CHAPTER

# Dynamics of Bloch Electrons

8

## CHAPTER OUTLINE



## 8.1 SEMICLASSICAL MODEL

We determined in Chapter 4 (Eq. 4.45) that the eigenfunction of the Hamiltonian of an electron moving in a crystalline solid with a periodic potential $V(\mathbf{r})$ is a Bloch function $\psi_{n\mathbf{k}}(\mathbf{r})$ that can be expressed as

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \tag{8.1}$$

where $u_{n\mathbf{k}}(\mathbf{r})$ is the periodic part of the Bloch function. Here, $n$ is a band index, $\mathbf{k}$ is a vector in the first Brillouin zone in the restricted zone scheme but extends to infinity in the periodic zone scheme, and $u_{n\mathbf{k}}(\mathbf{r})$ has the unique property that it remains unchanged when translated by any direct lattice vector $\mathbf{R}_i$ (Eq. 4.46), i.e.,

$$u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}_i) = u_{n\mathbf{k}}(\mathbf{r}). \tag{8.2}$$

Thus, the Schrodinger equation

$$H\psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_n(\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r}) \tag{8.3}$$

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can be rewritten in the alternate form (Eq. 4.36)

$$H_{\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_n(\mathbf{k}) u_{n\mathbf{k}}(\mathbf{r}), \tag{8.4}$$

where

$$H_{\mathbf{k}} = \left[\frac{\hbar^2}{2m}(-i\nabla + \mathbf{k})^2 + V(\mathbf{r})\right]. \tag{8.5}$$

In this chapter, we have written $H_{eff}$ as $H_{\mathbf{k}}$ for convenience. Here, the boundary conditions for $u_{n\mathbf{k}}(\mathbf{r})$ are specified in Eq. (8.2). In the periodic zone scheme, which will be used in the derivations that follow, the eigenfunctions and eigenvalues are periodic functions of $\mathbf{k}$ in the reciprocal lattice, i.e.,

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \psi_{n,\mathbf{k}+\mathbf{K}}(\mathbf{r}) \tag{8.6}$$

and

$$\varepsilon_n(\mathbf{k}) = \varepsilon_n(\mathbf{k}+\mathbf{K}). \tag{8.7}$$

The set of electronic levels $\varepsilon_n(\mathbf{k})$, for each $n$, is known as the energy band because the band index $n$ is a constant of motion. In addition, the energy levels $\varepsilon_n(\mathbf{k})$ vary continuously as $\mathbf{k}$ varies because $\mathbf{k}$ is essentially a parameter in Eq. (8.5). Further, the size of the crystal is not a factor in Eq. (8.4), and as we noted earlier, the Born–von Karman boundary condition (Eq. 3.31),

$$\begin{aligned}
\psi_{\mathbf{k}}(x+L,y,z) &= \psi_{\mathbf{k}}(x,y,z)\\
\psi_{\mathbf{k}}(x,y+L,z) &= \psi_{\mathbf{k}}(x,y,z)\\
\psi_{\mathbf{k}}(x,y,z+L) &= \psi_{\mathbf{k}}(x,y,z),
\end{aligned} \tag{8.8}$$

specifies that $\mathbf{k}$ is continuous when $L \to \infty$ (Eq. 3.14). We will use the property that $\mathbf{k}$ is a continuous parameter in what follows. These same boundary conditions are also valid for the Bloch functions $\psi_{n\mathbf{k}}(\mathbf{r})$.

## 8.2 VELOCITY OPERATOR

For a crystal with inversion symmetry, the velocity operator

$$\mathbf{v} = \dot{\mathbf{r}} = -\frac{i}{\hbar}[\mathbf{r}, \mathbf{H}] \tag{8.9}$$

can be rewritten in the alternate form

$$\mathbf{v} = -\frac{i\hbar}{m}\nabla. \tag{8.10}$$

If we define the velocity operator using the effective Hamiltonian in Eq. (8.5),

$$\mathbf{v}_{\mathbf{k}} = -\frac{i}{\hbar}[\mathbf{r}, H_{\mathbf{k}}], \tag{8.11}$$

we obtain

$$\mathbf{v}_{\mathbf{k}} = \frac{\hbar}{m}(-i\nabla + \mathbf{k}). \tag{8.12}$$

We will use this relation for the velocity operator to obtain an expression for the velocity of the Bloch electrons.

## 8.3 k · p PERTURBATION THEORY

We assume that $\mathbf{k}$ is increased by an infinitesimal amount $\Delta\mathbf{k}$. When $\mathbf{k} \rightarrow \mathbf{k} + \Delta\mathbf{k}$, Eq. (8.5) can be rewritten in the form

$$H_{\mathbf{k}+\Delta\mathbf{k}} = \left[\frac{\hbar^2}{2m}(-i\nabla + \mathbf{k} + \Delta\mathbf{k})^2 + V(\mathbf{r})\right], \tag{8.13}$$

which can be rewritten in the alternate form

$$H_{\mathbf{k}+\Delta\mathbf{k}} = H_{\mathbf{k}} + \frac{\hbar^2}{m}(-i\nabla + \mathbf{k}) \cdot \Delta\mathbf{k} + \frac{\hbar^2}{2m}(\Delta\mathbf{k})^2. \tag{8.14}$$

We use nondegenerate second-order perturbation theory and write

$$H_{\mathbf{k}+\Delta\mathbf{k}} = H_{\mathbf{k}} + H'_{\mathbf{k}}. \tag{8.15}$$

The perturbation term $H'_{\mathbf{k}}$ is obtained from Eqs. (8.14) and (8.15),

$$H'_{\mathbf{k}} = \frac{\hbar^2}{m}(-i\nabla + \mathbf{k}) \cdot \Delta\mathbf{k} + \frac{\hbar^2}{2m}(\Delta\mathbf{k})^2. \tag{8.16}$$

If we express the energy eigenvalue in different orders of $\varepsilon$ as

$$\varepsilon_n(\mathbf{k} + \Delta\mathbf{k}) = \varepsilon_n(\mathbf{k}) + \varepsilon_n^{(1)}(\mathbf{k}) + \varepsilon_n^{(2)}(\mathbf{k}) + \ldots, \tag{8.17}$$

we obtain from second-order perturbation theory,

$$\varepsilon_n(\mathbf{k}) = <u_{n\mathbf{k}}|H_{\mathbf{k}}|u_{n\mathbf{k}}> = <\psi_{n\mathbf{k}}|H|\psi_{n\mathbf{k}}> \tag{8.18}$$

and

$$\varepsilon_n^{(1)}(\mathbf{k}) = <u_{n\mathbf{k}}|H'_{\mathbf{k}}|u_{n\mathbf{k}}> = <u_{n\mathbf{k}}|\frac{\hbar^2}{m}(-i\nabla + \mathbf{k}) \cdot \Delta\mathbf{k}|u_{n\mathbf{k}}>, \tag{8.19}$$

where the term $\frac{\hbar^2}{2m}(\nabla\mathbf{k})^2$, which is second order in $\nabla\mathbf{k}$, has been included in $\varepsilon_n^{(2)}(\mathbf{k})$,

$$\varepsilon_n^{(2)}(\mathbf{k}) = \frac{\hbar^2}{2m}(\nabla\mathbf{k})^2 + \sum_{n' \neq n} \frac{|<u_{n\mathbf{k}}|\frac{\hbar^2}{m}\Delta\mathbf{k} \cdot (-i\nabla + \mathbf{k})|u_{n'\mathbf{k}}>|^2}{\varepsilon_{n\mathbf{k}} - \varepsilon_{n'\mathbf{k}}}. \tag{8.20}$$

If we also expand $\varepsilon_n(\mathbf{k}+\Delta\mathbf{k})$ as

$$\varepsilon_n(\mathbf{k}+\Delta\mathbf{k}) = \varepsilon_n(\mathbf{k}) + \sum_i \frac{\partial \varepsilon_n(\mathbf{k})}{\partial k_i}\Delta k_i + \frac{1}{2}\sum_{ij}\frac{\partial^2 \varepsilon_n(\mathbf{k})}{\partial k_i \partial k_j}\Delta k_i \Delta k_j + \ldots, \tag{8.21}$$

we obtain from Eqs. (8.12), (8.17), (8.19), and (8.21),

$$\frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}} = \hbar <u_{n\mathbf{k}}|\mathbf{v}_\mathbf{k}|u_{n\mathbf{k}}>, \tag{8.22}$$

which can be rewritten in the alternate form (Problem 8.2)

$$\frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}} = \hbar <\psi_{n\mathbf{k}}|\mathbf{v}|\psi_{n\mathbf{k}}> = \hbar \mathbf{v}_{n\mathbf{k}}. \tag{8.23}$$

Thus, the mean velocity of a Bloch electron is given by

$$\mathbf{v}_{n\mathbf{k}} = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}}. \tag{8.24}$$

It is interesting to note that one can derive a similar expression for the velocity of electrons in a periodic potential and an external field. We will show by using quasiclassical dynamics that

$$\mathbf{v}_\mathbf{k} = \frac{\hbar\mathbf{k}}{m} = \frac{1}{\hbar}\frac{\partial \varepsilon(\mathbf{k})}{\partial \mathbf{k}}. \tag{8.25}$$

It is also interesting to note that the group velocity of a wave packet moving freely in space is given by the same expression as Eq. (8.25).

## 8.4 QUASICLASSICAL DYNAMICS

The classical Hamilton equations are expressed as[11]

$$\dot{q}_k = \frac{\partial H}{\partial p_k}, \dot{p}_k = -\frac{\partial H}{\partial q_k}, \tag{8.26}$$

where $H$ is the classical Hamiltonian function, and $q_k$ and $p_k$ are the generalized coordinates and momenta, respectively. In the quantum mechanical formulation, the Hamiltonian operator is obtained by replacing the classical momentum $\mathbf{p}$ by $-i\hbar\nabla$. In an external electrostatic field, the Hamiltonian operator can be written as

$$\hat{H} = \hat{H}_0 + U(\mathbf{r}) = \hat{\varepsilon}(-i\nabla) + U(\mathbf{r}), \tag{8.27}$$

where $\hat{H}_0$ is the Hamiltonian operator in the perfect lattice, $U(\mathbf{r})$ is the perturbing potential of the external field, and $\hat{\varepsilon}(-i\nabla)$ is the equivalent Hamiltonian operator. If we reverse these steps by replacing $-i\nabla$ by $\mathbf{p}/\hbar$, the classical Hamiltonian function is given by

$$H(\mathbf{r},\mathbf{p}) = \varepsilon(\mathbf{p}/\hbar) + U(\mathbf{r}). \tag{8.28}$$

From Eqs. (8.26) and (8.28), we obtain

$$\dot{\mathbf{r}} = \mathbf{v} = \frac{\partial H}{\partial \mathbf{p}} = \frac{\partial \varepsilon(\mathbf{p}/\hbar)}{\partial \mathbf{p}} = \frac{1}{\hbar}\frac{\partial \varepsilon(\mathbf{k})}{\partial \mathbf{k}}, \tag{8.29}$$

where

$$\mathbf{p} = \hbar\mathbf{k}. \tag{8.30}$$

It may be noted that $\hbar\mathbf{k}$ is the crystal momentum and not the actual momentum of an electron, as was obtained in the Sommerfeld model for free electrons. This is a consequence of the fact that in the Bloch formulation, the effect of the periodic potential has been already included.

The second Hamiltonian equation in Eq. (8.26) can be written as

$$\dot{\mathbf{p}} = \hbar\dot{\mathbf{k}} = -\frac{\partial H}{\partial \mathbf{r}} = -\nabla U(\mathbf{r}). \tag{8.31}$$

Because $U(\mathbf{r})$ is the potential energy of the electron in an external field, $\hbar\dot{\mathbf{k}}$ is essentially the force $\mathbf{F}$ acting on the Bloch electron. According to Newton's law,

$$\mathbf{F} = m\frac{d\mathbf{v}}{dt} = \hbar\dot{\mathbf{k}}, \tag{8.32}$$

where $m$ is the mass of the electron.

## 8.5 EFFECTIVE MASS

It is often convenient to define an effective mass to describe the motion of Bloch electrons in an external field. Later, we will use the same concept to describe the motion of electrons and holes in a semiconductor. If we assume that the external field (electrostatic) acting on the electrons is weak and the change in $\mathbf{k}$ is slow, we can write

$$\frac{d}{dt}\mathbf{v}_{n\mathbf{k}} = \sum_{ij} \hat{\epsilon}_i \frac{\partial v^i_{n\mathbf{k}}}{\partial k_j}\frac{\partial k_j}{\partial t}, \tag{8.33}$$

where $\hat{\epsilon}_i$ is one of the three unit vectors $\hat{x}, \hat{y}$, and $\hat{z}$. We can also introduce the effective mass tensor $\mathbf{M}_n^{-1}(\mathbf{k})$ (it is actually an inverse effective mass tensor) of the Bloch electrons (it is important to note that the effect of the periodic potential of the lattice has already been included in the Bloch formulation) in analogy with Eq. (8.32) as

$$\frac{d}{dt}\mathbf{v}_{n\mathbf{k}} = \hbar\mathbf{M}_n^{-1}(\mathbf{k})\cdot\dot{\mathbf{k}}. \tag{8.34}$$

From Eqs. (8.24), (8.33), and (8.34), we obtain

$$[\mathbf{M}_n^{-1}(\mathbf{k})]_{ij} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon_n}{\partial k_i \partial k_j}. \tag{8.35}$$

We can derive an expression for the effective mass tensor from the results of the perturbation theory. From Eqs. (8.20) and (8.21), we obtain

$$\begin{aligned}\varepsilon_n^{(2)}(\mathbf{k}) &= \frac{\hbar^2}{2m}(\nabla\mathbf{k})^2 + \sum_{n'\neq n}\frac{|<u_{n\mathbf{k}}|\frac{\hbar^2}{m}\Delta\mathbf{k}\cdot(-i\nabla+\mathbf{k})|u_{n'\mathbf{k}}>|^2}{\varepsilon_n(\mathbf{k})-\varepsilon_{n'}(\mathbf{k})} \\ &= \frac{1}{2}\sum_{ij}\frac{\partial^2\varepsilon_n(\mathbf{k})}{\partial k_i\partial k_j}\Delta k_i\Delta k_j.\end{aligned} \tag{8.36}$$

From Eqs. (8.35) and (8.36), we obtain (Problem 8.4)

$$[\mathbf{M}_n^{-1}(\mathbf{k})]_{ij} = \frac{1}{m}\delta_{ij} + \frac{\hbar^2}{m^2}\sum_{n'\neq n}\frac{<n\mathbf{k}|-i\nabla_i|n'\mathbf{k}><n'\mathbf{k}|-i\nabla_j|n\mathbf{k}> + c.c.}{\varepsilon_n(\mathbf{k})-\varepsilon_{n'}(\mathbf{k})}. \tag{8.37}$$

Here, the summation is over all band indices $n'$ except $n$. The inverse mass tensor plays an important role in the formulation of dynamics of Bloch electrons. As we will see, the inverse effective mass tensor can be either positive or negative. Because the concept of a negative effective mass associated with the negatively charged Bloch electrons is contrary to our physical understanding, we will also introduce the concept of "holes," which are positively charged particles associated with positive effective mass. The holes play a very important role in semiconductors. In addition, the mystery of a positive charge in the Hall coefficient (in the free electron model, $R_H = -nec$), in the measurement of the Hall effect in certain metals such as aluminum in high magnetic fields, is also explained by the concept of holes.

## 8.6 BLOCH ELECTRONS IN EXTERNAL FIELDS

In an external electric field $\mathbf{E}$, the force acting on a free electron is given by

$$\hbar\dot{\mathbf{k}} = -e\mathbf{E}. \tag{8.38}$$

The effect of a magnetic field $\mathbf{B}$ is included by assuming that the Lorentz force equation is valid, i.e.,

$$\hbar\dot{\mathbf{k}} = -e\left(\mathbf{E} + \frac{1}{c}\mathbf{V}\times\mathbf{B}\right). \tag{8.39}$$

The proof of an equivalent result for Bloch electrons is much more difficult for a magnetic field. We will first derive an equivalent result for Bloch electrons in a static electric field and then generalize the results by using a more rigorous method. In a static electric field $\mathbf{E}$, the general expression

$$\mathbf{E}(\mathbf{r},t) = -\frac{1}{c}\frac{\partial\mathbf{A}(\mathbf{r},t)}{\partial t} - \nabla\phi(\mathbf{r},t) \tag{8.40}$$

reduces to

$$\mathbf{E} = -\nabla\phi(\mathbf{r}). \tag{8.41}$$

Here, $\mathbf{A}(\mathbf{r}, t)$ is the vector potential, and $\phi(\mathbf{r})$ is the scalar potential. We showed in Eq. (8.24) that for Bloch electrons,

$$\dot{\mathbf{r}} = \mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\mathbf{k})}{\partial t}. \tag{8.42}$$

The wave packet moves in such a way that the energy

$$\varepsilon = \varepsilon_n(\mathbf{k}(t)) - e\phi(\mathbf{r}(t)) = \text{constant}. \tag{8.43}$$

Because the energy $\varepsilon$ of the wave packet is constant, we obtain, by taking the time derivative of the energy,

$$\frac{\partial \varepsilon}{\partial t} = \frac{\partial \varepsilon_n(\mathbf{k})}{\partial t} \cdot \dot{\mathbf{k}} - e\nabla\phi \cdot \dot{\mathbf{r}} = 0. \tag{8.44}$$

From Eqs. (8.42) and (8.44), we obtain

$$\mathbf{V}_n(\mathbf{k}) \cdot [\hbar\dot{\mathbf{k}} - e\nabla\phi] = 0. \tag{8.45}$$

From Eq. (8.45), we obtain the desired result

$$\hbar\dot{\mathbf{k}} = e\nabla\phi = -e\mathbf{E}. \tag{8.46}$$

However, there are problems associated in this derivation because the periodic boundary conditions that were implicitly assumed in this derivation (by assuming that the eigenfunctions of the Hamiltonian are the Bloch functions) are no longer valid. The electrostatic potential $U(\mathbf{r})$, due to the uniform electric field $\mathbf{E}$, grows linearly in space because $U(\mathbf{r}) = -\mathbf{E} \cdot \mathbf{r}$. Therefore, when a metal is placed in an electric field, the surface charges build up and cancel the interior field. Thus, the basic assumption that the Bloch formulation is still valid is questionable, and the periodicity associated with our formulation of the problem in a Brillouin zone with a band index $n$ and crystal momentum $\mathbf{k}$ is invalid. We will derive Eq. (8.46) by using a second method where the periodicity of the potential is not lost. However, we will first use the previous derivation to justify (in a hand-waving way) the effect of a magnetic field.

It may be noted that the results of Eq. (8.45) are valid if any term perpendicular to $\mathbf{V}_n(\mathbf{k})$ is added in the square bracket. For example, anticipating that the Lorentz equations are valid, we can rewrite Eq. (8.45) as

$$\mathbf{V}_n(\mathbf{k}) \cdot [\hbar\dot{\mathbf{k}} - e\nabla\phi + \frac{e}{c}\mathbf{V}_n(\mathbf{k}) \times \mathbf{B}] = 0. \tag{8.47}$$

Because $e\nabla\phi = -e\mathbf{E}$ (from Eq. 8.46), Eq. (8.47) leads to the desired semiclassical expression for the Bloch electron in an electric field $\mathbf{E}$ and magnetic field $\mathbf{B}$,

$$\hbar\dot{\mathbf{k}} = -e\mathbf{E} - \frac{e}{c}\mathbf{V}_n(\mathbf{k}) \times \mathbf{B}. \tag{8.48}$$

We note that Eq. (8.48) is in no way a rigorous derivation of the motion of the Bloch electrons in an electric and magnetic field.

### 8.6.1 Time Evolution of Bloch Electrons in an Electric Field

If we use the expression for the electric field **E** through a time-dependent vector potential **A** that increases linearly with time and set the scalar potential $\phi(\mathbf{r})$ to zero, i.e.,

$$\mathbf{A} = -c\mathbf{E}t,\ \phi(\mathbf{r}) = 0, \tag{8.49}$$

we verify that

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} - \nabla\phi = \mathbf{E}. \tag{8.50}$$

Such a vector potential **A**, which allows the electric field **E** to coexist with the periodic boundary conditions (in a ring-shaped crystal) is shown in Figure 8.1.

The use of a time-dependent vector potential instead of a scalar potential allows us to use the periodic boundary conditions. We can generalize this method to a Bloch state under the influence of a time-dependent electric field, $E(t)$, turned on at $t = 0$.[6]

The time-dependent Schrodinger equation for an electron in a Bloch state under the influence of an electric field, $E(t)$, turned on at $t = 0$, is given by

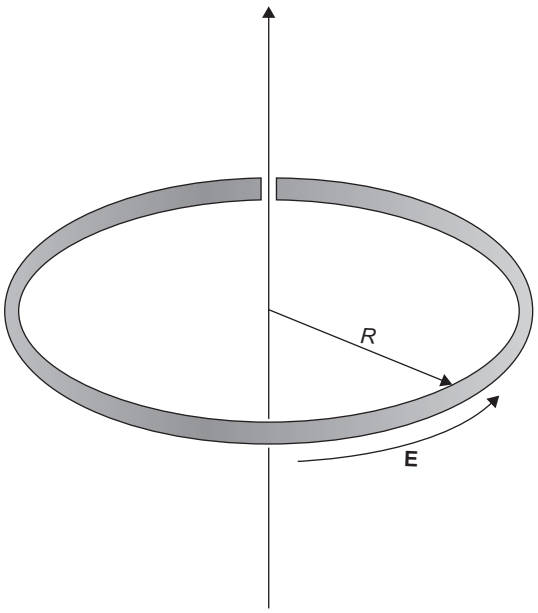


**FIGURE 8.1**

The vector potential $\mathbf{A} = -c\mathbf{E}t$ can be established in a ring-shaped crystal by changing the magnetic flux at a uniform rate $B_z = 2\pi RcEt\delta(\mathbf{r})$ through an infinite solenoid inside the ring.

$$H\psi(\mathbf{r},t) = \left[\frac{\left(\mathbf{p} + (e/c)\mathbf{A}\right)^2}{2m} + V(\mathbf{r})\right]\psi = i\hbar\frac{\partial\psi}{\partial t}, \tag{8.51}$$

where

$$\mathbf{A} = -c\int_0^t E(t')dt', \tag{8.52}$$

$V(\mathbf{r})$ is the lattice periodic potential, and the time-dependent electric field is included as a vector potential, as described earlier. We can obtain $\psi(\mathbf{r},t)$ from $\psi(\mathbf{r},0)$ by using eigenfunction expansion of which the elements are

$$\left[\frac{\left(\mathbf{p} + (e/c)\mathbf{A}\right)^2}{2m} + V(\mathbf{r})\right]\phi_i'(\mathbf{r},t) = \varepsilon_i(t)\phi_i'(\mathbf{r},t). \tag{8.53}$$

For each $t$, the Hamiltonian is invariant under a crystal lattice translation because $\mathbf{A}$ is independent of $\mathbf{r}$ for a homogeneous electric field, and $V(\mathbf{r})$ is periodic. If we substitute

$$\phi_i'(\mathbf{r},t) = e^{-ie\mathbf{A}\cdot\mathbf{r}/\hbar c}\phi_i(\mathbf{r},t), \tag{8.54}$$

in Eq. (8.53), we obtain

$$\left[\frac{p^2}{2m} + V(\mathbf{r})\right]\phi_i = \varepsilon_i\phi_i. \tag{8.55}$$

The solutions of Eq. (8.55) are the Bloch functions and energy band functions of the unperturbed crystal,

$$\phi_i = \phi_{n\mathbf{k}}(\mathbf{r}) \tag{8.56}$$

and

$$\varepsilon_i = \varepsilon_n(\mathbf{k}). \tag{8.57}$$

From Eqs. (8.54) and (8.56), we obtain

$$\phi_i'(\mathbf{r},t) = e^{-ie\mathbf{A}\cdot\mathbf{r}/\hbar c}\phi_{n\mathbf{k}}(\mathbf{r}). \tag{8.58}$$

Because $H$ is invariant under a lattice translation, the allowed values of $\mathbf{k}$ are defined using periodic boundary conditions on the $\phi_i'$. We obtain

$$\mathbf{k} - \frac{e\mathbf{A}}{\hbar c} = \sum_i \frac{n_i}{N_i}\mathbf{K}_i, \tag{8.59}$$

where $\mathbf{K}_i (i = 1, 2, 3)$ are the primitive reciprocal-lattice translation vectors, $N_i$ are the number of cells in the $i$ direction, and $-N_i/2 < n_i \leq N_i/2$. For the periodic boundary condition to be satisfied, $\mathbf{k}$ must be a function of $t$ and

$$\hbar\dot{\mathbf{k}} = \frac{e}{c}\dot{\mathbf{A}} = \frac{e}{c}(-c\mathbf{E}(t)) = -e\mathbf{E}(t). \tag{8.60}$$

From Eq. (8.59) and the time dependence of $\mathbf{A}(t)$, it follows that the Brillouin zone describing the allowed $\mathbf{k}(t)$ values is time dependent. The periodic boundary conditions that lead to Brillouin zone boundaries move in time. Thus, the wave vector does not undergo an Umklapp process (or U-process) back to the other side of the Brillouin zone, but continues with continuous values of $\mathbf{k}(t)$ in the time-dependent zone. Having considered the general case of a time-dependent electric field, if we restrict to a time-independent electric field,

$$\hbar\dot{\mathbf{k}} = -e\mathbf{E} \tag{8.61}$$

and

$$\mathbf{A} = -c\mathbf{E}t. \tag{8.62}$$

Thus, the $\mathbf{k}$ vectors are time dependent and should be written as $\mathbf{k}(t)$. From Eqs. (8.55) and (8.56), we also obtain the Bloch equation

$$\phi_{n\mathbf{k}(t)}(\mathbf{r}) = e^{i\mathbf{k}(t)\cdot\mathbf{r}} u_{n\mathbf{k}(t)}(\mathbf{r}). \tag{8.63}$$

The functions defined in (8.53) and (8.58) are also known as Houston functions. It may be noted that the Houston functions are not exact solutions of the Schrodinger equation because the eigenvalues are time dependent. The amplitude of Houston states with nearby $\mathbf{k}$ becomes nonzero and grows, a behavior typical of wave packets. In addition, the electron can jump from one band to another, which is known as Zener tunneling and which we will discuss later.

We note that if we use the Houston functions instead of the Bloch functions, we obtain expressions for the effective Hamiltonians by a using a similar technique followed earlier (Problem 8.5). The effective Hamiltonian for $U_{n\mathbf{k}}(\mathbf{r}, \mathbf{E}, t)$ is

$$H_{eff} = \frac{1}{2m}(-i\hbar\nabla + \hbar\mathbf{k} - e\mathbf{E}t)^2 + V(\mathbf{r}). \tag{8.64}$$

One important aspect to note is that the electric field $\mathbf{E}$ is incorporated through $\mathbf{k}(t)$ as described in Eq. (8.61).

When the electron jumps from one band to another because of a strong electric field, it is called *electric breakdown* or the *Zener breakdown*. It is easier for the electron to jump to a neighboring band in a magnetic field. This is known as *magnetic breakdown*. We will discuss these breakdowns later. We will describe the Zener breakdown after discussing an alternate (but essentially flawed) derivation of the motion of Bloch electrons in an electric and magnetic field. The controversy in this derivation is that one cannot use Bloch functions for Hamiltonians that are not periodic.

### 8.6.2 Alternate Derivation for Bloch Functions in an External Electric and Magnetic Field

The Hamiltonian in an electric and magnetic field can be written as

$$H = \frac{1}{2m}\left(\mathbf{p} + \frac{e\mathbf{A}}{c}\right)^2 + V(\mathbf{r}) + e\mathbf{E}\cdot\mathbf{r}. \tag{8.65}$$

In a small interval $dt$, the Bloch function $\psi = \psi_n(\mathbf{k}_0, \mathbf{r})$ at $t = 0$ will change by

$$\psi_n(\mathbf{k}, \mathbf{r}, dt) = e^{-i/\hbar H dt}\psi_n(\mathbf{k}_0, \mathbf{r}) \approx \left(1 - \frac{i}{\hbar}Hdt\right)\psi_n(\mathbf{k}_0, \mathbf{r}). \tag{8.66}$$

If we operate with the translation operator, with properties described in Eq. (4.47), we obtain

$$\hat{T}(\mathbf{R}_i)\psi = \hat{T}(\mathbf{R}_i)\left(1 - \frac{i}{\hbar}Hdt\right)\psi_n(\mathbf{k}_0, \mathbf{r}), \tag{8.67}$$

which can be written as

$$\hat{T}(\mathbf{R}_i)\psi = \left(1 - \frac{i}{\hbar}Hdt\right)\hat{T}(\mathbf{R}_i)\psi_n - \frac{i}{\hbar}dt[T(\mathbf{R}_i), H]\psi_n. \tag{8.68}$$

It can be shown that (Problem 8.6)

$$[\hat{T}(\mathbf{R}_i), H] = \left(\overrightarrow{\xi} \cdot \mathbf{R}_i + \frac{e^2B^2}{2m} R_{ix}^2\right)\hat{T}(\mathbf{R}_i), \tag{8.69}$$

where

$$\overrightarrow{\xi} = \frac{e}{c}\mathbf{v}\times\mathbf{B} + e\mathbf{E} + \frac{e}{c}\dot{\mathbf{A}}. \tag{8.70}$$

We neglect the last term in Eq. (8.69) in a weak magnetic field approximation and obtain

$$\hat{T}(\mathbf{R}_i)\psi = \left[1 - \frac{i}{\hbar}(H + \overrightarrow{\xi} \cdot \mathbf{R}_i)dt\right]\hat{T}(\mathbf{R}_i)\psi_n = (\ldots)e^{i\mathbf{k}_0\cdot\mathbf{R}_i}\psi_n = e^{i\mathbf{k}\cdot\mathbf{R}_i}\psi. \tag{8.71}$$

Here,

$$\mathbf{k} = \mathbf{k}_0 - \frac{\overrightarrow{\xi}}{\hbar}dt \tag{8.72}$$

or

$$\hbar\dot{\mathbf{k}} = -\overrightarrow{\xi}. \tag{8.73}$$

If we neglect the last term in Eq. (8.70), we obtain

$$\hbar\dot{\mathbf{k}} = -e\left(\mathbf{E} + \frac{\mathbf{v}\times\mathbf{B}}{c}\right). \tag{8.74}$$

Eq. (8.74) is the standard Lorentz force equation.

### 8.6.3 Motion in an Applied DC Field

Eq. (8.61) can be rewritten in the alternate form

$$\mathbf{k}(t) = \mathbf{k}(0) - \frac{e\mathbf{E}t}{\hbar}, \tag{8.75}$$

from which we obtain

$$\mathbf{v}_n(\mathbf{k}(t)) = \mathbf{v}_n\left(\mathbf{k}(0) - \frac{e\mathbf{E}t}{\hbar}\right). \tag{8.76}$$

We note from Eq. (8.42) that $\mathbf{v}_n(\mathbf{k})$ is periodic in the reciprocal lattice vector $\mathbf{K}$ and when $\mathbf{E} \| \mathbf{K}$, Eq. (8.76) is oscillatory. This oscillatory behavior in one dimension is shown in Figure 8.2. The velocity, which is linear in $k$ near the band minimum, reaches a maximum and then decreases to zero at the Brillouin zone boundary. It is surprising

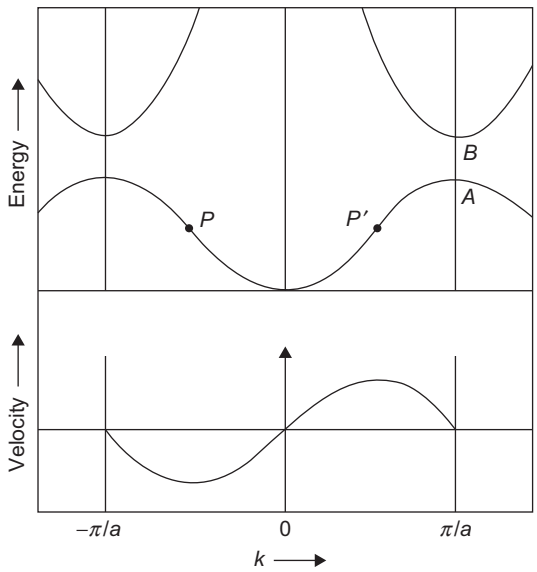


**FIGURE 8.2**

$v(k)$ and $\varepsilon(k)$ versus $k$ in one dimension.

to note that in the region in which the velocity decreases with increasing $k$, the acceleration of the electron is opposite to the external applied field.

We first note the periodic behavior of the $\varepsilon(k)$ versus $k$ curve in Figure 8.2. The Bloch electrons have positive effective masses at $k = 0$ and negative effective masses at $k = \pm\pi/a$. The oscillatory behavior of the velocity of the Bloch electron with $k$ (and with time that is related to $k$ through Eq. 8.69) is a consequence of the effect of the periodic potential that exerts an additional force. Hypothetically, the external DC electric field could induce alternating current, but collisions with phonons and impurities present in a crystal do not allow any such possibility. In fact, in the absence of damping, a perfect crystal with a periodic potential would not have any resistivity at zero temperature.

## 8.7 BLOCH OSCILLATIONS

The Bloch oscillations result from the fact that $\varepsilon_{n\mathbf{k}}$ is a periodic function of $\mathbf{k}$. For example, we consider the energy of a band in one dimension using the tight-binding method. From Eq. (5.13), we obtain the expression for energy of a one-dimensional crystal of lattice constant $a$ (in the $x$ direction) as

$$\varepsilon(k) = \varepsilon_a - \beta - 2\gamma \cos ka, \tag{8.77}$$

where the constants were defined in Eq. (5.13). When there is an external electric field $E$ parallel to the linear chain of the lattice (in the $x$ direction), we have from Eq. (8.61)

$$\hbar\dot{k} = -eE \tag{8.78}$$

and

$$k = -eEt/\hbar. \tag{8.79}$$

From Eqs. (8.42), (8.77), and (8.79), we have

$$\frac{dr}{dt} = \dot{r} = \frac{1}{\hbar}\frac{\partial\varepsilon}{\partial t} = -\frac{2a\gamma}{\hbar}\sin\left(\frac{aeEt}{\hbar}\right). \tag{8.80}$$

Integrating with respect to $t$, we obtain

$$r = \frac{2\gamma}{eE}\cos\left(\frac{aeEt}{\hbar}\right). \tag{8.81}$$

Eq. (8.81) implies that when the external electric field is very large, the Bloch electrons would oscillate around a mean position. Instead of being a good conductor, a metal would become an insulator. However, it can be easily shown that a small amount of damping can destroy this oscillation.

The existence of such Bloch oscillations was experimentally observed by Dahan et al (Ref. 3). Dahan et al. prepared ultracold cesium

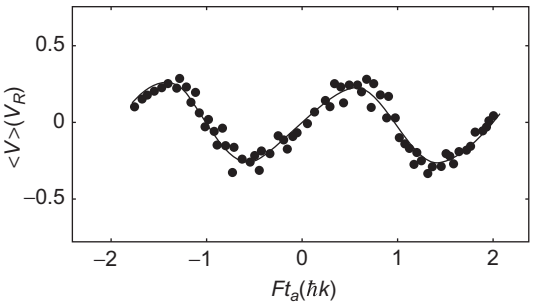


**FIGURE 8.3**

Bloch oscillations of cesium atoms in an optical periodic potential driven by a constant external force observed experimentally. The negative values of $Ft_a$ were measured by changing the sign of $F$.

*Reproduced from Dahan et al.[3] with the permission of the American Physical Society.*

atoms in the ground-state energy band of the potential induced by an optical standing wave. The periodic potential results from the light shift of the ground state of cesium atoms illuminated by a laser standing wave. The constant external force was mimicked by introducing a tunable frequency difference $\delta v(t)$ between two counter propagating laser waves creating the optical potential. The reference frame in which the optical potential is stationary moves with velocity $\delta v(t)\lambda/2$. For a linear variation of time in $\delta v(t)$, a constant inertial force $F = -ma = -m\lambda \frac{d}{dt}\delta v(t)/2$ is exerted on the atoms in this frame. They observed Bloch oscillations of the atoms driven by this constant inertial force shown in Figure 8.3. The recoil velocity of the cesium atom was 0.35 cm/s, and the acceleration was $\pm 0.85\,\mathrm{m/s^2}$. Figure 8.3 shows the results for potential depth $U_0 = 4.4\,E_R$.

## 8.8 HOLES

We can write the expression for the contribution of all the electrons in a given band to the current density as

$$\mathbf{j} = -e \int_{occupied} \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}(\mathbf{k}). \tag{8.82}$$

Because the current in a completely filled band is zero, we can also write

$$\mathbf{j} = e \int_{unoccupied} \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}(\mathbf{k}). \tag{8.83}$$

If only one electron is missing from the occupied band, the current is

$$\mathbf{j} = e\mathbf{v}(\mathbf{k}). \tag{8.84}$$

The absence of an electron in state $\mathbf{k}$ from an otherwise filled band is known as a "hole" in state $\mathbf{k}$. There are a couple of important physical properties to note about a hole:

1. The hole is a positive charge, as evidenced by Eq. (8.84).
2. The velocity of the "wave packet" of the hole will be the same as the velocity of the electrons in either side of the hole, i.e.,

$$\mathbf{v}_{n\mathbf{k}} = \frac{1}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}}. \tag{8.85}$$

There are several ways in which a hole can be formed in a filled band. An electron can absorb a photon and can be excited to the empty band above the filled band. Similarly, an electron can be thermally excited at room temperature to the empty band above the filled band provided the energy gap is small, as is the case for intrinsic semiconductors like Si or Ge. In fact, "holes" play a significant role in semiconductors, which is the topic of Chapter 9. The formation of a hole by the absorption of a photon by an electron in state $\mathbf{k}$ to an empty band is shown in Figure 8.4.

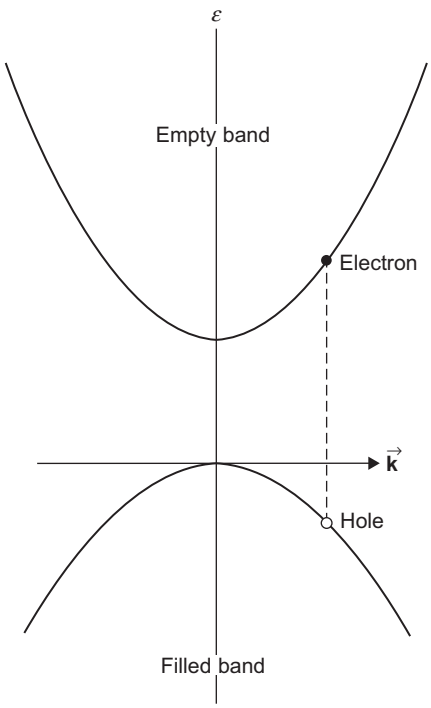


**FIGURE 8.4**

An electron of vector **k** absorbs a photon and is excited to the empty band, leaving behind a positively charged "hole" of the same vector **k** in the filled band.

Because the unoccupied levels normally lie near the top of the band and the band energy $\varepsilon_n(\mathbf{k})$ has its maximum value at $\mathbf{k}_m$, we can expand $\varepsilon_n(\mathbf{k})$ about $\mathbf{k}_m$ assuming that $\mathbf{k}$ is sufficiently close to $\mathbf{k}_m$. We obtain (assuming that $\mathbf{k}_m$ is a point of high symmetry)

$$\varepsilon_n(\mathbf{k}) \approx \varepsilon_n(\mathbf{k}_m) + a(\mathbf{k}-\mathbf{k}_m) - b(\mathbf{k}-\mathbf{k}_m)^2 + \ldots \tag{8.86}$$

However, the linear term on the right side will vanish because $\varepsilon_n(\mathbf{k}_m)$ is a maximum and the coefficient of $b$ will be negative. From Eqs. (8.85) and (8.86), we obtain

$$\mathbf{v}_n(\mathbf{k}) = -\frac{2}{\hbar} b\mathbf{k} \tag{8.87}$$

and

$$\frac{d}{dt}\mathbf{v}_n(\mathbf{k}) = \mathbf{a} = -\frac{2}{\hbar} b\dot{\mathbf{k}}. \tag{8.88}$$

Comparing Eq. (8.88) with Eq. (8.34) for the effective mass tensor, we obtain

$$\hbar\mathbf{M}_n^{-1}(\mathbf{k}) \cdot \dot{\mathbf{k}} = -\frac{2}{\hbar} b\dot{\mathbf{k}} = \mathbf{a}. \tag{8.89}$$

Thus, the inverse mass tensor is negative if $\mathbf{k}$ is near a band maximum. Because a negative mass is physically unacceptable, a *hole* can be considered as a *positive charge* with a *positive effective mass.*

Thus, the general expression of the equation of motion can be written as

$$\mathbf{M}_n(\mathbf{k}) \cdot \mathbf{a} = \hbar\dot{\mathbf{k}}. \tag{8.90}$$

From Eqs. (8.74) and (8.90), we obtain

$$\mathbf{M}_n(\mathbf{k}) \cdot \mathbf{a} = \mp e\left(\mathbf{E} + \frac{1}{c}\mathbf{v}_n(\mathbf{k}) \times \mathbf{B}\right). \tag{8.91}$$

It is easier to understand the motion of the electrons and holes if we consider only the electric field $\mathbf{E}$. In that case, Eq. (8.91) can be rewritten as

$$\mathbf{M}_n(\mathbf{k}) \cdot \mathbf{a} = \mp e\mathbf{E}. \tag{8.92}$$

As shown in Figure 8.5, the symbol ∘ indicates the position of the hole in **k** space. However, the behavior of the hole, which is governed by its **k** vector, is marked ⊗. In an electric field, the electron and hole states in the same band, which are marked (•) and (∘), respectively, always move rigidly like beads on a string. However, $d\mathbf{k}/dt$ for these two particles, which have opposite charges, are of opposite signs. For the holes, $d\mathbf{k}/dt$ is *always positive,* and the points ⊗ move in the same direction as the applied electric field. Because the electrons have negative charge, the electron state (•) moves opposite to the direction of the electric field.

The positive and negative effective mass (in units of mass of cesium atom) as a function of the potential depth, when $k = 0$ and $k = K$, respectively (in a simulated periodic potential), were demonstrated in the experiment described previously. The experimental results are shown in Figure 8.6.

It is often convenient to describe the physical behavior in terms of the hole states, especially when a Brillouin zone is nearly full. An example is shown in Figure 8.7, which shows a plane

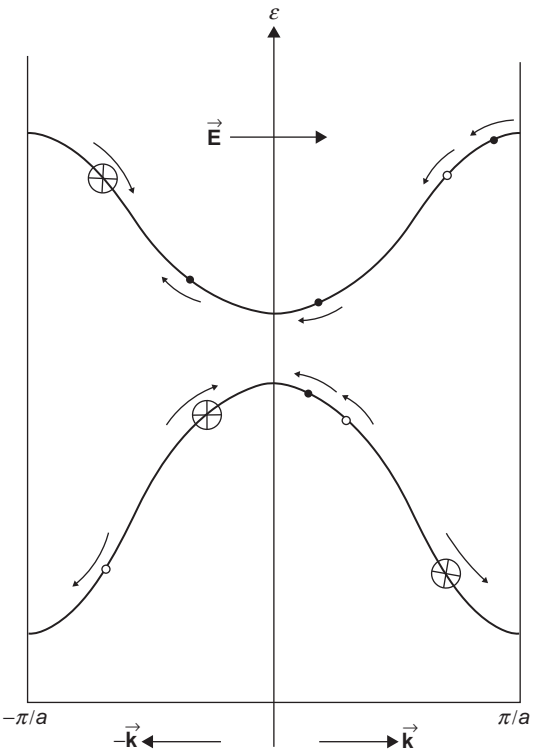


**FIGURE 8.5**

The electrons (•) and hole (∘) states always move together under the action of an electric field **E,** as shown by arrows. The behavior of the holes is governed by its **k** vector and is marked ⊗.

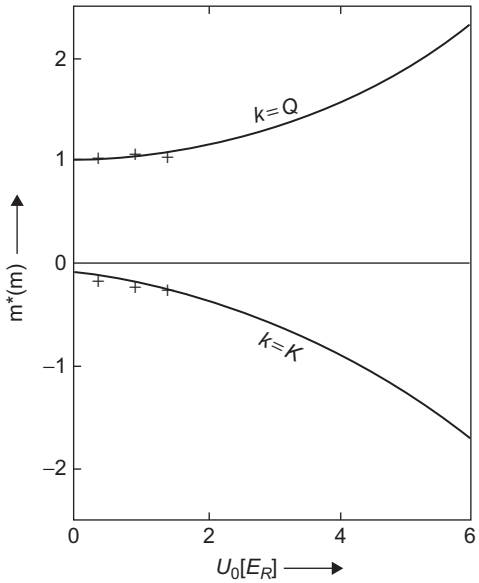


**FIGURE 8.6**

Effective masses $m^*$ for $k = 0$ and $k = K$ (in units of cesium atomic mass) versus potential depth $U_0$.

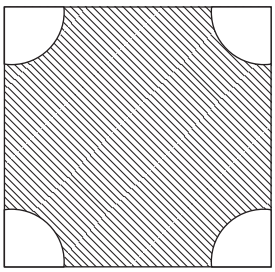

**FIGURE 8.7**

Occupied states in the first zone shown by a plane section perpendicular to (001).

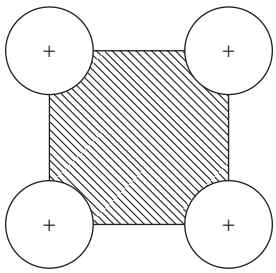


**FIGURE 8.8**

The circular areas of hole states at the zone corners (in two dimensions). They are spheres in three dimensions.

section perpendicular to (001) in a cubic zone structure where the occupied states are only in the first zone.

We note that the empty states of the nearly filled zone are in the corners of the zone. These empty states form spheres of hole states in the repeated zone scheme in the three-dimensional **k** space, a two-dimensional equivalent of which is shown in Figure 8.8. It is much easier to deal with these spheres of positive charges (holes) than the electrons in the Brillouin zone. The Fermi surface of divalent metals has small sections of holes in the first Brillouin zone as a consequence of electrons spilling over into the second Brillouin zone. The electrons in the second zone are ellipses of occupied states (ellipsoids in three dimensions), as shown in Figure 8.9.

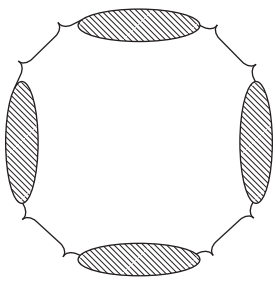

**FIGURE 8.9**

The electrons of the second zone in the Fermi surface of a divalent metal in the repeated zone scheme. The major portion of the first zone is filled with electrons, but these states are replaced by the hole states.

## 8.9 ZENER BREAKDOWN (APPROXIMATE METHOD)

We will consider the Zener breakdown (Ref. 12) in an electric field in two alternate ways. First, we will consider a simple and traditional method that is very controversial because the fundamental postulate on which the Bloch functions and the concept of the Brillouin zones have been built—i.e., the potential is periodic and the crystal has symmetry in the sense that one can consider the opposite ends to be equivalent—is lost in an external electric field. In fact, as we have seen, the wave vector **k** becomes time dependent, and the Brillouin zone boundary keeps moving with time. Nevertheless, we will first discuss the simple case neglecting these objections. Later, we will discuss the more rigorous theory of Zener breakdown (Ref. 12).

When we consider the motion of a Bloch electron (in one dimension) in an external electric field **E** along the x-axis, there are two ways in which we can represent the motion of the electron. The motion along the **k** space is shown in Figure 8.10 in the repeated zone scheme. These are the familiar Bloch oscillations in which the electron travels from 0 to A and then to B and C, and so on. The zone boundaries A and C are equivalent, and one can describe the oscillatory motion of the electron by stating that the electron has jumped from C to A.

However, the path of the electron in the external electric field in real space (in one dimension) shown in Figure 8.11 appears very different. The electron slows down as it moves from 0 to A, where it has a Bragg reflection. It cannot go forward because there is an energy gap at A, and the electron is forbidden to move in that region. The electron reverses direction until it reaches B and then accelerates again until it reaches the zone boundary at C.

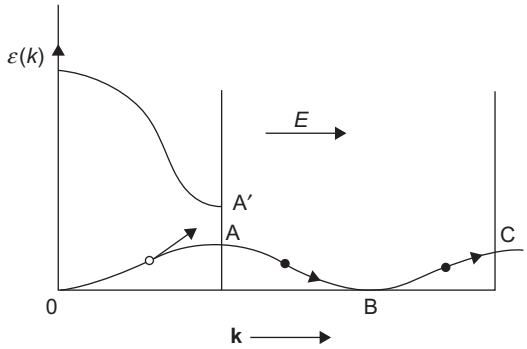


**FIGURE 8.10**

Electron trajectory in **k** space.

In addition, in a strong electric field E, the bands are tilted as shown in Figure 8.12.

An electron moving from P to Q will be reflected back into the band, or it can move from Q to R by crossing the energy gap $\varepsilon_g$ if the electric field is strong enough to satisfy the condition $\varepsilon_g = eEd$, where $d = \text{QR}$. Thus, we obtain

$$d \approx \frac{\varepsilon_g}{eE}. \tag{8.93}$$

It may be noted that QR is a forbidden region, and the electron has to tunnel through this region. This tunneling problem was originally solved by Zener by using WKB approximation. However, this is a semiclassical derivation with a lot of controversies because the periodicity of the Bloch functions is lost in an electric field. We will first outline a brief derivation of tunneling

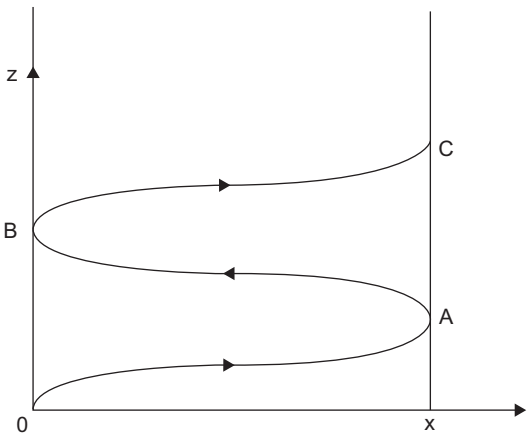


**FIGURE 8.11**

Path of electron in real space in an electric field E along the x axis.

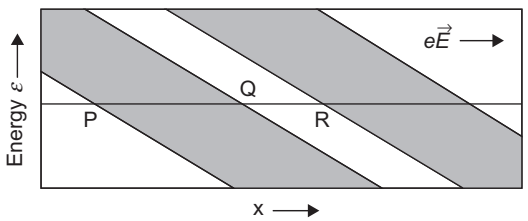


**FIGURE 8.12**

The energy bands in the $\varepsilon - x$ diagram are tilted in an applied electric field.

using the WKB approximation and then derive the effect of electric field on the Bloch functions for derivation of a more rigorous formula.

The tunneling of an electron in a square potential barrier is shown in Figure 8.13. This is solved by the WKB approximation.[4]

The approximate solution of the Schrodinger equation in the WKB approximation is

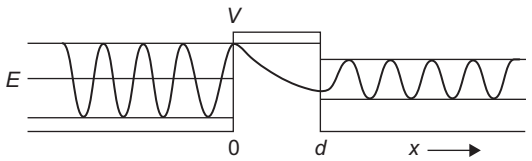


**FIGURE 8.13**

Square potential barrier. Penetration of a barrier by a wave function $\psi(x)$ when $V > d$.

$$\psi(x) = Ae^{i/\hbar \int^{x} dx \sqrt{2m(\varepsilon - V)}}. \tag{8.94}$$

If $V - \varepsilon = u$, where $u$ is positive, an electron wave function that starts on the left side of Figure 8.13 and travels distance $d$ through the gap will have a transmission coefficient[7]

$$T = e^{-2d\sqrt{2mu/\hbar^2}}. \tag{8.95}$$

However, in the case of a Bloch electron moving on an electric field, if $\varepsilon_v$ and $\varepsilon_c$ are the energies of the valence and conduction bands, respectively, while $\varepsilon - \varepsilon_v$ is negative in the energy gap, $\varepsilon_c - \varepsilon = 0 = \varepsilon_v - \varepsilon$ at the zone boundaries, and once the electron tunnels to the conduction band, $\varepsilon_v - \varepsilon$ is positive. If we include these specific conditions for tunneling through the bands, a rough estimate of the Zener tunneling problem can be made by rewriting the WKB approximation, and the probability for an electron to tunnel from one band to another is of the form

$$T = e^{2i/\hbar \int_0^{d} dx \sqrt{2m\sqrt{(\varepsilon_c - \varepsilon)(\varepsilon_v - \varepsilon)}}}. \tag{8.96}$$

Eq. (8.96) can be rewritten in the alternate form (in a very rough approximation)

$$T \approx e^{-2d\sqrt{\frac{2m\varepsilon_g}{\hbar^2}}}. \tag{8.97}$$

From Eqs. (8.87) and (8.97), we obtain the expression for tunneling probability as

$$T \approx e^{-\frac{2\varepsilon_g}{eE}\sqrt{\frac{2m\varepsilon_g}{\hbar^2}}}. \tag{8.98}$$

The probability of the electron to tunnel through the barrier obtained in Eq. (8.98) is a *very rough estimate* of the tunneling problem.

## 8.10 RIGOROUS CALCULATION OF ZENER TUNNELING

We expanded $\psi(\mathbf{r},t)$—in Eqs. (8.53) and (8.58)—in terms of the Houston states

$$\psi(\mathbf{r},t)=\sum_i a_i(t)\phi_i'(\mathbf{r},t), \tag{8.99}$$

which can be rewritten in the alternate form from Eq. (8.58)

$$\psi(\mathbf{r},t)=\sum_{n'\mathbf{k}'} a_{n'\mathbf{k}'}(t)e^{-ie\mathbf{A}\cdot\mathbf{r}/\hbar c}\phi_{n'\mathbf{k}'(t)}(\mathbf{r}), \tag{8.100}$$

$$H\psi(\mathbf{r},t)=\sum_{n'\mathbf{k}'} a_{n'\mathbf{k}'}(t)\varepsilon_{n'}(\mathbf{k}'(t))e^{i(\mathbf{k}'-e\mathbf{A}/\hbar c)\cdot\mathbf{r}}U_{n'\mathbf{k}'(t)}(\mathbf{r}). \tag{8.101}$$

Here, we replaced $a_i(t)$ by $a_{n'\mathbf{k}'}(t)$ and replaced the summation over $i$ by $n'k'$ and expressed the Houston functions as

$$\phi_{n\mathbf{k}(t)}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}U_{n\mathbf{k}(t)}(\mathbf{r}). \tag{8.102}$$

We also obtain

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t)=i\hbar\sum_{n'\mathbf{k}'}\frac{\partial a_{n'\mathbf{k}'}(t)}{\partial t}e^{i(\mathbf{k}'-\frac{e\mathbf{A}}{\hbar c})\cdot\mathbf{r}}U_{n'\mathbf{k}'(t)}(\mathbf{r})+i\hbar\sum_{n'\mathbf{k}'}a_{n'\mathbf{k}'}(t)e^{i(\mathbf{k}'-\frac{e\mathbf{A}}{\hbar c})\cdot\mathbf{r}}\frac{\partial}{\partial t}U_{n'\mathbf{k}'}(\mathbf{r}). \tag{8.103}$$

Here, we used the condition that $\mathbf{k}'-\frac{e\mathbf{A}}{\hbar c}$ is time independent from Eq. (8.59).

Further,

$$\frac{\partial}{\partial t}U_{n\mathbf{k}(t)}(\mathbf{r})=\frac{\partial}{\partial k_x}U_{n\mathbf{k}}\frac{dk_x}{dt}=-\frac{eE}{\hbar}\frac{\partial}{\partial k_x}U_{n\mathbf{k}}. \tag{8.104}$$

Substituting Eqs. (8.101) through (8.103) in Eq. (8.51), multiplying both sides by $e^{-i(\mathbf{k}-\frac{e\mathbf{A}}{\hbar c})\cdot\mathbf{r}}U^*_{n\mathbf{k}}(\mathbf{r})$, using $\mathbf{E}=\hat{i}E(t)$, integrating over the volume of the crystal, and using the orthonormal conditions of the Bloch functions (Problem 8.9), we obtain

$$\varepsilon_n(\mathbf{k},t)a_{n\mathbf{k}(t)}=i\hbar\frac{\partial a_{n\mathbf{k}(t)}}{\partial t}-eE(t)\sum_{n'}A_{nn'}(\mathbf{k}(t))a_{n'\mathbf{k}(t)}, \tag{8.105}$$

where

$$A_{nn'}(\mathbf{k}(t))\equiv -i\int U^*_{n\mathbf{k}(t)}\frac{\partial}{\partial k_x}U_{n'\mathbf{k}(t)}d\tau. \tag{8.106}$$

From Eq. (8.105), it follows that the coefficients $a_{n\mathbf{k}(t)}$ are coupled only to $a_{n'\mathbf{k}(t)}$, i.e., coupled to the same $\mathbf{k}$. Therefore, for a given $\mathbf{k}$, we can write

$$a_{n\mathbf{k}(t)}=\alpha_n(t)e^{-\frac{i}{\hbar}\int_0^t\varepsilon_n(\mathbf{k}(t')dt'}. \tag{8.107}$$

Substituting Eq. (8.107) in Eq. (8.105), we obtain

$$\dot{\alpha}_n(t) = \frac{ieE(t)}{\hbar}\sum_{n'}\alpha_{n'}(t)A_{nn'}(\mathbf{k}(t))\exp\left[\frac{i}{\hbar}\int_0^t[\varepsilon_n(\mathbf{k}(t'))-\varepsilon_{n'}(\mathbf{k}(t'))]dt'\right]. \tag{8.108}$$

This general expression can be used for derivation of Wannier–Stark ladders for time-dependent $E$ as well as for Zener tunneling between the valence and conduction bands.

At $t = 0$, before the field $E$ is turned on, $\mathbf{k}(t) = \mathbf{k}(t = 0)$, the electron state can be described by a Bloch wave in band $n$ with $\mathbf{k}(t) = \mathbf{k}(t = 0)$; then at $t = 0$,

$$\alpha_{n'} = \delta_{nn'}. \tag{8.109}$$

After a time $T = -\frac{\hbar K}{eE}$, where $T$ is the period of one Bloch oscillation, which is a sufficiently short time so that $\alpha_{n'} \ll 1$, $n' \neq n$, we can substitute Eq. (8.109) in Eq. (8.108) to obtain

$$\alpha_{n'}(t) = \int_0^t \frac{ieE(t')}{\hbar}A_{n'n}(\mathbf{k}(t'))\exp\left[\frac{i}{\hbar}\int_0^{t'}[\varepsilon_{n'}(\mathbf{k}(t''))-\varepsilon_n(\mathbf{k}(t''))]dt''\right]dt'. \tag{8.110}$$

We consider the case in which $E$ is constant and is in the direction of the reciprocal-lattice vector $K$ (which is along the x axis) and use $\hbar\dot{k} = -eE$ to change the variables

$$dt = -\frac{\hbar}{eE}dk. \tag{8.111}$$

From Eqs. (8.110) and (8.111), it can be shown that the transmission probability per period $T$,

$$P_{nn'} = |\alpha_{n'}(T)|^2 = \left|\int_{-K/2}^{K/2} A_{n'n}(\mathbf{k})\exp\left[-\tfrac{i}{eE}\int_0^{k_x}[\varepsilon_{n'}(k_x',\mathbf{k}_\perp)-\varepsilon_n(k_x',\mathbf{k}_\perp)]dk_x'\right]dk_x\right|^2. \tag{8.112}$$

Any calculation of $P_{nn'}$ requires actual band calculations for the particular metal or the semiconductor to calculate $A_{n'n}(\mathbf{k})$, and evaluation of the integrals requires the use of a computer. However, in what follows, we will make several drastic approximations to derive an expression for the Zener tunneling between a valence band and a conduction band. In the process, we will explain why the Zener tunneling between the two bands is much easier for semiconductors than for metals.

To be able to consider Zener tunneling, we consider two parabolic bands that are of the form

$$\varepsilon_{1k} = \varepsilon_v - \frac{\hbar^2k^2}{2m_v^*} \tag{8.113}$$

and

$$\varepsilon_{2k} = \varepsilon_c + \frac{\hbar^2k^2}{2m_c^*}. \tag{8.114}$$

Thus,

$$\varepsilon_{2k} - \varepsilon_{1k} = \varepsilon_g + \frac{\hbar^2 k^2}{2m^*}, \tag{8.115}$$

where $\varepsilon_g = \varepsilon_c - \varepsilon_v$, and $m^*$ is the reduced mass defined by

$$\frac{1}{m^*} = \frac{1}{m_v^*} + \frac{1}{m_c^*}. \tag{8.116}$$

With these conditions, Eq. (8.105) can be rewritten as

$$\varepsilon_{1\mathbf{k}(t)} a_{1\mathbf{k}(t)} = i\hbar \frac{\partial a_{1\mathbf{k}(t)}}{\partial t}, \tag{8.117}$$

from which we obtain

$$a_{1\mathbf{k}(t)} = \exp\left[-\frac{i}{\hbar}\int_0^t dt' \varepsilon_{1\mathbf{k}}(t')\right]. \tag{8.118}$$

If the time interval is short such that $\alpha_{n'} \ll 1$, $n' \neq n$, we can substitute Eq. (8.118) in Eq. (8.108) to obtain an expression for the rate of tunneling from band 1 to band 2 after time $t$ as

$$\alpha_2(t) = \int_0^t \frac{ieE}{\hbar} A_{21}(\mathbf{k}(t')) \exp\left[\frac{i}{\hbar}\int_0^{t'} [\varepsilon_{2\mathbf{k}(t'')} - \varepsilon_{1\mathbf{k}(t'')}] dt''\right] dt'. \tag{8.119}$$

For a linear lattice, it can be shown that apart from the oscillatory terms in $k$, $iA_{21} \approx a$, where $a$ is the lattice constant. Further, if $\tau$ is the time needed for $k$ to move by a reciprocal lattice vector $K = 2\pi/a$,

$$\alpha_2(\tau) \approx a \int_0^{2\pi/a} dk \exp\left[\frac{-i}{eE}\int_0^k dk' (\varepsilon_{2k'} - \varepsilon_{1k'})\right]. \tag{8.120}$$

Here, we used the relation $\hbar\dot{k} = -eE$ to change the variables $dt = -\frac{\hbar}{eE} dk$. From Eqs. (8.115) and (8.120), we obtain

$$\alpha_2(\tau) \approx a \int_0^{2\pi/a} dk \exp\left[\frac{-i}{eE}\int_0^k dk' \left(\varepsilon_g + \frac{\hbar^2 k'^2}{2m^*}\right)\right]. \tag{8.121}$$

The integral is impossible to perform exactly, but an approximate result achieved by using the method of steepest descent yields the expression for the rate of tunneling:

$$\alpha_2(\tau) \approx a \exp\left[-\frac{2\varepsilon_g^{3/2}}{3eE}\sqrt{\frac{2m^*}{\hbar^2}}\right]. \tag{8.122}$$

The probability of tunneling, which is given by $|\alpha_2(\tau)|^2$, is much smaller in metals than in semiconductors because both the band gaps and the effective masses are much smaller for semiconductors.

## 8.11 ELECTRON–PHONON INTERACTION

The electron–phonon interaction process is basically the absorption (annihilation) or emission of a phonon $(\mathbf{q}, \lambda)$ with a simultaneous change of the electron states from $|\mathbf{k}, \sigma>$ to $|\mathbf{k} \pm \mathbf{q}, \sigma>$. Here, $\sigma$ is the spin index and $\lambda = x, y, z$ directions. These two processes are shown as (a) and (b) in Figure 8.14 (the spin index $\sigma$ and $\lambda$ are not shown).

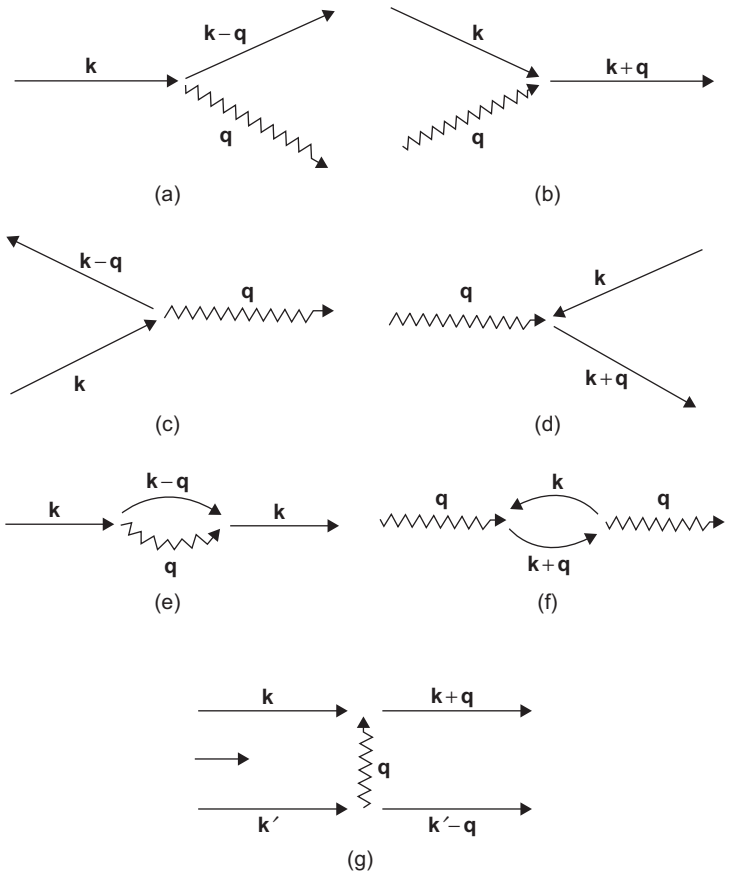


**FIGURE 8.14**

Graphs for various types of electron–phonon interaction. The Umklapp process is not shown here.

Process (a) is called phonon emission, and process (b) is called phonon absorption. In processes (c) and (d), the time axis runs from left to right. The electrons are assumed to run backward in time, and holes run forward in time. Process (c) describes the recombination of an electron-hole pair where a phonon is emitted. Process (d) describes the generation of an electron-hole pair by a phonon. One can describe processes (a) through (d) by using first-order perturbation theory. The conservation laws for the sum of the wave vectors (momentum) and energy are obeyed.

Processes (e) through (g) are due to contributions of perturbation calculations of higher order. Process (e) describes the emission and reabsorption of a virtual phonon. Process (f) describes the emission and reabsorption of a virtual electron-hole pair. Process (g) describes the electron–electron interaction of a virtual phonon. In these graphs, the intermediate states are not stationary states of the system. The laws of conservation of energy do not apply to these intermediate states because these processes occur in a very short time. The uncertainty relation between energy and time holds for these virtual states. The electron–electron interaction by exchange of virtual phonons will be neglected in the following discussions.

The Hamiltonian of a crystal can be written as

$$H_c = H_{el} + H_{ion} + H_{el-ion}. \tag{8.123}$$

Here, the contribution due to exchange is neglected. Using the Born–Oppenheimer (adiabatic) approximation discussed in Chapter 7, we can separate the movement of the electrons in a stationary lattice and the movement of the ions in a uniform space of electrons. The Hamiltonian $H_{ion}$ is considered separately and is used to study lattice dynamics, which we considered in Chapter 2. We write

$$H_{el-ion} = H^0_{el-ion} + H_{el-ph}, \tag{8.124}$$

where $H^0_{el-ion}$ describes the electron interaction with the periodic potential in the one-electron band model.

We express

$$H_e = H_{el} + H^0_{el-ion}. \tag{8.125}$$

Thus, we can write the Schrodinger equation for the electrons—from Eqs. (8.123) through (8.125)—as

$$H\psi = (H_e + H_{el-ph})\psi = E\psi. \tag{8.126}$$

We also note that we can write

$$H_{el-ion} = \sum_{j,i,\alpha} V(\mathbf{r}_j - \mathbf{R}_{i\alpha}(t)), \tag{8.127}$$

where $\mathbf{r}_j$ is the position of an electron, and $\mathbf{R}_{i\alpha}(t) = \mathbf{R}_i + \mathbf{d}_\alpha + \mathbf{u}_{\alpha i}(t)$ (see Figure 2.1 in Chapter 2). Here, the position vector of the ion is the sum of the equilibrium position of the $\alpha$th ion in the $i$th Wigner–Seitz cell, and $\mathbf{u}_{\alpha i}(t)$ is the instantaneous deviation of the $\alpha$th ion from the equilibrium position.

We assume that the interaction potential depends only on the electron–ion separation (Nordheim's rigid ion model). We can expand the potential

$$V_\alpha(\mathbf{r}_j - \mathbf{R}_{i\alpha} - \mathbf{u}_{\alpha i}) \approx V_\alpha(\mathbf{r}_j - \mathbf{R}_{i\alpha}) - \sum_{\alpha ij} \mathbf{u}_{\alpha i} \cdot \nabla V_\alpha(\mathbf{r}_j - \mathbf{R}_{i\alpha}). \tag{8.128}$$

From Eqs. (8.22), (8.127), and (8.128), we obtain

$$H_{el-ph} = -\sum_{\alpha ij} \mathbf{u}_{\alpha i} \cdot \nabla V_\alpha(\mathbf{r}_j - \mathbf{R}_{i\alpha}). \tag{8.129}$$

In Eq. (2.159), we also derived (note that we have changed the notation from $\mathbf{k}$ to $\mathbf{q}$ because we will use $\mathbf{k}$ for electrons and generalized to a lattice with a basis, and from $n$ to $\alpha$)

$$\mathbf{u}_{\alpha i} = \frac{1}{\sqrt{M_\alpha N}} \sum_{\mathbf{q}\lambda} \hat{\epsilon}_{\alpha\lambda}(\mathbf{q}) \hat{Q}_{\mathbf{q}\lambda} e^{i\mathbf{q}\cdot\mathbf{R}_i}, \tag{8.130}$$

where the expression for the normal coordinate $Q_{\mathbf{q}\lambda}$ was derived in Eq. (2.182) as

$$\hat{Q}_{\mathbf{q}\lambda} = \left(\frac{\hbar}{2\omega_{\mathbf{q}\lambda}}\right)^{\frac{1}{2}} (\hat{a}_{\mathbf{q}\lambda} + \hat{a}^\dagger_{-\mathbf{q}\lambda}). \tag{8.131}$$

From Eqs. (8.129) through (8.131), we obtain

$$H_{el-ph} = -\sum_{\alpha ij} \frac{1}{\sqrt{M_\alpha N}} \sum_{\mathbf{q}\lambda} \hat{Q}_{\mathbf{q}\lambda} e^{i\mathbf{q}\cdot\mathbf{R}_i} \hat{\epsilon}_{\alpha\lambda}(\mathbf{q}) \cdot \nabla V_\alpha(\mathbf{r}_j - \mathbf{R}_{i\alpha}). \tag{8.132}$$

We will now convert quantum mechanical equations for $H_e$ from the $\mathbf{r}$-representation into the occupation number representation. We assume that the Hamiltonian is a sum of one-electron operators

$$\hat{H} = \sum_i \hat{H}(\mathbf{r}_i, s_i). \tag{8.133}$$

We recall that, for fermions, we derived in Chapter 2 (Eq. 2.110) that

$$\hat{c}^\dagger_{\mathbf{k}} \hat{c}_{\mathbf{k}} = n_{\mathbf{k}} \tag{8.134}$$

(In this chapter, we use $\hat{c}^\dagger_{\mathbf{k}}$ and $\hat{c}_{\mathbf{k}}$ for creation and annihilation operators for electrons to distinguish from the phonon operators.)

Similarly, from Eqs. (2.99) through (2.101) and (2.109), we derived

$$[c_{\mathbf{k}}, c^\dagger_{\mathbf{k}}]_+ = \delta_{\mathbf{k},\mathbf{k}'}, \tag{8.135}$$

$$c^\dagger_{\mathbf{k}} | n_1, n_2, \ldots, n_{\mathbf{k}} \ldots, > = \sqrt{1 - n_{\mathbf{k}}} (-1)^m | n_1, n_2, \ldots, n_{\mathbf{k}} + 1, \ldots, > \tag{8.136}$$

and

$$c_{\mathbf{k}} | n_1, n_2, \ldots, n_{\mathbf{k}} \ldots, > = \sqrt{n_{\mathbf{k}}} (-1)^m | n_1, n_2, \ldots, n_{\mathbf{k}} - 1, \ldots, >, \tag{8.137}$$

where

$$m = \sum_{j<\mathbf{k}} n_i. \tag{8.138}$$

We also showed in Chapter 7 (Eq. 7.18) that the wave function is a Slater determinant, which can be written in the form

$$\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \ldots, \mathbf{r}_N s_N) = \frac{1}{\sqrt{N!}} \sum_n (-1)^n \psi_{n_1}(\mathbf{r}_1 s_1)\psi_{n_2}(\mathbf{r}_2 s_2) \ldots \psi_{n_N}(\mathbf{r}_N s_N), \tag{8.139}$$

where the sum $n$ is over all permutations $n$ of $1 \ldots N$.

We can rewrite Eq. (8.139) in the alternate form

$$\Psi = \frac{1}{\sqrt{N!}} \sum_P P(-1)^P \psi_\alpha(\mathbf{r}_1 s_1)\psi_\beta(\mathbf{r}_2 s_2) \ldots \psi_\omega(\mathbf{r}_N s_N), \tag{8.140}$$

where the sum $P$ is over all permutations of the indices $\alpha, \beta, \ldots$, etc.

From Eq. (8.140), we can write

$$H\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \ldots, \mathbf{r}_N s_N) = \frac{1}{\sqrt{N!}} H \sum_P P(-1)^P \psi_\alpha(\mathbf{r}_1 s_1)\psi_\beta(\mathbf{r}_2 s_2) \ldots \psi_\omega(\mathbf{r}_N s_N). \tag{8.141}$$

From Eqs. (8.133) and (8.141), we obtain

$$H\Psi = \frac{1}{\sqrt{N!}} \sum_i \sum_P P(-1)^P \psi_\alpha(\mathbf{r}_1 s_1)\psi_\beta(\mathbf{r}_2 s_2) \ldots H(\mathbf{r}_i s_i)\psi_\lambda(\mathbf{r}_i s_i) \ldots \psi_\omega(\mathbf{r}_N s_N). \tag{8.142}$$

If the Hamiltonian does not involve the spin explicitly (Eq. 7.20),

$$\int \psi_\lambda^*(\mathbf{r}_i s_i) H(\mathbf{r}_i) \psi_{\lambda'}(\mathbf{r}_i s_i') = \int \phi_\lambda^*(\mathbf{r}_i) H(\mathbf{r}_i) \phi_{\lambda'}(\mathbf{r}_i) \delta_{s_i, s_i'} \tag{8.143}$$

because

$$\psi_\lambda(\mathbf{r}_j s_j) = \phi_\lambda(\mathbf{r}_j)\chi_\lambda(s_j). \tag{8.144}$$

We can write the Hamiltonian as a sum of operators on single particles,

$$H = \sum_i H(\mathbf{r}_i s_i) \equiv \sum_i H_i. \tag{8.145}$$

Because $\psi_\lambda$ forms a complete set, we can rewrite Eq. (8.145) in a more convenient way by writing

$$\hat{H} = \sum_{i\lambda\lambda'} |\psi_{\lambda'}(i)><\psi_{\lambda'}(i)|\hat{H}_i|\psi_\lambda(i)>|<\psi_\lambda(i)|. \tag{8.146}$$

The one-particle equivalent of Eq. (8.146) is

$$H(\mathbf{r}_i s_i)\psi_\lambda(\mathbf{r}_i s_i) = \sum_{\lambda'} \psi_{\lambda'}(\mathbf{r}_i s_i) <\lambda'|H_i|\lambda>, \tag{8.147}$$

which has $i$-independent matrix elements. Here, the spin index $s$ is dropped from $\lambda$ because the Hamiltonian $H$ does not explicitly contain spin terms, whereas the summation over $\lambda'$ explicitly contains spin summation.

We define the operator

$$\hat{A}_{\lambda'\lambda} = \sum_i |\psi_{\lambda'}(i)><\psi_\lambda(i)|. \tag{8.148}$$

The operator $\hat{A}_{\lambda'\lambda}$ searches for each electron (one at a time) in state $\psi_\lambda$ and moves it to $\psi_{\lambda'}$. From Eqs. (8.146) and (8.148), we obtain

$$\hat{H} = \sum_{\lambda\lambda'} \hat{A}_{\lambda'\lambda} <\psi_{\lambda'}(1)|\hat{H}_1|\psi_\lambda(1)>, \tag{8.149}$$

where the label 1 is used instead of $i$ because the matrix elements of a one-particle operator do not depend on which particle is involved.

We first consider a wave function $\Psi$ and wish to evaluate

$$\sum_{i=1}^{N} <\Psi_a|\psi_{\lambda'}(i)><\psi_\lambda(i)|\Psi_b>. \tag{8.150}$$

We consider one term

$$<\Psi_a|\psi_{\lambda'}(1)><\psi_\lambda(1)|\Psi_b>. \tag{8.151}$$

This term is nonzero only if in $|\Psi_b>$, $\psi_\lambda$ is unoccupied and $\psi_{\lambda'}$ is occupied while in $|\Psi_a>$, $\psi_\lambda$ is unoccupied and $\psi_{\lambda'}$ is occupied, and otherwise $\Psi_a$ and $\Psi_b$ are identical. Thus, one has to permute $\psi_{\lambda'}$ past all the states in the ordering to obtain $|\psi_{\lambda'}(1)>$, and one obtains a factor of $(-1)^{m_{\lambda'}}$. Similarly, one obtains a factor $(-1)^{m_\lambda}$ to permute $\psi_\lambda$ past all the states below it to obtain $|\psi_\lambda(1)>$. Here,

$$m_\lambda = \sum_{i<\lambda} n_i \text{ and } m_{\lambda'} = \sum_{i<\lambda'} n_i. \tag{8.152}$$

Thus, we obtain

$$\sum_{i=1}^{N} <\Psi_a|\psi_{\lambda'}(i)><\psi_\lambda(i)|\Psi_b> = (-1)^{m_\lambda + m_{\lambda'}}, \tag{8.153}$$

if it is not zero. Thus, in the occupation number representation,

$$\hat{A}_{\lambda'\lambda}|n_1, n_2, n_{\lambda'} \ldots n_{\lambda'} \ldots> = (-1)^{m_{\lambda'}}(-1)^{m_\lambda}\sqrt{(1-n_{\lambda'})n_\lambda}\,|n_1, n_2, \ldots, n_{\lambda'+1} \ldots n_{\lambda-1} \ldots>. \tag{8.154}$$

From Eqs. (8.149) and (8.154), we obtain (Problem 8.11)

$$\hat{H}|n_1, n_2, \ldots, n_1, n_2, \ldots, n_{\lambda'}, \ldots, n_\lambda, \ldots>$$

$$= \sum_{\lambda,\lambda'} \sqrt{n_\lambda(1-n_{\lambda'})}(-1)^{m_\lambda + m_{\lambda'}'} <\lambda'|H_1|\lambda>|n_1, n_2, \ldots, n_{\lambda'+1}, \ldots, n_{\lambda-1}, \ldots> \text{ if } \lambda \neq \lambda', \tag{8.155}$$

$$= \sum_\lambda n_\lambda <\lambda|H_1|\lambda>|n_1, n_2, \ldots, n_\lambda \ldots>, \text{ if } \lambda = \lambda'. \tag{8.156}$$

Here, the terms $\sum\sqrt{n_\lambda(1-n_\lambda)}$ and $n_\lambda$ occur due to the property of the fermions that $n_\lambda$ can be either zero or 1.

From Eqs. (8.152) through (8.154), the operator

$$\hat{A}_{\lambda'\lambda} = \hat{c}^\dagger_{\lambda'}\,\hat{c}_\lambda, \tag{8.157}$$

where the creation and annihilation operators for fermions were defined in Eqs. (8.136) and (8.137). From Eqs. (8.149), (8.153), and (8.155) through (8.157), we obtain by replacing $\lambda$ and $\lambda'$ by $\mathbf{k}s$ and $\mathbf{k}'s$,

$$H|n_1, n_2, \ldots, n_{\mathbf{k}} \ldots > = \sum_{\mathbf{k}\mathbf{k}'s} <\mathbf{k}'s|H_1(\mathbf{r})|\mathbf{k}s> c^\dagger_{\mathbf{k}'s} c_{\mathbf{k}s}|n_1, n_2, \ldots, n_{\mathbf{k}'} \ldots n_{\mathbf{k}} \ldots >. \tag{8.158}$$

The Hamiltonian $H$ in the occupation number representation becomes

$$H = \sum_{\mathbf{k},\mathbf{k}',s} <\mathbf{k}'s|H_1(\mathbf{r})|\mathbf{k}s> c^\dagger_{\mathbf{k}'s} c_{\mathbf{k}s}, \tag{8.159}$$

where

$$<\mathbf{k}'s|H_1(\mathbf{r})|\mathbf{k}s> = \int \psi^*_{\mathbf{k}'s}(\mathbf{r}) H_1(\mathbf{r}) \psi_{\mathbf{k}s}(\mathbf{r}) d\mathbf{r}. \tag{8.160}$$

Here, we dropped the index $i$ in $\mathbf{r}_i$. We note that because spin is conserved in $\mathbf{k} \rightarrow \mathbf{k}'$ transition, we have to carry out only one spin summation. The matrix elements on the right side of Eq. (8.160) are formed from the Bloch functions.

To calculate $H_{el-ph}$ from Eqs. (8.132) and (8.160), we expand $V_\alpha(\mathbf{r}-\mathbf{R}_{i\alpha})$ in a Fourier series

$$V_\alpha(\mathbf{r}-\mathbf{R}_i) = \sum_{\vec{\kappa}} e^{i\vec{\kappa}\cdot(\mathbf{r}-\mathbf{R}_i)} V_{\alpha\vec{\kappa}}, \tag{8.161}$$

from which we obtain

$$<\mathbf{k}'s|\nabla V_\alpha|\mathbf{k}s> = \sum_{\vec{\kappa}} e^{-i\vec{\kappa}\cdot\vec{R}_i} V_{\alpha\vec{\kappa}}\, i\vec{\kappa} <\mathbf{k}'s|e^{i\vec{\kappa}\cdot\vec{r}}|\mathbf{k}s>. \tag{8.162}$$

From Eqs. (8.132) and (8.162), the sum over $i$ contains the factor

$$\sum_i e^{i(\vec{q}-\vec{\kappa})\cdot\vec{R}_i} = N \sum_{\vec{K}_l} \delta_{\vec{\kappa},\,\vec{q}+\vec{K}_l}. \tag{8.163}$$

Thus, in the sum over $\vec{\kappa}$ in Eq. (8.162), only the term $\vec{\kappa} = \vec{q} + \vec{K}_l$ survives. If we write the Bloch functions $|\mathbf{k}> \equiv e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$ (note that we have also used bold letters as vectors) in Eq. (8.162), the integrand $I$ contains the term

$$I = \int d\mathbf{r}\, e^{i(\mathbf{k}+\mathbf{q}+\mathbf{K}_l-\mathbf{k}')\cdot\mathbf{r}} u^*_{n'\mathbf{k}'}(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}). \tag{8.164}$$

Because $u^*_{n'\mathbf{k}'}(\mathbf{r})u_{n\mathbf{k}}(\mathbf{r})$ is a periodic function in $\mathbf{R}$,

$$I = \int d\mathbf{r}\, u^*_{n'\mathbf{k}'}(\mathbf{r})u_{n\mathbf{k}}(\mathbf{r})\delta_{\mathbf{k}',\,\mathbf{k}+\mathbf{q}+\mathbf{K}_l}. \tag{8.165}$$

From Eqs. (8.132), (8.159), and (8.162) through (8.165), and letting $n' = n$ (because the electron remains in the same band $n = n'$ when making the transition $\mathbf{k}$ to $\mathbf{k}'$ except for the U-process to be discussed later), we obtain

$$\begin{aligned} H_{el-ph} = &-\sum_{\mathbf{k}\mathbf{K}_l\mathbf{q}\alpha\lambda s} i\sqrt{\frac{N}{M_\alpha}}\, V_{\alpha,\,\mathbf{q}+\mathbf{K}_l}(\mathbf{q}+\mathbf{K}_l)\cdot\hat{\epsilon}_{\alpha\lambda}\left(\frac{\hbar}{2\omega_{\mathbf{q}\lambda}}\right) \\ &\times \int u^*_{n,\,\mathbf{q}+\mathbf{K}_l+\mathbf{k}}(\mathbf{r})u_{n\mathbf{k}}(\mathbf{r})d\mathbf{r}\,(\hat{a}^\dagger_{-\mathbf{q}\lambda}+\hat{a}_{\mathbf{q}\lambda})\hat{c}^\dagger_{\mathbf{k}+\mathbf{q}+\mathbf{K}_l,s}c_{\mathbf{k},s}. \end{aligned} \tag{8.166}$$

We note that if $\mathbf{k}$ and $\mathbf{q}$ are added vectorially, the resultant vector can lie outside the first Brillouin zone (where $\mathbf{k}, \mathbf{k}', \mathbf{q}$, and $\mathbf{q}'$ lie in the reduced zone scheme) in the repeated zone scheme, so that $\mathbf{k}' = \mathbf{k}+\mathbf{q}+\mathbf{K}_l$. The sum over $\mathbf{K}_l$ in Eq. (8.164) is thus reduced to one term. If $\mathbf{K}_l = 0$, the transition is called a normal process (N-process) while if $\mathbf{K}_l \neq 0$, the transition is called the Umklapp process (U-process). (Umklapp is a German word for "flopping over.")

To simplify further, we assume that we restrict ourselves to Bravais lattices so that there is only one atom in the Wigner–Seitz cell. Thus, we can omit the index $\alpha$ and $\lambda$ and count the different acoustic branches since the optical branches do not exist. We also restrict the derivation to the N-process such that $\mathbf{K}_l = 0$. We also assume that phonons are either longitudinal or transverse so that $\hat{\epsilon}_\lambda$ is either parallel or perpendicular to $\mathbf{q}$. With these assumptions, Eq. (8.166) can be written as

$$H_{el-ph} = -\sum_{\mathbf{k}\mathbf{q}\lambda s} i\sqrt{\frac{\hbar N}{2M\omega_{\mathbf{q}\lambda}}}\, V_{\mathbf{q}}\mathbf{q}\cdot\hat{\epsilon}_\lambda \times \int d\mathbf{r}\, u^*_{n,\,\mathbf{k}+\mathbf{q}}(\mathbf{r})u_{n\mathbf{k}}(\mathbf{r})\,(\hat{a}^\dagger_{-\mathbf{q}\lambda}+\hat{a}_{\mathbf{q}\lambda})\hat{c}^\dagger_{\mathbf{k}+\mathbf{q},\,s}c_{\mathbf{k},\,s}. \tag{8.167}$$

Because $\hat{\epsilon}_\lambda \perp \mathbf{q}$ for *transverse phonons*, $\hat{\epsilon}_\lambda \cdot \mathbf{q} = 0$. Thus, only *longitudinal acoustic phonons* are coupled to the electrons. Eq. (8.167) can be rewritten in the alternate form

$$H_{el-ph} = \sum_{\mathbf{k}\mathbf{q}s} B_{\mathbf{k}\mathbf{q}}(\hat{a}^\dagger_{-\mathbf{q}}+\hat{a}_{\mathbf{q}})\hat{c}^\dagger_{\mathbf{k}+\mathbf{q},\,s}\hat{c}_{\mathbf{k},s}. \tag{8.168}$$

We can calculate the probability of transition of an electron from state $|\mathbf{k}>$ into state $|\mathbf{k}+\mathbf{q}>$. Because the spin is unchanged in this transition, it can be ignored.

From Fermi's "golden rule" (originally derived by Dirac from perturbation theory), the transition probability

$$P(i\to f) = \frac{2\pi}{\hbar}|<f|H_{el-ph}|i>|^2\,\delta(\varepsilon_f-\varepsilon_i). \tag{8.169}$$

Here, the initial states are $|i>$ and the final states $|f>$ are characterized by the occupation numbers $n_{\mathbf{k}}$ and $n_{\mathbf{k}+\mathbf{q}}$ of the electron state and $n_{\mathbf{q}}$ and $n_{-\mathbf{q}}$ of the phonon states involved in the transition

$$|n_{\mathbf{k}+\mathbf{q}}, n_{\mathbf{k}};\, n_{\mathbf{q}}, n_{-\mathbf{q}}>. \tag{8.170}$$

If we consider the transition involving the absorption of a phonon, we apply the operator $\hat{c}^{\dagger}_{\mathbf{k+q}}\hat{c}_{\mathbf{k}}a_{\mathbf{q}}$ to Eq. (8.170). It can be shown that (Problem 8.12)

$$< n_{\mathbf{k+q}}+1, n_{\mathbf{k}}-1; n_{\mathbf{q}}-1|\hat{c}^{\dagger}_{\mathbf{k+q}}\hat{c}_{\mathbf{k}}\hat{a}_{\mathbf{q}}|n_{\mathbf{k+q}}, n_{\mathbf{k}}; n_{\mathbf{q}}> = \sqrt{(1-n_{\mathbf{k+q}})n_{\mathbf{k}}n_{\mathbf{q}}}. \tag{8.171}$$

The matrix elements vanish for all cases except when $n_{\mathbf{k}} = 1;\ n_{\mathbf{k+q}} = 0$. The energy relations for the absorption of a phonon are

$$\varepsilon_f - \varepsilon_i = \varepsilon(\mathbf{k}+\mathbf{q}) - \varepsilon(\mathbf{k}) - \hbar\omega_{\mathbf{q}}. \tag{8.172}$$

Similarly, the transitions involving emission of phonons can be written as (Problem 8.13)

$$< n_{\mathbf{k+q}}+1, n_{\mathbf{k}}-1; n_{-\mathbf{q}}+1|\hat{c}^{\dagger}_{\mathbf{k+q}}\hat{c}_{\mathbf{k}}\hat{a}^{\dagger}_{-\mathbf{q}}|n_{\mathbf{k+q}}, n_{\mathbf{k}}; n_{-\mathbf{q}}> = \sqrt{(1-n_{\mathbf{k+q}})n_{\mathbf{k}}(n_{-\mathbf{q}}+1)}, \tag{8.173}$$

and

$$\varepsilon_f - \varepsilon_i = \varepsilon(\mathbf{k}+\mathbf{q}) - \varepsilon(\mathbf{k}) + \hbar\omega_{\mathbf{q}}. \tag{8.174}$$

From Eqs. (8.168) through (8.174), we obtain

$$\begin{aligned} P(\mathbf{k}\rightarrow\mathbf{k}+\mathbf{q}) = \frac{2\pi}{\hbar}|B_{\mathbf{kq}}|^2 n_{\mathbf{k}}(1-n_{\mathbf{k+q}})\{n_{\mathbf{q}}\delta(\varepsilon(\mathbf{k}+\mathbf{q}) - \varepsilon(\mathbf{k}) - \hbar\omega_{\mathbf{q}}) \\ + (n_{-\mathbf{q}}+1)\delta(\varepsilon(\mathbf{k}+\mathbf{q}) - \varepsilon(\mathbf{k}) + \hbar\omega_{\mathbf{q}})\}. \end{aligned} \tag{8.175}$$

In this case, $n_{\mathbf{k}} = 1,\ n_{\mathbf{k+q}} = 0$, and the matrix element vanishes in all other cases. However, the factor $(1-n_{\mathbf{k+q}})n_{\mathbf{k}}$ is retained because if and when we consider a large number of states instead of the transition probability from *one occupied state to one empty state*, the Fermi and Bose distributions have to be used for electrons and phonons if the system is in equilibrium.

## PROBLEMS

**8.1.** Derive Eqs. (8.19) and (8.20) from Eq. (8.16).

**8.2.** We can write

$$(-i\nabla + \mathbf{k})u_{n\mathbf{k}}(\mathbf{r}) = (-i\nabla + \mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{r}}\psi_{n\mathbf{k}}(\mathbf{r}). \tag{1}$$

Show that

$$(-i\nabla + \mathbf{k})e^{-\mathbf{k}\cdot\mathbf{r}}\psi_{n\mathbf{k}}(\mathbf{r}) = e^{-\mathbf{k}\cdot\mathbf{r}}(-i\nabla)\psi_{n\mathbf{k}}(\mathbf{r}). \tag{2}$$

Hence, show that

$$< u_{n\mathbf{k}}|(-i\nabla + \mathbf{k})|u_{n\mathbf{k}}> = <\psi_{n\mathbf{k}}|-i\nabla|\psi_{n\mathbf{k}}>. \tag{3}$$

**8.3.** Show that the inverse effective mass tensor can be written as

$$[\mathbf{M}_n^{-1}(\mathbf{k})]_{ij} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon_n}{\partial k_i \partial k_j}. \tag{1}$$

**8.4.** Using Eqs. (8.35) and (8.36), show that

$$[\mathbf{M}_n^{-1}(\mathbf{k})]_{ij} = \frac{1}{m}\delta_{ij} + \frac{\hbar^2}{m^2}\sum_{n' \neq n} \frac{<n\mathbf{k}|-i\nabla_i|n'\mathbf{k}><n'\mathbf{k}|-i\nabla_j|n\mathbf{k}> + c.c.}{\varepsilon_n(\mathbf{k}) - \varepsilon_{n'}(\mathbf{k})}. \tag{1}$$

**8.5.** Show that if in Eq. (8.53), we can write

$$\phi_i'(\mathbf{r}, t) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}, \mathbf{E}, t), \tag{1}$$

the effective Hamiltonian for $u_{n\mathbf{k}}(\mathbf{r}, \mathbf{E}, t)$ is

$$\frac{1}{2m}(-i\hbar\nabla + \hbar\mathbf{k} - e\mathbf{E}t)^2 + V(\mathbf{r}). \tag{2}$$

**8.6.** Show that

$$[\hat{T}(\mathbf{R}_i), H] = (\overrightarrow{\xi}\cdot\mathbf{R}_i + \frac{e^2B^2}{2m}R_{ix}^2)\hat{T}(\mathbf{R}_i). \tag{1}$$

**8.7.** The eigenfunction $\varepsilon_n(\mathbf{k})$ is periodic in $\mathbf{k}$ space and can be expanded as

$$\varepsilon_n(\mathbf{k}) = \sum_m C_{nm} e^{i\mathbf{k}\cdot\mathbf{R}_m}. \tag{1}$$

If $\mathbf{k}$ is replaced by $-i\nabla$, show that

$$\varepsilon_n(-i\nabla)\psi_n(\mathbf{k}, \mathbf{r}) = \sum_m C_{nm} e^{i\mathbf{R}_m\cdot\nabla}\psi_n(\mathbf{k}, \mathbf{r}) = \varepsilon_n(\mathbf{k})\psi_n(\mathbf{k}, \mathbf{r}). \tag{2}$$

If we write the time-dependent Schrodinger equation as

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) - e\phi\right]\psi = i\hbar\dot{\psi}, \tag{3}$$

and represent the electron as a wave packet constructed from all the Bloch states of all bands,

$$\psi = \sum_{n\mathbf{k}} A_n(\mathbf{k}, t)\psi_n(\mathbf{k}, \mathbf{r}), \tag{4}$$

show that

$$[E_n(-i\nabla) - e\phi]\psi = i\hbar\dot{\psi}. \tag{5}$$

**8.8.** If we substitute $\phi_i^{'}(\mathbf{r},t) = e^{ie\mathbf{A}\cdot\mathbf{r}/\hbar c}\phi_i(\mathbf{r},t)$ in

$$\left[\frac{\left(\mathbf{p}+(e/c)\mathbf{A}\right)^2}{2m}+V(\mathbf{r})\right]\phi_i^{'}(\mathbf{r},t)=\varepsilon_i(t)\phi_i^{'}(\mathbf{r},t), \tag{1}$$

show that Eq. (1) reduces to

$$\left[\frac{p^2}{2m}+V(\mathbf{r})\right]\phi_i=\varepsilon_i\phi_i. \tag{2}$$

**8.9.** Derive the expression

$$\varepsilon_n(\mathbf{k},t)a_{n\mathbf{k}(t)}=i\hbar\frac{\partial a_{n\mathbf{k}(t)}}{\partial t}-eE(t)\sum_{n'}A_{nn'}(\mathbf{k}(t))a_{n'\mathbf{k}(t)}. \tag{1}$$

**8.10.** Use the expression

$$\dot{\alpha}_n(t)=\frac{ieE(t)}{\hbar}\sum_{n'}\alpha_{n'}(t)A_{nn'}(\mathbf{k}(t))\exp\left[\frac{i}{\hbar}\int_0^t[\varepsilon_n(\mathbf{k}(t'))-\varepsilon_{n'}(\mathbf{k}(t'))]dt'\right], \tag{1}$$

which is a general expression used for derivation of Wannier–Stark ladders for time-dependent $E$ as well as for Zener tunneling between the valence and conduction bands.

At $t=0$, before the field $E$ is turned on, $\mathbf{k}(t)=\mathbf{k}(t=0)$, the electron state can be described by a Bloch wave in band $n$ with $\mathbf{k}(t)=\mathbf{k}(t=0)$, then at $t=0$,

$$\alpha_{n'}=\delta_{nn'}. \tag{2}$$

After a time $T=-\frac{\hbar K}{eE}$, where $T$ is the period of one Bloch oscillation, which is a sufficiently short time so that $\alpha_{n'}\ll 1$, $n'\neq n$, show that we can substitute Eq. (2) in Eq. (1) to obtain

$$\alpha_{n'}(t)=\int_0^t\frac{ieE(t')}{\hbar}A_{n'n}(\mathbf{k}(t'))\exp\left[\frac{i}{\hbar}\int_0^{t'}[\varepsilon_{n'}(\mathbf{k}(t''))-\varepsilon_n(\mathbf{k}(t''))]dt''\right]dt'. \tag{3}$$

**8.11.** Using Eqs. (8.149) and (8.154), show that

$$\begin{aligned}&\hat{H}|n_1,n_2,\ldots,n_1,n_2,\ldots,n_{\lambda'},\ldots,n_\lambda,\ldots>\\&=\sum_{\lambda,\lambda'}\sqrt{n_\lambda(1-n_{\lambda'})}\,(-1)^{m_\lambda+m_{\lambda'}^{'}}<\lambda'|H_1|\lambda>|n_1,n_2,\ldots,n_{\lambda'+1},\ldots n_{\lambda-1},\ldots>\text{if }\lambda\neq\lambda',\end{aligned} \tag{1}$$

$$=\sum_\lambda n_\lambda<\lambda|H_1|\lambda>|n_1,n_2,\ldots,n_\lambda\ldots>,\text{if }\lambda=\lambda'. \tag{2}$$

**8.12.** By using the expressions derived in Eqs. (2.75) and (2.76) for bosons,

$$a_{\mathbf{q}}^{\dagger}|n_1, n_2, \ldots, n_{\mathbf{q}}, \ldots > = \sqrt{n_{\mathbf{q}}+1}|n_1, n_2, \ldots, n_{\mathbf{q}}+1, \ldots >, \tag{1}$$

$$a_{\mathbf{q}}|n_1, n_2, \ldots, n_{\mathbf{q}}, \ldots > = \sqrt{n_{\mathbf{q}}}|n_1, n_2, \ldots, n_{\mathbf{q}}-1, \ldots >, \tag{2}$$

and from Eqs. (8.133) through (8.136) for fermions, show that

$$< n_{\mathbf{k+q}}+1, n_{\mathbf{k}}-1; n_{\mathbf{q}}-1 > |\hat{c}_{\mathbf{k+q}}^{\dagger}\hat{c}_{\mathbf{k}}a_{\mathbf{q}}|n_{\mathbf{k+q}}, n_{\mathbf{k}}; n_{\mathbf{q}} > = \sqrt{(1-n_{\mathbf{k+q}})n_{\mathbf{k}}n_{\mathbf{q}}}. \tag{3}$$

**8.13.** Using the properties of the creation and annihilation operators for bosons and fermions outlined in Problem 8.12, show that

$$< n_{\mathbf{k+q}}+1, n_{\mathbf{k}}-1; n_{-\mathbf{q}}+1 |\hat{c}_{\mathbf{k+q}}^{\dagger}\hat{c}_{\mathbf{k}}\hat{a}_{-\mathbf{q}}^{\dagger}|n_{\mathbf{k+q}}, n_{\mathbf{k}}; n_{-\mathbf{q}} > = \sqrt{(1-n_{\mathbf{k+q}})n_{\mathbf{k}}(n_{-\mathbf{q}}+1)}. \tag{1}$$

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