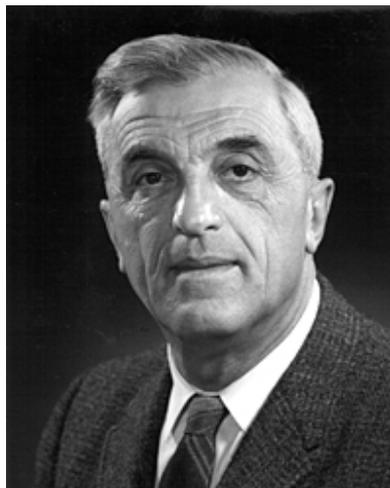


**Bloch theorem and energy band**  
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**Felix Bloch** was born in Zürich, Switzerland to Jewish parents Gustav and Agnes Bloch. He was educated there and at the Eidgenössische Technische Hochschule, also in Zürich. Initially studying engineering he soon changed to physics. During this time he attended lectures and seminars given by Peter Debye and Hermann Weyl at ETH Zürich and Erwin Schrödinger at the neighboring University of Zürich. A fellow student in these seminars was John von Neumann. Graduating in 1927 he continued his physics studies at the University of Leipzig with Werner Heisenberg, gaining his doctorate in 1928. His doctoral thesis established the quantum theory of solids, using Bloch waves to describe the electrons.

He remained in European academia, studying with Wolfgang Pauli in Zürich, Niels Bohr in Copenhagen and Enrico Fermi in Rome before he went back to Leipzig assuming a position as privatdozent (lecturer). In 1933, immediately after Hitler came to power, he left Germany, emigrating to work at Stanford University in 1934. In the fall of 1938, Bloch began working with the University of California at Berkeley 37" cyclotron to determine the magnetic moment of the neutron. Bloch went on to become the first professor for theoretical physics at Stanford. In 1939, he became a naturalized citizen of the United States. During WW II he worked on nuclear power at Los Alamos National Laboratory, before resigning to join the radar project at Harvard University.

After the war he concentrated on investigations into nuclear induction and nuclear magnetic resonance, which are the underlying principles of MRI. In 1946 he proposed the Bloch equations which determine the time evolution of nuclear magnetization. He and Edward Mills Purcell were awarded the 1952 Nobel Prize for "their development of new ways and methods for nuclear magnetic precision measurements." In 1954–1955, he served for one year as the first Director-General of CERN. In 1961, he was made Max Stein Professor of Physics at Stanford University.



[http://en.wikipedia.org/wiki/Felix\\_Bloch](http://en.wikipedia.org/wiki/Felix_Bloch)

## 1. Bloch theorem

Here we present a restricted proof of a Bloch theorem, valid when  $\psi(x)$  is non-degenerate. That is, when there is no other wavefunction with the same energy and wavenumber as  $\psi(x)$ .

We assume that a periodic boundary condition is satisfied,

$$\psi(x + Na) = \psi(x).$$

The potential energy is periodic in a period  $a$ ,

$$V(x + a) = V(x).$$

We now consider the wavefunction  $\psi(x + a)$ . For convenience we rewrite this equation as

$$\psi(x + a) = T(a)\psi(x).$$

Then we have

$$\begin{aligned} T(a)H(x, p)\psi(x) &= H(x + a, p)\psi(x + a) \\ &= H(x, p)\psi(x + a) \\ &= H(x, p)T(a)\psi(x) \end{aligned}$$

where the Hamiltonian is invariant under the translation by  $a$ .

$$H(x + a, p) = H(x, p).$$

This means that

$$T(a)H(x, p) = H(x, p)T(a).$$

Suppose that  $\psi(x)$  is the eigenfunction of  $H(= H(x, p))$  with the energy  $E$ .

$$H\psi(x) = E\psi(x).$$

Then we have

$$T(a)H\psi(x) = HT(a)\psi(x).$$

or

$$H[T(a)\psi(x)] = T(a)H\psi(x) = E[T(a)\psi(x)].$$

This means that  $T(a)\psi(x)$  is the eigenfunction of  $H$  with the energy  $E$ . Since  $\psi(x)$  is nondegenerate,  $\psi(x+a) = T(a)\psi(x)$  is described by

$$\psi(x+a) = C\psi(x),$$

where  $C$  is a constant. Similarly we have

$$\psi(x+2a) = C\psi(x+a) = C^2\psi(x)$$

$$\psi(x+3a) = C\psi(x+2a) = CC^2\psi(x) = C^3\psi(x)$$

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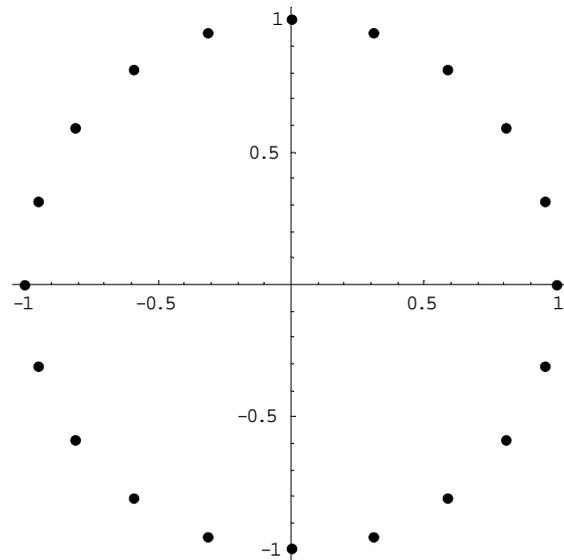
$$\psi(x+Na) = C^N\psi(x) = \psi(x) \quad (\text{from the periodic condition}).$$

Then we have

$$C^N = 1$$

Note that  $C$  is a complex number.  $|C|^N = 1$  or  $|C| = 1$ .

**((Example))**



**Fig.** The solution of  $C^{20} = 1$  in the complex plane.

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$$C = e^{i\theta}, \quad C^N = e^{iN\theta} = 1$$

Then we get

$$N\theta = 2\pi s \quad (s: \text{integer})$$

or

$$\theta = \frac{2\pi s}{N} = \frac{2\pi s}{Na} a = \frac{2\pi}{L} sa = ka$$

where

$$k = \frac{2\pi}{L} s \quad \text{and} \quad C = e^{ika}$$

((Bloch theorem))

$$\psi_k(x+a) = e^{ika} \psi_k(x)$$

or

$$\psi_k(x+la) = e^{ikla} \psi_k(x)$$

where  $l$  is an integer.

## 2. Brillouin zone in one dimensional system

We know that the reciprocal lattice  $G$  is defined by

$$G = \frac{2\pi}{a} n, \quad (n: \text{integer}).$$

When  $k$  is replaced by  $k + G$ ,

$$\psi_{k+G}(x+a) = e^{i(k+G)a} \psi_{k+G}(x) = e^{ika} \psi_{k+G}(x),$$

since  $e^{iGa} = e^{i2\pi m} = 1$ . This implies that  $\psi_{k+G}(x)$  is the same as  $\psi_k(x)$ .

$$\psi_{k+G}(x) = \psi_k(x).$$

or the energy eigenvalue of  $\psi_{k+G}(x)$  is the same as that of  $\psi_k(x)$ ,

$$E_{k+G} = E_k.$$

Note that the restriction for the value of  $s$  arises from the fact that  $\psi_{k+G}(x) = \psi_k(x)$ .

$$k = \frac{2\pi s}{L} = \frac{2\pi s}{Na} = \frac{\pi}{a} \left( \frac{2s}{N} \right),$$

where

$$-\frac{N}{2} \leq s \leq \frac{N}{2}.$$

The first Brillouin zone is defined as  $|k| \leq \frac{\pi}{a}$ . There are  $N$  states in the first Brillouin zone.

When the spin of electron is taken into account, there are  $2N$  states in the first Brillouin zone. Suppose that the number of electrons per unit cell is  $n_c$  ( $= 1, 2, 3, \dots$ ). Then the number of the total electrons is  $n_c N$ .

- (a)  $n_c = 1$ . So there are  $N$  electrons.  $N/2N = 1/2$  (band-1: half-filled)
- (b)  $n_c = 2$ .  $2N/2N = 1$  (band-1: filled).
- (c)  $n_c = 3$ .  $3N/2N = 1.5$  (band-1: filled, band-2: half-filled).
- (d)  $n_c = 4$ .  $4N/2N = 2$  (band-1: filled, band-2: filled).

When there are even electrons per unit cell, bands are filled. Then the system is an insulator. When there are odd electrons per unit cell, bands are not filled. Then the system is a conductor.

### 3. Bloch wavefunction

Here we assume that

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

Then we have

$$\psi_k(x-a) = e^{ikx} e^{-ika} u_k(x-a) = e^{-ika} e^{ikx} u_k(x-a),$$

which should be equal to

$$e^{-ika} \psi_k(x) = e^{-ika} e^{ikx} u_k(x),$$

or

$$u_k(x-a) = u_k(x),$$

which is a periodic function of  $x$  with a period  $a$ . The solution of the Schrodinger equation for a periodic potential must be of a special form such that  $\psi_k(x) = e^{ikx} u_k(x)$ ,

where  $u_k(x+a) = u_k(x)$ . In other words, the wave function is a product of a plane wave and a periodic function which has the same periodicity as a potential.

Here we consider the 3D case. The solutions of the Schrödinger equation for a periodic potential must be of a special form:

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \quad (\text{Bloch function}),$$

where

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{T}).$$

Bloch functions can be assembled into localized wave packets to represent electrons that propagate freely through the potential of the ion cores.  $\mathbf{T}$  is any translation vectors which is expressed by  $\mathbf{T} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$  ( $n_1, n_2, n_3$  are integers,  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$  are fundamental lattice vectors). The function  $u_{\mathbf{k}}(\mathbf{r})$  can be expanded as follows. (Fourier transform)

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}}.$$

where  $\mathbf{G}$  is the reciprocal lattice vector. We use the same discussion for the periodic charge density in the x-ray scattering.

Then the wave function in a periodic potential is given by

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} = C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + C_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} + \dots$$

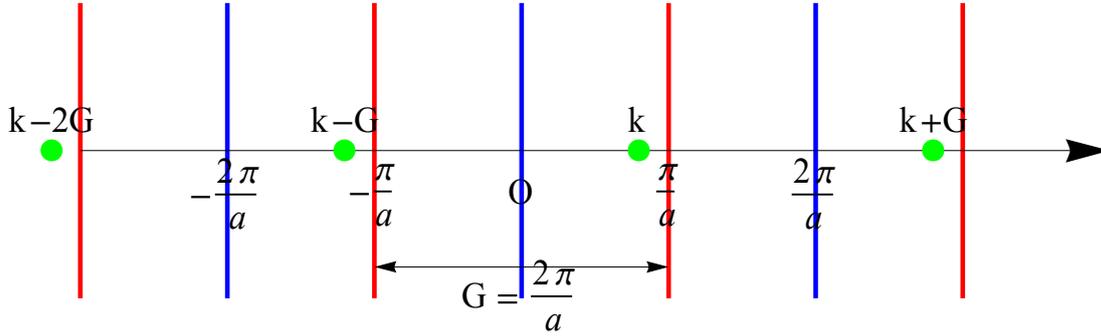
or

$$\psi_{\mathbf{k}}(\mathbf{r}) = \dots + C_{\mathbf{k}-2\mathbf{G}} e^{i(\mathbf{k}-2\mathbf{G})\cdot\mathbf{r}} + C_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} + C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + C_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} + C_{\mathbf{k}+2\mathbf{G}} e^{i(\mathbf{k}+2\mathbf{G})\cdot\mathbf{r}} + \dots$$

or

$$\begin{aligned} |\psi_{\mathbf{k}}\rangle = & \dots + C_{\mathbf{k}-2\mathbf{G}} |\mathbf{k}-2\mathbf{G}\rangle + C_{\mathbf{k}-\mathbf{G}} |\mathbf{k}-\mathbf{G}\rangle + C_{\mathbf{k}} |\mathbf{k}\rangle \\ & + C_{\mathbf{k}+\mathbf{G}} |\mathbf{k}+\mathbf{G}\rangle + C_{\mathbf{k}+2\mathbf{G}} |\mathbf{k}+2\mathbf{G}\rangle + \dots \end{aligned}$$

using the Dirac ket vector.



The eigenvalue-problem

$$\hat{H}|\psi_{\mathbf{k}}\rangle = E_{\mathbf{k}}|\psi_{\mathbf{k}}\rangle, \quad \text{or} \quad H\psi_{\mathbf{k}}(x) = E_{\mathbf{k}}\psi_{\mathbf{k}}(x).$$

$E_{\mathbf{k}}$  is the eigenvalue of the Hamiltonian and has the following properties.

- (i)  $E_{\mathbf{k}} = E_{\mathbf{k}+\mathbf{G}}$ .
- (ii)  $E_{\mathbf{k}} = E_{-\mathbf{k}}$ .

The first property means that any reciprocal lattice point can serve as the origin of  $E_{\mathbf{k}}$ . The relation  $E_{\mathbf{k}} = E_{-\mathbf{k}}$  is always valid, whether or not the system is centro-symmetric.

The proof of this is already given using the time-reversal operator. The proof can be also made analytically as follows.

$$H\psi_{\mathbf{k}}(x) = E_{\mathbf{k}}\psi_{\mathbf{k}}(x),$$

$$H\psi_{\mathbf{k}}^*(x) = E_{\mathbf{k}}\psi_{\mathbf{k}}^*(x) \quad (\hat{H} \text{ is Hermitian}),$$

or

$$H\psi_{-\mathbf{k}}^*(x) = E_{-\mathbf{k}}\psi_{-\mathbf{k}}^*(x).$$

From the Bloch theorem given by

$$\psi_{\mathbf{k}}(x-a) = e^{-ika}\psi_{\mathbf{k}}(x),$$

or

$$\psi_{\mathbf{k}}(x) = e^{ikx}u_{\mathbf{k}}(x), \quad \text{and} \quad \psi_{\mathbf{k}}^*(x) = e^{-ikx}u_{\mathbf{k}}^*(x),$$

we have

$$\psi_{\mathbf{k}}^*(x-a) = e^{-ik(x-a)}u_{\mathbf{k}}^*(x-a) = e^{-ik(x-a)}u_{\mathbf{k}}^*(x) = e^{ika}\psi_{\mathbf{k}}^*(x),$$

or

$$\psi_{-k}^*(x-a) = e^{-ika} \psi_{-k}^*(x).$$

Thus the wave functions  $\psi_k(x)$  and  $\psi_{-k}^*(x)$  are the same eigenfunctions of  $\hat{T}_x(a)$  with the same eigenvalue  $e^{-ika}$ . Thus we have

$$\psi_{-k}^*(x) = \psi_k(x),$$

with

$$E_{\mathbf{k}} = E_{-\mathbf{k}}.$$

What does this relation mean?

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} = C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + C_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} + \dots$$

$$\psi_{\mathbf{k}}^*(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}}^* e^{-i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}},$$

or

$$\psi_{-\mathbf{k}}^*(\mathbf{r}) = \sum_{\mathbf{G}} C_{-\mathbf{k}-\mathbf{G}}^* e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = \sum_{\mathbf{G}} C_{-\mathbf{k}+\mathbf{G}}^* e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}}.$$

Then we have the relation

$$C_{-\mathbf{k}+\mathbf{G}}^* = C_{\mathbf{k}-\mathbf{G}},$$

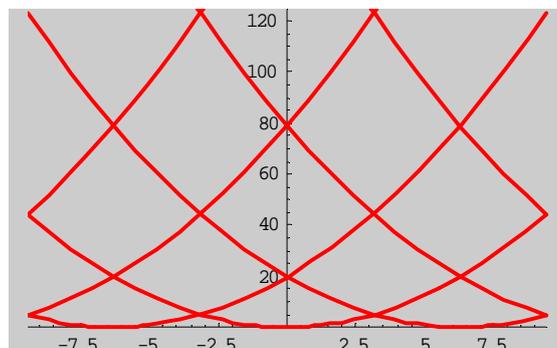
or

$$C_{\mathbf{k}-\mathbf{G}}^* = C_{-\mathbf{k}+\mathbf{G}}.$$

#### 4. Properties of energy band

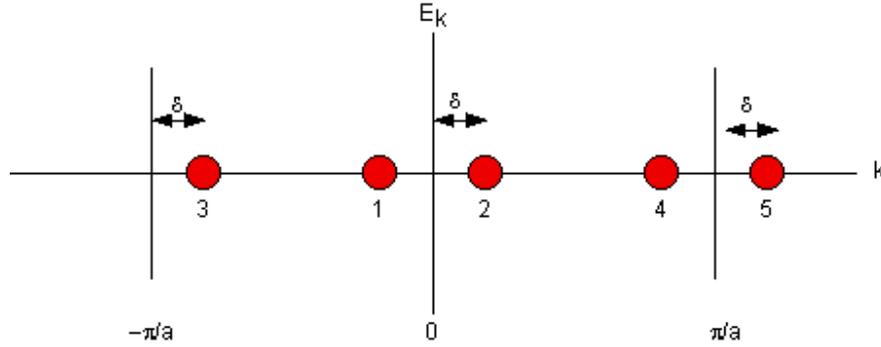
(i)  $E_k = E_{k+G}$

We consider the case of an infinitely small periodic potential. The curve  $E_k$  is practically the same as in the case of free electron, but starting at every point in reciprocal lattice at  $G = (2\pi/a)n$  ( $n$ : integer). We have  $E_{k+G} = E_k$ , but for the dispersion curves that have a different origin.



**Fig.** The energy dispersion ( $E_k$  vs  $k$ ) of electrons in the weak limit of periodic potential (the periodic zone scheme), where  $E_k = E_{k+G}$ .  $m \rightarrow 1$ .  $a \rightarrow 1$ .  $\hbar \rightarrow 1$ .  $G \rightarrow 2\pi n$  ( $n = 0, \pm 1, \pm 2, \dots$ ).

(ii)  $E_{-k} = E_k$



**Fig.** The relation of  $E_{-k} = E_k$  in the reciprocal lattice plane.  $k = \pm\pi/a$  is the boundary of the first Brillouin zone ( $|k| \leq \pi/a$ ).

It follows that from the condition ( $E_k = E_{-k}$ ), in Fig.,  $E(1) = E(2)$ . On taking  $\delta \rightarrow 0$ , the group velocity defined by  $[E(2) - E(1)]/2\delta$  reduces to zero ( $dE_k/dk \rightarrow 0$ ). On applying the periodicity condition  $E_k = E_{k+G}$  this result can immediately be extended as follows.  $dE_k/dk \rightarrow 0$  at  $k = 0, \pm 2\pi/a, \pm 4\pi/a, \dots$

We now consider the value of this derivative at the Brillouin zone boundary.

From the condition  $E_k = E_{-k}$ ,  $E(3) = E(4)$ .

From the condition  $E_k = E_{k+G}$ ,  $E(3) = E(5)$ .

Therefore, we have  $E(4) = E(5)$ .

On taking  $\delta \rightarrow 0$ , the group velocity at the boundary of Brillouin zone is defined as  $[E(5) - E(4)]/2\delta$ , which reduces to zero ( $dE_k/dk \rightarrow 0$ ). In other words, the group velocity ( $dE_k/dk$ ) is equal to zero at  $k = 0, \pm G/2, \pm G, \pm 3G/2, \pm 2G$ .

## 5. Solution of the Schrödinger equation

### 5.1 Secular equation

We consider the Schrödinger equation of an electron in a periodic potential  $U(x)$  with a period  $a$ .

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x)\right]\psi_k(x) = E\psi_k(x), \quad (1)$$

where

$$U(x) = \sum_G U_G e^{-iGx} \quad [(G = n(2\pi/a), n: \text{integer})],$$

with

$$U_G^* = U_{-G},$$

$$\psi_{\mathbf{k}}(x) = \sum_G C_{k-G} e^{i(k-G)x} = C_k e^{ikx} + C_{k-G} e^{i(k-G)x} + \dots,$$

with

$$C_{k-G}^* = C_{-k+G},$$

$$\sum_G \frac{\hbar^2}{2m} C_{k-G} (k-G)^2 e^{i(k-G)x} + \left( \sum_{G'} U_{G'} e^{-iG'x} \right) \left( \sum_G C_{k-G} e^{i(k-G)x} \right) = E \sum_G C_{k-G} e^{i(k-G)x}.$$

Here we note that

$$I = \left( \sum_{G'} U_{G'} e^{-iG'x} \right) \left( \sum_G C_{k-G} e^{i(k-G)x} \right) = \sum_G \sum_{G'} U_{G'} C_{k-G} e^{-iG'x} e^{i(k-G)x}.$$

For simplicity, we put  $G'' = G + G'$  or  $G' = G'' - G$

$$I = \sum_G \sum_{G''} U_{G''-G} C_{k-G} e^{i(k-G'')x} = \sum_{G'} \sum_G U_{G-G'} C_{k-G'} e^{i(k-G)x},$$

where we have a replacement of variables:  $G'' \rightarrow G, G \rightarrow G'$  in the second term. Then the Schrödinger equation is

$$\sum_G \frac{\hbar^2}{2m} C_{k-G} (k-G)^2 e^{i(k-G)x} + \sum_{G'} \sum_G U_{G-G'} C_{k-G'} e^{i(k-G)x} = E \sum_G C_{k-G} e^{i(k-G)x},$$

or

$$\left[ \frac{\hbar^2}{2m} (k-G)^2 - E \right] C_{k-G} + \sum_{G'} U_{G-G'} C_{k-G'} = 0.$$

When  $k \rightarrow k + G$

$$\left( \frac{\hbar^2}{2m} k^2 - E \right) C_k + \sum_{G'} U_{G-G'} C_{k+G-G'} = 0.$$

Here we put  $\lambda_k = \frac{\hbar^2}{2m} k^2$ .

$$[\lambda_{k-G} - E]C_{k-G} + \sum_{G'} U_{G-G'} C_{k-G'} = 0,$$

or

$$\begin{aligned} & [\lambda_{k-G} - E]C_{k-G} + (\dots + U_{-4G}C_{k-5G} + U_{-3G}C_{k-4G} + U_{-2G}C_{k-3G} + U_{-G}C_{k-2G} + U_0C_{k-G} + \\ & + U_G C_k + U_{2G}C_{k+G} + U_{3G}C_{k+2G} + U_{4G}C_{k+3G} + \dots) = 0 \end{aligned} \quad (2)$$

When  $k \rightarrow k + G$  in Eq.(2)

$$\begin{aligned} & [\lambda_k - E]C_k + (\dots + U_{-4G}C_{k-4G} + U_{-3G}C_{k-3G} + U_{-2G}C_{k-2G} + U_{-G}C_{k-G} + U_0C_k + \\ & + U_G C_{k+G} + U_{2G}C_{k+2G} + U_{3G}C_{k+3G} + U_{4G}C_{k+4G} + \dots) = 0 \end{aligned} \quad (3)$$

When  $k \rightarrow k + 2G$  in Eq.(2)

$$\begin{aligned} & [\lambda_{k+G} - E]C_{k+G} + (\dots + U_{-4G}C_{k-3G} + U_{-3G}C_{k-2G} + U_{-2G}C_{k-G} + U_{-G}C_k + U_0C_{k+G} + \\ & + U_G C_{k+2G} + U_{2G}C_{k+3G} + U_{3G}C_{k+4G} + U_{4G}C_{k+5G} + \dots) = 0 \end{aligned} \quad (4)$$

The secular equation is expressed by

$$\begin{pmatrix} \lambda_{k+3G} - E & U_{-G} & U_{-2G} & U_{-3G} & U_{-4G} & U_{-5G} & U_{-6G} \\ U_G & \lambda_{k+2G} - E & U_{-G} & U_{-2G} & U_{-3G} & U_{-4G} & U_{-5G} \\ U_{2G} & U_G & \lambda_{k+G} - E & U_{-G} & U_{-2G} & U_{-3G} & U_{-4G} \\ U_{3G} & U_{2G} & U_G & \lambda_k - E & U_{-G} & U_{-2G} & U_{-3G} \\ U_{4G} & U_{3G} & U_{2G} & U_G & \lambda_{k-G} - E & U_{-G} & U_{-2G} \\ U_{5G} & U_{4G} & U_{3G} & U_{2G} & U_G & \lambda_{k-2G} - E & U_{-G} \\ U_{6G} & U_{5G} & U_{4G} & U_{3G} & U_{2G} & U_G & \lambda_{k-3G} - E \end{pmatrix} \begin{pmatrix} C_{k+3G} \\ C_{k+2G} \\ C_{k+G} \\ C_k \\ C_{k-G} \\ C_{k-2G} \\ C_{k-3G} \end{pmatrix} = 0,$$

with  $U_0 = 0$  for convenience, where we assume that  $C_{k+mG} = 0$  for  $m = \pm 4, \pm 5, \pm 6, \dots$

## 5.2 Solution for the simple case

Now we consider the simplest case: mixing of only the two states:  $|k\rangle$  and  $|k-G\rangle$  ( $k \approx \pi/a$ ,  $k-G = -\pi/a$ ,  $G \approx 2\pi/a$ ). Only the coefficients  $C_k$  and  $C_{k-G}$  are dominant.

$$\begin{pmatrix} \lambda_k - E & U_G^* \\ U_G & \lambda_{k-G} - E \end{pmatrix} \begin{pmatrix} C_k \\ C_{k-G} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}.$$

From the condition that the determinant is equal to 0,

$$(\lambda_k - E)(\lambda_{k-G} - E) - |U_G|^2 = 0,$$

or

$$E = \frac{\lambda_k + \lambda_{k-G} \pm \sqrt{(\lambda_k - \lambda_{k-G})^2 + 4|U_G|^2}}{2}.$$

Now we consider that  $\lambda_k \approx \lambda_{k-G}$  ( $|k| = |k - G|$  with  $k \approx \pi/a$ , Bragg reflection)

$$(\lambda_k - E)^2 - |U_G|^2 = 0,$$

or

$$E = \lambda_k \pm |U_G|.$$

Note that the potential energy  $U(x)$  is described by

$$U(x) = U_0 + U_G e^{-iGx} + U_G e^{iGx} = U_0 + 2U_G \cos(Gx),$$

where we assume that  $U_G$  is real:

$$U_G = U_{-G}^* = U_{-G}.$$

At  $k = G = 2\pi/a$  only the coefficients  $C_{k-2G}$  and  $C_k$  are dominant. In this case we have the secular equation only for  $C_{k-2G}$  and  $C_k$ .

$$\begin{pmatrix} \lambda_k - E & U_{-2G} \\ U_{2G} & \lambda_{k-2G} - E \end{pmatrix} \begin{pmatrix} C_k \\ C_{k-2G} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}.$$

The condition of  $\det(M) = 0$  leads to

$$\begin{vmatrix} \lambda_k - E & U_{2G}^* \\ U_{2G} & \lambda_{k-2G} - E \end{vmatrix} = 0.$$

Since  $\lambda_k = \lambda_{k-2G}$ , we have

$$(\lambda_k - E)^2 - |U_{2G}|^2 = 0,$$

or

$$E = \lambda_k \pm |U_{2G}|.$$

(a)  $U_G < 0$ ;

For  $E = \lambda_k + |U_G| = \lambda_k - U_G$  (upper energy level)

$$\begin{pmatrix} U_G & U_G \\ U_G & U_G \end{pmatrix} \begin{pmatrix} C_k \\ C_{k-G} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix},$$

or

$$\frac{C_k}{C_{k-G}} = -1.$$

Then the wave function is described by

$$\psi_{\mathbf{k}}(x) = C_k e^{ikx} + C_{k-G} e^{i(k-G)x} = C_k [e^{ikx} - e^{i(k-G)x}] = 2iC_k e^{i(k-\frac{G}{2})x} \sin\left(\frac{Gx}{2}\right),$$

or

$$|\psi_{\mathbf{k}}(x)|^2 = 4|C_k|^2 \sin^2\left(\frac{Gx}{2}\right) \text{ (upper energy level).}$$

For  $E = \lambda_k - |U_G| = \lambda_k + U_G$  (lower energy level)

$$\begin{pmatrix} -U_G & U_G \\ U_G & -U_G \end{pmatrix} \begin{pmatrix} C_k \\ C_{k-G} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix},$$

or

$$\frac{C_k}{C_{k-G}} = 1.$$

The wave function is described by

$$\psi_{\mathbf{k}}(x) = C_k e^{ikx} + C_{k-G} e^{i(k-G)x} = C_k [e^{ikx} + e^{i(k-G)x}] = 2C_k e^{i(k-\frac{G}{2})x} \cos\left(\frac{Gx}{2}\right),$$

or

$$|\psi_{\mathbf{k}}(x)|^2 = 4|C_k|^2 \cos^2\left(\frac{Gx}{2}\right) \text{ (lower energy level).}$$

(b)  $U_G > 0$

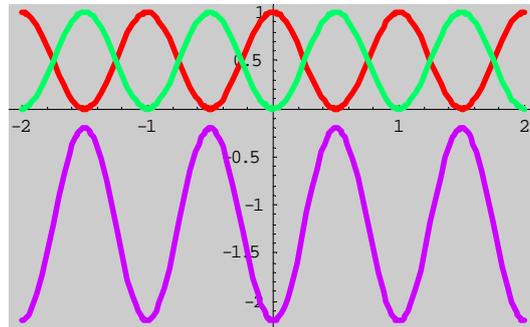
$$|\psi_{\mathbf{k}}(x)|^2 = 4|C_{\mathbf{k}}|^2 \cos^2\left(\frac{Gx}{2}\right) \quad \text{for } E = \lambda_{\mathbf{k}} + U_G \text{ (upper energy level),}$$

and

$$|\psi_{\mathbf{k}}(x)|^2 = 4|C_{\mathbf{k}}|^2 \sin^2\left(\frac{Gx}{2}\right) \quad \text{for } E = \lambda_{\mathbf{k}} - U_G \text{ (lower energy level).}$$

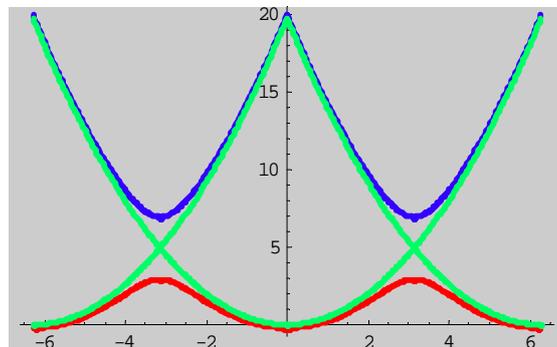
**((Probability of finding electrons))**

Comparison of the two standing wave solutions at  $k \rightarrow \pi/a$  is presented. Note that the wave motion is in phase with the lattice.



**Fig.** At  $k = \pi/a$ , Bragg reflection of the electron arises, leading to two possible charge distributions  $f_1(x)$  and  $f_2(x)$ . The case of  $U_G < 0$  (attractive potential due to positive ions).  $f_1(x)$  (red) probability of the wave function (lower energy level),  $f_2(x)$  (green) probability of the wave function (upper energy level), and the potential energy  $U(x)$ . The phases of  $f_1(x)$  and  $U(x)$  are out of phase, while the phase of  $f_2(x)$  and  $U(x)$  are in phase. When the electrons are close to the ions located at the lattice sites, the energy of the electrons becomes lower. When the electrons are far away from ions, on the other hand, the energy of the electrons becomes higher. (see the book of C. Kittel<sup>5</sup> for more detail).

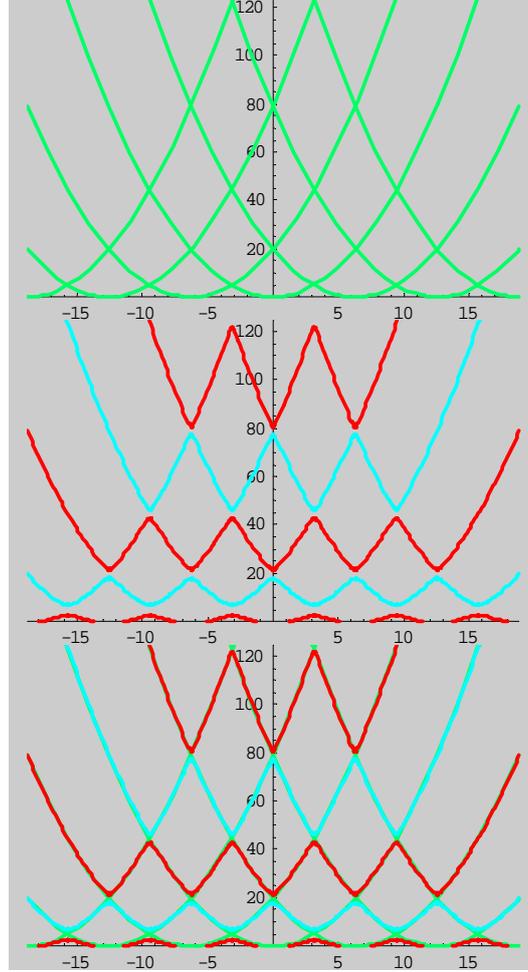
**((Eigenvalue problem for the system with only  $U_G$ ))**



**Fig.** The energy dispersion curves of  $E_k$  vs  $k$  with  $U_G = -2$  (red and yellow curves) and with  $U_G \rightarrow 0$  (blue curve).  $a \rightarrow 1$ .  $\hbar \rightarrow 1$ .  $m \rightarrow 1$ .  $K = G \rightarrow 2\pi$ . There are energy gaps

at  $k = \pm G/2 = \pm\pi/a$  for the energy dispersion curve with  $U_G = -2$ . The energy gap is  $2|U_G|$  there. Note that  $dE_k/dk = 0$  at  $k = G/2 = \pm\pi/a$ .

### 5.3. Eigenvalue problem for the system with $U_G, U_{2G}, U_{3G}, U_{4G}, U_{5G}$ , and $U_{6G}$

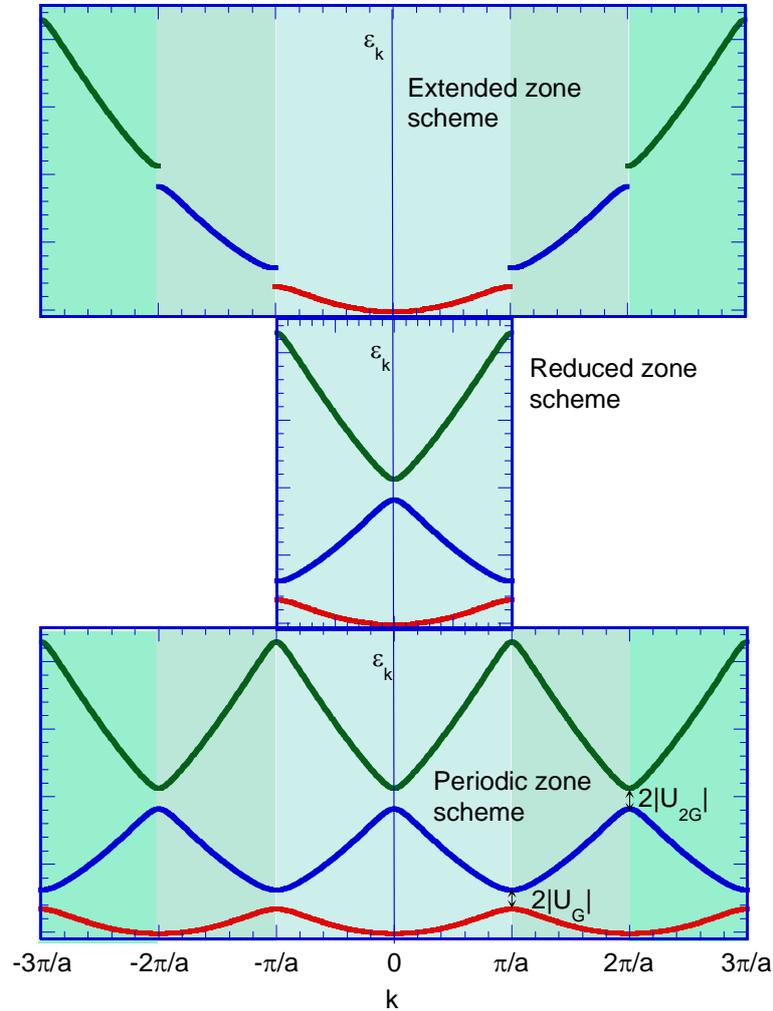


**Fig.** The energy dispersion of  $E_k$  vs  $k$  for free electrons (in the limit of weak potential) and the Bloch electrons with  $U_G, U_{2G}, U_{3G}, U_{4G}, U_{5G}, U_{6G}$  ( $U_G \rightarrow -2, U_{2G} \rightarrow -2, U_{3G} \rightarrow -2, U_{4G} \rightarrow -2, U_{5G} \rightarrow -2, U_{6G} \rightarrow -2$ ) in the extended zone scheme.  $a \rightarrow 1, \hbar \rightarrow 1, m \rightarrow 1, K = G \rightarrow 2\pi$ . There are energy gaps with  $2|U_G|, 2|U_{2G}|, 2|U_{3G}|, 2|U_{4G}|, 2|U_{5G}|, 2|U_{6G}|$ , of at the Brillouin zone ( $k = \pi/a$ ).

### 5.4 Energy dispersion curves in different scheme zones

The above results on the energy dispersion relation are summarized as follows. Three different zone schemes are useful. (a) The extended zone scheme where different bands are drawn in different zones in wavevector space. (b) The reduced zone scheme where all bands are drawn in the first Brillouin zone. (c) The periodic zone scheme where every

band is drawn in every zone. The formation of energy bands and gaps are generated. The main effects are at the zone boundary of the Brillouin zone.



**Fig.** Three zone schemes for the 1D system. Extended zone scheme. Reduced zone scheme. Periodic zone scheme.

## 5.5 Bragg reflection at the boundary of the Brillouin zone

The Bragg reflection occurs when the degeneracy condition  $E(\mathbf{k}) = E(\mathbf{k}-\mathbf{G})$  or  $|\mathbf{k}-\mathbf{G}| = |\mathbf{k}|$ . This condition is equivalent to the condition  $2\mathbf{k}\cdot\mathbf{G} = G^2$ . For the 1D system the Bragg reflection occurs when  $k = \pm G/2 = \pm \pi/a$ , or at the zone boundary of the first Brillouin zone. For the 2D system, the boundaries form lines in the reciprocal lattice plane. The degeneracy condition  $|\mathbf{k}-\mathbf{G}| = |\mathbf{k}|$  geometrically means that  $\mathbf{k}$  lies on the perpendicular bisector of the reciprocal lattice vector  $\mathbf{G}$ . For the 3D system, the Bragg reflection occurs when  $\mathbf{k}$  is located at the zone boundary surfaces of the first Brillouin zone.

### 5.5.1 1D system:

For For the 1D system this condition at the zone boundary at  $k = G/2 = \pm\pi/a$ .

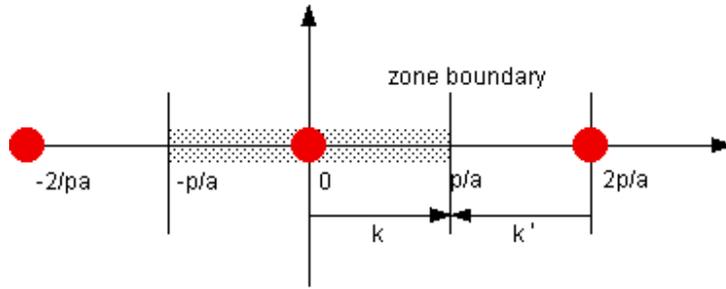


Fig. Condition of the Bragg reflection for the 1D case.  $|k| = |k - G|$ .  $G = 2\pi/a$ .  $k' = k - G$ .

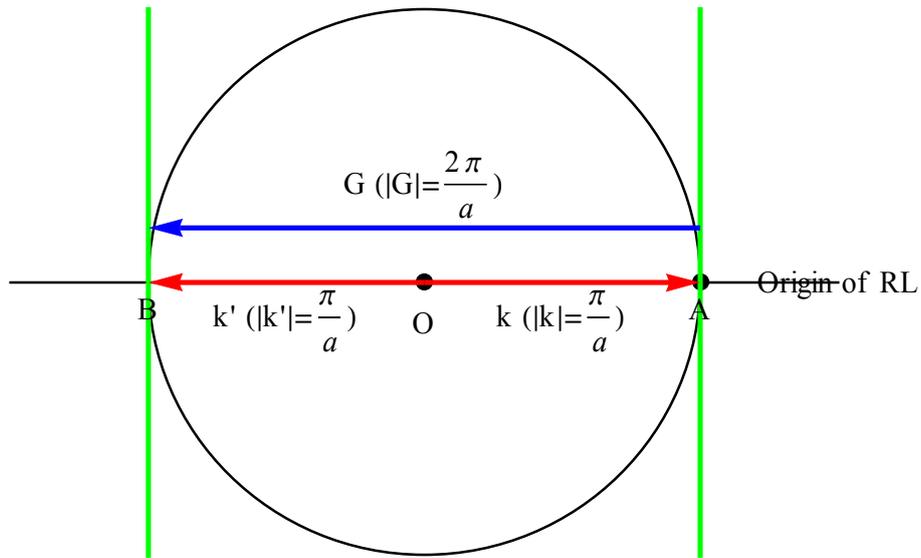
### 5.5.2 Ewald's sphere

The electron behaves like x-ray as a wave inside the crystal. It undergoes a Bragg reflection when the wavelength is  $\lambda = 2\pi/k$  at  $k = \pi/a$  (the boundary of the Brillouin zone). When the electron has the wavevector  $k$ , it also has the wavevector  $k' = k + G$ . Then the standing wave can occur when these two waves with  $k = \pm\pi/a$  are superimposed. The resulting wave does not propagate inside the crystal. In other words, the group velocity at  $k = \pm\pi/a$  is equal to zero.

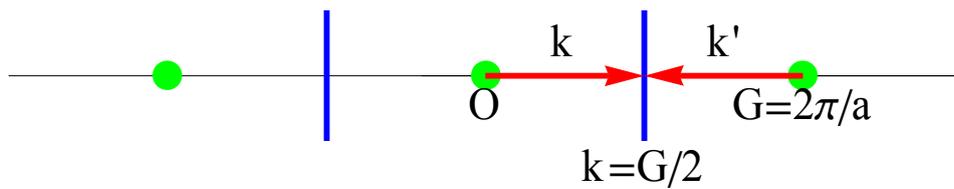
We consider the Bragg reflection using the Ewald sphere.  $k$  and  $k'$  are the wavevectors of the incident and outgoing electrons. The origin of the reciprocal lattice plane is located at the end of the wavevector  $k$  (the point A). In this Fig. the green lines show the Bragg planes at  $G = 0$  (the point A) and  $G = -2\pi/a$  (the point B). Since the lattice is one-dimensional, the reciprocal lattice forms a plane at  $k_x = 2\pi/a$ . The Bragg reflection can occur only at

$$k_x - k_x' = \frac{2\pi}{a}$$

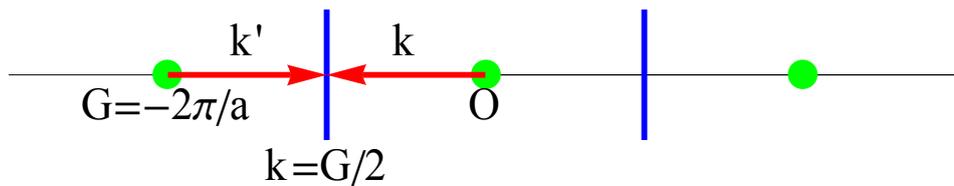
in this figure.



From this we can define the Brillouine zone for the one dimensional case as follows.



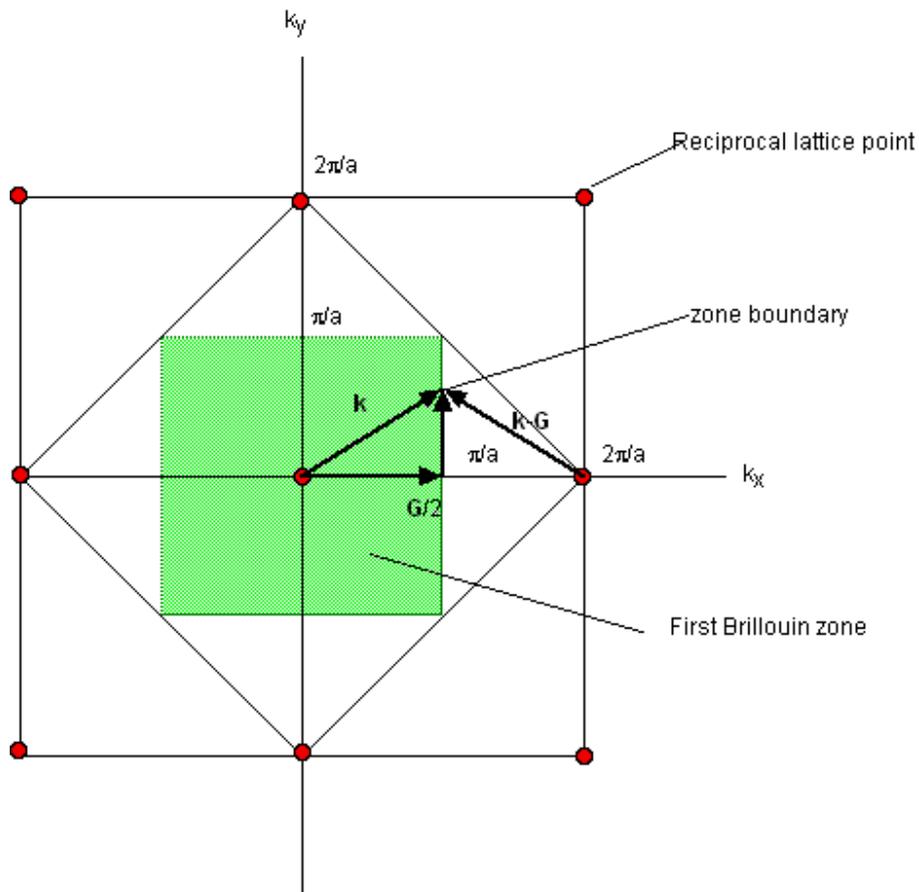
**Fig.** The first Brillouin zone.  $|k| < \pi/a$ . The Bragg condition  $(\mathbf{k} - \mathbf{k}' = \mathbf{G})$  is satisfied only at  $k = \pi/a$ . The blue line are the boundary of the first Brillouin zone.



**Fig.** The first Brillouin zone.  $|k| < \pi/a$ . The Bragg condition  $(\mathbf{k} - \mathbf{k}' = \mathbf{G})$  is satisfied only at  $k = -\pi/a$ . The blue line are the boundary of the first Brillouin zone.

### 5.5.3 2D system:

The Bragg reflection occurs when  $\mathbf{k}$  is on the zone boundary of the first Brillouin zone.  $\mathbf{G} \cdot (\mathbf{k} - \mathbf{G}/2) = 0$ . In other words,  $\mathbf{G}$  is perpendicular to  $\mathbf{k} - \mathbf{G}/2$ . This implies that  $\mathbf{k}$  is at the zone boundary of the first Brillouin zone for the Bragg reflection.



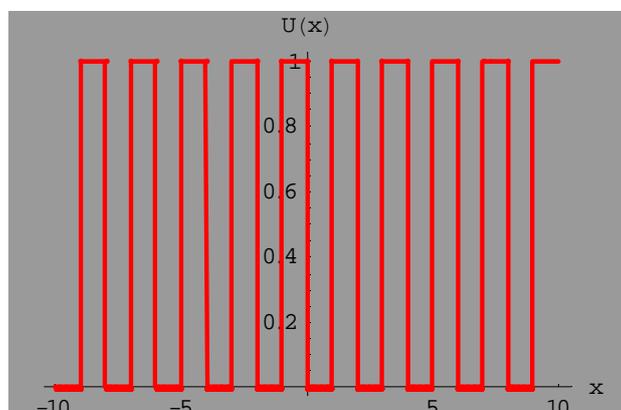
**Fig.** Condition of the Bragg reflection for the 2D case.  $|\mathbf{k}| = |\mathbf{k} - \mathbf{G}|$ .

## 6 Kronig Penny model as an application of the Bloch theorem

### 6.1 Secular equation

Here we consider a Kronig-Penny model. Using this model we can get an exact solution for the Schrödinger equation of an electron in a periodic potential. The potential is defined by

$$U(x) = U_0 \text{ for } -b \leq x \leq 0 \text{ and } U(x) = 0 \text{ for } 0 \leq x \leq a \text{ (the periodicity, } a+b).$$



**Fig.** Square-well periodic potential where  $a = b = 1$  and  $U_0 = 1$ .

We now consider a Schrödinger equation,

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + U(x)\psi(x) = E\psi(x),$$

where  $E$  is the energy eigenvalue.

(i)  $U(x) = 0$  for  $0 \leq x \leq a$

$$\psi_1(x) = Ae^{iKx} + Be^{-iKx}, \quad d\psi_1(x)/dx = iK(Ae^{iKx} - Be^{-iKx}),$$

with  $E = \hbar^2 K^2 / 2m$ .

(ii)  $U(x) = U_0$  for  $-b \leq x \leq 0$

$$\psi_2(x) = Ce^{Qx} + De^{-Qx}, \quad d\psi_2(x)/dx = Q(Ce^{Qx} - De^{-Qx}),$$

with

$$U_0 - E = \hbar^2 Q^2 / 2m.$$

The Bloch theorem can be applied to the wave function

$$\psi(x + a + b) = e^{ik(a+b)}\psi(x),$$

where  $k$  is the wave number. The constants  $A$ ,  $B$ ,  $C$ , and  $D$  are chosen so that  $\psi$  and  $d\psi/dx$  are continuous at  $x = 0$  and  $x = a$ .

(a) At  $x = 0$ ,

$$A + B = C + D,$$

$$iK(A - B) = Q(C - D).$$

(b) At  $x = a$ ,

$$\psi(a) = e^{ik(a+b)}\psi(-b), \quad \text{or} \quad \psi_1(a) = e^{ik(a+b)}\psi_2(-b),$$

$$\psi'(a) = e^{ik(a+b)}\psi'(-b), \quad \text{or} \quad \psi_1'(a) = e^{ik(a+b)}\psi_2'(-b),$$

or

$$Ae^{iKa} + Be^{-iKa} = e^{ik(a+b)}(Ce^{-Qb} + De^{Qb}),$$

$$iK(Ae^{iKa} - Be^{-iKa}) = Qe^{ik(a+b)}(Ce^{-Qb} - De^{Qb}).$$

The above four equations for  $A$ ,  $B$ ,  $C$ , and  $D$  have a solution only if  $\det[M]=0$ , where the matrix  $M$  is given by

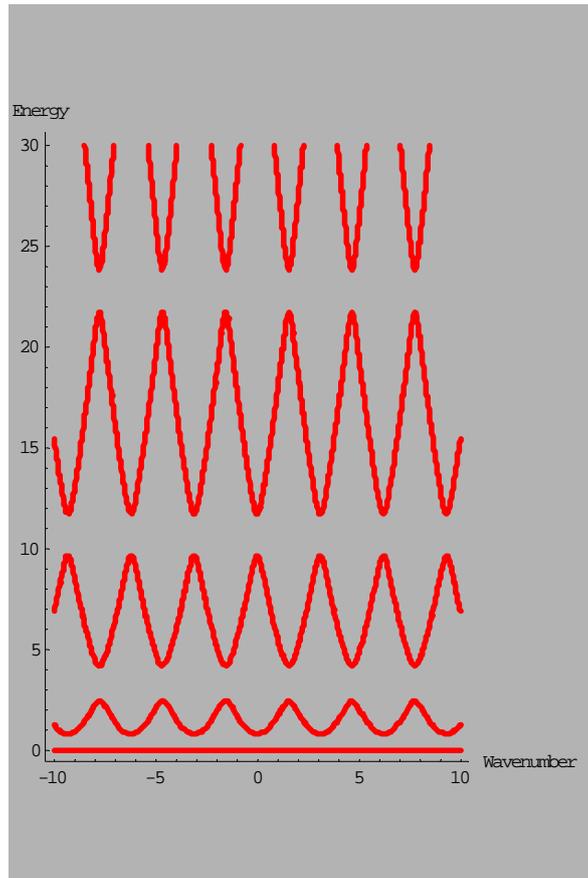
$$M = \begin{pmatrix} 1 & 1 & -1 & -1 \\ iK & -iK & -Q & Q \\ e^{iKa} & e^{-iKa} & -e^{-Qb+ik(a+b)} & -e^{Qb+ik(a+b)} \\ iKe^{iKa} & -iKe^{-iKa} & -Qe^{-Qb+ik(a+b)} & Qe^{Qb+ik(a+b)} \end{pmatrix}.$$

The condition of  $\det[M] = 0$  leads to

$$\cos[k(a+b)] = \cos(Ka) \cosh(Qb) + \frac{(Q^2 - K^2)}{2KQ} \sin(Ka) \sinh(Qb).$$

The energy dispersion relation ( $E$  vs  $k$ ) can be derived from this equation.

## 6.2 Energy dispersion relation



**Fig.** Plot of energy  $E$  vs wave number  $k$  in the Kronig-Penny model (periodic zone scheme).  $a = 2$ ,  $b = 0.022$ .  $K = \sqrt{\varepsilon}$ .  $Q = \sqrt{100 - \varepsilon}$ .  $0 \leq \varepsilon \leq 30$ .  $U_0 = 50\hbar^2 / m$ .

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## REFERENCES

1. M. Suzuki and I.S. Suzuki, Lecture note on solid state Physics, Bloch theorem and energy band. <http://www2.binghamton.edu/physics/docs/note-energy-band.pdf>
2. See *Out of the Crystal Maze*, Chapters from the history of solid state physics edited by L. Hoddeson, E. Braun, J. Teichmann, and S. Wert (Oxford University Press, New York, 1992).
3. S.L. Altmann, *Band Theory of Metals* (Pergamon Press, Oxford 1970). S.L. Altmann, *Band Theory of Solids An Introduction from the point of view of symmetry* (Clarendon Press, Oxford 1991).
4. J.M. Ziman, *Principle of the Theory of Solids* (Cambridge University Press 1964).
5. C. Kittel, *Introduction to Solid State Physics*, seventh edition (John Wiley & Sons, New York, 1996).
6. C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, 1963).
7. N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Holt, Rinheart and Winston, New York, 1976).
8. E.M. Lifshitz and L.P. Pitaevskii, *Statistical Physics Part2 Landau and Lifshitz Course of Theoretical Physics* volume 9 (Pergamon Press, Oxford 1980).

9. J. Callaway, *Quantum Theory of the Solid State*, second edition (Academic Press, New York, 1991).
10. A.A. Abrikosov, *Introduction to the Theory of Normal Metals* (Academic Press, New York, 1972).