smaller than the amplitude of the potential A and, thus, the electron must be confined near the bottom of the cosine-type potential. This means that only the motion near $\xi = 0$ needs to be considered. The potential in equation (5.3) is then approximated as

$$\eta \cos 2\xi \approx \eta (1 - 2\xi^2),$$

since ξ is small. The resulting Schrödinger equation is reduced to

$$\frac{d^2\psi}{d\xi^2} + (\varepsilon' - 2\eta\xi^2)\psi = 0.$$

The potential in this equation is proportional to the square of the coordinate ξ, thereby representing the motion of a harmonic oscillator. As discussed in Section 4.6, its energy eigenvalue is given by

$$\varepsilon' = \left(n + \frac{1}{2}\right)\hbar\omega \quad (n = 0, 1, 2, 3, \ldots),$$

where ω represents the angular frequency characterizing the oscillation of the electron at the bottom of the potential. The energy eigenvalue obtained under the two extreme cases is illustrated schematically in Fig. 5.1. In case (1), the electron can propagate freely in space, since the amplitude of the potential is negligibly small relative to the kinetic energy of the electron. The energy eigenvalue is given by equation (2.5) and forms a continuous band, as discussed in Chapter 2. In contrast, the electron is captured in the potential well in case (2). The discrete energy level is given by that of a harmonic oscillator. In this chapter, we deal with the situation where the energy of the electron is comparable to the amplitude of the potential or $E \approx A$. We will learn that energy gaps open up within the continuous band, as schematically illustrated in Fig. 5.1.

5.3 Bloch theorem

We study in this section the Bloch theorem and prove it by using a one-dimensional periodic lattice consisting of N monatomic ions with lattice constant a. The ionic potential located at the origin $x = 0$ is defined in the range $-a/2 < x \leq a/2$ and denoted as $V(x)$. The ionic potential located at its nearest neighbor position $x = a$ is then expressed as $V(x + a)$ in the range $a/2 < x \leq 3/2a$. Because of its identical nature, $V(x) = V(x + a)$ holds. In the same manner, we obtain

$$V(x) = V(x + a) = V(x + 2a) = \cdots = V(x + (N-1)a), \quad (5.4)$$

where $V(x+ma)$ is defined in the range $(-a/2)+ma < x \leq (a/2)+ma$ ($m=0, 1, 2, \ldots, N-1$).

The periodic boundary condition is imposed in such a way that the ion at $x=0$ coincides with that at the position $x=Na$. This forms a ring of length Na, onto which N lattice points are evenly distributed with the lattice constant a. Now we have the relation

$$V(x) \equiv V(x+Na), \tag{5.5}$$

where the symbol $\equiv$ emphasizes that both $V(x)$ and $V(x+Na)$ refer to the same potential. The Schrödinger equation in each unit cell can be expressed as

$$\left(\frac{-\hbar^2}{2m}\right)\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

$$\left(\frac{-\hbar^2}{2m}\right)\frac{d^2\psi(x+a)}{dx^2} + V(x+a)\psi(x+a) = E\psi(x+a)$$

$$\vdots$$

$$\left(\frac{-\hbar^2}{2m}\right)\frac{d^2\psi(x+(N-1)a)}{dx^2} + V(x+(N-1)a)\psi(x+(N-1)a) = E\psi(x+(N-1)a). \tag{5.6}$$

Note that ionic potentials periodically arranged with the lattice constant a are identical. For example, the identity of the wave functions $\psi(x)$ with $\psi(x+a)$ means that they should possess the same energy eigenvalue E but that $\psi(x)$ can differ from $\psi(x+a)$ by a phase factor. They are therefore written as

$$\psi(x+a) = \lambda\psi(x) \quad |\lambda| = 1. \tag{5.7}$$

By repeating this process N times to reach the N-th unit cell, we finally obtain the relation

$$\psi(x+Na) = \lambda^N\psi(x).$$

However, the N-th one is nothing but the cell at $x=0$ and, hence, $\psi(x+Na) = \psi(x)$ holds. This results in

$$\lambda^N = 1,$$

which is solved as

$$\lambda = \exp\left(\frac{2\pi ni}{N}\right),$$

where n is an integer in the range of 0 up to $N-1$.

The Bloch theorem in a one-dimensional lattice is stated as follows. The wave function $\psi(x)$ for an electron propagating in the periodic potential with the period a can be expressed as

$$\psi(x) = \exp\left(\frac{2\pi inx}{Na}\right)u(x), \qquad (5.8)$$

where an arbitrary function $u(x)$ is a periodic function of a and satisfies the relation

$$u(x + ma) = u(x), \qquad (5.9)$$

with a positive integer m. In order to prove the Bloch theorem, we first assume equation (5.8) to hold. Then, we can prove below that the function $u(x)$ must satisfy equation (5.9). Let the variable x in equation (5.8) to be replaced by $x + ma$. We have

$$\psi(x + ma) = \exp\left[\frac{2\pi ni(x + ma)}{Na}\right]u(x + ma)$$

$$= \exp\left(\frac{2\pi mni}{N}\right)\exp\left(\frac{2\pi nix}{Na}\right)u(x + ma)$$

$$= \lambda^m \exp\left(\frac{2\pi nix}{Na}\right)u(x + ma). \qquad (5.10)$$

The relation $\lambda = \exp(2\pi ni/N)$ obtained above is inserted to reach the last line. If we apply equation (5.7) m times to $\psi(x)$, then we get the relation $\psi(x + ma) = \lambda^m \psi(x)$. By inserting equation (5.8) into it, we have

$$\psi(x + ma) = \lambda^m \psi(x) = \lambda^m \exp\left(\frac{2\pi nix}{Na}\right)u(x). \qquad (5.11)$$

A comparison of equations (5.10) and (5.11) immediately leads us to conclude that an arbitrary function $\psi(x)$ must satisfy equation (5.9).

A quantity of $(2\pi/Na)n$ or $(2\pi/L)n$ in equation (5.8) may be replaced by a new variable k, since it is of the same form as the wave number defined by equation (2.9) for free electrons. By this replacement, the wave function (5.8) is simplified to $\psi(x) = \exp(ikx)u(x)$, allowing us to envisage $\psi(x)$ as the plane wave $\exp(ikx)$ modulated by the periodic function $u(x)$. Here it is important to keep in mind that the variable k of the free electron was originally introduced as the wave number of the plane wave in free space, whereas the new variable above appeared in relation to the periodicity of the lattice. Before discussing its

unique nature, we extend the Bloch theorem to a three-dimensional periodic lattice.

Let us assume the periodic potential in a crystal where the position of each ion is specified by the lattice vector $\mathbf{l} = l_x\mathbf{a}_x + l_y\mathbf{a}_y + l_z\mathbf{a}_z$ (l_x, l_y, l_z = integers) in equation (4.7). The wave function $\psi(\mathbf{r})$ of the electron in the periodic potential can be expressed in the form

$$\psi_\mathbf{k}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u_\mathbf{k}(\mathbf{r}), \tag{5.12}$$

where $u_\mathbf{k}(\mathbf{r})$ satisfies the relation

$$u_\mathbf{k}(\mathbf{r}+\mathbf{l}) = u_\mathbf{k}(\mathbf{r}). \tag{5.13}$$

Here the vector $\mathbf{k}$ is of the same form as the wave vector in equation (2.11) for the free electron. This is called the Bloch theorem. The wave function expressed by equation (5.12) is called the Bloch wave or Bloch state.

The Bloch theorem is very important. By applying this theorem, the wave function in a macroscopic crystal containing as many atoms as the Avogadro number can be determined by solving the Schrödinger equation into which information from just one unit cell is inserted. This unique advantage stems from the fact that the wave function everywhere in a crystal is automatically decided, once $u_\mathbf{k}(\mathbf{r})$ in the unit cell, say, at $\mathbf{l} = 0$ is specified. Therefore, the Bloch theorem is responsible for the successful development of band structure calculations for a 'macroscopic' crystal, which we will study in Chapter 8. We show, in Fig. 5.2, an example of the Bloch wave in a one-dimensional system, where $u_\mathbf{k}(x)$ is positioned at the center of the unit cell. Once the function $u_\mathbf{k}(\mathbf{r})$ in the unit cell is given, the wave function extending over the crystal is completely decided by the product of the plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ and the periodic function $u_\mathbf{k}(\mathbf{r})$, as shown in Fig. 5.2(b).

It is of great importance for the reader to recognize how physical quantities associated with the wave vector $\mathbf{k}$ in the Bloch wave differ from those derived from the free-electron model. For example, $\hbar\mathbf{k}$ is found to be the eigenvalue of the momentum operator $-i\hbar\nabla$ in the free-electron model (see equation (2.14)). If it is operated to the Bloch wave function (5.12), one can easily find that $\hbar\mathbf{k}$ is no longer its eigenvalue. This is because the ionic potential exerts a force on the electron through the function $u_\mathbf{k}(\mathbf{r})$.

To study further the characteristic features of the Bloch wave function, we can rewrite equation (5.12) in the following form:

$$\psi_\mathbf{k}(\mathbf{r}+\mathbf{l}) = \exp(i\mathbf{k}\cdot\mathbf{l})\psi_\mathbf{k}(\mathbf{r}). \tag{5.14}$$

As discussed in Section 4.2, the reciprocal lattice vector $\mathbf{g}$ is defined so as to satisfy the relation $\exp(\pm i\mathbf{g}\cdot\mathbf{l}) = 1$, where $\mathbf{l}$ is the lattice vector defined by
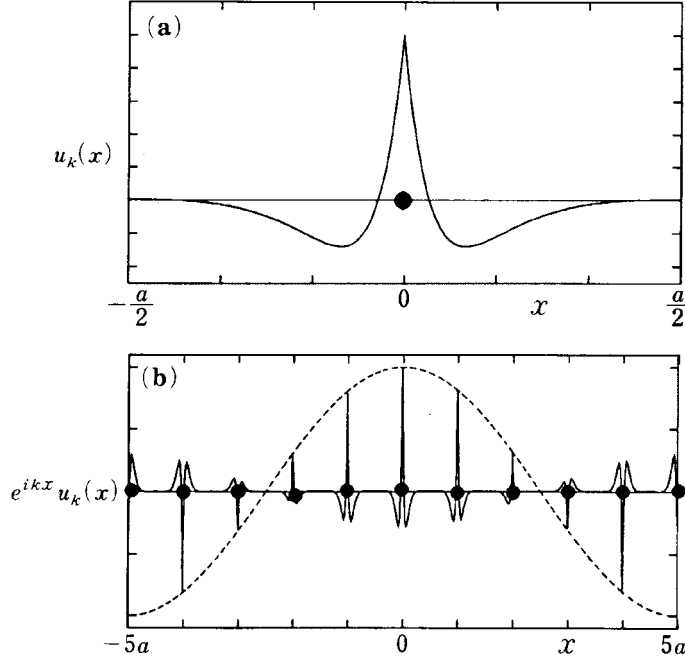
Figure 5.2.   (a) The periodic function $u_k(x)$ centered at the origin of the unit cell in the range $-a/2 < x \leq a/2$. (b) The Bloch wave constructed by using the function shown in (a). Only the real part is shown. The function $u_k(x)$ is placed at every origin of the unit cell and modulated by the plane wave $\exp(ikx)$. A solid circle represents the ion at the center of each unit cell.

equation (4.7). Keeping this in mind, we can replace the wave vector $\mathbf{k}$ of the Bloch wave by the wave vector $\mathbf{k} = \mathbf{k}' \pm \mathbf{g}$:

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{l}) = \exp(i\mathbf{k} \cdot \mathbf{l})\psi_{\mathbf{k}}(\mathbf{r})$$

$$= \exp(\pm i\mathbf{g} \cdot \mathbf{l}) \exp(i\mathbf{k}' \cdot \mathbf{l})\psi_{\mathbf{k}}(\mathbf{r})$$

$$= \exp(i\mathbf{k}' \cdot \mathbf{l})\psi_{\mathbf{k}}(\mathbf{r}). \tag{5.15}$$

A comparison of equations (5.14) and (5.15) tells us that the Bloch state of the wave vector $\mathbf{k}$ is equally describable in terms of the wave vector $\mathbf{k}'$ different from it by the reciprocal lattice vector $\mathbf{g}$.

This is a property unique to the Bloch wave or Bloch electron. Multiply both sides of $\mathbf{k} = \mathbf{k}' \pm \mathbf{g}$ by $\hbar$. Then, it is viewed as representing the momentum conservation law of the Bloch electron, indicating that the Bloch electron exchanges its momentum with the lattice by the amount $\pm\hbar\mathbf{g}$. What does $\pm\hbar\mathbf{g}$ mean? It is assigned to an infinite array of identical lattice planes specified by

the reciprocal lattice vector **g** and has nothing to do with phonons. It may merely refer to the motion of the lattice as a whole. Thus, the momentum $\hbar\mathbf{k}$ of the Bloch wave cannot be uniquely determined as the momentum inherent to an electron but involves arbitrariness associated with a whole motion of the lattice. This is the reason why the momentum $\hbar\mathbf{k}$ is often called the crystal momentum of the Bloch wave.

Let us consider a special case where the magnitude of the periodic potential is reduced infinitesimally small. We call it the periodic empty-lattice, under which the electron should resume the free-electron band structure but the periodicity of the lattice and, hence, the concept of the Bloch wave remains valid. This is a hypothetical model but helps the reader to gain further insight into the role of the periodic potential. The free-electron wave function $\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})$ must be its eigenfunction but still obeys the Bloch theorem. The wave function may be rewritten as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp[i(\mathbf{k} \pm \mathbf{g})\cdot\mathbf{r}]\exp(\mp i\mathbf{g}\cdot\mathbf{r})$$

$$= \exp(i\mathbf{k}'\cdot\mathbf{r})u_{\mp\mathbf{g}}(\mathbf{r}), \tag{5.16}$$

where $\mathbf{k}' = \mathbf{k} \pm \mathbf{g}$ and $u_{\mp\mathbf{g}}(\mathbf{r}) = \exp(\mp i\mathbf{g}\cdot\mathbf{r})$. Equation (5.16) satisfies the Bloch theorem, since $u_{\mp\mathbf{g}}(\mathbf{r} + \mathbf{l}) = \exp[\mp i\mathbf{g}\cdot(\mathbf{r} + \mathbf{l})] = \exp(\mp i\mathbf{g}\cdot\mathbf{r}) = u_{\mp\mathbf{g}}(\mathbf{r})$. It is now interesting to examine the *E–k* relation of the Bloch electron in the periodic empty-lattice potential. By reflecting the periodic nature of the lattice, the Bloch state of the wave vector **k** should be identical to that of the wave vector $\mathbf{k} \pm \mathbf{g}$ but yet the energy eigenvalue is given by the free-electron value (see Exercise 5.2).

A one-dimensional monatomic lattice with lattice constant a is assumed. In this particular case, the reciprocal lattice vector becomes multiples of $2\pi/a$. Since the Bloch states **k** and $\mathbf{k} \pm \mathbf{g}$ possess the same eigenstate, we can always transfer the Bloch state of any wave vector into the region $-\pi/a < k_x \leq \pi/a$. This is called the reduction to the first Brillouin zone. We will learn more about the operation of the reduction in Section 5.11. This unique property in reciprocal space is caused by the periodic array of ions in a crystal and has already been discussed in relation to lattice vibrations in Section 4.4.

5.4 Kronig–Penney model

By making full use of the Bloch theorem, we can study the effect of the periodic potential on the *E–k* relation of the conduction electron. For this purpose, the Kronig–Penney model is known to be quite instructive. The model assumes a periodic square-well potential in one-dimensional space, as indicated in Fig. 5.3. The Schrödinger equation in one-dimensional space is generally written as