Bloch theorem and Energy band II

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(May 9, 2006)

Abstract

Here we consider a wavefunction of an electron in a periodic potential of metal. The translation symmetry of periodic potential is imposed on the wave function. The wave function of electrons is a product of a plane wave and a periodic function which has the same periodicity as a potential. These electrons are often called Bloch electrons to distinguish them from the ideally free electrons. A peculiar aspect of the energy spectrum of the Bloch electrons is the formation of energy band (allowed energy regions) and band gap (forbidden energy region).

In this note we discuss the Bloch theorem using the concept of the translation operator, the parity operator, and the time-reversal operator in quantum mechanics. Our approach is similar to that used by S.L. Altmann (Band theory of metals: the elements, Pergamon Press, Oxford, 1970). This book is very useful in our understanding the concept of the Bloch theorem. The eigenvalue problems are solved, depending on the strength of the periodic potential (we use Mathematica 5.2 to solve the problems). The exact solution of the Kronig-Penny model is presented using Mathematica 5.2. We also discuss the persistent current of conducting metal ring in the presence of magnetic field located at the center (the same configuration as the Aharonov-Bohm effect) as an application of the Bloch theorem.

Content

1 Translation operator[1]

1.1 Analogy from the classical mechanics for *x*

Here we discuss the translation operator $\hat{T}(a)$ in quantum mechanics,

$$|\psi'\rangle = \hat{T}(a)|\psi\rangle, \tag{1}$$

or

$$\langle\psi'| = \langle\psi'|\hat{T}^{+}(a). \tag{2}$$

In an analogy from the classical mechanics, it is predicted that the average value of $\hat{x}$ in the new state $|\psi'\rangle$ is equal to that of $\hat{x}$ in the old state $|\psi\rangle$ plus the *x*-displacement *a* under the translation of the system

$$\langle\psi'|\hat{x}|\psi'\rangle = \langle\psi|\hat{x}+a|\psi\rangle,$$

or

$$\langle\psi|\hat{T}^{+}(a)\hat{x}\hat{T}(a)|\psi\rangle = \langle\psi|\hat{x}+a|\psi\rangle,$$

or

$$\hat{T}^{+}(a)\hat{x}\hat{T}(a) = \hat{x} + a\hat{1}. \tag{3}$$

Normalization condition:

$$\langle\psi'|\psi'\rangle = \langle\psi|\hat{T}^{+}(a)\hat{T}(a)|\psi\rangle = \langle\psi|\psi\rangle,$$

or

$$\hat{T}^{+}(a)\hat{T}(a) = \hat{1}\,. \tag{4}$$

[$\hat{T}(a)$ is an unitary operator].

From Eqs.(3) and (4), we have

$$\hat{x}\hat{T}(a) = \hat{T}(a)(\hat{x}+a) = \hat{T}(a)\hat{x} + a\hat{T}(a)\,,$$

or the commutation relation:

$$[\hat{x},\hat{T}(a)] = a\hat{T}(a)\,. \tag{5}$$

From this, we have

$$\hat{x}\hat{T}(a)|x\rangle = \hat{T}(a)\hat{x}|x\rangle + a\hat{T}(a)|x\rangle = (x+a)\hat{T}(a)|x\rangle\,.$$

Thus, $\hat{T}(a)|x\rangle$ is the eigenket of $\hat{x}$ with the eigenvalue (x+a).

or

$$\hat{T}(a)|x\rangle = |x+a\rangle\,, \tag{6}$$

or

$$\hat{T}^{+}(a)\hat{T}(a)|x\rangle = \hat{T}^{+}(a)|x+a\rangle = |x\rangle\,. \tag{7}$$

When x is replaced by x-a in Eq.(7), we get

$$|x-a\rangle = \hat{T}^{+}(a)|x\rangle\,, \tag{8}$$

or

$$\langle x-a| = \langle x|\hat{T}(a)\,. \tag{9}$$

Note that

$$\langle x|\psi'\rangle = \langle x|\hat{T}(a)|\psi\rangle = \langle x-a|\psi\rangle = \psi(x-a)\,. \tag{10}$$

1.2 Analogy from the classical mechanics for *p*

The average value of $\hat{p}$ in the new state $|\psi'\rangle$ is equal to the average value of $\hat{p}$ in the old state $|\psi\rangle$ under the translation of the system

$$\langle\psi'|\hat{p}|\psi'\rangle = \langle\psi|\hat{p}|\psi\rangle\,, \tag{11}$$

or

$$\langle\psi|\hat{T}^{+}(a)\hat{p}\hat{T}(a)|\psi\rangle = \langle\psi|\hat{p}|\psi\rangle\,,$$

or

$$\hat{T}^{+}(a)\hat{p}\hat{T}(a) = \hat{p}\,. \tag{12}$$

So we have the commutation relation

$$[\hat{T}(a),\hat{p}] = \hat{0}\,.$$

From this commutation relation, we have

$$\hat{p}\hat{T}(a)|p\rangle = \hat{T}(a)\hat{p}|p\rangle = p\hat{T}(a)|p\rangle\,.$$

Thus, $\hat{T}(a)|p\rangle$ is the eigenket of $\hat{p}$ associated with the eigenvalue p.

1.3 Infinitesimal translation operator

We now define the infinitesimal translation operator by

$$\hat{T}(dx) = \hat{1} - \frac{i}{\hbar}\hat{G}dx, \tag{13}$$

$\hat{G}$ is called a generator of translation. The dimension of $\hat{G}$ is that of the linear momentum. The operator $\hat{T}(dx)$ satisfies the relations:

$$\hat{T}^{+}(dx)\hat{T}(dx) = \hat{1}, \tag{14}$$

$$\hat{T}^{+}(dx)\hat{x}\hat{T}(dx) = \hat{x} + dx,$$

or

$$\hat{x}\hat{T}(dx) - \hat{T}(dx)\hat{x} = dx\hat{T}(dx), \tag{15}$$

and

$$[\hat{T}(dx), \hat{p}] = \hat{0}, \tag{16}$$

Using the relation (14), we get

$$(\hat{1} - \frac{i}{\hbar}\hat{G}dx)^{+}(\hat{1} - \frac{i}{\hbar}\hat{G}dx) = \hat{1},$$

or

$$(\hat{1} + \frac{i}{\hbar}\hat{G}^{+}dx)(\hat{1} - \frac{i}{\hbar}\hat{G}dx) = \hat{1} + \frac{i}{\hbar}(\hat{G}^{+} - \hat{G})dx + O[(dx)^2] = \hat{1},$$

or

$$\hat{G}^{+} = \hat{G}. \tag{17}$$

The operator $\hat{G}$ is a Hermite operator. Using the relation (15), we get

$$\hat{x}(\hat{1} - \frac{i}{\hbar}\hat{G}dx) - (\hat{1} - \frac{i}{\hbar}\hat{G}dx)\hat{x} = dx(\hat{1} - \frac{i}{\hbar}\hat{G}dx) = dx\hat{1} + O(dx)^2,$$

or

$$-\frac{i}{\hbar}[\hat{x}, \hat{G}]dx = dx\hat{1},$$

or

$$[\hat{x}, \hat{G}] = i\hbar\hat{1}. \tag{18}$$

Using the relation (16), we get

$$[\hat{1} - \frac{i}{\hbar}\hat{G}dx, \hat{p}] = \hat{0}.$$

Then we have

$$[\hat{G}, \hat{p}] = \hat{0}. \tag{19}$$

From these two commutation relations, we conclude that

$$\hat{G} = \hat{p},$$

and

$$\hat{T}(dx) = \hat{1} - \frac{i}{\hbar}\hat{p}dx. \tag{20}$$

We see that the position operator $\hat{x}$ and the momentum operator $\hat{p}$ obeys the commutation relation

$$[\hat{x}, \hat{p}] = i\hbar\hat{1}, \tag{21}$$

which leads to the Heisenberg's principle of uncertainty.

1.4 Momentum operator $\hat{p}$ in the position basis

$$\hat{T}(\delta x)|\psi\rangle = \hat{T}(\delta x)\int dx'|x'\rangle\langle x'|\psi\rangle = \int dx'|x'+\delta x\rangle\langle x'|\psi\rangle$$
$$= \int dx'|x'\rangle\langle x'-\delta x|\psi\rangle = \int dx'|x'\rangle\psi(x'-\delta x).$$

We apply the Taylor expansion:

$$\psi(x'-\delta x) = \psi(x') - \delta x\frac{\partial}{\partial x'}\psi(x').$$

Substitution:

$$\hat{T}(\delta x)|\psi\rangle = \int dx'|x'\rangle\psi(x'-\delta x) = \int dx'|x'\rangle[\psi(x') - \delta x\frac{\partial}{\partial x'}\psi(x')] =$$
$$= \int dx'|x'\rangle[\langle x'|\psi\rangle - \delta x\frac{\partial}{\partial x'}\langle x'|\psi\rangle] = |\psi\rangle - \delta x\int dx'|x'\rangle\frac{\partial}{\partial x'}\langle x'|\psi\rangle = (\hat{1} - \frac{i}{\hbar}\hat{p}\delta x)|\psi\rangle.$$

Thus we have

$$\hat{p}|\psi\rangle = \frac{\hbar}{i}\int dx'|x'\rangle\frac{\partial}{\partial x'}\langle x'|\psi\rangle,$$
$$\langle x|\hat{p}|\psi\rangle = \frac{\hbar}{i}\int dx'\langle x|x'\rangle\frac{\partial}{\partial x'}\langle x'|\psi\rangle = \frac{\hbar}{i}\int dx'\,\delta(x-x')\frac{\partial}{\partial x'}\langle x'|\psi\rangle = \frac{\hbar}{i}\frac{\partial}{\partial x}\langle x|\psi\rangle.$$

We obtain a very important formula

$$\langle x|\hat{p}|\psi\rangle = \frac{\hbar}{i}\frac{\partial}{\partial x}\langle x|\psi\rangle. \qquad (22)$$

$$\langle\psi|\hat{p}|\psi\rangle = \int dx\langle\psi|x\rangle\frac{\hbar}{i}\langle x|\hat{p}|\psi\rangle = \int dx\langle\psi|x\rangle\frac{\hbar}{i}\frac{\partial}{\partial x}\langle x|\psi\rangle = \frac{\hbar}{i}\int dx\langle x|\psi\rangle^*\frac{\hbar}{i}\frac{\partial}{\partial x}\langle x|\psi\rangle.$$

1.5 The finite translation operator

What is the operator $\hat{T}(a)$ corresponding to a finite translation a? We find it by the following procedure. We divide the interval a into N parts of size $dx = a/N$. As $N\to\infty$, a/N becomes infinitesimal.

$$\hat{T}(dx) = \hat{1} - \frac{i}{\hbar}\hat{p}(\frac{a}{N}).$$

Since a translation by a equals N translations by a/N, we have

$$\hat{T}(a) = \lim_{N\to\infty}[\hat{1} - \frac{i}{\hbar}\hat{p}(\frac{a}{N})]^N = \exp(-\frac{i}{\hbar}\hat{p}a).$$

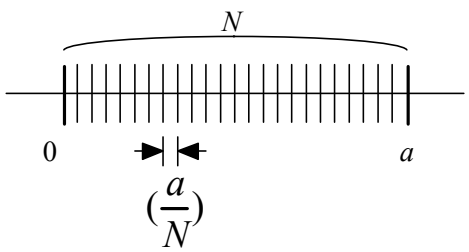


Fig.1 The separation of a divided by N, which becomes infinitesimally small when $N\to\infty$.

Here we use the formula

$$\lim_{N\to\infty}(1+\frac{1}{N})^N = e\,, \qquad \lim_{N\to\infty}(1-\frac{1}{N})^N = e^{-1}\,,$$

$$\lim_{N\to\infty}[(1-\frac{ax}{N})^{\frac{N}{ax}}]^{ax} = \lim_{N\to\infty}(1-\frac{ax}{N})^N = (e^{-1})^{ax} = e^{-ax}\,.$$

In summary, we have

$$\hat{T}(a) = \exp(-\frac{i}{\hbar}\hat{p}a)\,. \tag{23}$$

It is interesting to calculate

$$\hat{T}^{+}(a)\hat{x}\hat{T}(a) = e^{\frac{i}{\hbar}\hat{p}a}\hat{x}e^{-\frac{i}{\hbar}\hat{p}a}\,,$$

by using the Baker-Hausdorff theorem:

$$\exp(\hat{A}x)\hat{B}\exp(-\hat{A}x) = \hat{B} + \frac{x}{1!}[\hat{A},\hat{B}] + \frac{x^2}{2!}[\hat{A},[\hat{A},\hat{B}]] + \frac{x^3}{3!}[\hat{A},[\hat{A},[\hat{A},\hat{B}]]] + ...$$

When x = 1, we have

$$\exp(\hat{A})\hat{B}\exp(-\hat{A}) = \hat{B} + \frac{1}{1!}[\hat{A},\hat{B}] + \frac{1}{2!}[\hat{A},[\hat{A},\hat{B}]] + \frac{1}{3!}[\hat{A},[\hat{A},[\hat{A},\hat{B}]]] + ...$$

Then we have

$$\hat{T}^{+}(a)\hat{x}\hat{T}(a) = e^{\frac{i}{\hbar}\hat{p}a}\hat{x}e^{-\frac{i}{\hbar}\hat{p}a} = \hat{x} + [\frac{i}{\hbar}\hat{p}a,\hat{x}] = \hat{x} + \frac{i}{\hbar}a[\hat{p},\hat{x}] = \hat{x} + \frac{i}{\hbar}a\frac{\hbar}{i} = \hat{x} + a\hat{1}\,.$$

So we confirmed that the relation

$$\hat{T}^{+}(a)\hat{x}\hat{T}(a) = \hat{x} + a\hat{1}\,.$$

holds for any finite translation operator.

2 Parity operator[1]

2.1 Property

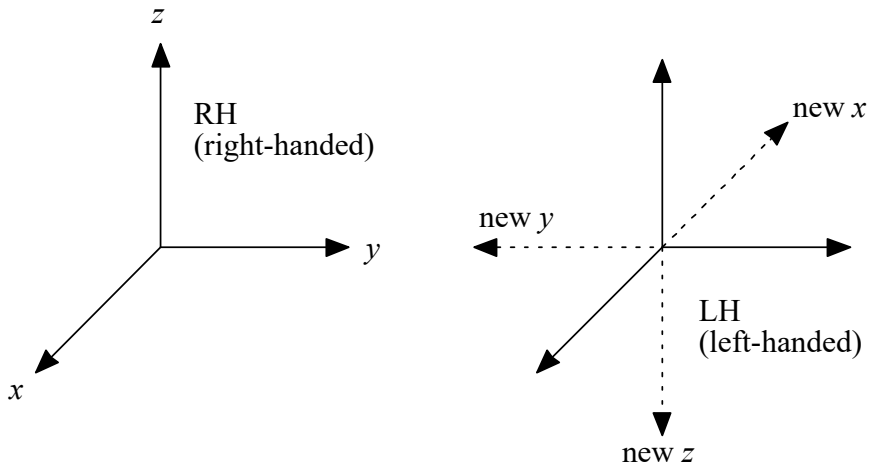


Fig.2 Right-handed (RH) and left-handed (LH) systems.

$\hat{\pi}$: parity operator (unitary operator)

$$|\psi'\rangle = \hat{\pi}|\psi\rangle\,, \tag{24}$$

or

$$\langle\psi'| = \langle\psi|\hat{\pi}^+ . \tag{25}$$

We assume that the average of $\hat{x}$ in the new state $|\psi'\rangle$ is opposite to to that in the old state $|\psi\rangle$

$$\langle\psi'|\hat{x}|\psi'\rangle = -\langle\psi|\hat{x}|\psi\rangle ,$$

or

$$\langle\psi|\hat{\pi}^+\hat{x}\hat{\pi}|\psi\rangle = -\langle\psi|\hat{x}|\psi\rangle ,$$

or

$$\hat{\pi}^+\hat{x}\hat{\pi} = -\hat{x} . \tag{26}$$

The position vector is called a polar vector.

We define the normalization by

$$\langle\psi'|\psi'\rangle = \langle\psi|\hat{\pi}^+\hat{\pi}|\psi\rangle = \langle\psi|\psi\rangle = \hat{1},$$

or

$$\hat{\pi}^+\hat{\pi} = \hat{1} . \tag{27}$$

Thus the parity operator is an unitary operator.

From Eqs.(26) and (27),

$$\hat{x}\hat{\pi} + \hat{\pi}\hat{x} = \hat{0} ,$$

or

$$\hat{x}\hat{\pi}|x\rangle = -\hat{\pi}\hat{x}|x\rangle = -x\hat{\pi}|x\rangle .$$

Thus $\hat{\pi}|x\rangle$ is the eigenket of $\hat{x}$ with the eigenvalue (–x).

or

$$\hat{\pi}|x\rangle = |-x\rangle , \tag{28}$$

or

$$\hat{\pi}\hat{\pi}|x\rangle = \hat{\pi}|-x\rangle = |x\rangle ,$$

or

$$\hat{\pi}^2 = \hat{1} . \tag{29}$$

Since $\hat{\pi}^+\hat{\pi} = \hat{1}$ and $\hat{\pi}^2 = \hat{1}$,

$$\hat{\pi}^+\hat{\pi}\hat{\pi} = \hat{\pi} ,$$

or

$$\hat{\pi}^+ = \hat{\pi} . \tag{30}$$

So the parity operator is a Hermite operator.

$$\hat{\pi}|p\rangle = \hat{\pi}\int_{-\infty}^{\infty} dx'|x'\rangle\langle x'|p\rangle = \int_{-\infty}^{\infty} dx'\,\hat{\pi}|x'\rangle\langle x'|p\rangle = \int_{-\infty}^{\infty} dx'|-x\rangle\langle x'|p\rangle$$

$$= \int_{-\infty}^{\infty} dx|-x'\rangle\frac{1}{\sqrt{2\pi\hbar}}\exp(\frac{ipx'}{\hbar}) = \int_{-\infty}^{\infty} dx|x\rangle\frac{1}{\sqrt{2\pi\hbar}}\exp(-\frac{ipx}{\hbar}) = \int_{-\infty}^{\infty} dx|x\rangle\langle x|-p\rangle .$$

Note that $x' = -x$ and $dx' = -dx$. Then we have

$$\hat{\pi}|p\rangle = |-p\rangle , \tag{31}$$

and

$$\hat{p}|p\rangle = p|p\rangle .$$

So we have

$$\hat{\pi}\hat{p}|p\rangle = p\hat{\pi}|p\rangle = p|-p\rangle,$$

or

$$\hat{p}\hat{\pi}|p\rangle = \hat{p}|-p\rangle = -p|-p\rangle.$$

Thus we have

$$\hat{\pi}\hat{p} + \hat{p}\hat{\pi} = \hat{0}, \tag{32}$$

or

$$\hat{\pi}^+\hat{p}\hat{\pi} = -\hat{p}.$$

Thus the linear momentum is called a polar vector.

2.2 Commutation relation

Here we show the commutation relation between the parity operator and several operators including $\hat{T}_x(a)$. The orbital angular momentum $\hat{L}_z$ (the x axis component) is defined by $\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}p_x$. The commutation relation ($[\hat{\pi}, \hat{L}_z] = \hat{0}$ or $\hat{\pi}^+\hat{L}_z\hat{\pi} = \hat{L}_z$) holds valid, since $\hat{x}$, $\hat{y}$, $\hat{p}_x$, and $\hat{p}_y$ are odd under parity. Similar commutation relations hold for the spin angular momentum $\hat{\mathbf{S}}$ and general angular momentum $\hat{\mathbf{J}}$: $\hat{\pi}^+\hat{\mathbf{S}}\hat{\pi} = \hat{\mathbf{S}}$ and $\hat{\pi}^+\hat{\mathbf{J}}\hat{\pi} = \hat{\mathbf{J}}$. We show that there is a commutation relation between $\hat{\pi}$ and $\hat{T}_x(a)$; $\hat{\pi}\hat{T}_x(a) = \hat{T}_x^{\,+}(a)\hat{\pi}$, or $[\hat{\pi}, \hat{T}_x(a)] = \hat{0}$.

$$\hat{\pi}^+\hat{T}_x(a)\hat{\pi} = \hat{\pi}^+\exp(-\frac{i}{\hbar}\hat{p}a)\hat{\pi} = \exp(-\frac{i}{\hbar}\hat{\pi}^+\hat{p}\hat{\pi}a) = \exp(\frac{i}{\hbar}\hat{p}a) = \hat{T}_x(-a) = \hat{T}_x^{\,+}(a),$$

or

$$\hat{\pi}^+\hat{T}_x(a) = \hat{T}_x^{\,+}(a)\hat{\pi},$$

or

$$\hat{\pi}\hat{T}_x(a) = \hat{T}_x^{\,+}(a)\hat{\pi}, \tag{33}$$

since $\hat{\pi}^+ = \hat{\pi}$.

The Hamiltonian is given by $\hat{H} = \frac{1}{2m}\hat{p}^2 + V(\hat{x})$. Here we assume that the potential is symmetric with respect to $x = 0$: $V(\hat{x}) = V(-\hat{x})$. Then we have the commutation relation $\hat{\pi}^+\hat{H}\hat{\pi} = \hat{H}$ or $[\hat{\pi}, \hat{H}] = \hat{0}$, since $\hat{\pi}^+V(\hat{x})\hat{\pi} = V(-\hat{x}) = V(\hat{x})$ and $\hat{\pi}^+\hat{p}^2\hat{\pi} = (-\hat{p})^2 = \hat{p}^2$.

In conclusion, we have the following commutation relations.

(1) $\hat{\pi}^+\hat{\mathbf{S}}\hat{\pi} = \hat{\mathbf{S}}$, $\hat{\pi}^+\hat{\mathbf{L}}\hat{\pi} = \hat{\mathbf{L}}$, and $\hat{\pi}^+\hat{\mathbf{J}}\hat{\pi} = \hat{\mathbf{J}}$.

(2) $\hat{\pi}\hat{T}_x(a) = \hat{T}_x^{\,+}(a)\hat{\pi}$.

(3) $\hat{\pi}^+\hat{H}\hat{\pi} = \hat{H}$ for $\hat{H} = \hat{p}^2/(2m) + V(\hat{x})$, only if $V(\hat{x}) = V(-\hat{x})$.

2.3 Parity operator on electron-spin state

Electrons has a spin (s = 1/2). The spin angular momentum is $\boldsymbol{S}$ (= $\hbar\boldsymbol{\sigma}/2$) and the spin magnetic moment is given by $\mu_s = -(2\mu_B/\hbar)\boldsymbol{S}$, where μ_B (= $e\hbar/2mc$) is a Bohr magneton. We now consider how the electron-spin state changes under the parity operator. The spin

operator $\hat{\mathbf{S}}$ of electron commutates with $\hat{\pi}$: $\hat{\pi}\hat{\mathbf{S}}\hat{\pi}^{-1} = \hat{\mathbf{S}}$. Since $\hat{\pi}\hat{S}_z = \hat{S}_z\hat{\pi}$, $\hat{S}_z\hat{\pi}|+\rangle = \hat{\pi}\hat{S}_z|+\rangle = \frac{\hbar}{2}\hat{\pi}|+\rangle$, where $|+\rangle$ is the spin-up state. So the state $\hat{\pi}|+\rangle$ is the eigenket of $\hat{\pi}$ with the eigenvalue $\hbar/2$, or $\hat{\pi}|+\rangle = |+\rangle$. Similary we have $\hat{S}_z\hat{\pi}|-\rangle = \hat{\pi}\hat{S}_z|-\rangle = \frac{\hbar}{2}\hat{\pi}|-\rangle$, where $|-\rangle$ is the spin-down state. So the state $\hat{\pi}|-\rangle$ is the eigenket of $\hat{\pi}$ with the eigenvalue $-\hbar/2$, or $\hat{\pi}|-\rangle = |-\rangle$.

In conclusion the spin state remains unchanged under the parity operator:

$\hat{\pi}|+\rangle = |+\rangle$ and $\hat{\pi}|-\rangle = |-\rangle$. (34)

3. Time-reversal operator[1]

3.1 Definition

The time reversal is an odd kind of symmetry. It suggests that a motion picture of a physical event could be run without the viewer being able to tell something is wrong. We now consider the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(t) = H\psi(t).$$

Suppose that $\psi(t)$ is a solution. We can easily verify that $\psi(-t)$ is not a solution because of the first-order time derivative. However,

$$-i\hbar\frac{\partial}{\partial t}\psi^*(t) = H^*\psi^*(t) = H\psi^*(t).$$

When $t \to -t$, we have

$$i\hbar\frac{\partial}{\partial t}\psi^*(-t) = H\psi^*(-t).$$

This means that $\psi^*(-t)$ is a solution of the Schrödinger equation. The time reversal state is defined by

$$\Theta\psi(t) = \psi^*(-t). \quad (35)$$

If we consider a stationary state, $\psi(t) = e^{-\frac{i}{\hbar}Et}\psi(0)$,

$$\psi^*(-t) = e^{-\frac{i}{\hbar}Et}\psi^*(0),$$

or

$$\Theta\psi(t) = \Theta[e^{-\frac{i}{\hbar}Et}\psi(0)] = e^{-\frac{i}{\hbar}Et}\psi^*(0),$$

or

$$\Theta e^{-\frac{i}{\hbar}Et}\psi(0) = e^{-\frac{i}{\hbar}Et}\psi^*(0),$$

where $\Theta\psi(0) = \psi^*(0) = K\psi(0)$ and K is an operator which takes the complex conjugate.

3.2. Property

The state before the time reversal ($|\psi\rangle$) and the state after the time reversal ($|\tilde{\psi}\rangle$) are related through the relation

$$|\psi\rangle \to |\tilde{\psi}\rangle = \hat{\Theta}|\psi\rangle,$$

where $\hat{\Theta}(C_1|\alpha\rangle + C_2|\beta\rangle) = C^*_1\hat{\Theta}|\alpha\rangle + C_2{}^*\hat{\Theta}|\beta\rangle)$. The time-reversal operator acts only to the right because it entails taking the complex conjugate. The inner product of the time-reversal states $|\tilde{\alpha}\rangle = \hat{\Theta}|\alpha\rangle$ and $|\tilde{\beta}\rangle = \hat{\Theta}|\beta\rangle$ is defined by

$$\langle\tilde{\beta}|\tilde{\alpha}\rangle = \langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle^*. \tag{36}$$

One can then show that the expectation operators must satisfy the identity

$$\langle\tilde{\beta}|\hat{\Theta}\hat{A}\hat{\Theta}^{-1}|\tilde{\alpha}\rangle = \langle\alpha|\hat{A}^+|\beta\rangle = \langle\beta|\hat{A}|\alpha\rangle^*. \tag{37}$$

Suppose that $\hat{\Theta}\hat{A}\hat{\Theta}^{-1} = \pm\hat{A}$, then we have

$$\langle\alpha|\hat{A}|\beta\rangle = \langle\tilde{\beta}|\hat{\Theta}\hat{A}\hat{\Theta}^{-1}|\tilde{\alpha}\rangle = \langle\tilde{\beta}|\pm\hat{A}|\tilde{\alpha}\rangle = \pm\langle\tilde{\beta}|\hat{A}|\tilde{\alpha}\rangle = \pm\langle\tilde{\alpha}|\hat{A}|\tilde{\beta}\rangle^*.$$

If $|\alpha\rangle = |\beta\rangle$, we have

$$\langle\alpha|\hat{A}|\alpha\rangle = \pm\langle\tilde{\alpha}|\hat{A}|\tilde{\alpha}\rangle. \tag{38}$$

In conclusion, most operators of interest are either even or odd under the time reversal. $\hat{\Theta}\hat{A}\hat{\Theta}^{-1} = \pm\hat{A}$ (+: even, -: odd).

(1) $\hat{\Theta}i\hat{\Theta}^{-1} = -i\hat{1}$ (i is a pure imaginary, $\hat{1}$ is the identity operator).

(2) $\hat{\Theta}\hat{\mathbf{p}}\hat{\Theta}^{-1} = -\hat{\mathbf{p}}$: ($\hat{\Theta}|\mathbf{p}\rangle = |-\mathbf{p}\rangle$).

(3) $\hat{\Theta}\hat{\mathbf{p}}^2\hat{\Theta}^{-1} = \hat{\mathbf{p}}^2$.

(4) $\hat{\Theta}\ \hat{\mathbf{r}}\ \hat{\Theta}^{-1} = \hat{\mathbf{r}}$: ($\hat{\Theta}|\mathbf{r}\rangle = |\mathbf{r}\rangle$).

(5) $\hat{\Theta}V(\hat{\mathbf{r}})\hat{\Theta}^{-1} = V(\hat{\mathbf{r}})$: ($V(\hat{\mathbf{r}})$ is a potential).

(6) $\hat{\Theta}\hat{\mathbf{S}}\hat{\Theta}^{-1} = -\hat{\mathbf{S}}$ ($\hat{\mathbf{S}}$ is the spin angular momentum).

(7) $\hat{\Theta}\hat{H}\hat{\Theta}^{-1} = \hat{H}$, when $\hat{H} = \dfrac{\hat{p}^2}{2m} + V(\hat{x})$ and $V(\hat{x})$ is a potential energy. The relation is independent of the form of $V(\hat{x})$.

(8) $\hat{\Theta}\hat{T}_x(a)\hat{\Theta}^{-1} = \hat{T}_x(a)$ or $\hat{\Theta}\hat{T}_x(a) = \hat{T}_x(a)\hat{\Theta}$.

3.3 Time reversal operator on electron-spin state

We now consider how the electron-spin state change under the time-reversal operator. Since $\hat{\Theta}\hat{S}_z\hat{\Theta}^{-1} = -\hat{S}_z$ and $\hat{\Theta}\hat{S}_z = -\hat{S}_z\hat{\Theta}$, we have

$$\hat{S}_z\hat{\Theta}|+\rangle = -\hat{\Theta}\hat{S}_z|+\rangle = -\frac{\hbar}{2}\Theta|+\rangle.$$

The time reverse state $\hat{\Theta}|+\rangle$ is the eigenket of $\hat{S}_z$ with an eigenvalue $-\hbar/2$. Then we have $\hat{\Theta}|+\rangle = \eta|-\rangle$, where η is a phase factor (a complex number of modulus unity). Here we choose $\eta = 1$. In this case, $\hat{\Theta}$ can be expressed by

$$\hat{\Theta} = -i\hat{\sigma}_y\hat{K}, \tag{39}$$

where $\hat{K}$ is an operator which takes the complex conjugate and $\hat{\sigma}_y$ is a Pauli spin operator. Note that $\hat{\sigma}_y|+\rangle = i|-\rangle$ and $\hat{\sigma}_y|-\rangle = -i|+\rangle$. First we calculate

$$\hat{\Theta}(C_+|+\rangle + C_-|-\rangle) = -i\hat{\sigma}_y\hat{K}(C_+|+\rangle + C_-|-\rangle) = -i\hat{\sigma}_y(C_+^*|+\rangle + C_-^*|-\rangle)$$
$$= -i(C_+^*\hat{\sigma}_y|+\rangle + C_-^*\hat{\sigma}_y|-\rangle) = C_+^*|-\rangle - C_-^*|+\rangle .$$

where C_1 and C_2 are arbitrary complex numbers. We try to apply $\hat{\Theta}$ again to the above state

$$\hat{\Theta}^2(C_+|+\rangle + C_-|-\rangle) = \hat{\Theta}(C_+^*|-\rangle - C_-^*|+\rangle) = -i\hat{\sigma}_y\hat{K}(C_+^*|-\rangle - C_-^*|+\rangle)$$
$$= -i\hat{\sigma}_y(C_+|-\rangle - C_-|+\rangle) = -i[(C_+\hat{\sigma}_y|-\rangle - C_-\hat{\sigma}_y|+\rangle)]$$
$$= -i[(C_+(-i)|+\rangle - C_-i|+\rangle)] = -(C_+|+\rangle + C_-|-\rangle)$$

or

$$\hat{\Theta}^2 = -\hat{1} . \tag{40}$$

4 Bloch theorem

Felix Bloch entered the Federal Institute of Technology (Eidgenössische Technische Hochschule) in Zürich. After one year's study of engineering he decided instead to study physics, and changed therefore over to the Division of Mathematics and Physics at the same institution. After Schrödinger left Zürich in the fall of 1927 he continued his studies with Heisenberg at the University of Leipzig, where he received his degree of Doctor of Philosophy in the summer of 1928 with a dissertation dealing with the quantum mechanics of electrons in crystals and developing the theory of metallic conduction.

By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation. This was so simple that I did not think it could be much of a discovery, but when I showed it to Heisenberg, he said right away; "That's it!! (F. Bloch, July, 1928) (from the book edited by Hoddeson et al.[2]).

His paper was published in 1928 [F. Bloch, Zeitschrift für Physik 52, 555 (1928)]. There are many standard textbooks[3-10] which discuss the properties of the Bloch electrons in a periodic potential.

4.1 Derivation of the Bloch theorem

We consider the motion of an electron in a periodic potential (the lattice constant *a*). The system is one-dimensional and consists of *N* unit cells (the size $L = Na$, N: integer).

$$V(\hat{x} + a\hat{1}) = V(\hat{x}) ,$$
$$\hat{T}_x^{+}(\ell)\hat{x}\hat{T}_x(\ell) = \hat{x} + \ell\hat{1} , \tag{41}$$
$$\hat{T}_x(\ell)|x\rangle = |x + \ell\rangle , \tag{42}$$
$$\hat{T}_x(\delta x) = \hat{1} - \frac{i}{\hbar}\hat{p}_x\delta x , \tag{43}$$

where l is any finite translation (one dimensional) and δx is the infinitesimal translation. a is the lattice constant. The commutation relations hold

$$[\hat{T}_x(\delta x), \hat{p}_x] = \hat{0},$$

and

$$[\hat{T}_x(\delta x), \hat{p}_x{}^2] = \hat{0}.$$

Therefore the kinetic energy part of the Hamiltonian is invariant under the translation. When $\ell = a$ (a is a period of potential $V(x)$),

$$\hat{T}_x{}^+(a)\hat{x}\hat{T}_x(a) = \hat{x} + a\hat{1},$$

$$\hat{T}_x{}^+(a)V(\hat{x})\hat{T}_x(a) = V(\hat{x} + a\hat{1}) = V(\hat{x}).$$

Thus we have

$$[\hat{H}, \hat{T}_x(a)] = \hat{0},$$

or

$$\hat{T}_x{}^+(a)\hat{H}\hat{T}_x(a) = \hat{H}. \tag{44}$$

The Hamiltonian is invariant under the translation with a.

Since $\hat{T}(a)|x\rangle = |x + a\rangle$ and $\hat{T}^+(a)|x\rangle = |x - a\rangle$ or $\hat{T}^+(-a)|x\rangle = |x + a\rangle$,

we have

$$\hat{T}_x{}^+(a) = \hat{T}_x(-a). \tag{45}$$

So $\hat{T}^+(a)$ is not a Hermite operator.

We consider the simultaneous eigenket of $\hat{H}$ and $\hat{T}_x(a)$ for the system with a periodicity of $L = Na$ (there are N unit cells), since $[\hat{H}, \hat{T}_x(a)] = \hat{0}$.

$$\hat{H}|\psi_k\rangle = E_k|\psi_k\rangle, \tag{46}$$

and

$$\hat{T}_x(a)|\psi_k\rangle = \frac{1}{p}|\psi_k\rangle, \tag{47}$$

or

$$[\hat{T}_x(a)]^N|\psi_k\rangle = \left(\frac{1}{p}\right)^N|\psi_k\rangle.$$

Note that

$$\hat{T}_x(a)|x\rangle = |x + a\rangle, \tag{48}$$

$$[\hat{T}_x(a)]^N|x\rangle = |x + Na\rangle = |x\rangle \text{ (periodic condition).}$$

Thus we have

$$p^N = 1,$$

or

$$p = \exp(i\frac{2\pi s}{N}) = \exp(i\frac{2\pi as}{Na}) = \exp(ika), \tag{49}$$

with

$$k = \frac{2\pi}{Na}s = \frac{2\pi}{L}s \text{ (s: integer).} \tag{50}$$

Therefore, we have

$$\hat{T}_x(a)|\psi_k\rangle = e^{-ika}|\psi_k\rangle. \tag{51}$$

The state $|\psi_k\rangle$ is the eigenket of $\hat{T}_x(a)$ with the eigenvalue e^{-ika}.

or

$$\langle x|\hat{T}_x(a)|\psi_k\rangle = \exp(-ika)\langle x|\psi_k\rangle,$$
$$\langle x|\hat{T}_x(a) = \langle x-a|,$$
$$\langle x-a|\psi_k\rangle = e^{-ika}\langle x|\psi_k\rangle, \tag{52}$$

or

$$\psi_k(x-a) = e^{-ika}\psi_k(x). \tag{53}$$

By changing for a to $-a$, we have

$$\psi_k(x+a) = e^{ika}\psi_k(x). \tag{54}$$

This is called as the Bloch theorem.

4.2 Symmetry of E_k and E_{-k}: the time-reversal state

We assume that the Hamiltonian $\hat{H}$ is invariant under the time-reversal operator (this assumption is valid in general): $\hat{\Theta}\hat{H} = \hat{H}\hat{\Theta}$. Then the state $|\psi_k\rangle$ is the simultaneous eigenket (the Bloch state) of $\hat{H}$ and $\hat{\Theta}$:

$$\hat{H}|\psi_k\rangle = E_k|\psi_k\rangle \text{ and } \hat{T}_x(a)|\psi_k\rangle = e^{-ika}|\psi_k\rangle. \tag{55}$$

Since $\hat{H}\hat{\Theta}|\psi_k\rangle = \hat{\Theta}\hat{H}|\psi_k\rangle = E_k\Theta|\psi_k\rangle$, the time-reversal state $|\tilde{\psi}_k\rangle = \hat{\Theta}|\psi_k\rangle$ is also the eigenket of $\hat{H}$ with the energy eigenvalue E_k. Since $[\hat{T}_x(a), \hat{\Theta}] = \hat{0}$,

$$\hat{T}_x(a)|\tilde{\psi}_k\rangle = \hat{T}_x(a)\hat{\Theta}|\psi_k\rangle = \hat{\Theta}\hat{T}_x(a)|\psi_k\rangle = \Theta(e^{-ika}|\psi_k\rangle) = e^{ika}\Theta|\psi_k\rangle = e^{ika}|\tilde{\psi}_k\rangle.$$

The time-reversal state $|\tilde{\psi}_k\rangle = \hat{\Theta}|\psi_k\rangle$ is the eigenket of $\hat{T}_x(a)$ with the eigenvalue e^{ika}. So the state $|\tilde{\psi}_k\rangle$ is different from the state $|\psi_k\rangle$ and coincide with the state $|\psi_{-k}\rangle$, where $\hat{H}|\tilde{\psi}_k\rangle = E_{-k}|\tilde{\psi}_k\rangle$.

In conclusion, the property of $E_k = E_{-k}$ is a consequence of the symmetry under the time reversal:

(1) $$\hat{\Theta}|\psi_k\rangle = |\psi_{-k}\rangle. \tag{56}$$

(2) Both states ($\hat{\Theta}|\psi_k\rangle = |\psi_{-k}\rangle$ and $|\psi_k\rangle$) are degenerate states with the same energy eigenvalue:

$$E_k = E_{-k}. \tag{57}$$

4.3 Kramer's theorem for electron-spin state

We consider how the electron-spin state changes under the time reversal. The Hamiltonian $\hat{H}$ is invariant under time reversal, $[\hat{H}, \hat{\Theta}] = \hat{0}$. Let $|\psi_{k,s}\rangle$ and $\hat{\Theta}|\psi_{k,s}\rangle = |\psi_{-k,-s}\rangle$ be the simultaneous eigenket of $\hat{H}$ and $\hat{S}_z$ ($[\hat{H}, \hat{S}_z] = \hat{0}$) and its time-reversed states, respectively. $\hat{H}|\psi_{k,s}\rangle = E_{k,s}|\psi_{k,s}\rangle$, where $E_{k,s}$ is the eigenket with the wavenumber k and spin state s (s = up or down).

$$\hat{H}\hat{\Theta}|\psi_{k,s}\rangle = \hat{\Theta}\hat{H}|\psi_{k,s}\rangle = \hat{\Theta}E_{k,s}|\psi_{k,s}\rangle = E_{k,s}\hat{\Theta}|\psi_{k,s}\rangle = E_{k,s}|\psi_{-k,-s}\rangle.$$

It follows that $\hat{\Theta}|\psi_{k,s}\rangle$ is the eigenket of $\hat{H}$ with the eigenvalue $E_{k,s}$. On the other hand, $\hat{\Theta}|\psi_{k,s}\rangle = |\psi_{-k,-s}\rangle$ is the eigenket of $\hat{H}$ with the eigenvalue $E_{-k,-s}$. Therefore $E_{k,s}$ is equal to $E_{-k,-s}$. When $\hat{\Theta}^2 = -\hat{1}$ (half-integer), $\hat{\Theta}|\psi_{k,s}\rangle$ and $|\psi_{k,s}\rangle$ are orthogonal. This means that $\hat{\Theta}|\psi_{k,s}\rangle$ and $|\psi_{k,s}\rangle$ (having the same energy $E_{k,s}$) must correspond to distinct states (degenerate) [Kramer's theorem].

In order to prove this orthogonality, we use the formula

$$\langle\tilde{\beta}|\tilde{\alpha}\rangle = \langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle^*,$$

where

$$|\alpha\rangle = \hat{\Theta}|\psi_{k,s}\rangle,\ |\tilde{\alpha}\rangle = \hat{\Theta}|\alpha\rangle = \hat{\Theta}(\hat{\Theta}|\psi_{k,s}\rangle) = \hat{\Theta}^2|\psi_{k,s}\rangle$$

$$|\beta\rangle = |\psi_{k,s}\rangle,\ |\tilde{\beta}\rangle = \hat{\Theta}|\psi_{k,s}\rangle = |\alpha\rangle.$$

Since $\hat{\Theta}^2|\psi_{k,s}\rangle = -|\psi_{k,s}\rangle$, we have $|\tilde{\alpha}\rangle = \hat{\Theta}^2|\psi_{k,s}\rangle = -|\psi_{k,s}\rangle$.

Then

$$\langle\tilde{\beta}|\tilde{\alpha}\rangle = -\langle\alpha|\beta\rangle = \langle\alpha|\beta\rangle,$$

or

$$\langle\alpha|\psi_{k,s}\rangle = 0,$$

indicating that for such systems, time-reversed states are orthogonal.

In conclusion, when the effect of spin on the energy eigenket is taken into account

(1) $\hat{\Theta}|\psi_{k,s}\rangle = |\psi_{-k,-s}\rangle$. (58)

(2) Both states ($\hat{\Theta}|\psi_{k,s}\rangle = |\psi_{-k,-s}\rangle$ and $|\psi_{k,s}\rangle$) are degenerate states (the same energy but different states):

$E_{k,s} = E_{-k,-s}$, or $E_{k,\uparrow} = E_{-k,\downarrow}$ and $E_{k,\downarrow} = E_{-k,\uparrow}$. (59)

4.4 Parity operator for symmetric potential

What is the effect of the parity operator on the eigenket $|\psi_k\rangle$? Using the following relations

$$\hat{T}_x(a)|\psi_k\rangle = e^{-ika}|\psi_k\rangle,$$

$$\hat{\pi}\hat{T}_x(a) = \hat{T}_x^{+}(a)\hat{\pi},$$

we have

$$\hat{\pi}\hat{T}_x(a)|\psi_k\rangle = \hat{T}_x^{+}(a)\hat{\pi}|\psi_k\rangle = e^{-ika}\hat{\pi}|\psi_k\rangle,$$

or

$$\hat{T}_x^{+}(a)\hat{\pi}|\psi_k\rangle = e^{-ika}\hat{\pi}|\psi_k\rangle,$$

or

$$\hat{T}_x(-a)\hat{\pi}|\psi_k\rangle = e^{-ika}\hat{\pi}|\psi_k\rangle.$$

When a is changed to $-a$ in the above equation, we get

$$\hat{T}_x(a)\hat{\pi}|\psi_k\rangle = e^{ika}\hat{\pi}|\psi_k\rangle. \quad (60)$$

In other words, the state $\hat{\pi}|\psi_k\rangle$ is the eigenket of $\hat{T}_x(a)$ with the eigenvalue e^{ika}.

Here we consider the limited case that the potential energy $V(x)$ is an even function of x:or $V(-\hat{x}) = V(\hat{x})$. Then the Hamiltonian $\hat{H}$ commutes with $\hat{\pi}$: $[\hat{H}, \hat{\pi}] = \hat{0}$. In other words, $\hat{H}$ is invariant under the parity operation. The state $|\psi_{k,s}\rangle$ is a simultaneous eigenket of $\hat{H}$ and $\hat{T}_x(a)$: $\hat{H}|\psi_{k,s}\rangle = E_{k,s}|\psi_{k,s}\rangle$ and $\hat{T}_x(a)|\psi_{k,s}\rangle = e^{-ika}|\psi_{k,s}\rangle$.

$$\hat{H}\hat{\pi}|\psi_{k,s}\rangle = \hat{\pi}\hat{H}|\psi_{k,s}\rangle = E_{k,s}\hat{\pi}|\psi_{k,s}\rangle .$$

Thus $\hat{\pi}|\psi_{k,s}\rangle$ is the simultaneous eigenket of $\hat{H}$ with $E_{k,s}$ and $\hat{T}_x(a)$ with e^{ika}. The state $\hat{\pi}|\psi_{k,s}\rangle$ coincides with $|\psi_{-k,s}\rangle$ with $E_{-k,s}$. Therefore we can conclude that $E_{k,s} = E_{-k,s}$; $E_{k,\uparrow} = E_{-k,\uparrow}$ and $E_{k,\downarrow} = E_{-k,\downarrow}$.

4.5 Brillouin zone in one dimensional system

We know that the reciprocal lattice G is defined by

$$G = \frac{2\pi}{a} n \text{, } (n\text{: integer}). \tag{61}$$

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

$$\psi_{k+G}(x) = \psi_k(x) . \tag{62}$$

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

$$E_{k+G} = E_k . \tag{63}$$

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

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

The first Brillouin zone is defined as $|k| \le \frac{\pi}{a}$. 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 Brilloiun zone. Suppose that the number of electrons per unit cell is n_c (= 1, 2, 3, …). 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.

4.6 Bloch wavefunction

Here we assume that

$$\psi_k(x) = e^{ikx}u_k(x), \tag{64}$$

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

which should be equal to

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

or

$$u_k(x-a) = u_k(x), \tag{65}$$

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:

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \text{ (Bloch function)}, \tag{66}$$

where

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{T}). \tag{67}$$

Bloch functions can be assembled into localized wave packets to represent electrons that propagate freely through the potential of the ion cores. $\boldsymbol{T}$ is any translation vectors which is expressed by $\boldsymbol{T} = n_1\boldsymbol{a}_1+n_2\mathbf{a}_2+n_3\boldsymbol{a}_3$ (n_1, n_2, n_3 are integers, $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ are fundamental lattice vectors). From Eq.(67), $u_{\mathbf{k}}(\mathbf{r})$ can be expanded as follows. (Fourier transform)

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}}e^{-i\mathbf{G}\cdot\mathbf{r}}. \tag{68}$$

where $\boldsymbol{G}$ 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

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

or

$$\psi_{\mathbf{k}}(\mathbf{r}) = \ldots + C_{\mathbf{k}-2\mathbf{G}}e^{i(\mathbf{k}-2\mathbf{G})\cdot\mathbf{r}} + C_{\mathbf{k}-\mathbf{G}}e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} + C_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}} + C_{\mathbf{k}+\mathbf{G}}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} + C_{\mathbf{k}+2\mathbf{G}}e^{i(\mathbf{k}+2\mathbf{G})\cdot\mathbf{r}} + \ldots. \tag{69}$$

The eigenvalue-problem

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

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

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

(ii) $E_{\mathbf{k}} = E_{-\mathbf{k}}$. (70)

The first property means that any reciprocal lattice point can serve as the origin of E_{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.

$$H\psi_k(x) = E_k\psi_k(x),$$

$$H\psi_k^*(x) = E_k\psi_k^*(x) \quad (\hat{H} \text{ is Hermitian}),$$

or

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

From the Bloch theorem given by

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

or

$$\psi_k(x) = e^{ikx}u_k(x), \text{ and } \psi_k^{*}(x) = e^{-ikx}u_k^{*}(x),$$

we have

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

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

$$\psi_{-k}^{*}(x) = \psi_k(x), \tag{71}$$

with

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

What does this relation mean?

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

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

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

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

or

$$C_{\mathbf{k}-\mathbf{G}}^{*} = C_{-\mathbf{k}+\mathbf{G}}. \tag{72}$$

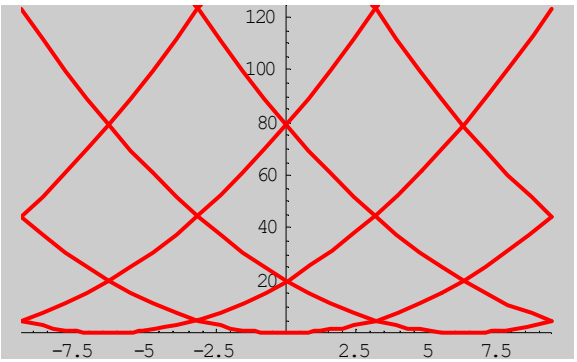
4.7 Properties of energy band

(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.

((Mathematica 5.2))

```
f = ħ^2/(2 m) (k - 2 π/a n)^2; rule1 = {m → 1, ħ → 1, a → 1}; g = f /. rule1;
s1 = Plot[Evaluate[Table[g, {n, -3, 3}]], {k, -3 π, 3 π}, PlotRange → {{-3 π, 3 π}, {0, 125}},
  Prolog → AbsoluteThickness[2.0], PlotStyle → {Hue[0], Hue[0]}, Background → GrayLevel[0.8]]
```



-Graphics-

Fig.3 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, ±1, ±…).

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

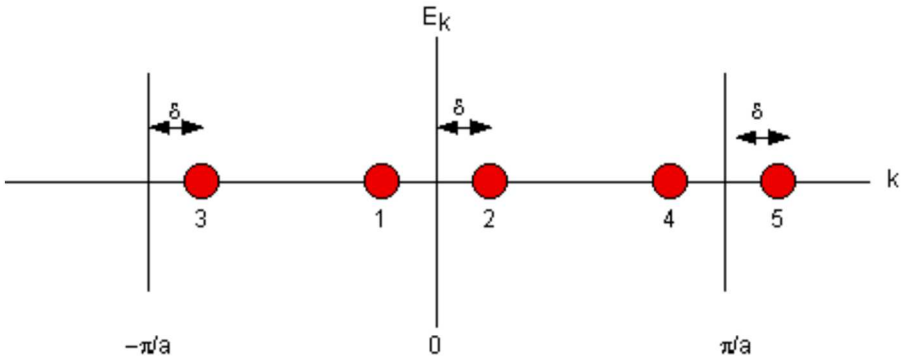


Fig.4 The relation of $E_{-k} = E_k$ in the reciprocal lattice plane. $k = \pm\pi/a$ is the boundary of the first Brillouin zone ($|k| \leq \pi/a$).

It follows that from the condition ($E_k = E_{-k}$), in Fig.4, $E(1) = E(2)$. 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 $k = 0, \pm 2\pi/a, \pm 4\pi/a, \ldots,$

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 conclusion, the group velocity (dE_k/dk) is equal to zero at $k = 0, \pm G/2, \pm G, \pm 3G/2, \pm 2G,$. (see the books written by S.L. Altmann[3] for more detail.)

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.

$$[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+U(x)]\psi_k(x)=E\psi_k(x), \tag{73}$$

where

$$U(x)=\sum_G U_G e^{-iGx} \quad [(G=n\,(2\pi/a),\ n\text{: integer})], \tag{74}$$

with

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

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

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: $G''\to G, G\to G'$ 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

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

When $k\to k+G$

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

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

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

or

$$[\lambda_{k-G}-E]C_{k-G}+(\ldots+U_{-4G}C_{k-5G}+U_{-3G}C_{k-4G}+U_{-2G}C_{k-3G}+U_{-G}C_{k-2G}+U_0C_{k-G}+$$

$$+U_GC_k+U_{2G}C_{k+G}+U_{3G}C_{k+2G}+U_{4G}C_{k+3G}+\ldots)=0 \tag{75}$$

When $k \to k+G$ in Eq.(75)

$$[\lambda_k - E]C_k + (... + U_{-4G}C_{k-4G} + U_{-3G}C_{k-3G} + U_{-2G}C_{k-2G} + U_{-G}C_{k-G} + U_0 C_k +$$

$$+ U_G C_{k+G} + U_{2G}C_{k+2G} + U_{3G}C_{k+3G} + U_{4G}C_{k+4G} + ...) = 0 \tag{76}$$

When $k \to k+2G$ in Eq.(75)

$$[\lambda_{k+G} - E]C_{k+G} + (... + U_{-4G}C_{k-3G} + U_{-3G}C_{k-2G} + U_{-2G}C_{k-G} + U_{-G}C_k + U_0 C_{k+G} +$$

$$+ U_G C_{k+2G} + U_{2G}C_{k+3G} + U_{3G}C_{k+4G} + U_{4G}C_{k+5G} + ...) = 0 \tag{77}$$

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 $m = \pm 4, \pm 5, \pm 6, \ldots$.

5.2 Solution for the simple case

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

$$\begin{pmatrix} \lambda_k - E & U_G^* \\ U_G & \lambda_{k-G} - E \end{pmatrix} \begin{pmatrix} C_k \\ C_{k-G} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{78}$$

From the condition that the determinant is equal to 0,

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

or

$$E = \frac{\lambda_k + \lambda_{k-G} \pm \sqrt{(\lambda_k - \lambda_{k-G})^2 + 4|U_G|^2}}{2}. \tag{79}$$

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

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

5.2.1 $U_G < 0$

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

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

or

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

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

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

or

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

5.2.2 $U_G > 0$

$$|\psi_{\mathbf{k}}(x)|^2 = 4|C_k|^2 \cos^2(\frac{Gx}{2}) \qquad \text{for } E = \lambda_k + U_G \text{ (upper energy level),}$$

and

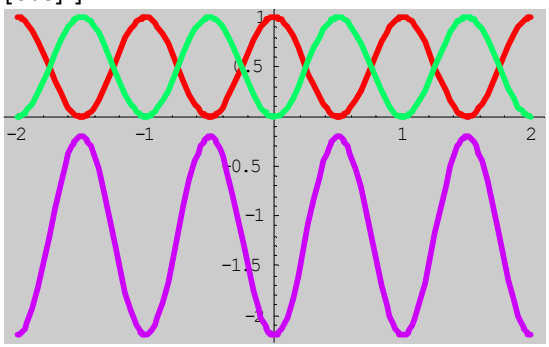
$$|\psi_{\mathbf{k}}(x)|^2 = 4|C_k|^2 \sin^2(\frac{Gx}{2}) \qquad \text{for } E = \lambda_k - U_G \text{ (lower energy level).}$$

5.2.3 Probability of finding electrons

((Mathematica 5.2))

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.

```
f1 = Cos[π x]^2; f2 = Sin[π x]^2; f3 = -1.2 - Cos[2 π x];
Plot[{f1, f2, f3}, {x, -2, 2}, PlotStyle → Table[Hue[0.4 i], {i, 0, 3}], Prolog → AbsoluteThickness[3],
 Background → GrayLevel[0.8] ]
```




```
-Graphics-
```

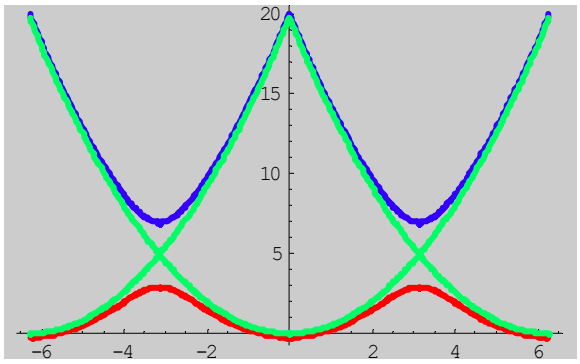
Fig.5 At $k = \pi/a$, Bragg reflection of the electron arises, leading to two possible charge distributions $f_1(x)$ and $f_2(x)$. The case of $U_G<0$ (attractive potential due to positive ions). $f_1(x)$ (red) probability of the wave function (lower energy level), $f_2(x)$ (green) probability of the 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[5] for more detail).

5.2.4 Eigenvalue problem for the system with only U_G

((Mathematica 5.2))

```
(*  attractive potential Vk = -2*)
```

```
f[k_] = ħ^2/(2 m) k^2; M = {{f[k], Vk}, {Vk, f[k - K]}}; rule1 = {ħ → 1, m → 1, K → 2 π, Vk → -2};
M1 = M /. rule1; A = Eigenvalues[M1];
p1 = Plot[{A[[1]], A[[2]], k^2/2, 1/2 (k - 2 π)^2}, {k, 0, 2 π}, Prolog → AbsoluteThickness[3.0],
  PlotPoints → 200, PlotStyle → {Hue[0], Hue[0.7], Hue[0.4], Hue[0.4]},
  Background → GrayLevel[0.8]]; rule2 = {ħ → 1, m → 1, K → -2 π, Vk → -2}; M2 = M /. rule2;
B = Eigenvalues[M2];
p2 = Plot[{B[[1]], B[[2]], k^2/2, 1/2 (k + 2 π)^2}, {k, -2 π, 0},
  PlotStyle → {Hue[0], Hue[0.7], Hue[0.4], Hue[0.4]}, PlotPoints → 200,
  Prolog → AbsoluteThickness[3.0], Background → GrayLevel[0.8]];
Show[p1, p2]
```



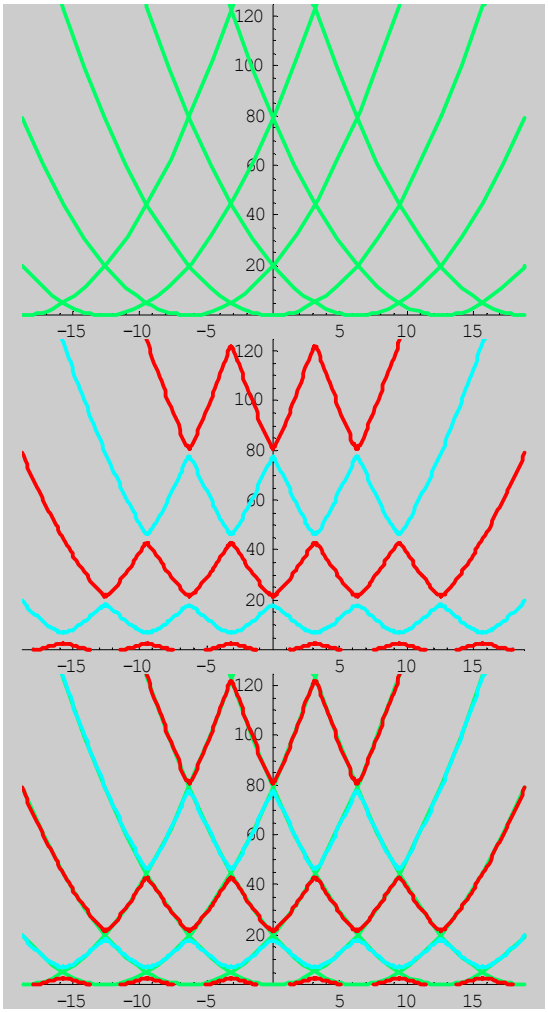

```
-Graphics-
```

Fig.6 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} ((Mathematica 5.2))

```
(* Nearly free electron approximation*)
```

```
h = ħ^2/(2 m) (k - 2 π/a n)^2; rule1 = {m → 1, ħ → 1, a → 1}; h1 = h /. rule1;
s1 = Plot[Evaluate[Table[h1, {n, -3, 3}]], {k, -6 π, 6 π}, PlotRange → {{-6 π, 6 π}, {0, 125}},
  Prolog → AbsoluteThickness[2.5], PlotStyle → {Hue[0.4], Hue[0.4]}, Background → GrayLevel[0.8]];
f[k1_] = ħ^2/(2 m) k1^2;
M = {{f[k+3 K], U, V, W, X, Y, Z}, {U, f[k+2 K], U, V, W, X, Y}, {V, U, f[k+K], U, V, W, X},
  {W, V, U, f[k], U, V, W}, {X, W, V, U, f[k-K], U, V}, {Y, X, W, V, U, f[k-2 K], U},
  {Z, Y, X, W, V, U, f[k-3 K]}};
rule2 = {ħ → 1, m → 1, K → -2 π, U → -2, V → -2, W → -2, X → -2, Y → -2, Z → -2}; M1 = M /. rule2;
A = Eigenvalues[M1];
p1 = Plot[Evaluate[Table[A[[i]], {i, 1, 5}]], {k, -6 π, 6 π}, Prolog → AbsoluteThickness[2.5],
  PlotStyle → {Hue[0], Hue[0.5]}, PlotPoints → 300, Background → GrayLevel[0.8],
  PlotRange → {{-6 π, 6 π}, {0, 125}}];
Show[s1, p1]
```



-Graphics-

Fig.7 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.

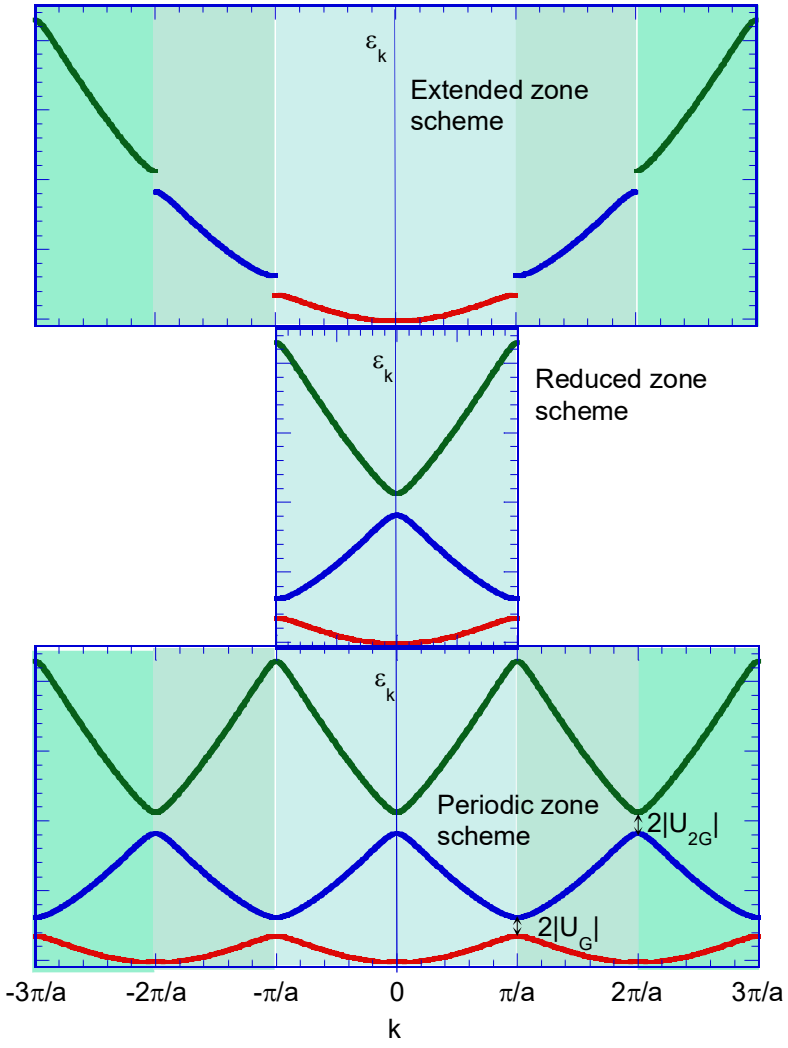


Fig.8 Three zone schemes for the 1D system. Extended zone scheme. Reduced zone scheme. Periodic zone scheme.

5.5 Bragg reflection at the boundary of the Brillouin zone

The Bragg reflection occurs when the degeneracy condition $E(\boldsymbol{k}) = E(\boldsymbol{k}\text{-}\boldsymbol{G})$ or $|\boldsymbol{k}\text{-}\boldsymbol{G}| = |\boldsymbol{k}|$. This condition is equivalent to the condition $2\boldsymbol{k}\cdot\boldsymbol{G} = \boldsymbol{G}^2$. 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 (Fig.9). For the 2D system, the boundaries form lines in the reciprocal lattice plane (Fig.10). The degeneracy condition $|\boldsymbol{k}\text{-}\boldsymbol{G}| = |\boldsymbol{k}|$ geometrically means that $\boldsymbol{k}$ lies on the perpendicular bisector of the reciprocal lattice vector $\boldsymbol{G}$. For the 3D system, the Bragg reflection occurs when $\boldsymbol{k}$ 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 $k = G/2 = \pm\pi/a$.

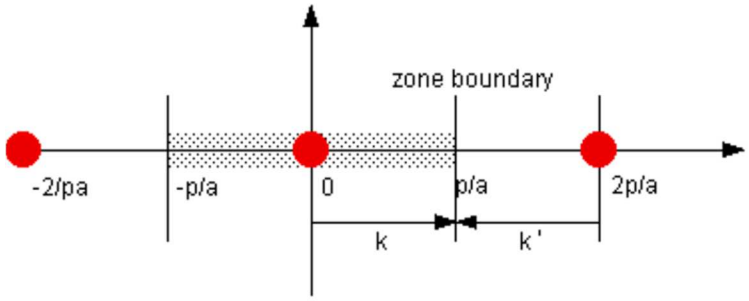


Fig.9 Condition of the Bragg reflection for the 1D case. $|k| = |\mathrm{k} - G|$. $G = 2\pi/a$. $k' = k - G$.

5.5.2 2D system:

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

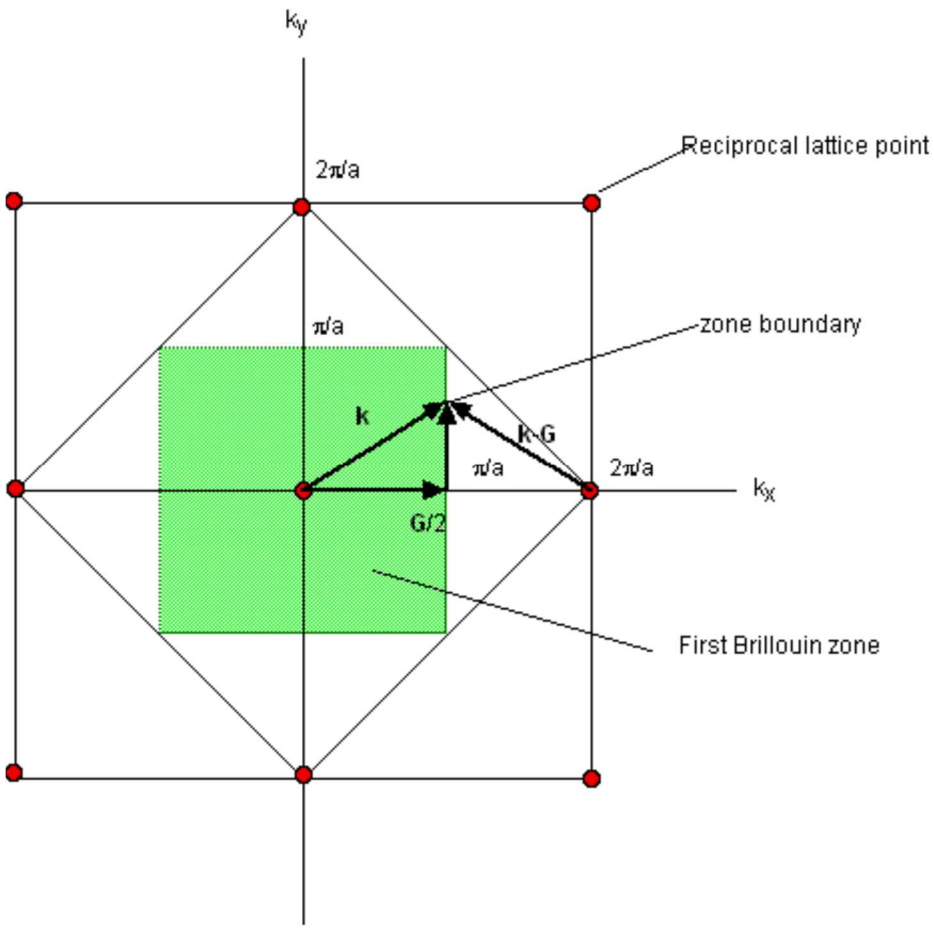


Fig.10 Condition of the Bragg reflection for the 2D case. $|\boldsymbol{k}| = |\boldsymbol{k} - \boldsymbol{G}|$.

6 Kronig Penny model as an application of the Bloch theorem

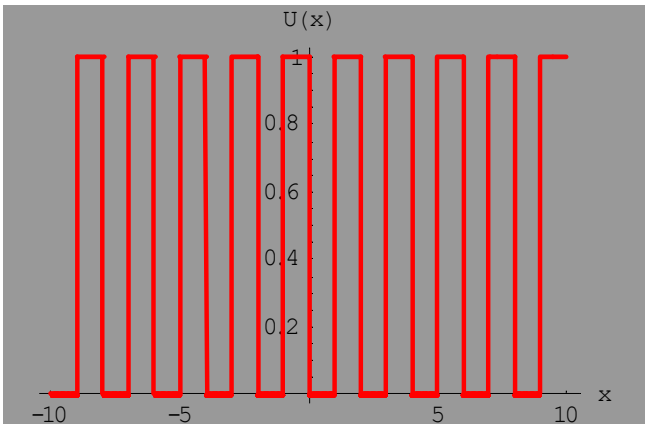
6.1 Secular equation

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,

$U(x)=U_0$ for $-b \le x \le 0$ and $U(x)= 0$ for $0 \le x \le a$ (the periodicity, $a+b$).

((Mathgematica 5.2)) Periodic potential $U(x)$

```
(*A periodic potential Kronig Penny model *)
 f[x_]:=1/;-1≤x≤0;f[x_]:=0/;0≤x≤1;a[x_]:=f[x]/;-
1≤x≤1;a[x_]:=a[x-2]/;x>1;a[x_]:=a[x+2]/;x<-1;Plot[a[x],{x,-
10,10},PlotStyle→Hue[0],Background→GrayLevel[0.6],PlotPoint
s→200,Prolog→AbsoluteThickness[2.5],AxesLabel→{"x","U(x)"}]
```



-Graphics-

Fig.11 Square-well periodic potential where $a = b = 1$ and $U_0 = 1$.

We now consider a Schrödinger equation,

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)+U(x)\psi(x)=E\psi(x), \tag{80}$$

where E is the energy eigenvalue.

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

$$\psi_1(x)=Ae^{iKx}+Be^{-iKx}, \qquad d\psi_1(x)/dx=iK(Ae^{iKx}-Be^{-iKx}), \tag{81}$$

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

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

$$\psi_2(x)=Ce^{Qx}+De^{-Qx}, \qquad d\psi_2(x)/dx=Q(Ce^{Qx}-De^{-Qx}), \tag{82}$$

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

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 ψ and $d\psi/dx$ are continuous at $x = 0$ and $x = a$.

At $x = 0$,

$$A+B=C+D, \tag{83}$$

$$iK(A-B)=Q(C-D). \tag{84}$$

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

$$Ae^{iKa}+Be^{-iKa}=e^{ik(a+b)}(Ce^{-Qb}+De^{Qb}), \tag{85}$$

$$iK(Ae^{iKa}-Be^{-iKa})=Qe^{ik(a+b)}(Ce^{-Qb}-De^{Qb}). \tag{86}$$

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

$$\cos[k(a+b)] = \cos(Ka)\cosh(Qb) + \frac{(Q^2 - K^2)}{2KQ}\sin(Ka)\sinh(Qb)\,. \qquad (87)$$

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

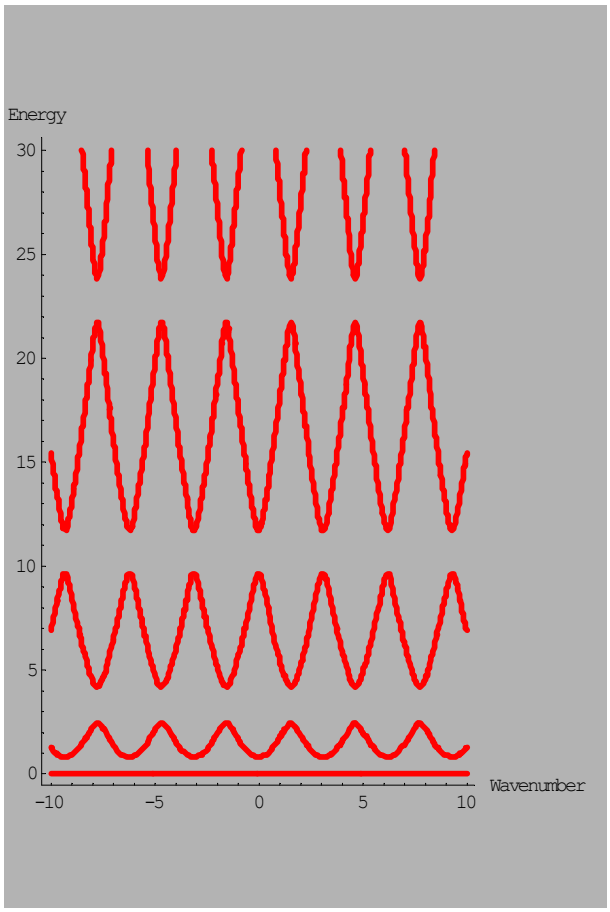
6.2 Energy dispersion relation

((Mathematica 5.2)) solution of the secular equation
Here we use the program which was originally written by Noboru Wada.[11]

```
M={{1,1,-1,-1},{i K,-i K, -Q,Q},{Exp[i K a],Exp[-i K a],-
Exp[i k (a+b)-Q b],-Exp[i k (a+b)+Q b]},{i K Exp[i K a], -i
K Exp[-i K a],-Q Exp[i k (a+b)-Q b],Q Exp[i k (a+b)+Q
b]}};M2=Det[M];Simplify[ExpToTrig[M2]]
```

```
4 i (Cos[(a + b) k] + i Sin[(a + b) k])
 (2 K Q Cos[(a + b) k] - 2 K Q Cos[a K] Cosh[b Q] + (K^2 - Q^2) Sin[a K] Sinh[b Q])
```

```
<<Graphics`ImplicitPlot`
p11 =
 ImplicitPlot[
  Evaluate[
    (2 K Q Cos[(a + b) k] - 2 K Q Cos[a K] Cosh[b Q] +
       (K^2 - Q^2) Sin[a K] Sinh[b Q]) /.
     {a → 2, b → 0.022, K → Sqrt[ϵ], Q → Sqrt[100 - ϵ]}] == 0,
  {k, -10, 10}, {ϵ, 0, 30}, PlotPoints → 200,
  PlotStyle → {Hue[0], Thickness[0.015]}, Background → GrayLevel[0.7],
  AxesLabel → {"Wavenumber", "Energy"}]
```



-ContourGraphics-

Fig.12 Plot of energy E vs wave number k in the Kronig-Penny model (periodic zone scheme). $a = 2$, $b = 0.022$. $K = \sqrt{\varepsilon}$. $Q = \sqrt{100 - \varepsilon}$. $0 \leq \varepsilon \leq 30$. $U_0 = 50\hbar^2 / m$.

7 Theory of persistent current in conducting metallic ring

7.1 Model similar to the Aharonov-Bohm effect

This was, in part, anticipated in a widely known but unpublished piece of work by Felix Bloch in the early thirties, who argued that the equilibrium free energy of a metallic circuit must be a periodic function of the flux through the circuit with period hc/e; this was jokingly known as a theorem which disproved all theories of the metastable current in superconductors. (from a book written by D.J. Thouless[12]).

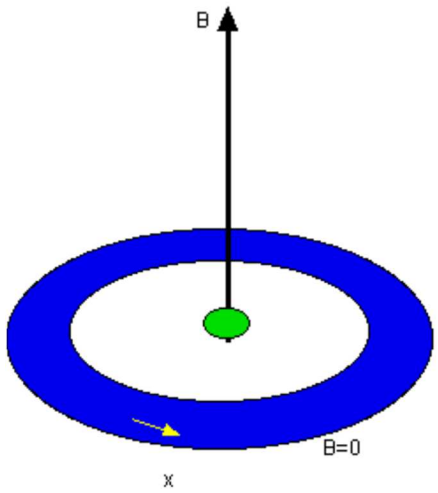


Fig.13 Circular conducting metal wire (one-dimensional along the x axis). The coordinate x is along the circular ring. The magnetic field is located only at the center (green part) of the ring (the same configuration as the Aharonov-Bohm effect). $a = 2\pi R$ (R: radius).

We consider a circular metal ring. A magnetic field is located only at the center of the ring (the same configuration as the Aharonov-Bohm effect[13]). We assume that $q = -e$ ($e>0$). There is no magnetic field on the conducting metal ring ($\boldsymbol{B} = 0$). The vector potential $\boldsymbol{A}$ is related to $\boldsymbol{B}$ by

$$\mathbf{B} = \nabla \times \mathbf{A} = 0 ,$$

or

$$\mathbf{A} = \nabla \chi .$$

The scalar potential χ is described by

$$\chi(x) = \int_{x_0}^{x} dx A(x) , \tag{88}$$

where the direction of x is along the circular ring and x_0 is an arbitrary initial point in the ring.

We now consider the gauge transformation. $\boldsymbol{A}$' and $\boldsymbol{A}$ are the new and old vector potentials, respectively. ψ' and ψ are the new and old wave functions, respectively.

$$\mathbf{A}' = \mathbf{A} + \nabla(-\chi) = 0 ,$$

$$\psi'(\mathbf{r}) = \exp(\frac{ie\chi}{\hbar c})\psi(\mathbf{r}) . \tag{89}$$

Since $\boldsymbol{A}' = 0$, ψ' is the field-free wave function and satisfies the Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi' = i\hbar\frac{\partial}{\partial t}\psi' . \tag{90}$$

In summary, we have

$$\psi(x) = \psi'(x)\exp[-\frac{ie}{\hbar c}\int_{x_0}^{x} A(x)dx] , \tag{91}$$

$$\psi(x+a) = \psi'(x+a)\exp[-\frac{ie}{\hbar c}\int_{x_0}^{x+a} A(x)dx], \tag{92}$$

where a is a perimeter of the circular ring. From these equation we get

$$\frac{\psi(x+a)}{\psi(x)} = \frac{\psi'(x+a)}{\psi'(x)}\exp[-\frac{ie}{\hbar c}\int_{x}^{x+a} A(x)dx] = \frac{\psi'(x+a)}{\psi'(x)}\exp[-\frac{ie\Phi}{\hbar c}].$$

Here we use the relation

$$\int_{x}^{x+a} A(x)dx = \oint(\nabla \times A)\cdot d\mathbf{a} = \Phi, \tag{93}$$

where Φ is the total magnetic flux. It is reasonable to assume the periodic boundary condition

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

for the free particle wave function. Then we have

$$\psi(x+a) = \psi(x)\exp(-\frac{ie\Phi}{\hbar c}) = \exp(ika)\psi(x). \tag{94}$$

with the wavenumber

$$k = -\frac{e\Phi}{\hbar ca}. \tag{95}$$

This equation indicates that $\psi(x)$ is the Bloch wave function. The electronic energy spectrum of the system has a band structure.

We now consider the case of $k+G$ with $G=2\pi/a$.

$$\exp[i(k+G)a]\psi(x) = \exp(ika)\psi(x) = \psi(x+a),$$

since $\exp(iGa) = 1$. Therefore we have the periodicity of the energy eigenvalue

$$E(k+G) = E(k), \quad \text{or} \quad E(\Phi + 2n\Phi_0) = E(\Phi). \tag{96}$$

From the Bloch theory, we can also derive

$$E(-k) = E(k), \quad \text{or} \quad E(-\Phi) = E(\Phi). \tag{97}$$

The energy $E(k)$ depends on Φ. It is actually a periodic function of Φ with the periodicity $2\Phi_0$.

$$G = \frac{2\pi}{a} = \frac{e\Delta\Phi}{\hbar ca}, \quad \text{or} \quad \Delta\Phi = 2\frac{2\pi\hbar c}{2e} = 2\Phi_0. \tag{98}$$

The magnetization $M(\Phi)$ is defined as

$$M(\Phi) = -\frac{\partial E(\Phi)}{\partial B} = -A\frac{\partial E(\Phi)}{\partial \Phi} = \frac{Ae}{\hbar ca}\frac{\partial E(k)}{\partial k}, \tag{99}$$

where A is the total area. This is proportional to the group velocity defined by

$$v_k = \frac{1}{\hbar}\frac{\partial E(k)}{\partial k}. \tag{100}$$

The magnetic moment $M(\Phi)$ is related to the current flowing in the ring as

$$M(\Phi) = \frac{1}{c}I(\Phi)A = -A\frac{\partial E(\Phi)}{\partial \Phi}, \tag{101}$$

or

$$I(\Phi) = -c\frac{\partial E(\Phi)}{\partial \Phi}. \tag{102}$$

7.2 Derivation of $E(\Phi)$[14]

We consider the persistent current system in the ring in the presence of magnetic flux. $a = 2\pi R$.

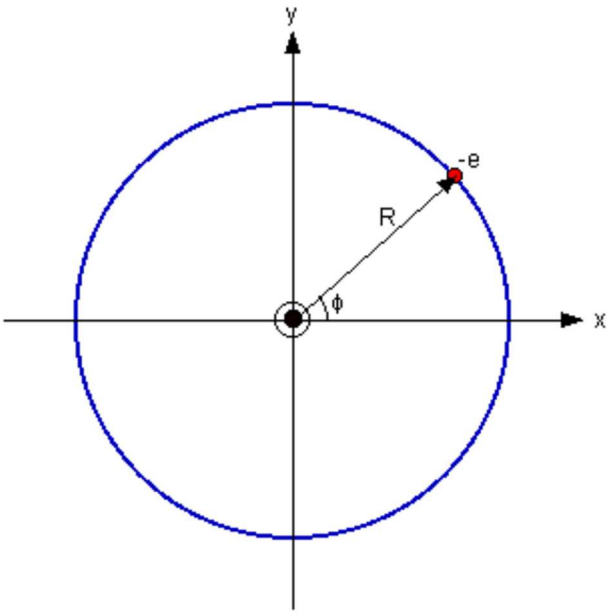


Fig.14 Circular conducting ring with radius R. The magnetic field $\boldsymbol{B}$ is located only at the center and is along the z axis (out of the page).

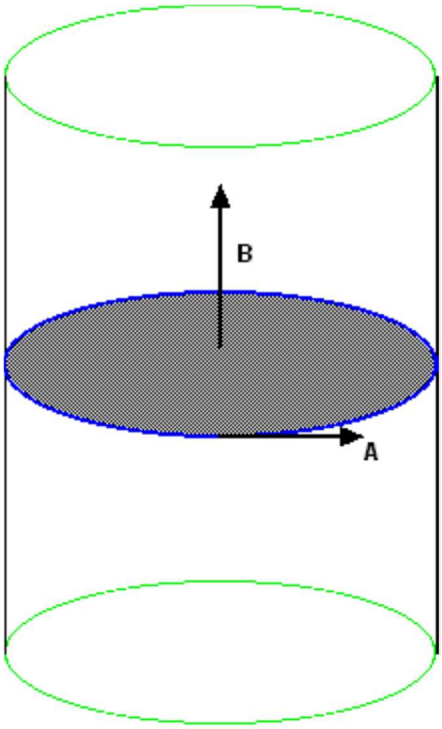


Fig.15 The vector potential $\boldsymbol{A}$ is along the $\boldsymbol{e}_\phi$ direction. The magnetic field is along the cylindrical axis (z axis) and is located only at the center of cylinder.

An electron is constrained to move on a 1D ring of radius R. At the center of the ring, there is a constant magnetic flux in the z direction. The magnetic flux through the surface bounded by the ring

$$\Phi = \oint (\nabla \times \mathbf{A}) \cdot d\mathbf{a} = \oint \mathbf{B} \cdot d\mathbf{a} .$$

Using Stoke's theorem,

$$\oint (\nabla \times \mathbf{A}) \cdot d\mathbf{a} = \oint \mathbf{A} \cdot d\ell = \oint \mathbf{B} \cdot d\mathbf{a} = \Phi .$$

From the azimuthal symmetry of the system, the magnitude of the azimuthal component of $\boldsymbol{A}$ must be the same everywhere along the path ($\rho = R$)

$$\mathbf{A} = \frac{\Phi}{2\pi R}\mathbf{e}_\phi . \tag{103}$$

Now we consider the Schrödinger equation for electron (q = -e) constrained to move on the ring, we have

$$\rho = R \text{ and } z = \text{constant}.$$

We use the new vector potential

$$\mathbf{A}' = \mathbf{A} + \nabla\chi = 0 ,$$

or

$$A_\phi' = A_\phi + \frac{1}{R}\frac{\partial}{\partial\phi}\chi = 0 ,$$

or

$$0 = \frac{\Phi}{2\pi R} + \frac{1}{R}\frac{\partial\chi}{\partial\phi} = 0 ,$$

or

$$\chi = -\frac{\Phi}{2\pi}\phi .$$

The Hamiltonian is given by

$$\hat{H} = \frac{1}{2m}(\hat{\mathbf{p}} + \frac{e}{c}\mathbf{A}')^2 = \frac{1}{2m}\hat{\mathbf{p}}^2 .$$

The Schrödinger equation is given by

$$\langle \mathbf{r}|\hat{H}|\psi'\rangle = E\langle \mathbf{r}|\psi'\rangle ,$$

or

$$\langle \mathbf{r}|\hat{H}|\psi\rangle = -\frac{\hbar^2}{2m}\frac{1}{R^2}\frac{\partial^2}{\partial\phi^2}\psi'(r) = E\psi'(r) ,$$

or

$$\frac{\partial^2}{\partial\phi^2}\psi'(r) = -\lambda^2\psi'(r) , \tag{104}$$

where

$$\lambda = \sqrt{\frac{2mE}{\hbar^2}R^2} . \tag{105}$$

Then the wave function is obtained as

$$\psi'(\phi) = \frac{1}{\sqrt{2\pi R}} e^{i\lambda\phi} . \tag{106}$$

The old wave function is related to the new wave function (q = -e, gauge transformation) by

$$\psi(\phi) = e^{-\frac{iq\chi}{c\hbar}} \psi'(\phi) = e^{-\frac{ie\Phi\phi}{2\pi c\hbar}} \frac{e^{i\lambda\phi}}{\sqrt{2\pi R}} = \frac{1}{\sqrt{2\pi R}} e^{i(\lambda - \frac{e\Phi}{2\pi c\hbar})\phi} . \tag{107}$$

From the periodic boundary

$$\psi(\phi + 2\pi) = \psi(\phi) , \tag{108}$$

we have

$$2\pi(\lambda - \frac{e\Phi}{2\pi c\hbar}) = -2n\pi \ \ (n\text{: integer}),$$

or

$$\lambda - \frac{e\Phi}{2\pi c\hbar} = -n . \tag{109}$$

Here we define the quantum fluxoid Φ_0 as

$$\Phi_0 = \frac{2\pi c\hbar}{2e} = 2.06783372 \text{ x } 10^{-7} \text{ Gauss cm}^2 \text{ (from the NIST Website}^{15}\text{)}$$

then we have

$$\lambda = \frac{\Phi}{2\Phi_0} - n .$$

Then the energy eigenvalue is obtained as

$$E = \frac{\hbar^2}{2mR^2}\left(\frac{\Phi}{2\Phi_0} - n\right)^2 . \tag{110}$$

The ground states depend on Φ (or $\Phi/2\Phi_0$). For $-1/2 \le \Phi/2\Phi_0 \le 1/2$, the minimum energy corresponds to n = 0. For $\Phi/2\Phi_0 \ge 1/2$, the energy with n = 0 is no longer the minimum energy. For $1/2 \le \Phi/2\Phi_0 \le 3/2$, the minimum energy corresponds to n = 1. For $3/2 \le \Phi/2\Phi_0 \le 5/2$, the minimum energy corresponds to n = 2. In general, for $(n-1)/2 \le \Phi/2\Phi_0 \le (n+1)/2$, the minimum energy corresponds to n. So the ground state is periodic in $\Phi/2\Phi_0$ as shown in Fig.16.

We now consider the current density $\boldsymbol{J}$ defined by (quantum mechanics)

$$\mathbf{J} = q[\frac{\hbar}{2mi}(\psi^*\nabla\psi - \psi\nabla\psi^*) - \frac{q}{mc}\mathbf{A}\psi^*\psi] , \tag{111}$$

where

$$\mathbf{A} = \frac{\Phi}{2\pi R}\mathbf{e}_\phi , \quad \psi(\phi) = \frac{1}{\sqrt{2\pi R}} e^{ia\phi} , \qquad \nabla\psi(\phi) = \mathbf{e}_\phi \frac{1}{\rho}\frac{\partial}{\partial\phi}\psi(\phi) ,$$

with

$$a = \lambda - \frac{e\Phi}{2\pi c\hbar} , \qquad \text{and} \qquad q = -e.$$

Then we have

$$\mathbf{J} = -e(\frac{\hbar a}{2\pi mR^2} + \frac{e\Phi}{4\pi^2 mcR^2})\mathbf{e}_\phi = -e[\frac{\hbar}{2\pi mR^2}(\lambda - \frac{e\Phi}{2\pi c\hbar}) + \frac{e\Phi}{4\pi^2 mcR^2}]\mathbf{e}_\phi$$

$$= -\frac{e\hbar\lambda}{2\pi mR^2}\mathbf{e}_\phi$$

or

$$J_\phi = \frac{e\hbar}{2\pi mR^2}(-\frac{\Phi}{2\Phi_0} + n). \tag{112}$$

This is compared with

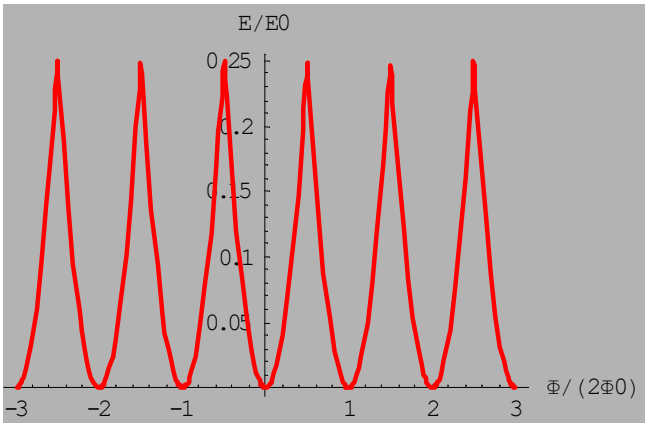
$$\frac{\partial E}{\partial \Phi} = \frac{\hbar^2}{mR^2}\frac{1}{2\Phi_0}(\frac{\Phi}{2\Phi_0} - n) = \frac{e\hbar}{2\pi mcR^2}(\frac{\Phi}{2\Phi_0} - n),$$

or

$$J_\phi = -c\frac{\partial E}{\partial \Phi} = \frac{e\hbar}{2\pi mR^2}(-\frac{\Phi}{2\Phi_0} + n).$$

7.3 Energy eigenvalues and persistent current density as a function of magnetic flux ((Mathematica 5.2))

```
(*Ground state energy vs magnetic flux*)
 f[x_] := x^2; a[x_] := f[x] /; -1/2 ≤ x ≤ 1/2; a[x_] := a[x - 1] /; x > 1/2;
 a[x_] := a[x + 1] /; x < -1/2;
 Plot[a[x], {x, -3, 3}, PlotStyle → Hue[0], Background → GrayLevel[0.7],
  Prolog → AbsoluteThickness[2], AxesLabel → {"Φ/(2Φ0)", "E/E0"}]
```




```
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 (*Current vs magnetic flux*)
 g[x_]:=-x;b[x_]:=g[x]/;-1/2≤x≤1/2;b[x_]:=b[x-
1]/;x>1/2;b[x_]:=b[x+1]/;x<-1/2;Plot[b[x],{x,-
3,3},PlotStyle→Hue[0],Background→GrayLevel[0.7],Prolog→Abso
luteThickness[2],AxesLabel→{"Φ/(2Φ0)","Jφ/J0"}]
```

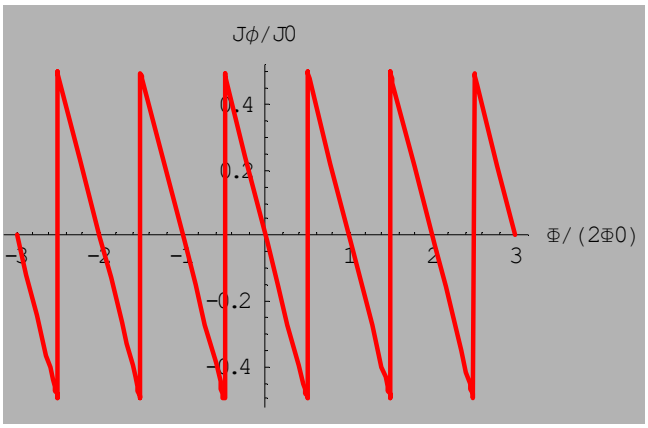

-Graphics-

Fig.16 The energy eigenvalue E/E_0 as a function of $\Phi/(2\Phi_0)$. $E_0 = \hbar^2/2mR^2$.

Fig.17 The persistent current density J_ϕ/J_0 as a function of $\Phi/(2\Phi_0)$. $J_0 = e\hbar/2\pi mR^2$.

8 Conclusion

We have discussed the energy spectrum of the Bloch electrons in a periodic potential. The energy spectrum consists of energy band and energy gap. The difference between the metals and insulators are understood in terms of this concept. The system behaves as an insulator if the allowed energy bands are either filled or empty, and as a metal if the bands are partly filled.

Appendix

Mathematica 5.2 program (see Sec. 5.3) for the Eigenvalue problem for the system with U_G, U_{2G}, U_{3G}, U_{4G}, U_{5G}, and U_{6G} is attached for the convenience.

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