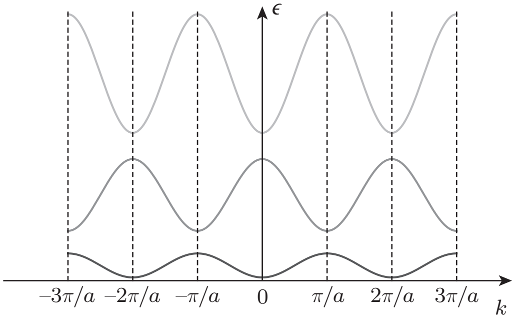


Figure 7.7 The 1D band structure plotted in the extended-zone scheme. Van Hove singularities are associated with extrema of the dispersion curves.

guarantees the existence of singularities in the density of states, since near each extremum there lies a large number of states with nearly the same energy.

Consider the (single-spin) density of states per unit volume for band n:

$$\rho_n(E) = \int_{\mathrm{BZ}} \frac{d^3\vec{k}}{(2\pi)^3}\delta(E - \epsilon_{n\vec{k}}). \tag{7.94}$$

Consider now the surface $S(E)$ in k space having $\epsilon_{n\vec{k}} = E$. We can define a local coordinate $\vec{k}_\perp$ perpendicular to this surface. The energy eigenvalue near the surface is given by

$$\epsilon_{n\vec{k}} = E + \vec{k}_\perp \cdot \nabla_{\vec{k}}\epsilon_{n\vec{k}}, \tag{7.95}$$

where the gradient is evaluated on the surface (i.e. at $\vec{k}_\perp = \vec{0}$). The density of states therefore is

$$\rho_n(E) = \int_{S(E)} \frac{dS}{(2\pi)^3} \int dk_\perp \, \delta(-\vec{k}_\perp \cdot \nabla_{\vec{k}}\epsilon_{n\vec{k}}). \tag{7.96}$$

Using the fact that the energy gradient is necessarily parallel to $\vec{k}_\perp$ we have

$$\rho_n(E) = \int_{S(E)} \frac{dS}{(2\pi)^3} \frac{1}{|\nabla_{\vec{k}}\epsilon_{n\vec{k}}|}, \tag{7.97}$$

which clearly shows that extrema in the energy will lead to singularities.

7.3.3 Velocity of Bloch Electrons

As another example of how band structure determines the physical properties of Bloch electrons, and that crystal momentum is *not* momentum, we consider the relation between the velocity of a Bloch electron and its crystal momentum $\vec{k}$, and prove Eq. (7.56). Our starting points are Eqs. (7.64) and (7.65). Treating $\vec{k}$ as a set of *parameters* of $h_{\vec{k}}$ and using the **Hellmann–Feynman theorem** (see Exercise 7.6), which states that

$$\frac{\partial E(\lambda)}{\partial \lambda} = \langle n(\lambda)|\frac{\partial H(\lambda)}{\partial \lambda}|n(\lambda)\rangle, \tag{7.98}$$

where $H(\lambda)$ is a λ-dependent Hamiltonian, $|n(\lambda)\rangle$ is one of its eigenstates and $E(\lambda)$ is the corresponding eigenvalue, we have

$$\begin{aligned}\frac{1}{\hbar}\nabla_{\vec{k}}\epsilon(\vec{k}) &= \frac{1}{\hbar}\langle u_{n\vec{k}}|\frac{\partial h_{\vec{k}}}{\partial \vec{k}}|u_{n\vec{k}}\rangle = \langle u_{n\vec{k}}|\frac{\vec{p}+\hbar\vec{k}}{m_{\mathrm{e}}}|u_{n\vec{k}}\rangle \\ &= \langle \psi_{n\vec{k}}|\frac{\vec{p}}{m_{\mathrm{e}}}|\psi_{n\vec{k}}\rangle;\end{aligned} \tag{7.99}$$

thus Eq. (7.56) follows. Note that here the lattice momentum $\vec{k}$ is viewed as a *parameter* that lives in the first Brillouin zone, which specifies a member in a *family* of Hamiltonians, $\{h_{\vec{k}}\}$, $\vec{k} \in$ 1BZ. This is a viewpoint we will take again and again in this book.

Exercise 7.6. Prove the Hellmann–Feynman theorem, Eq. (7.98). Hint: take advantage of the fact that the norm of the eigenfunction is fixed at unity, which implies that $(\partial/\partial\lambda)\langle n(\lambda)|n(\lambda)\rangle = 0$.

Exercise 7.7. A 1D lattice has lattice constant a and a band with energy dispersion

$$\epsilon_k = -t\cos(ka).$$

Find the density of states and identify the nature of the van Hove singularities.

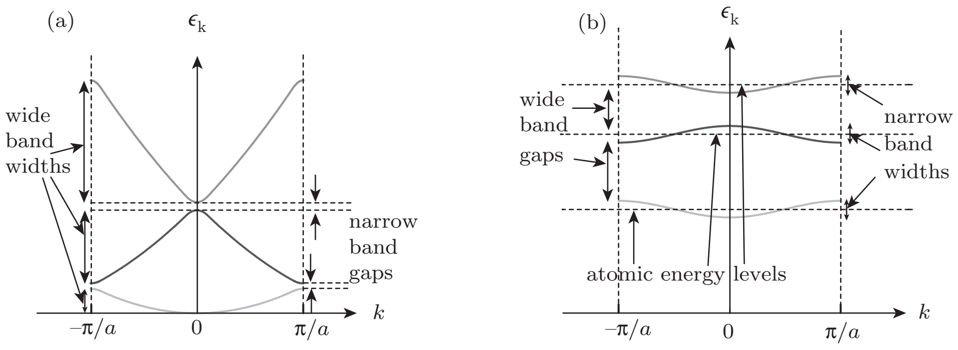
Exercise 7.8. Now consider the 2D version of Exercise 7.7, where the dispersion is $\epsilon_{\vec{k}} = -t(\cos(k_x a)+\cos(k_y a))$. Identify the energy where there is a van Hove singularity, and determine the leading energy dependence of the density of states near the van Hove singularity.

Exercise 7.9. Calculate the velocity of electrons with the band dispersion in Exercise 7.7, and identify the regions in momentum space where the velocity is parallel and anti-parallel to the momentum, respectively.

7.4 Tight-Binding Method

So far we have been studying nearly free electrons that are only weakly perturbed by a periodic potential. Generically we found broad bands separated by narrow gaps, as shown in Fig. 7.8(a). Now we will look at the opposite limit of strong periodic potentials which produce narrow bands separated by large gaps, as shown in Fig. 7.8(b).

One way to achieve this situation is to imagine a crystal made up of very widely separated atoms. To a good approximation, the atomic orbitals remain undistorted. The only change is that an electron in one atom has a small amplitude for tunneling to states on the neighboring atoms (see Appendix C



(a) (b)

Figure 7.8 Band structures with (a) large band widths and small band gaps, and (b) large band gaps and small band widths. The latter can often be well described using the tight-binding method, which starts from atomic electron levels.

for an introduction). This tunneling (also referred to as hopping in this context), as we shall soon see, broadens the sharp atomic energy levels into narrow bands.

To describe this type of band structure we will now introduce the so-called "**tight-binding model**." Let $|j\rangle$ be the relevant state on the jth atom having wave function

$$\langle \vec{r}\,|j\rangle \equiv \varphi_0(\vec{r} - \vec{R}_j) \tag{7.100}$$

centered on the atomic position $\vec{R}_j$. If we restrict our attention to this single orbital on each atom, then Bloch's theorem *uniquely* constrains the form of the eigenfunction in a Bravais lattice with lattice wave vector $\vec{q}$ to be

$$|\psi_{\vec{q}}\rangle \equiv \frac{1}{\sqrt{N}}\sum_{j=1}^{N} e^{i\vec{q}\cdot\vec{R}_j}|j\rangle. \tag{7.101}$$

To see why this is so, consider

$$\langle \vec{r}|\psi_{\vec{q}}\rangle \equiv \psi_{\vec{q}}(\vec{r}\,) = \frac{1}{\sqrt{N}}\sum_{j} e^{i\vec{q}\cdot\vec{R}_j}\varphi_0(\vec{r} - \vec{R}_j) \tag{7.102}$$

$$= e^{i\vec{q}\cdot\vec{r}}u_{\vec{q}}(\vec{r}\,), \tag{7.103}$$

where

$$u_{\vec{q}}(\vec{r}\,) \equiv \frac{1}{\sqrt{N}}\sum_{j=1}^{N} e^{-i\vec{q}\cdot(\vec{r}-\vec{R}_j)}\varphi_0(\vec{r} - \vec{R}_j). \tag{7.104}$$

Now clearly $u_{\vec{q}}(\vec{r} + \vec{a}) = u_{\vec{q}}(\vec{r}\,)$ for any lattice vector $\vec{a}$. Hence Bloch's theorem is satisfied. There is no other linear combination of these orbitals that satisfies the requirements of translation symmetry (with the same lattice wave vector). Hence, within the approximation of neglecting mixing between different atomic orbitals, there is only a single state for each $\vec{q}$, and it must be an energy eigenstate with eigenvalue (within this approximation) given by

$$\epsilon_{\vec{q}} = \frac{\langle\psi_{\vec{q}}|H|\psi_{\vec{q}}\rangle}{\langle\psi_{\vec{q}}|\psi_{\vec{q}}\rangle}. \tag{7.105}$$

Let us first evaluate the denominator in this expression. Recall that for a single atom (in the independent-electron approximation) each atomic orbital $\varphi_n(\vec{r} - \vec{R}_j)$ is orthogonal to the others:

$$\int d^3\vec{r}\;\varphi_n^*(\vec{r} - \vec{R}_j)\varphi_m(\vec{r} - \vec{R}_j) = \delta_{nm}, \tag{7.106}$$

because they are all eigenstates of a Hermitian Hamiltonian operator, each with a different eigenvalue (ignoring degeneracies). This does *not* imply, however, that orbitals on *different* atoms are orthogonal. In particular,

$$\langle j|j'\rangle \equiv \int d^3\vec{r}\;\varphi_0^*(\vec{r} - \vec{R}_j)\varphi_0(\vec{r} - \vec{R}_{j'}) \tag{7.107}$$

is generically non-zero (though of course exponentially small if the atoms are widely separated). Thus the Bloch states are not normalized to unity:

$$\langle\psi_{\vec{q}}|\psi_{\vec{q}}\rangle = \frac{1}{N}\sum_{j,\ell} e^{-i\vec{q}\cdot(\vec{R}_j-\vec{R}_\ell)}\langle j|\ell\rangle$$

$$= \sum_{\ell} e^{i\vec{q}\cdot\vec{R}_\ell}\langle j = 0|\ell\rangle \equiv \eta(\vec{q}\,). \tag{7.108}$$

Despite the non-orthogonality of the atomic orbitals, the Bloch states *are* automatically orthogonal:

$$\langle\psi_{\vec{q}}|\psi_{\vec{q}\,'}\rangle = \eta(\vec{q})\delta_{\vec{q},\vec{q}\,'}. \tag{7.109}$$

This is because the Bloch states are eigenvectors of the unitary (not Hermitian) translation operators:

$$T_{\vec{a}}\psi_{\vec{q}} = e^{i\vec{q}\cdot\vec{a}}\psi_{\vec{q}}, \tag{7.110}$$

$$\langle\psi_{\vec{q}}|T_{\vec{a}}|\psi_{\vec{q}\,'}\rangle = e^{i\vec{q}\,'\cdot\vec{a}}\langle\psi_{\vec{q}}|\psi_{\vec{q}\,'}\rangle. \tag{7.111}$$

We can also evaluate this by means of

$$\langle\psi_{\vec{q}}|T_{\vec{a}}|\psi_{\vec{q}\,'}\rangle = \left(\langle\psi_{\vec{q}\,'}|T_{\vec{a}}^{\dagger}|\psi_{\vec{q}}\rangle\right)^{*} \tag{7.112}$$

and using $T_{\vec{a}}^{\dagger} = T_{\vec{a}}^{-1} = T_{-\vec{a}}$ to obtain

$$\left(\langle\psi_{\vec{q}\,'}|\psi_{\vec{q}}\rangle e^{-i\vec{q}\cdot\vec{a}}\right)^{*} = e^{i\vec{q}\cdot\vec{a}}\langle\psi_{\vec{q}}|\psi_{\vec{q}\,'}\rangle. \tag{7.113}$$

Equating these two results yields

$$(e^{i\vec{q}\,'\cdot\vec{a}} - e^{i\vec{q}\cdot\vec{a}})\langle\psi_{\vec{q}}|\psi_{\vec{q}\,'}\rangle = 0. \tag{7.114}$$

The term in parentheses vanishes if $\vec{q}\,' = \vec{q} + \vec{G}$, where $\vec{G}$ is a reciprocal lattice vector. However, since $\vec{q}$ and $\vec{q}\,'$ are restricted to the first Brillouin zone, the term in parentheses vanishes only for $\vec{q} = \vec{q}\,'$. Hence the states must be orthogonal for $\vec{q} \neq \vec{q}\,'$.

To evaluate the matrix element of the numerator, write the Hamiltonian in the form

$$H = \frac{\vec{p}^{\,2}}{2m} + \sum_{\ell} v(\vec{r} - \vec{R}_{\ell}), \tag{7.115}$$

$$H|j\rangle = \left[\frac{\vec{p}^{\,2}}{2m} + v(\vec{r} - \vec{R}_{j}) + \Delta v_{j}\right]|j\rangle, \tag{7.116}$$

where

$$\Delta v_{j} \equiv \sum_{\ell\neq j} v(\vec{r} - \vec{R}_{\ell}). \tag{7.117}$$

Here v is the individual atomic potential, unmodified by the presence of the other atoms. Hence

$$H|j\rangle = \varepsilon_0|j\rangle + \Delta v_j|j\rangle, \tag{7.118}$$

where ε_0 is the atomic energy eigenvalue. Thus

$$H|\psi_{\vec{q}}\rangle = \varepsilon_0|\psi_{\vec{q}}\rangle + \frac{1}{\sqrt{N}}\sum_{j} e^{i\vec{q}\cdot\vec{R}_{j}}\ \Delta v_{j}|j\rangle \tag{7.119}$$

and

$$\langle\psi_{\vec{q}}|H|\psi_{\vec{q}}\rangle = \varepsilon_0\eta(\vec{q}\,) + \Lambda(\vec{q}\,), \tag{7.120}$$

where

$$\Lambda(\vec{q}\,) \equiv \frac{1}{N}\sum_{j,k} e^{i\vec{q}\cdot(\vec{R}_{j}-\vec{R}_{k})}\langle k|\Delta v_{j}|j\rangle. \tag{7.121}$$

Thus we obtain for the energy eigenvalue

$$\epsilon_{\vec{q}} = \varepsilon_0 + \frac{\Lambda(\vec{q}\,)}{\eta(\vec{q}\,)}. \tag{7.122}$$

For the case of widely separated atoms we anticipate that $\Lambda(\vec{q}\,)$ will be very small and $\eta(\vec{q}\,)$ will be close to unity. We can parameterize $\Lambda(\vec{q}\,)$ by assuming that

$$\langle j|\Delta v_j|j\rangle = \Delta\varepsilon \tag{7.123}$$

and

$$\langle k|\Delta v_j|j\rangle = t_0 \tag{7.124}$$

if k is a nearest neighbor of j. The parameter t_0 is often referred to as the transfer integral or hopping matrix element, as it is what allows the electron to hop from one atom to another (without it the electron would be bound to a single atom forever). We assume the remaining matrix elements vanish. Then we have

$$\Lambda(\vec{q}\,) = \Delta\varepsilon + t_0 z\gamma(\vec{q}\,), \tag{7.125}$$

where z is the coordination number of the lattice (the number of nearest-neighbors of each atom), and

$$\gamma(\vec{q}\,) \equiv \frac{1}{z}\sum_{\vec{\delta}} e^{-i\vec{q}\cdot\vec{\delta}}, \tag{7.126}$$

where $\vec{\delta}$ is summed over the set of vectors connecting a lattice site to its nearest neighbors.

Similarly, we can assume

$$\langle j|\ell\rangle = \begin{cases} 1 & \text{if } j = \ell \\ \zeta & \text{if } j \text{ and } \ell \text{ are nearest neighbors} \\ 0 & \text{otherwise.} \end{cases} \tag{7.127}$$

Then

$$\eta(\vec{q}\,) = 1 + z\zeta\gamma(\vec{q}\,), \tag{7.128}$$

and the energy is

$$\epsilon_{\vec{q}} = \varepsilon_0 + \frac{\Delta\varepsilon + t_0 z\gamma(\vec{q}\,)}{1 + z\zeta\gamma(\vec{q}\,)}. \tag{7.129}$$

Since all this is approximate anyway, one often does not bother to compute t_0 and ζ but rather treats them as phenomenological constants. Often one ignores ζ and just uses the following simple form:

$$\epsilon_{\vec{q}} = A + zt_0\gamma(\vec{q}\,), \tag{7.130}$$

which yields a band width $W = 2z|t_0|$ (since $-1 < \gamma < +1$).

The tight-binding dispersion in 1D would thus be (if $t_0 < 0$, which is often the case)

$$\epsilon_q = -\frac{W}{2}\cos(qa), \tag{7.131}$$

as shown in Fig. 7.9 (where it is assumed that $A = 0$). When the atoms are widely separated, t_0 will be very small, and the band will be nearly flat. This means that a wave packet

$$\phi(\vec{r}, t) = \int_{\mathrm{BZ}} d^d\vec{q}\ \psi_{\vec{q}}(\vec{r}\,)e^{-i\epsilon_{\vec{q}}\,t/\hbar} \tag{7.132}$$

that is localized near the origin will nearly be a stationary eigenstate of H and hence remain localized near the origin for a long time. The physical interpretation of this lack of dispersion is simply that it takes a long time $t \sim \hbar/W$ for the electron to tunnel between atomic sites if they are widely separated.

This simple example shows that the dispersion of tight-binding bands is often far from the simple parabola appropriate to free electrons. We can, however, define an **effective mass** m^* in terms of the

Table 7.1 Comparison of the band properties between nearly free electrons in a weak periodic potential and the tight-binding limit of a strong periodic potential

	Nearly free electrons	Tight-binding limit
Starting point	Plane waves	Atomic Orbitals
Band width	Large	Small
Origin of band width or band dispersion	Kinetic energy ("obvious")	Hopping (subtle)
Band gap	Small	Large
Origin of band gap	Bragg scattering from periodic potential (subtle)	Spacing between atomic energy levels ("obvious")

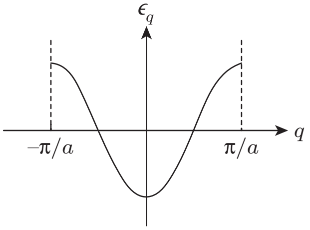


Figure 7.9 Dispersion of a 1D tight-binding band.

band curvature near the minimum. In the simple 1D example discussed above, the energy near the minimum is

$$\epsilon_q - \epsilon_0 \approx \frac{W}{4} q^2 a^2 = \frac{\hbar^2}{2m^*} q^2, \tag{7.133}$$

from which we can derive

$$m^* = \frac{2\hbar^2}{W a^2}. \tag{7.134}$$

For weak tunneling, W is small and m^* is large.

Before getting into discussions of more specific topics in the context of the tight-binding method, we compare in Table 7.1 the difference in size and origin of the band width and band gap between nearly free electrons and the tight-binding limit of a periodic potential. It is easy to understand the band dispersion, but harder to understand the band gap in the former, while the origin of the band gap is more obvious in the latter, but the presence of the band width/dispersion comes from the subtler effect of hopping.

Exercise 7.10. Consider a 1D tight-binding model with long-range hopping, such that the band dispersion is $\epsilon_k = \sum_{n=1}^{\infty} t_n \cos(kn)$, where t_n is the hopping matrix element between nth-nearest neighbors, and we have set the lattice constant $a = 1$ for simplicity. For carefully chosen t_n the band dispersion can be made exactly quadratic: $\epsilon_k = k^2$ for the entire first Brillouin zone. Find the t_n that accomplish this. (Hint: the band dispersion takes the form of a Fourier series.)

Exercise 7.11. Even if we are allowed to keep only one orbital for each atom, lattice translation symmetry does not completely determine the Bloch wave functions if we have a non-Bravais lattice. The following example illustrates this point. Consider a 1D crystal in the tight-binding

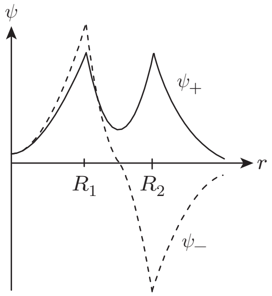


Figure 7.10 Illustration of bonding and anti-bonding electron wave functions of a diatomic molecule.

approximation (using a single atomic S-orbital only), and (for simplicity) treat the orbitals on different atoms as being orthogonal. (i) Suppose that the crystal dimerizes so that the nearest-neighbor hopping matrix elements alternate between two different values t_1 and t_2, corresponding to spacings between neighboring atoms of a_1 and a_2, respectively. Compute the complete band structure exactly (i.e. find all the eigenfunctions and eigenvalues of H). (Note: the eigenfunctions will have two components, one for each of the two atomic orbitals per unit cell.) (ii) Now consider the special case of no dimerization, so that $a_1 = a_2 = a$ and $t_1 = t_2 = t_0$, and show that in this case the band structure is equivalent to Eq. (7.131), but expressed here in a reduced-zone scheme. Note the similarity between the situation here and that of the phonon spectrum discussed in Section 5.3.

7.4.1 Bonds vs. Bands

We are familiar from chemistry with the concept of bonding and anti-bonding molecular orbitals made up of linear combinations of atomic orbitals (LCAOs). For instance, consider two hydrogen atoms forming a hydrogen molecule. The appropriate (unnormalized) diatomic molecular orbitals are approximately

$$\psi_\pm(\vec{r}\,) = \frac{1}{\sqrt{2}}\Big\{\phi_{1\mathrm{S}}(\vec{r} - \vec{R}_1) \pm \phi_{1\mathrm{S}}(\vec{r} - \vec{R}_2)\Big\}, \tag{7.135}$$

which are illustrated in Fig. 7.10. ψ_+ is the bonding orbital because it is nodeless and hence has lower kinetic energy. The potential energy is also lower since there is no node and the electron density is more concentrated in the region in between, but close to, the two nuclei.

Notice that the $+$ and $-$ phase factors are the same ones that occur in the 1D tight-binding model at $k = 0$ (zone center) and $k = \pm\pi/a$ (zone boundary). Hence we can roughly connect the bandwidth W to the chemistry by

$$W \sim z(\epsilon_{\mathrm{AB}} - \epsilon_{\mathrm{B}}), \tag{7.136}$$

where ϵ_{B} and ϵ_{AB} are the energies of the bonding and anti-bonding orbitals, respectively. For the case of one electron per atom, the band will be half full (due to spin), and chemical bonding occurs because electrons fill only the lower (bonding) half of the band. The six-atom benzene ring is a classic example. The chemist's "resonating bonds" are closely related to the condensed matter physicist's Bloch states.

7.4.2 Wannier Functions

We saw earlier that Bloch states with different wave vectors are automatically orthogonal even if the underlying atomic orbitals are not. One might inquire whether it is possible to use the Bloch states