Chapter 4.

Infinite One-Dimensional Lattice

Hall of Windows
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As an adolescent I aspired to lasting fame. I craved factual certainty, and I thirsted for a meaningful vision of human life – so I became a scientist. This is like becoming an archbishop so you can meet girls.

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Comment

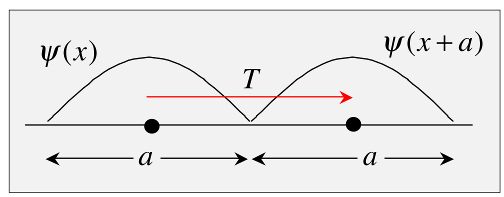
Periodic 1D lattices are examined here using a mathematical approach that is commonplace in solid-state physics, and that complements those used in Chapters $1-3$. The number of sites can range from small to infinite. The math does not change. Though the mathematical approach of the present chapter differs from those used in Chapters $1-3$, not surprisingly, similar results are obtained. My strategy is that the use of complementary perspectives facilitates the retention of concepts.

4.1. Bloch Waves

The first item on the agenda is the mathematical form that the eigenfunctions must assume as a consequence of the discrete lattice symmetry presented by evenly spaced sites. Toward this end, we start by introducing the translation operator, T, that brings about the transformation: $x \to x+a$, where a is the lattice spacing:

$$T\psi_k(x) = \psi_k(x+a). \tag{4.1}$$

Periodic boundary conditions shall be used throughout.



The operator T acts on a wave function that is defined over an interval of length a. It translates this wave function by the distance a, as indicated schematically on the right. The transformed wave function can acquire a phase but nothing more. Because T is a symmetry operation of the Hamiltonian, it commutes with H, and therefore T and H can have simultaneous eigenfunctions. The reason for labeling the eigenfunctions and eigenvalues of T and H with the index k will be discussed below. It is probably already clear, or at least not surprising, in light of the previous chapters. With the eigenvalues of T labeled λ_k we have

$$T\psi_k(x) = \lambda_k \psi_k(x). \tag{4.2}$$

The eigenvalues λ_k must satisfy $|\lambda_k| = 1$ to ensure that the probability density does not differ from site to site.[1] Thus, the λ_k can be expressed as

$$\lambda_k = e^{ika}. \tag{4.3}$$

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[1] Consider $|\psi_k(x)|^2$ for the site interval: $0 \le x \le a$. We require that the probability density for another site is $|\psi_k(x-na)|^2$, where the integer n denotes the location of the other site.

In other words, $\psi_k(x)$ can only vary from site to site by a phase factor whose argument is proportional to a.

Equation (4.3) defines the wave vector k. Though k appears in combination with the lattice spacing a, the allowed values of k do not reflect the lattice periodicity, except in the indirect sense that the allowed values of k depend on the length of the lattice, $L = Na$. The lattice spacing a is not a quantization length for k. Its quantization length is L.

Interesting things happen when k assumes values close to either edge of the Brillouin zones $\pm \pi / a$. Referring to eqn (4.3), because k serves to define the eigenvalue λ_k, it is an appropriate index for the eigenfunctions and eigenvalues of T. Because a is real, k must also be real to ensure that $|\lambda_k| = 1$.

We shall forego the placement of a subscript on k to denote its different possible values. It is understood that k assumes different values, and that for a large lattice there is a nearly continuous range of k values. We shall see in due course that there can be many k values for each energy eigenvalue. However, these additional k values do not correspond to physically distinct states. In other words, there is mathematical redundancy. We shall also see that there are many energy eigenvalues for each k value. Later, when the eigenvalue spectrum is discussed, a second index (n) will be introduced to label states according to their atomic orbital parentages. For now, n is taken as understood.

Returning to the discrete translational symmetry, putting eqn (4.3) into eqn (4.2) gives

$$T\psi_k(x) = e^{ika}\psi_k(x). \tag{4.4}$$

It is now assumed that $\psi_k(x)$ is of the form

$$\psi_k(x) = u_k(x)e^{ikx}. \tag{4.5}$$

This form for $\psi_k(x)$ satisfies the disparate limits of free versus highly localized. To visualize these limiting cases, assume that the magnitude of some periodic potential $V(x)$ that localizes electrons at lattice sites is V_0. The waves e^{ikx} are appropriate for the limit $V_0 \to 0$. Here, $u_k(x)$ approaches a constant value, and k can assume an essentially continuous range of values, because it is quantized only via the overall length of the lattice, which is taken as huge. Thus, for $V_0 = 0$, the solutions of the Schrödinger equation are free particle waves, e^{ikx}, whose energies are $\hbar^2k^2/2m$. The levels are degenerate for k values that have the same magnitude but differ in sign.

For $V_0 \neq 0$, the functions $u_k(x)$ conform to the lattice periodicity, namely, $|u_k(x)|^2$ does not vary from site to site. For small V_0 values, $u_k(x)$ can be said to modulate the plane waves. When V_0 is negative and has large magnitude, however, the functions $u_k(x)e^{ikx}$ are localized at the sites. With $u_k(x)$ localized to the extent that its amplitude is nearly zero between sites, there is little electron transport. An example of this is an atomic core level that hardly senses adjacent atoms.

Introducing the $\psi_k(x)$ given by eqn (4.5) into the right hand side of eqn (4.1) yields

$$T\psi_k(x) = u_k(x+a)e^{ikx}e^{ika}. \tag{4.6}$$

Likewise, putting this $\psi_k(x)$ into the right hand side of eqn (4.4) yields

$$T\psi_k(x) = e^{ika} u_k(x) e^{ikx} \tag{4.7}$$

$$= u_k(x)\, e^{ikx} e^{ika} \,. \tag{4.8}$$

A comparison of the right hand sides of eqns (4.6) and (4.8) indicates that

$$u_k(x+a) = u_k(x)\,. \tag{4.9}$$

The consistency that is achieved when eqn (4.5) is inserted into eqns (4.1) and (4.4), yielding eqn (4.9), verifies that $\psi_k(x)$ can be represented as:[2]

$$\boxed{\psi_k(x) = u_k(x) e^{ikx}\,.} \tag{4.10}$$

These are called Bloch waves, after Felix Bloch, who derived this equation and used it in crystal physics. It had been derived earlier in the field of mathematics, where it is referred to as Floquet's theorem. Figure 1 illustrates how it works by plotting the real part of $u_k(x)e^{ikx}$, with $u_k(x)$ taken to be real: $\mathrm{Re}\,\psi_k(x) = u_k(x)\cos kx$. You should figure out why it is acceptable to take $u_k(x)$ as real.

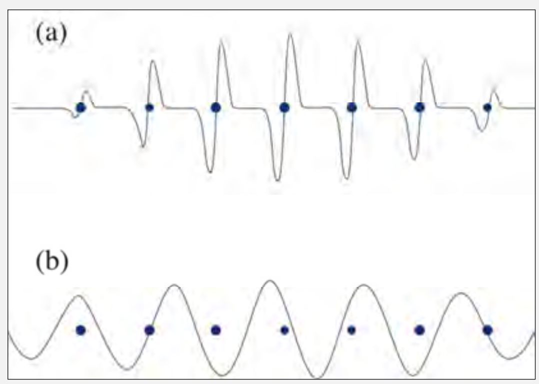

Figure 1. These plots show $\mathrm{Re}\,\psi_k(x) = u_k(x)\cos kx$ versus *x*. (a) $u_k(x)$ is proportional to $(x-x_i)\exp(-(x-x_i)^2)$, with lattice sites separated from one another by $|x_i - x_{i\pm1}| = 3$. There is essentially no electron transport. The long wavelength sinusoidal envelope is due to the fact that only $\mathrm{Re}\,\psi_k(x) = u_k(x)\cos kx$ is being plotted. The envelope of $\mathrm{Im}\,\psi_k(x)$ is out of phase with that of $\mathrm{Re}\,\psi_k(x)$. Of course $|\psi_k(x)| = |\psi_k(x+a)|$. In other words, peaks of $|\psi_k(x)|$ have constant site-to-site magnitude. (b) $u_k(x)$ is proportional to $\exp(-0.1(x-x_i)^2)$, so electrons are highly delocalized. The oscillations are due to $\cos kx$. In this case, the traveling wave can be said to modulate the $u_k(x)$. The value of *k* in (b) is larger than that in (a). Notice that the oscillations are not correlated with the positions of the nuclei. In this case, $|\psi_k(x)|$ is approximately constant throughout the lattice.

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[2] We have not derived the Bloch form given in eqn (4.10) with mathematical rigor. It is unlikely that doing so would lead to additional enlightenment.

The traveling wave character of $\psi_k(x)$ is given by e^{ikx}. Using either the real or imaginary part of e^{ikx} (as long as $u_k(x)$ is real) enables the phase progression to be seen, whereas this information is lost with the modulus $|\psi_k(x)|$. In Fig. 1(a), the value of k is small enough that the variation of $\cos kx$ is slow relative to that of $u_k(x)$.

The probability density $|\psi_k(x)|^2$ is equal to $|u_k(x)|^2$, so it is the overlap of the various $u_k(x)$ with adjacent functions $u_k(x \pm a)$ that determines whether or not there is electron transport. If $u_k(x)$ is such that there is negligible overlap between adjacent sites, then there is essentially no net traveling-wave character, regardless of the e^{ikx} factor, and the electrons reside at the sites. Figure 1(a) is analogous to a core level: $\psi_k(x)$ goes almost to zero between sites, so there is little site-to-site electron transport. Another way to appreciate this is to note that the probability flux J is conserved in these systems. It can be evaluated anywhere along the x-axis. If it is evaluated where $\psi_k(x) = 0$, then $J = 0$ everywhere.

At the other extreme, when the electron is highly delocalized, the functions $u_k(x)$ have large amplitude between sites, even extending over a number of sites. In this case, we can think of e^{ikx} as modulating a relatively constant $u_k(x)$, as shown in Fig. 1(b).

Crystal Momentum

One should not think of k as momentum. It has been introduced as a parameter, and $\hbar k$ is called crystal momentum. Though the function e^{ikx} is associated with traveling wave character, it multiplies $u_k(x)$. Thus, $\hbar k$ is not a momentum in the sense of a free particle, where $p = \hbar k$ applies. The linear momentum of a free particle is conserved because of the homogeneity of free space. The displacement operator applies to an infinitesimal displacement anywhere in free space, and consequently the translational invariance of p arises from a continuous symmetry. On the other hand, the T we have introduced for site-to-site displacement is a discrete symmetry. Therefore, its eigenfunctions are not eigenfunctions of p. To see how this works mathematically, let p operate on $\psi_k(x)$:

$$p\,\psi_k(x) = -i\hbar\nabla\left(u_k(x)e^{ikx}\right) \tag{4.11}$$

$$= \hbar k\psi_k(x) - i\hbar\, e^{ikx}\,\nabla u_k(x)\,. \tag{4.12}$$

Thus, $p\,\psi_k(x)$ is not equal to $\psi_k(x)$ times a constant, and therefore $\psi_k(x)$ is not an eigenfunction of p. When localization at the sites is weak, $\nabla u_k(x)$ is small and $p\,\psi_k(x)$ approaches $\hbar k\psi_k(x)$. Likewise, in this case the group velocity: $v_g = \partial E/\partial\hbar k$, approaches $\hbar k/m$. This is the nearly free electron regime. At the other extreme, when $u_k(x)$ is highly localized, there is little overlap between $u_k(x)$ and $u_k(x+a)$, as seen in Fig. 1(a). In this case, there is little site-to-site flux because $\psi_k(x)$ nearly vanishes between sites. This is the tight-binding regime. Though $\hbar k$ is not a momentum eigenfunction, it has units of momentum, and it is the momentum in the free electron limit. Therefore, we need to figure out just what kind of momentum it might be.

The relationship between $\hbar k$ and momentum can be determined by considering the affect of an applied electric field. Bloch waves are time independent solutions to the Schrödinger equation. They reflect the fact that in a perfect crystal with stationary nuclei there is no resistance to the flow of electric current. In other words, the ansatz that the nuclei are fixed in space means that no phonons can be created. Thus, to see what kind of momentum $\hbar k$ might be, a quasiclassical situation is constructed in which a wave packet comprising Bloch waves moves through the crystal under the influence of the electric field $\vec{E}$ without being scattered by phonons.

The energy of the electron increases as it gains energy from the field, and, because there is no loss, the sum of its translational and potential energies is constant:

$$E_0 - e\phi = \text{constant}\,, \tag{4.13}$$

where E_0 is the center translational energy of the wave packet, and ϕ is the electric potential. Differentiation yields

$$\dot{E}_0 - e\dot{\phi} = 0\,. \tag{4.14}$$

Minor manipulation gives

$$\frac{\partial E_0}{\partial k}\dot{k} - e\left(\nabla\phi\right)\dot{x} = 0. \tag{4.15}$$

In going from eqn (4.14) to eqn (4.15), use is made of the fact that, for a constant electric field, E_0 can be expressed as an explicit function of k, and ϕ can be expressed as an explicit function of x. Next, use is made of the facts that: (i) $\vec{E} = -\nabla\phi$ (the $-\partial_t\vec{A}$ term is neglected in this quasi-static regime); (ii) the group velocity v_g is equal to $\partial E_0 / \partial\hbar k$ (Appendix 2); and (iii) $\dot{x}$ is equal to v_g in the present case. Thus, eqn (4.15) becomes

$$\left(\hbar\dot{k} + e\vec{E}\right)v_g = 0. \tag{4.16}$$

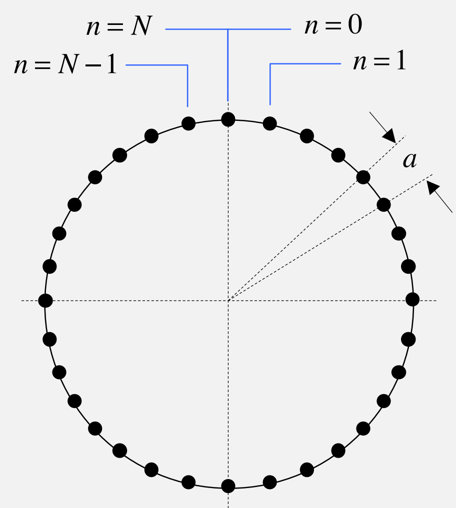
This shows that $\hbar k$ responds as a momentum to the applied electric field. The distinction between $\hbar k$ and p is clarified. Momentum p responds to all forces, including those from the binding sites. The crystal momentum behaves as a translational momentum, but to an applied field that causes current to flow. Its time rate of change $\hbar\dot{k}$ is equal to the force $\vec{F} = q\vec{E} = -e\vec{E}$. For core levels, there is essentially no electron transport, so $v_g \to 0$, in which case ($\hbar\dot{k} + e\vec{E}$) and v_g in eqn (4.16) vanishe separately.

Allowed k Values

The allowed values of k are obtained by considering a lattice of length $L = Na$, where N is the number of sites. As in Chapters 1 – 3, the ends are treated mathematically as being connected to one another, in which case the lattice is modeled as a giant ring, as indicated in Fig. 2. You should think of this figure as a mnemonic for imposing periodic boundary conditions. The requirement that the wave function is continuous where the ends of the 1D lattice join together demands

$$\psi_k(x) = \psi_k(x + Na)\,. \tag{4.17}$$

Figure 2. A one-dimensional lattice is wrapped into a giant ring: $Na = L$. In this case, the boundary condition on the wave function is $\psi_k(x) = \psi_k(x + Na)$. The wave function's phase varies with location on the circle. It can be expressed in terms of the phase progression between adjacent sites, e^{ika}.



Equation (4.17) is now used with eqn (4.2). Namely, applying the T operator N times in succession carries x to $x + Na$, and eqn (4.17) requires:

$$T^N \psi_k(x) = \lambda_k{}^N \psi_k(x) \tag{4.18}$$

$$= \psi_k(x + Na) \tag{4.19}$$

$$= \psi_k(x)\,. \tag{4.20}$$

Thus, $\lambda_k{}^N = 1$, which has N roots, each with unit magnitude and a phase. The eigenvalues λ_k are expressed as

$$\boxed{\lambda_k = \exp\left(i\frac{2\pi}{N}m\right) \quad \text{where } m = 0, 1, 2 \ldots N-1.} \tag{4.21}$$

The integer m assumes N sequential values. For example, this range can be 0, 1, 2 $\ldots N-1$ (as shown above). Alternatively, for odd N it could be: $-(N-1)/2 \ldots 0 \ldots (N-1)/2$, whereas for even N it could be: $-N/2 \ldots 0 \ldots N/2$, with the understanding that $-N/2$ and $N/2$ contribute one state, not two. Combining eqns (4.1) and (4.2), and using $\psi_k(x) = u_k(x)e^{ikx}$ and the expression for λ_k given by eqn (4.21) yields

$$\psi_k(x+a) = e^{i2\pi m/N} u_k(x) e^{ikx}, \tag{4.22}$$

and using $u_k(x) = u_k(x+a)$ gives

$$\psi_k(x+a) = u_k(x+a) e^{i(kx+2\pi m/N)}. \tag{4.23}$$

The right hand side of eqn (4.23) is equal to $u_k(x+a)e^{ik(x+a)}$ only if

$$k = \frac{2\pi}{Na} m = \frac{2\pi}{L} m, \tag{4.24}$$

where L is the circumference of the large ring. Make sure you understand how this stuff works before moving on.

Equation (4.24) is the quantization condition. The system is doubly degenerate: $|\pm m|$, with + and – corresponding to opposite senses of circulation. The smallest k values have wavelengths that are much larger than the lattice spacing. As k increases, the wavelength eventually becomes comparable to the lattice spacing. Though the large-L limit yields the infinite lattice, the Bloch theorem works for any value of $L = Na$.

The k that has been introduced is a parameter in the phase evolution factors e^{ikx} in the Bloch functions, and it labels the Bloch functions. It enters via the discrete symmetry of displacement by the lattice spacing a. As such, it is not related to the momentum p except when a is unimportant, that is, $u_k(x) \to$ a constant. Recall that in Chapter 1 it was seen that in the limit of a weak potential a periodic potential couples states such that gaps appear when $m' + m \sim 0$.

4.2. Brillouin Zones

Let us now examine the fact that the energy of a Bloch function is unaffected if k is increased or decreased by an integer multiple of $2\pi / a$. We shall, of course, invoke the system's discrete translational symmetry, which ensures that simultaneous eigenfunctions of T and H can be obtained. This symmetry lies at the heart of the matter, by definition, as it is the only spatial symmetry in the model. To begin, note that e^{ikx} undergoes no change from one site to the next when k is replaced by $k + G$, where the 1D reciprocal lattice vector, G, is given by $2\pi m_G / a$, where m_G is an integer.[3] Namely, phase progression from one site to the next is e^{ika}, and replacing k with $k + G$ yields

$$e^{i(k+G)a} = e^{ika}e^{iGa} = e^{ika}e^{i2\pi m_G} = e^{ika}. \tag{4.25}$$

Thus, $iGa = i2\pi m_G$ can be added to the argument of the exponential with impunity, and $T\psi_k(x)$ can be written:

$$T\psi_k(x) = e^{ika}\,\psi_k(x) = e^{i(k+G)a}\,\psi_k(x). \tag{4.26}$$

This shows that adding G to the k in e^{ika} does not change the state. Of course, if T operating on a state gives the eigenvalue $e^{i(k+G)a}$, the state must be $\psi_{k+G}(x)$. Therefore $\psi_k(x)$ must be equal to $\psi_{k+G}(x)$. Alternatively, one can start with $\psi_k(x) = e^{ikx}u_k(x)$ and multiply e^{ikx} by e^{iGx} and $u_k(x)$ by e^{-iGx}. This leaves $\psi_k(x)$ unaffected:

$$\psi_k(x) = e^{i(k+G)x}\left(e^{-iGx}u_k(x)\right). \tag{4.27}$$

The term in large parentheses is periodic in a, so the right hand side is $\psi_{k+G}(x)$. This means that E_k is equal to E_{k+G}, as k and $k + G$ each denote the same state.[4]

A mathematical redundancy has been revealed. For a given value of E, there can exist many values of $k + G$. This is best illustrated with an example. Figure 3 uses results from Fig. 7 of Chapter 1 for the case of 24 sites, with smooth curves replacing the 24 discrete

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[3] The subscript G on m_G is used to distinguish this integer from the one that appears in the quantization of k according to the length of the ring: $k = 2\pi m / L$.

[4] Yet another perspective considers the Bloch function $\psi_{k+G}(x) = e^{ikx}e^{iGx}u_{k+G}(x)$. Because $Ga = 2\pi m_G$ and $u_{k+G}(x) = u_{k+G}(x+a)$, this can be written

$$\psi_{k+G}(x) = e^{ikx}\left(e^{iG(x+a)}\,u_{k+G}(x+a)\right).$$

The term in large parentheses, being periodic in a, behaves the same way as $u_k(x)$. Thus, $\psi_{k+G}(x)$ and $\psi_k(x)$ have the same properties. When a value of E is found that corresponds to a specific value of k, it follows that $2\pi m_G / a$ ($m_G = \pm 1, \pm 2...$) can be added to this k without changing E.

points per band. Referring to Fig. 3(a), notice that the first Brillouin zone ($-\pi/a \leq k \leq \pi/a$) is repeated *ad infinitum* with increasing $|k|$. This is a direct consequence of the Bloch theorem, as noted with eqns (4.25) and (4.26). Referring to Fig. 3(b), there are 24 levels in the interval: $-\pi/a \leq k \leq \pi/a$. These were obtained in Fig. 7 of Chapter 1 for a weak binding potential by using matrix diagonalization and a particle-on-a-ring basis.

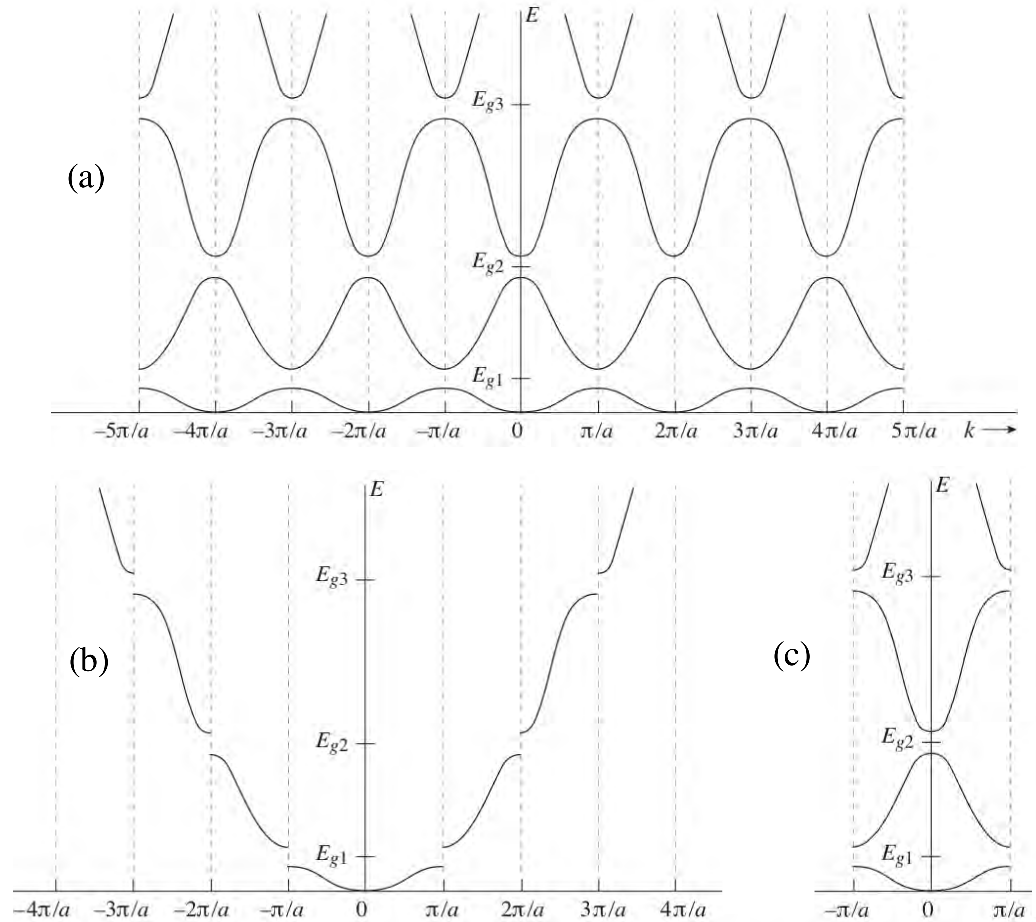


Figure 3. (a) For a given E within a band, there exist two k values within a $2\pi/a$ interval, as well as k values displaced from these by integer multiples of $2\pi/a$. All such possibilities are shown in the repeated zone representation. Only one $2\pi/a$ interval is unique and has physical meaning. (b) For the nearly free electron, E varies quadratically with k except near the gaps. The extended zone representation displays this. In (c), the restricted zone representation places all of the information in the first Brillouin zone.

The important point is that, for a given band, it is only possible to have 24 molecular orbitals because there are only 24 binding sites. For example, consider the lowest band in Fig. 3(b). When k fills the interval $-\pi/a \leq k \leq \pi/a$, that is it. Values of k outside this range (with $E < E_{g1}$) simply repeat states that are already present in the original 24. This redundancy is explicit in Fig. 3(a). For each band of allowed energies the shape within a single Brillouin zone is repeated in the horizontal directions.

At the same time, there must also be cases in which the wave vector $k+G$ belongs to a state that is distinct from ψ_k. For example, in the free electron limit, energies are given by $\hbar^2 k^2/2m$. Therefore, a state must exist whose energy is $\hbar^2(k+G)^2/2m$. This state can be written: $e^{i(k+G)x} = e^{ikx}u_k(x)$, where $u_k(x) = e^{iGx}$. We see that it is then straightforward to include higher momentum in which $G = 2\pi m_G/a$. As with the lowest band, a length of $2\pi/a$ in k-space contains 24 states. The rest are repeats. In Fig. 3(b) the length of $2\pi/a$ for the next highest band is the combined intervals π/a to $2\pi/a$ and $-\pi/a$ to $-2\pi/a$.

To summarize, the information that constitutes the 1D band structure can be viewed in different ways: fill the paper with repeating segments; assign the segments to physically meaningful portions of E versus k; or line up the bands vertically in the first Brillouin zone. When the bands are filled (no electron transport), the restricted zone representation shown in Fig. 3(c) is intuitive. When spin ½ is included, the number of states in a band is equal to twice the number of sites. Thus, in simple terms, when each site donates one electron to a band, the band is half full. When each site donates two electrons to a band, the band is full. When the energy gaps between the bands are large, electrons do not move between the bands to any significant extent. Figure 3(a) is of course correct, but it is too redundant to be practical. In (a) – (c), there is symmetry about the midpoint so only half of the Brillouin zones need to be shown. Keep in mind that Fig. 3 is a toy model in the extreme. It is not meant to mimic a real system.

4.3. Energy Eigenvalues

The above results can be viewed from the perspective of the energy eigenvalues by putting $\psi_k(x)$ into the Schrödinger equation

$$\left(\frac{p^2}{2m}+V(x)\right)\psi_k(x)=E(k)\psi_k(x). \tag{4.28}$$

In eqn (4.28), $E(k)$ is used instead of E_k because we are interested here in a lattice consisting of many sites, in which case k varies almost continuously, quantized only by the length $L = Na$. Note that $E(k)$ is not a density. It has units of energy, not energy per unit wave number, as would be the case for a density. Introducing $\psi_k(x) = e^{ikx}u_k(x)$, and following some algebra, eqn (4.28) becomes

$$\boxed{\left(-\frac{\hbar^2}{2m}(ik+\nabla)^2+V(x)\right)u_k(x)=E(k)u_k(x).} \tag{4.29}$$

Notice that the exponential factor e^{ikx} is no longer present. From the presence of k in the term $(ik+\nabla)$, we see why k is an appropriate label for Bloch functions. Equation (4.29) is a Hermitian eigenvalue equation, so for each value of k, there exists a spectrum of real eigenvalues. These can be labeled $E_n(k)$, where n indexes the eigenvalues of eqn

(4.29) for a given k. Thus, the Bloch function given by eqn (4.10) is now rewritten to include the index n:

$$\boxed{\psi_{k,n}(x) = u_{k,n}(x)e^{ikx}.} \tag{4.30}$$

The Bloch functions $\psi_{k,n}(x)$ are such that, for each value of k, a large number of eigenfunctions are labeled using the index n. Each different n has parentage in an atomic orbital. You might find it useful to think of n as a principal quantum number. Mathematically, the maximum n value can approach infinity, but in practice it is limited to orbitals without extreme excitations.

As mentioned above, all energy eigenvalues are contained in a range of ka values that spans 2π. The range $-\pi/a \le k \le \pi/a$ gets them all. Letting $k \to k + 2\pi m_G/a$, where m_G is an integer, does not change E. The region bounded by $-\pi/a \le k \le \pi/a$ is the first Brillouin zone. The second Brillouin zone is contained in the regions $-2\pi/a \le k \le -\pi/a$ and $\pi/a \le k \le 2\pi/a$. And so on for higher Brillouin zones.

Now return to Fig. 3(c), choose any k in the first Brillouin zone, and draw a vertical line through this k. The intersection points with the excited curves are the eigenvalues $E_n(k)$. This is the meaning of the Hermitian eigenvalue problem represented with eqn (4.29). You can also locate these solutions on Fig. 3(b) by shifting k by integer multiples of $2\pi/a$ and drawing vertical lines.

Fourier Analysis

A complementary way to view the eigenvalue problem enlists Fourier analysis. This focuses on the relationship between three things: wave vector k, the shape of the potential $V(x)$, and the eigenvalues. Let us expand the wave function in a plane wave basis that is periodic in the length of the lattice (Fig. 4). This is how the particle-on-a-ring model of Chapter 1 was approached. There, the quantization length was that of the large ring, with periodic boundary conditions, and we chose the basis $e^{im\phi}$. It was seen that when $m - m'$ was commensurate with the potential's periodicity the coupling matrix elements were nonzero.

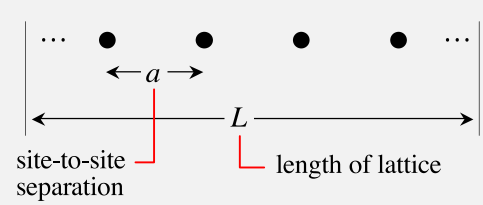


Fig. 4. The wave function quantization length is that of the lattice. The fundamental wave vector is $2\pi/L$ for periodic boundary conditions. The potential is expanded within one repeating interval. Its fundamental wave vector is $2\pi/a$.

The potential $V(x)$ shall be taken as symmetric about $x = 0$. It is expanded in terms of reciprocal lattice vectors G. This is another way of saying that its Fourier expansion consists of harmonics defined by the properties of an individual site. You should make a few sketches to see how this works. Fourier expansions for the wave function and potential can be written

$$\psi(x) = \sum_k C_k\, e^{ikx} \tag{4.31}$$

$$V(x) = \sum_{G>0} 2V_G \cos Gx \tag{4.32}$$

$$= \sum_{all\, G} V_G\, e^{iGx}\ . \tag{4.33}$$

Keep in mind that the $\psi(x)$ in eqn (4.31) is not written in the Bloch form given by eqn (4.30). Rather, it is expanded in a plane wave basis. The G's in eqn (4.33) have positive and negative values, as they must in order to ensure that $V(x)$ is real. The $G = 0$ term in the sum is excluded because it is an unimportant offset. In other words, summation over "all G" in eqn (4.33) means all positive and negative integer multiples of $2\pi / a$, excluding zero. In eqn (4.31), the smallest possible k value is $2\pi / L$ (periodic boundary condition), and the sum is over integer multiples of this. In eqn (4.33), the smallest possible G value is $2\pi / a$, and the sum is over integer multiples of this.

Putting eqns (4.31) and (4.33) into the Schrödinger equation will yield, in a few steps, conditions for the coefficients C_k. To start, the Schrödinger equation becomes

$$\frac{\hbar^2}{2m}\sum_k k^2 C_k e^{ikx} + \sum_k \sum_G V_G C_k e^{i(k+G)x} = E\sum_k C_k e^{ikx}\ . \tag{4.34}$$

The sum over k in the second term can be rewritten using the substitution: $k' = k + G$. The sum over k is then replaced by a sum over k'. Thus, C_k becomes $C_{k'-G}$, and the argument in the exponent is $ik'x$. Because the sum is over all k' (addition of G has the effect of shifting the origin) the prime is dropped, and eqn (4.34) reads

$$\sum_k \left(\left(\frac{\hbar^2 k^2}{2m} - E \right) C_k + \sum_G V_G C_{k-G} \right) e^{ikx} = 0\ . \tag{4.35}$$

Equation eqn (4.35) holds for each value of k. Thus, we have

$$\boxed{\left(\frac{\hbar^2 k^2}{2m} - E \right) C_k + \sum_G V_G C_{k-G} = 0\, .} \tag{4.36}$$

Equation (4.36) shows that, for a given k value, the only coefficients in the expansion of the wave function are those for which k changes by an integer multiple of the fundamental reciprocal lattice vector $2\pi / a$, as shown in Fig. 5. This result was obtained from a different perspective in eqn (4.27), where $\psi_{k+G}(x)$ was shown to have the same energy spectrum as $\psi_k(x)$. Thus, each value of E corresponds to all values of $k + G$, where G is an integer multiple of $2\pi/a$. You should think about this subtle point for a while before moving on.

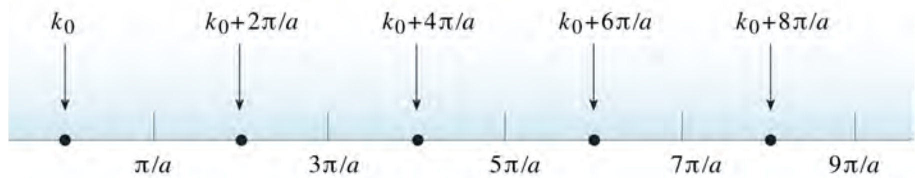


Figure 5. The system is unchanged when an integer multiple of $2\pi/a$ is added to any value of k. For example, k_0 can be changed to $k_0+2\pi/a$, $k_0+4\pi/a$, and so on.

Equation (4.36) of course is consistent with the fact that as the potential goes to zero E approaches the free particle limit $\hbar^2k^2/2m$. Alternatively, if the potential is sinusoidal with period a, for example, $V_0\cos(2\pi x/a)$, the sum contributes just two terms, corresponding to $\pm|G| = \pm\ 2\pi/a$. All other V_G values are equal to zero. The percentages of the higher harmonics in the expansion of the potential given by eqn (4.33) dictates the range of C_{k-G} values needed to express the eigenfunctions.

The result we have just obtained might strike you as formal. However, we encountered it earlier without the mathematical development that has been used here. Go back to Figs. 1.7 – 1.12 and recall the discussions accompanying these diagrams: harmonics of $V(x)$, avoided crossings, resonance conditions, and so on. It is more or less the same material.

Zone Boundary

Now consider a potential $V(x)$ that is sufficiently weak that plane waves are good descriptors except near the band edges. In particular, consider the edge of the first Brillouin zone where $k = \pm\pi/a$. In this case a half wavelength is equal to the site separation a, and $e^{i\pi x/a}$ and $e^{-i\pi x/a}$ combine to form sines and cosines, one peaked where the potential is maximum, the other where it is minimum (Fig. 6). This explains the band gap, which is the energy between these very different states. The numerical value of the band

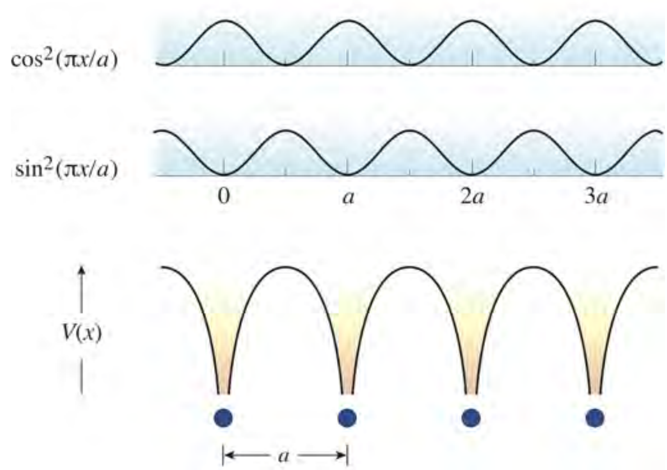


Figure 6. An electron experiences a weak periodic potential due to ionized nuclei separated by a. Standing waves are formed at $k = \pm\pi/a$.

gap is obtained by averaging $V(x)$ over the difference between the probability densities that correspond to the sine and cosine solutions:

$$E_g = \frac{2}{a}\int_0^a dx\left(\cos^2\left(\frac{\pi x}{a}\right)-\sin^2\left(\frac{\pi x}{a}\right)\right)V(x). \tag{4.37}$$

The factor $2/a$ normalizes the wave functions over the interval a. The trigonometric identity: $\cos^2 \mathrm{A} - \sin^2 \mathrm{A} = \cos 2\mathrm{A}$, yields

$$E_g = \frac{2}{a}\int_0^a dx \cos\left(\frac{2\pi x}{a}\right)V(x). \tag{4.38}$$

The cosine term contains the periodicity of the difference between the upper and lower level probability densities. The potential $V(x)$ is expanded in a Fourier series. Only the term in the Fourier series that varies as $\cos(2\pi x/a)$ (the lowest order term in the expansion) survives integration. Equation (4.38) yields the band gap energy at the edge of the first Brillouin zone.

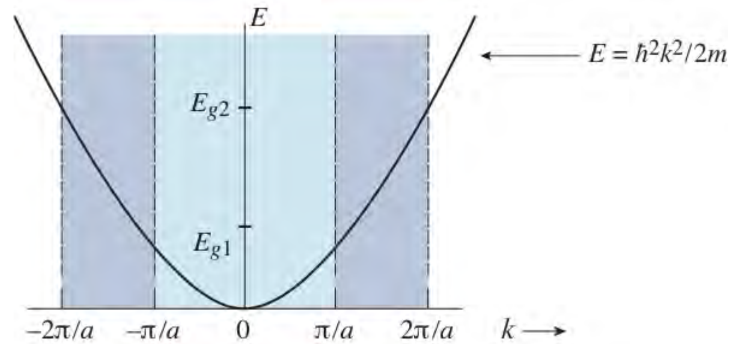
Two limiting cases are now examined: (i) binding is weak enough that, to a first approximation, the electron can be taken as nearly free; and (ii) binding is strong enough that, to a first approximation, site-to-site electron transport is quite modest.

Exercise: Explain why eqns (4.36) and (4.37) give the band gap. Should we not be taking the difference between eigenstates or between expectation values of the Hamiltonian?

4.4. Nearly Free Electron

Suppose an electron in a 1D lattice comprising many binding sites somehow managed to be oblivious to the sites. In this case, its motion would be restricted only in the sense that the electron wave function must respect the boundary condition imposed by the overall length of the lattice. The electron would have wave functions e^{ikx} and energies $\hbar^2k^2/2m$. Momentum would be quantized according to the length of the lattice, which is large, yielding the parabolic $E(k)$ indicated in Fig. 7. On the other hand, if the electron experiences a weak periodic potential, its eigenfunctions must be Bloch waves $\psi_{k,n}(x) = u_{k,n}(x)e^{ikx}$, where $u_{k,n}(x)$ is nearly constant. This case of the so-called nearly free electron is treated here. The electron is referred to as nearly free because there exists a lattice potential that, however slight, influences electrons having k values in the vicinities of $\pm\pi/a$, $\pm 2\pi/a$, and so on.

Figure 7. The $E(k)$ parabola is the dispersion relation for a free electron. In this limit, the sites and Brillouin zones are irrelevant.



For k values well away from the edges of the Brillouin zones, the e^{ikx} waves are good descriptors. At the Brillouin zone edges, however, strong effects arise from even weak interaction with the lattice. In the vicinities of the Brillouin zone edges, states whose k values differ by integer multiples of $2\pi / a$ (with $k \approx |k'|$) are coupled strongly to one another. The interpretation $p = \hbar k$ cannot be used, and energy is no longer given by $\hbar^2 k^2 / 2m$.

For example, we have seen that at the edge of the first Brillouin zone, the degenerate pair $e^{i\pi x/a}$ and $e^{-i\pi x/a}$ yield standing waves in which the upper and lower states correspond to probability densities peaked in regions of high and low potential, respectively. Applied to the other Brillouin zone boundaries, small gaps appear in the $E(k)$ curves when $k = \pm\, 2\pi / a$, $\pm\, 3\pi / a$, and so on, as indicated schematically in Fig. 8.

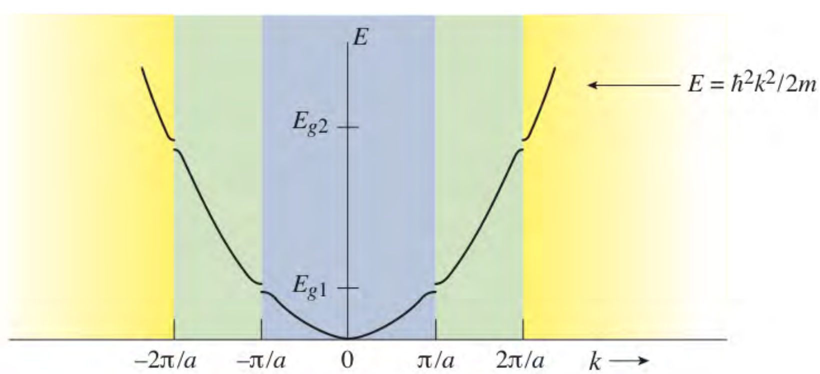


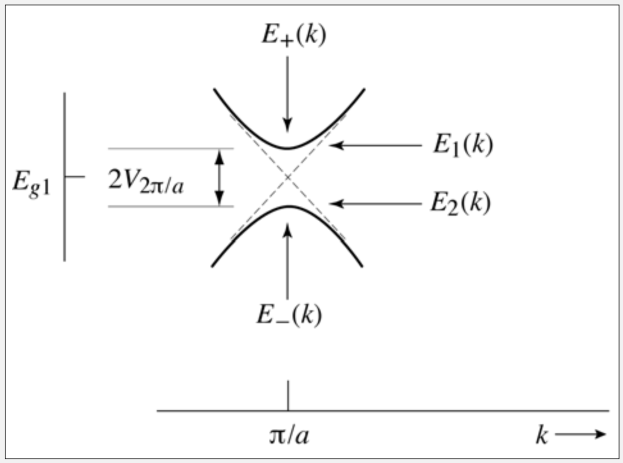
Figure 8. The nearly free electron model: small gaps appear at k values of $\pm\, \pi / a$, $\pm\, 2\pi / a$, and so on: the edges of the Brillouin zones.

The interactions at the Brillouin zone edges are curve crossings, as we saw way back in Chapter 1. Referring to Fig. 8, translating by $2\pi / a$ the region near $k = -\,\pi / a$ to the region near $k = \pi / a$ results in the crossing indicated in Fig. 9. In its vicinity, it is easy to evaluate the coupling matrix element in the traveling wave basis, and the eigenvalues are readily obtained using a 2×2 matrix. There is no need to consider influences brought about by interactions with higher levels, because of the fact that we are at a region of near-degeneracy and coupling is weak.

The coupling matrix element that is responsible for the energy gap at the edge of the first Brillouin zone is now evaluated between levels k in the first Brillouin zone and $k - 2\pi / a$ in the second Brillouin zone. In the plane wave basis, this matrix element is

$$\left\langle k \left| V(x) \right| k - \frac{2\pi}{a} \right\rangle = \frac{1}{L} \int_0^L dx\, e^{-i 2\pi x/a}\, V(x)\,. \tag{4.39}$$

Figure 9. In the vicinity of the curve crossing, only $E_1(k)$ and $E_2(k)$ (dashed lines) need to be considered. Plane waves interact via the periodic potential, creating a gap: $2\,|V_{2\pi/a}|$ at $k = \pi / a$. The $E_+(k)$ and $E_-(k)$ curves have parabolic shapes in the vicinity of $k = \pi / a$.



The integral retains only the leading term in the Fourier expansion of $V(x)$, which is expanded in harmonics of the fundamental reciprocal lattice vector $2\pi / a$. In short, integration retains only the $2\pi / a$ term in the expansion of $V(x)$. Diagonal matrix elements are zero. Earlier, the Fourier expansion of the periodic potential was introduced using sine, cosine, and complex exponential basis functions whose arguments were *iGx*, with G given by integer multiples of $2\pi / a$.[5] With $V(x)$ expressed in the exponential basis, eqn (4.39) becomes:

$$\left\langle k \left| V(x) \right| k - \frac{2\pi}{a} \right\rangle = \frac{1}{L} \int_0^L dx \left(e^{-i 2\pi x/a} \sum_G V_G\, e^{iGx} \right) \tag{4.40}$$

$$= \sum_G V_G \frac{1}{L} \int_0^L dx \exp\left(-i \left(\frac{2\pi}{a} - G \right) x \right). \tag{4.41}$$

As mentioned above, the only non-vanishing integration in the sum over all G is the one for which $G = 2\pi / a$. Thus, eqn (4.41) gives a simple and familiar result:

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[5] Note that there is a difference of a factor of two in the magnitudes of the expansion coefficients for real versus complex exponential bases.

$$\boxed{\left\langle k \left| V(x) \right| k - \frac{2\pi}{a} \right\rangle = V_{2\pi/a} .} \tag{4.42}$$

The off-diagonal matrix element $V_{2\pi/a}$ is now used with the 2×2 Hamiltonian matrix that describes coupling in the vicinity of the band gap. Referring to Fig. 9, the eigenvalues of the 2×2 matrix are

$$E_{\pm} = E_{g1} \pm \sqrt{\tfrac{1}{4}\left(E_1(k) - E_2(k)\right)^2 + |V_{2\pi/a}|^2} \ , \tag{4.43}$$

where E_{g1} is the crossing point indicated in Fig. 9, and $E_1(k)$ and $E_2(k)$ are the undisturbed curves, that is, the dashed lines in Fig. 9. Except for the continuous nature of $E_1(k)$ and $E_2(k)$, eqn (4.43) is the same as one encountered in the Chapter 1 section entitled: *Pairwise Interaction*. The curves $E_1(k)$ and $E_2(k)$ are now expanded in a Taylor series about the crossing point at $k = \pi / a$. Referring to Fig. 9, retaining the lowest order (linear) term in the expansion gives

$$E_{1,2}(k) = E_{g1} \pm \left(\frac{\partial E}{\partial k}\right)_{\pi/a} \left(k - \frac{\pi}{a}\right) \tag{4.44}$$

$$= E_{g1} \pm \frac{\hbar^2}{m}\frac{\pi}{a}\left(k - \frac{\pi}{a}\right), \tag{4.45}$$

where $E = \hbar^2 k^2 / 2m$ has been used. Thus, the first term inside the radical in eqn (4.43) is given by

$$\tfrac{1}{4}\left(E_1(k) - E_2(k)\right)^2 = \left(\frac{\hbar^2}{2m}\frac{2\pi}{a}\left(k - \frac{\pi}{a}\right)\right)^2 \tag{4.46}$$

$$= 4\left(\frac{\hbar^2 k'^2}{2m}\right)\left(\frac{\hbar^2 (\pi / a)^2}{2m}\right) \tag{4.47}$$

$$= \left(\frac{\hbar^2 k'^2}{2m}\right) 4E_{g1} . \tag{4.48}$$

where $E_{g1} = \hbar^2 (\pi / a)^2 / 2m$ has been used, and the definition $k' = k - \pi / a$ has been introduced. Introducing this into eqn (4.43) yields

$$E_{\pm}(k') = E_{g1} \pm \sqrt{\frac{\hbar^2 k'^2}{2m} 4E_{g1} + |V_{2\pi/a}|^2} \ . \tag{4.49}$$

Near $k' = 0$, the $|V_{2\pi/a}|^2$ term in the radical dominates. Expanding the radical, which is of the form $|V_{2\pi/a}|(1+\varepsilon)^{1/2}$, yields

$$E_\pm(k') \approx E_{g1} \pm |V_{2\pi/a}| \pm \alpha \frac{\hbar^2 k'^2}{2m}, \tag{4.50}$$

where $\alpha = 2E_{g1}/|V_{2\pi/a}|$ and $k' = k - \pi/a$.

Equation (4.50) shows that the $E_\pm(k')$ curves are parabolic near $k' = 0$. This is suggestive of states whose energies are "kinetic." However, given that the $k' = 0$ solutions are standing waves, the role of kinetic energy is curious. If one insists on assigning the k'^2 term to kinetic energy, it must be of the mathematical form $\hbar^2 k'^2/2m$. Moreover, to be consistent with eqn (4.50), the m in this expression must be replaced by a parameter. This parameter is referred to as the effective mass, and it is labeled m^*. The kinetic energy term in eqn (4.50) is then $\hbar^2 k'^2/2m^*$. Note that the $\pm$ that accompanies the term $\alpha\hbar^2 k'^2/2m$ has been absorbed into the effective mass, which therefore can be positive or negative.

The effective masses at the zone edges are defined from the curvatures of the $E_\pm(k')$ curves near their stationary points. Referring to eqn (4.50), at the edge of the first Brillouin zone, this gives

$$\left(\frac{\partial^2 E_\pm(k')}{\partial k'^2}\right)_0 = \pm\frac{\hbar^2\alpha}{m}. \tag{4.51}$$

This expression has been obtained using the nearly free electron model. The assignment: $\pm\hbar^2\alpha/m = \hbar^2/m^*$ is the definition of effective mass m^*. For the $E_\pm(k')$ curves described by eqn (4.50) and Fig. 9 we have

$$\boxed{E_\pm(k') = \left(E_{g1} \pm |V_{2\pi/a}|\right) + \frac{\hbar^2}{2\underbrace{m^*}_{\pm m/\underbrace{\alpha}_{2E_{g1}/|V_{2\pi/a}|}}}\left(k - \frac{\pi}{a}\right)^2.} \tag{4.52}$$

In the nearly free electron limit, the energy of the band gap $2|V_{2\pi/a}|$ is much smaller than the energy E_{g1} that locates the center of the gap. Thus, $\alpha = 2E_{g1}/|V_{2\pi/a}|$ is much larger than unity, and the electron's effective mass is much smaller than its real mass. This is due to the lattice. It appears to someone oblivious to the lattice potential that the electrons are lighter than is in fact the case. The effect brought about through the potential has been parameterized into the effective mass.

4.5. Tight Binding

The limit opposite that of the nearly free electron is referred to as tight binding. The electron, though strongly bound to a site, is not so strongly bound that it completely loses communication with adjacent sites. For example, it is assumed that the electron resides at a given site for long periods of time, tunneling infrequently to adjacent sites.

When electrons in a given atomic orbital are bound strongly to the sites, the function $u_{k,n}(x)$ and its counterparts at the immediately adjacent sites, $u_{k,n}(x \pm a)$, have only modest spatial overlap. The atomic orbitals are good first approximations, and the energy bands are narrow. This applies to the low energy filled bands that comprise atomic core orbitals and, to a lesser extent, to the highest occupied bands of insulators. For a given atomic orbital that we shall call ϕ_ν, the Bloch function can be written

$$\boxed{\psi_k(x) = \left(N^{-1/2} \sum_{i=1}^{N} e^{-ik(x-x_i)} \phi_\nu(x-x_i) \right) e^{ikx} .} \qquad (4.53)$$

In eqn (4.53), $x_i = ia$, where i is an integer that is not to be confused with the imaginary unit i. The subscript ν denotes the atomic orbital under consideration. The letter ν is used because it is the Greek counterpart to n. It is assumed that the atomic orbitals $\phi_\nu(x-x_i)$ are normalized. The index n for the corresponding band is suppressed in favor of a compact notation. It can be retrieved later. Thus, we write $\psi_k(x)$ instead of $\psi_{k,n}(x)$. The normalization factor $N^{-1/2}$ is an approximation based on the fact that electrons are tightly bound to the sites. It neglects the relatively small contribution due to overlap between wave functions centered at adjacent sites.

The large parenthetic term in eqn (4.53) is periodic in a, and therefore when it is multiplied by e^{ikx} we have a Bloch function. The electron atomic orbitals $\phi_\nu(x-x_i)$ are centered at the ion cores located at x_i. The phase evolution factor e^{ikx} on the right of the large parentheses does not imply electron transport, though it accommodates it when binding is not too tight. The tight binding limit, as its name implies, does not accommodate electron transport to any significant extent. This is made clear by writing eqn (4.53) as

$$\psi_k(x) = N^{-1/2} \sum_{i=1}^{N} e^{ikx_i} \phi_\nu(x-x_i) . \qquad (4.54)$$

Equation (4.54) shows that $\psi_k(x)$ can be represented using atomic orbitals whose site-to-site phase progression is e^{ika}. Let us now obtain an expression for $E(k)$ in terms of matrix elements whose values can be parameterized in a way that yields a neat form for $E(k)$. Start by writing $E(k)$ as the expectation value of H over $\psi_k(x)$:

$$E(k) = \langle \psi_k(x) | H | \psi_k(x) \rangle \tag{4.55}$$

$$= N^{-1} \sum_{i,i'} e^{ik(x_i - x_{i'})} \langle \phi_v(x - x_{i'}) | H | \phi_v(x - x_i) \rangle . \tag{4.56}$$

Without carrying out any calculation, we know that, because of the fact that $E(k)$ is real, a phase factor cannot appear in the final result. The $e^{ik(x_i - x_{i'})}$ term will not appear alone following summation.

The double sum can be reduced to a single sum. To see how this works, consider Fig. 10, which indicates the strategy. Focusing on the orbital with $x_{i'} = 0$ $[\phi_v(x - x_{i'}) = \phi_v(x)]$, its interactions with adjacent orbitals are $\langle \phi_v(x) | H | \phi_v(x \mp a) \rangle e^{\pm ika}$, and so on for its interactions with orbitals centered at $\pm 2a, \pm 3a \ldots$.

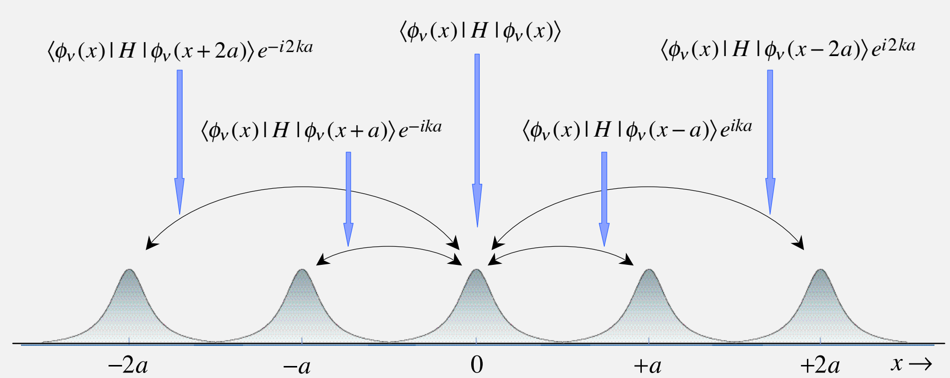

Figure 10. An atomic orbital $\phi_v(x)$ and its binding potential are each centered at $x = 0$ ($x_{i'} = 0$). This system interacts with its environment. Electron density from other orbitals is present at the potential centered at $x_{i'} = 0$. In addition, the electron in orbital $\phi_v(x)$ experiences a weak but non-negligible potential that arises from the other sites. Total energy is obtained by multiplying the energy for the single orbital $\phi_v(x)$ by N.

There is nothing special about the choice $x_{i'} = 0$, so the total energy is obtained by multiplying the result obtained at $x_{i'} = 0$ by N. That is, summing over i' is equivalent to multiplication by N. This cancels the factor of N^{-1} in eqn (4.56) and yields

$$E(k) = \sum_i e^{ikx_i} \langle \phi_v(x) | H | \phi_v(x - x_i) \rangle \tag{4.57}$$

$$= \langle \phi_v(x) | H | \phi_v(x) \rangle + \sum_{i \neq 0} e^{ikx_i} \langle \phi_v(x) | H | \phi_v(x - x_i) \rangle . \tag{4.58}$$

Evaluation of the first term in eqn (4.58) is facilitated by splitting H into $H_0 + V'(x)$, where H_0 is local to the site under consideration. It uses just the potential due to the ion present at $x = 0$, whereas $V'(x)$ takes into account the extended ranges of the potentials centered at the different sites.

$$H = H_0 + V'(x) \tag{4.59}$$

$$= \frac{p^2}{2m} + V_0(x) + V'(x) \tag{4.60}$$

Referring to Fig. 11(a), the potential due to the ion that is present at the site under consideration is $V_0(x)$. Thus, the atomic Hamiltonian for the electron is H_0. The term $V'(x)$ in Fig. 11(b) is the potential at the site under consideration due to the other sites. For the "other sites," we shall use just the immediately adjacent ones because in the tight binding approximation the potentials act rather locally in the regions around their respective ion cores. Consequently, sites farther away than a single displacement a are neglected. With H given by eqn (4.60), the first term on the right hand side of eqn (4.58) becomes

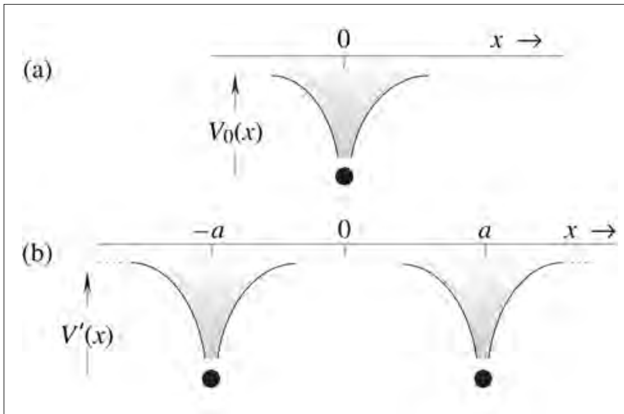

Figure 11. (a) An electron is bound to an ion at $x = 0$. (b) Potentials due to ions at $x = \pm a$ are weak but non-negligible in the vicinity of $x = 0$.

$$\langle \phi_v | H | \phi_v \rangle = \langle \phi_v | H_0 | \phi_v \rangle + \langle \phi_v | V' | \phi_v \rangle \tag{4.61}$$

$$= E_v - \beta \tag{4.62}$$

where E_v is the energy of the atomic orbital ϕ_v. The convention is that $E = 0$ corresponds to the electron removed completely from the atomic core. Thus, all of the atom's bound levels have negative energies. The term $-\beta$ is the average value of $V'(x)$. Because $V'(x)$ is negative, β is positive.

Let us now examine the second term on the right hand side of eqn (4.58). As mentioned earlier, the interaction terms are non-negligible only for adjacent sites in the tight binding model, so the sum reduces to two terms whose matrix elements are

$$\left\langle \phi_v(x) \middle| \, H_0 + V'(x) \, \middle| \phi_v(x \pm a) \right\rangle . \tag{4.63}$$

The H_0 contribution is equal to $E_v \langle\, \phi_v(x) | \phi_v(x \pm a) \,\rangle$, which we label $-\gamma$, where γ is positive. Though the magnitude of this term is small, it is not negligible. It is the same order-of-magnitude as β. On the other hand, the $V'(x)$ contribution in eqn (4.63) is sufficiently small that it can be neglected in the qualitative model under consideration, because it involves the product of two small factors: the overlap of $\phi_v(x)$ and $\phi_v(x \pm a)$, and the small magnitude of $V'(x)$ in the vicinity of the site under consideration. Equation (4.58) can thus be written

$$E(k) = E_v - \beta - \gamma\left(e^{ika} + e^{-ika}\right) \tag{4.64}$$

$$= E_v - \beta - 2\gamma \cos ka \,. \tag{4.65}$$

Using $\cos ka = 1 - 2\sin^2(ka/2)$, and defining $E_0 = E_v - \beta - 2\gamma$, eqn (4.65) becomes

$$\boxed{E(k) = E_0 + 4\gamma \sin^2\left(\tfrac{1}{2} ka\right).} \tag{4.66}$$

Figure 12 is a plot of this dispersion relation. The width of the band is 4γ, which is small. As the overlap integral: $\langle \phi_v(x) | \phi_v(x \pm a) \rangle$, diminishes in magnitude, so does the width of the band. As discussed earlier, the curvature of $E(k)$ can be used to define an effective mass m^*. Because the energy band is narrow in the tight binding limit, energy depends only weakly on k. Therefore, near the bottom of the dispersion curve ($k \sim 0$) curvature is small and the effective mass is larger than that of a free electron. This is a manifestation of the fact that it is hard for the electron to go anywhere when it is bound tightly to a site. In other words, it appears to be sluggish.

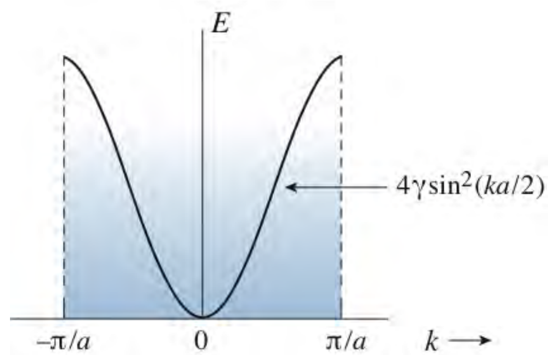

Figure 12. Equation (4.66) is the dispersion relation for the tight binding limit: $E(k) = E_0 + 4\gamma \sin^2(ka/2)$. The energy width is 4γ.

On the other hand, near $k = \pm\, \pi/a$, where the curvature is negative, the effective mass is negative. It has the same magnitude as at $k = 0$, because the curvature of sine-squared in eqn (4.66) differs only in sign for the stationary points $k = 0$ and $\pm\, \pi/a$.

An expression for m^* near the stationary points in the dispersion curve is obtained from eqn (4.66) by following the same procedure used in the nearly free electron model. For $k \sim 0$, replacing $\sin(ka/2)$ with $ka/2$ gives

$$\left(\frac{\partial^2 E(k)}{\partial k^2}\right)_0 = 2\gamma a^2 . \tag{4.67}$$

With this set equal to $\hbar^2/m^*$, the effective mass is

$$\boxed{m^* = \frac{\hbar^2}{2\gamma a^2} ,} \tag{4.68}$$

with the understanding that m^* is positive near $k = 0$ and negative near $k = \pi / a$.

This completes our peek into electrons in a 1D periodic lattice, including the limiting cases of nearly free electron and tight binding.