Bloch electron in a periodic potential of quantum box

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We discuss the energy band of conduction electron (spin 1/2 fermion) in metal, which is one-dimensional. In a quantum box with a well potential, the wave number of electrons becomes discrete due to the Heisenberg's principle of uncertainty. The energy dispersion of electrons is quantized. In a real metal, the electrons are not completely free but move in a weak periodic potential due to atoms in the unit cells of lattice. These electrons are called Bloch electrons. For a monovalent metal, there is one electron per unit cell, contributing to Bloch electrons. For a divalent metal, there are two electron per unit cell. The energy dispersion of the Bloch electrons is periodic as a function of wave number with the periodicity of the reciprocal lattice, forming an energy band. The energy gap is formed at the boundary of the Brillouin zone, as a result of the Bragg reflection of electrons. The electrons are fermions and obey the Pauli's exclusion principle. All the states below the Fermi energy are occupied by electrons at $T = 0$ K. If the number of electrons per unit cell is even, the Fermi energy coincides with the energy gap. The system becomes insulator. If the number of electrons per unit cell is odd, the Fermi energy is not equal to energy gap. The system is still metallic.

Felix Bloch

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.)."

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.

1. Energy dispersion for free electron

Electrons are quantum mechanical particles (fermions). They behave like a particle as well as a wave. The momentum p (= mv) of the electron is related to the Broglie wavelength λ as

$$p = \frac{h}{\lambda} = \hbar k ,$$

where k $(= \frac{2\pi}{\lambda})$ is the wave number, h is the Planck constant and $\hbar$ is the Dirac constant $(\hbar = \frac{h}{2\pi})$. The energy E of electron is given by the energy dispersion

$$\varepsilon_k = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m},$$

in a free space, where k is the wave number and k is continuous.

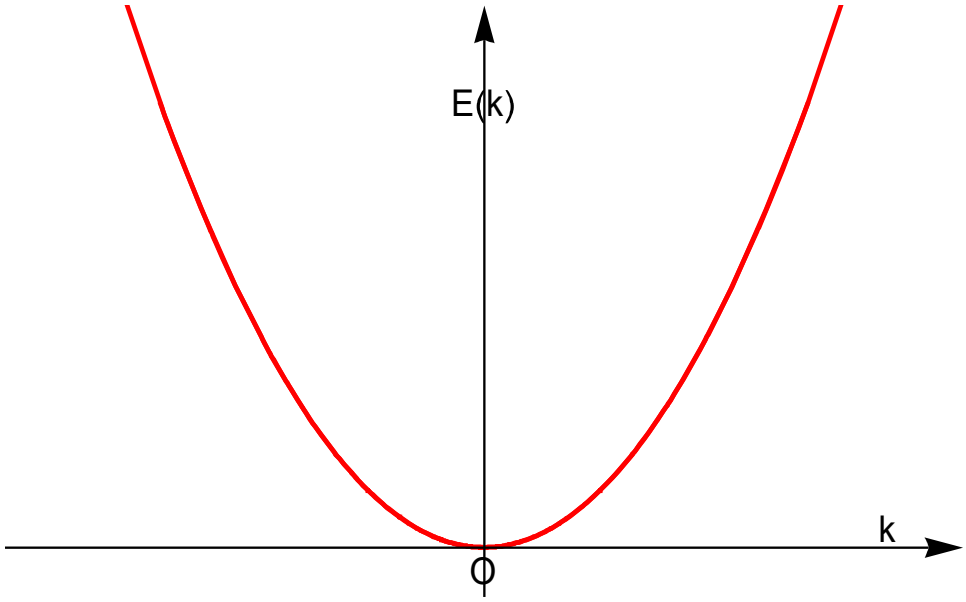


Fig. Plot of energy versus wavenumber for a free electron, where k is the wave number and is continuous.

2. Quantum box: Heisenberg's principle of uncertainty

We consider a free electron gas in 1D system. The Schrödinger equation is given by

$$H\psi_k(x) = \frac{p^2}{2m}\psi_k(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi_k(x)}{dx^2} = \varepsilon_k\psi_k(x) , \qquad (1)$$

where

$$p = \frac{\hbar}{i}\frac{d}{dx},$$

and ε_k is the energy of the electron in the orbital.

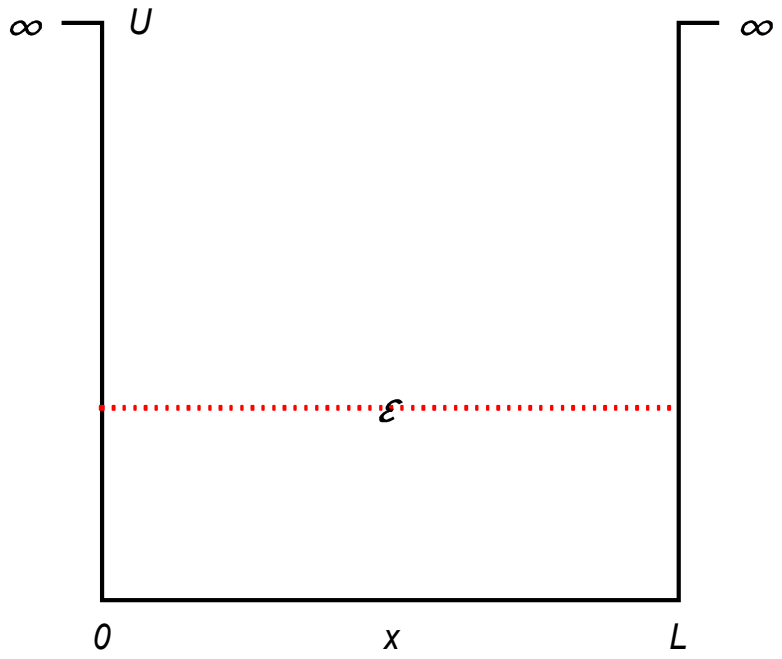


Fig. Electrons in a well-potential with size L. The potential is infinity outside the box. The determination of the energy eigenvalue of such an electron by using Schrödinger equation is called the quantum box problem.

The orbital is defined as a solution of the wave equation for a system of only one electron: ⟨⟨one-electron problem⟩⟩. Using a periodic boundary condition: $\psi_k(x+L) = \psi_k(x)$, we have

$$\psi_k(x) \sim e^{ikx}, \qquad (2)$$

with

$$\varepsilon_k = \frac{\hbar^2}{2m}k^2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}n\right)^2,$$

$$e^{ikL} = 1$$

or

$$k = \frac{2\pi}{L} n$$

where k has a discrete value

$$\Delta k = \frac{2\pi}{L}$$

The energy dispersion is essentially the same as that of free electron. However, the energy level is quantized, since the wave number becomes discrete.

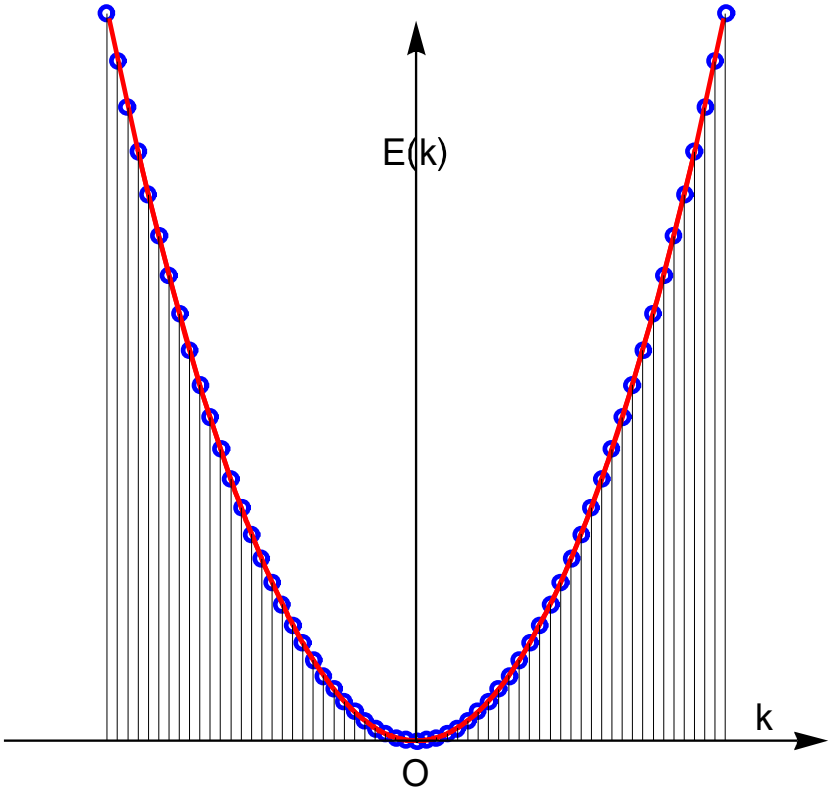


Fig. Energy dispersion curve for the electron in a quantum box.

The wave number is no longer continuous. It takes discrete values of k whose division is given by

$$\Delta k = \frac{2\pi}{L},$$

or

$$k_x = \frac{2\pi}{L} n_x \qquad (n = 0, \pm 1, \pm 2, \pm 3, \ldots)$$

((**Heisenberg's uncertainty of principle**))

The discreteness of the wave number is derived from the Heisenberg's principle of uncertainty.

$$\Delta x \Delta k \approx 2\pi$$

When $\Delta x = L$, we have

$$\Delta k = \frac{2\pi}{L}.$$

((The Pauli's exclusion principle))

The one-electron levels are specified by the wavevectors k and by the projection of the electron's spin along an arbitrary axis, which can take either of the two values $\pm\hbar/2$. Therefore associated with each allowed wave vector k are two levels:

$$|k,\uparrow\rangle, |k,\downarrow\rangle.$$

3. Periodic potential: Bloch theorem

In metals, there are many atoms. They are periodically arranged, forming a lattice with the lattice constant a. We consider conduction electron in the presence of periodic potential (due to a Coulomb potential of positive ions). The electrons undergo movements under the periodic potential as shown below. Such electrons are called the Bloch electrons. According to Bloch, the wave function of the Bloch electrons can be expressed by

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

where $u_k(x)$ is a periodic function of x with the periodicity a,

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

So we have

$$\psi_k(x+a) = e^{ik(x+a)}u_k(x+a) = e^{ika}e^{ikx}u_k(x) = e^{ika}\psi(x)$$

Note that the wave function satisfies the boundary condition

$$\psi_k(x+L) = e^{ikL}\psi(x) = \psi(x)\,.$$

since $e^{ikL} = 1$. We note that $u_k(x)$ can be expressed

$$u_k(x) = \sum_G u_{k-G}\exp(-iGx)\,,$$

by using the Fourier series, where G is the reciprocal lattice

$$G = \frac{2\pi}{a}n \qquad (n \text{ is integer}).$$

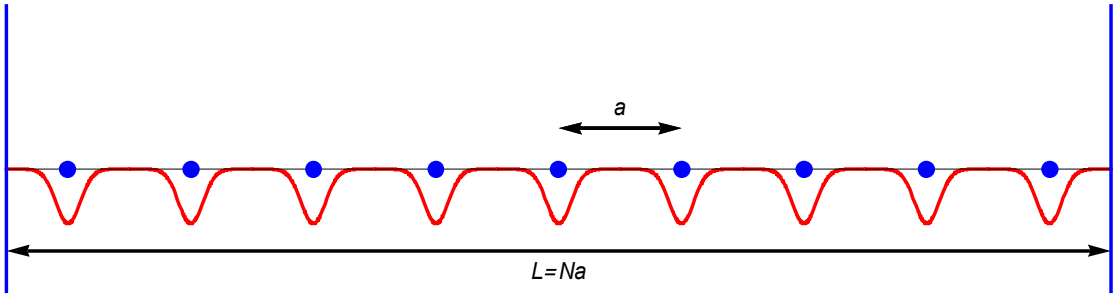


Fig. Periodic lattice of lattice constant a. The form of potential energy of an electron in a one-dimensional lattice The positions of the ion cores are indicated by the points (blue solid circles) with the separation a (lattice constant).

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 $\psi_k(x)$,

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

So the energy eigenvalue of $\psi_{k+G}(x)$ is the same as that of $\psi_k(x)$, leading to the periodicity of E_k as

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

We also note that the relation $\varepsilon_k = \varepsilon_{-k}$ is always valid, whether or not the system is centro-symmetric. Then the energy dispersion of ε_k vs k can be obtained by the superpositionof the curve of E_{k+G} vs k with G changed as a parameter.

$$\varepsilon_{k+G} = \frac{\hbar^2}{2m}(k+G)^2$$

Since

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

the value of k is chosen as

$$-\frac{\pi}{a} \le k \le \frac{\pi}{a}, \qquad \text{(the first Brillouin zone)}$$

or

$$-\frac{N}{2} \le n \le \frac{N}{2}, \qquad \text{(the total number is } N\text{, the number of unit cell).}$$

The energy dispersion thus obtained is shown in the Fig. as shown below.

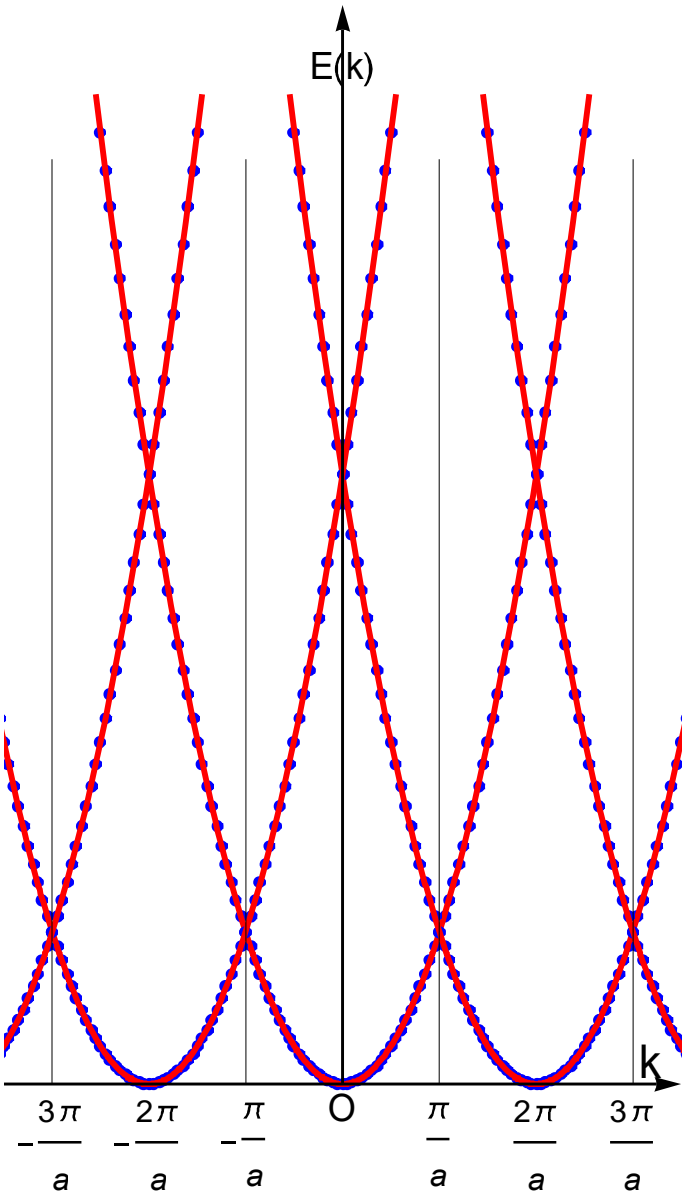
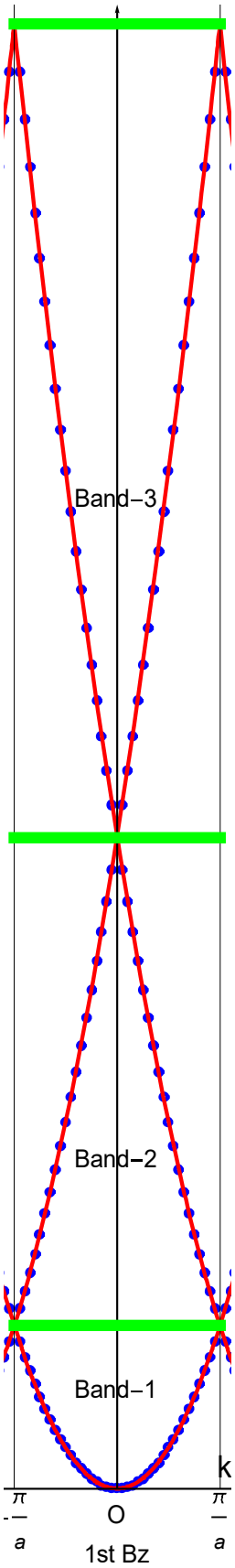


Fig. The parabolic energy curves of a free electron in one dimension, periodically continued in reciprocal space. The periodicity in real space is a periodic lattice with a vanishing periodic potential (empty lattice). The first Brillouin zone (

The energy vs k consists of branches denoted by the number of band (band-1, band-2, band-3,…) in the first Brillouin zone. As we discuss later, there are energy gaps between adjacent bands.


Band−3
Band−2
Band−1
K
π
a
O
π
a
1st Bz

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_cN.

(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. Bragg reflection at the boundary of the Brillouin zone

Just like x-ray, the electrons undergoes a Bragg reflection under the condition of

$$\Delta k = k' - k = G .$$

This can occurs when

$$k = \frac{\pi}{a} \text{ and } k' = -\frac{\pi}{a} \text{ (boundary of the Brillouin zone)}$$

where G is the reciprocal lattice,

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

As a result of the Bragg reflection, one can find a standing wave, leading to the energy gap at the boundary of the first Brillouin zone. We note that the magnitude of the energy gap can be evaluated from the time-dependent perturbation with the degenerate system. In the unperturbed system, the two independent states $\left| k = \frac{\pi}{a} \right\rangle$ and $\left| k' = -\frac{\pi}{a} \right\rangle$ are degenerate in energy. In the presence of weak perturbation due to the Fourier component of a periodic potential, these two states are combined into two different state with different energy. The difference of the energy leads to the energy gap.

1D system:

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

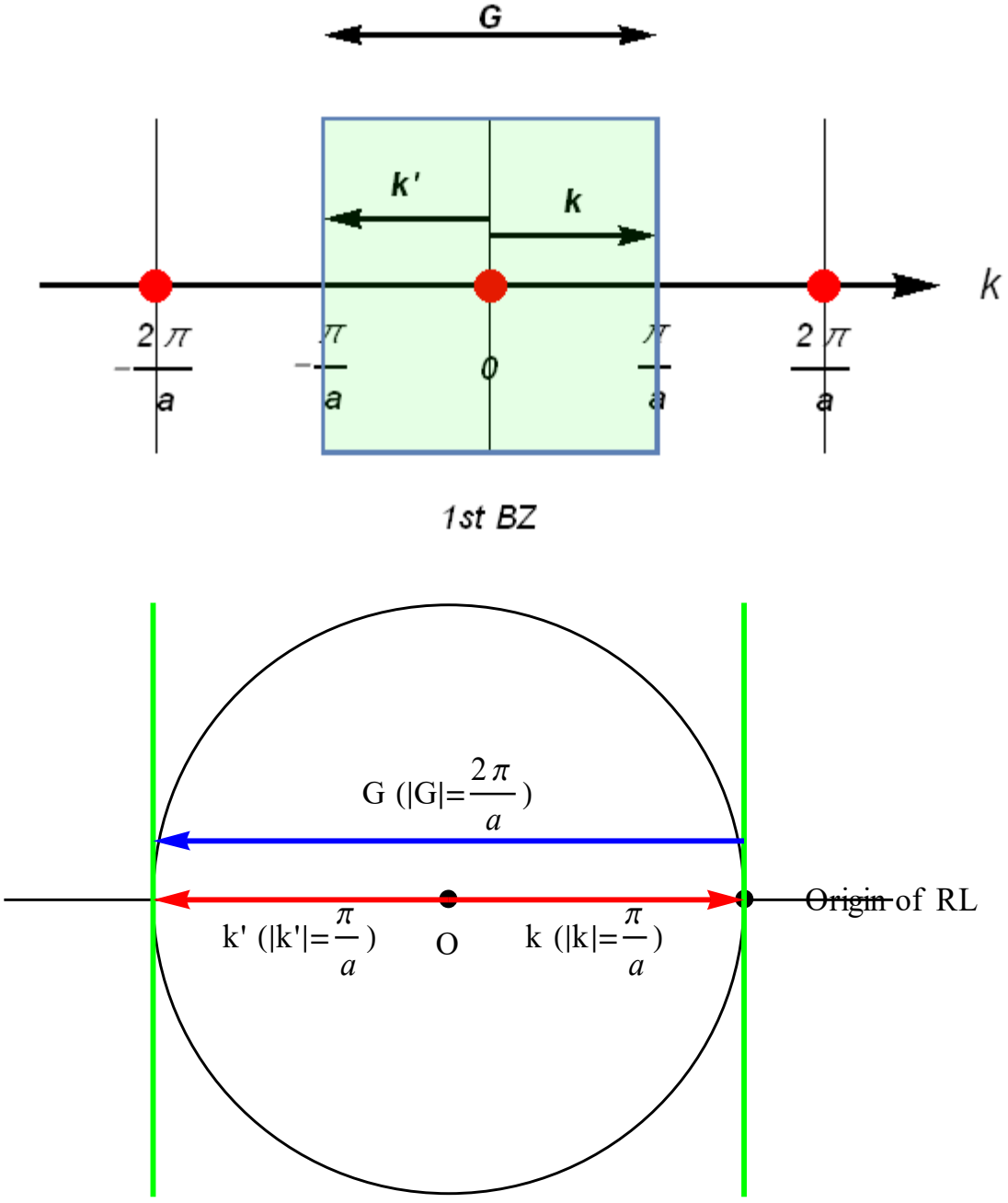


Fig. Condition of the Bragg reflection for the 1D case. $|k| = |k - G|$. $G = 2\pi/a$. $k' = k - G$.

5. The zone scheme of energy band

There are several zone schemes of energy band

(a) Extended zone scheme.
(b) Reduced zone scheme.
(c) Periodic zone scheme.

These three schemes are equivalent because of the two features,

$$\varepsilon_{k+G} = \varepsilon_k , \qquad \varepsilon_{-k} = \varepsilon_k$$

for the Bloch electrons.

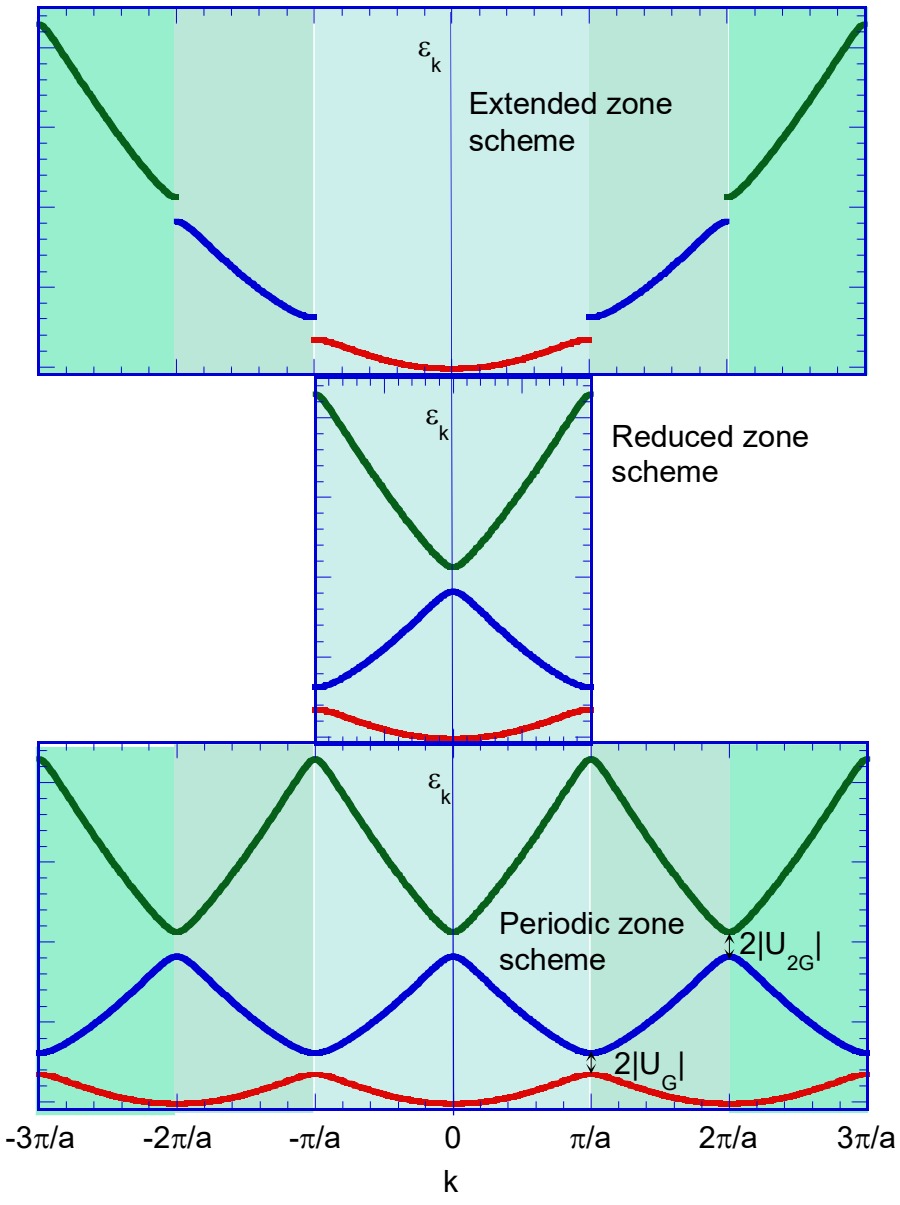


Fig. Three zone schemes for the 1D system. Extended zone scheme. Reduced zone scheme. Periodic zone scheme.

6. Occupied states below Fermi energy

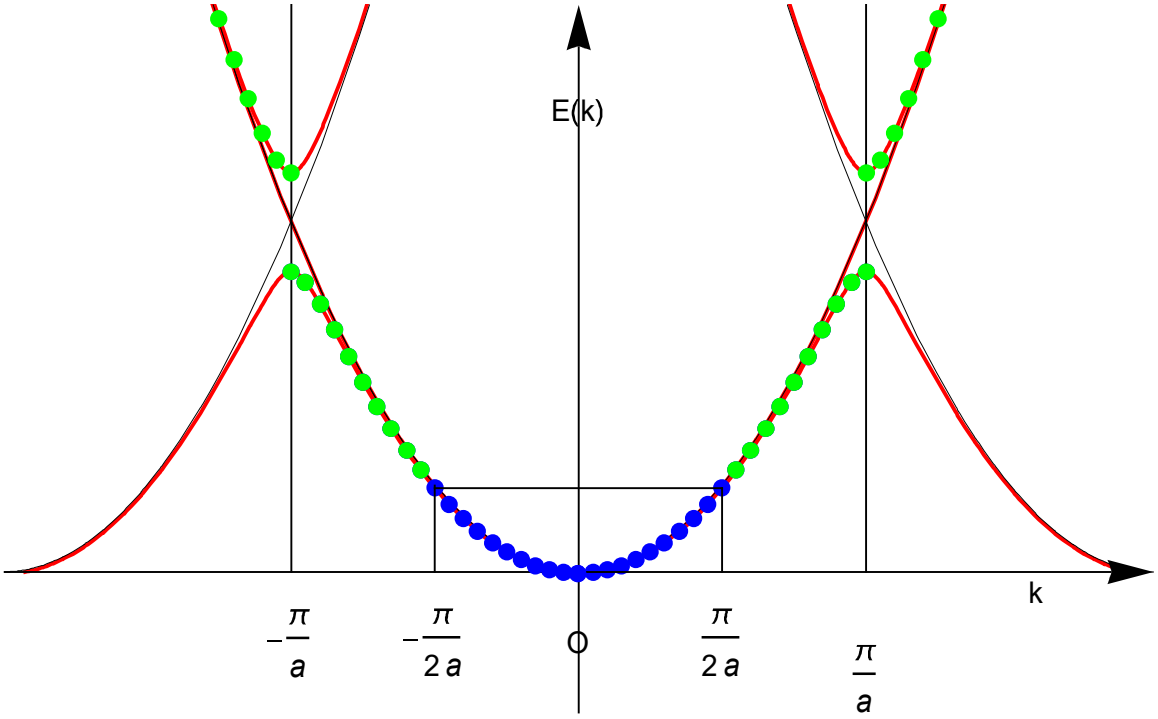


Fig. Half filled energy band (first Brillouin zone). Band-1 (in the first Brillouin zone) and band-2. The total number of states is $2N$ states for the first Brillouin zone when the system consists of N unit cells.

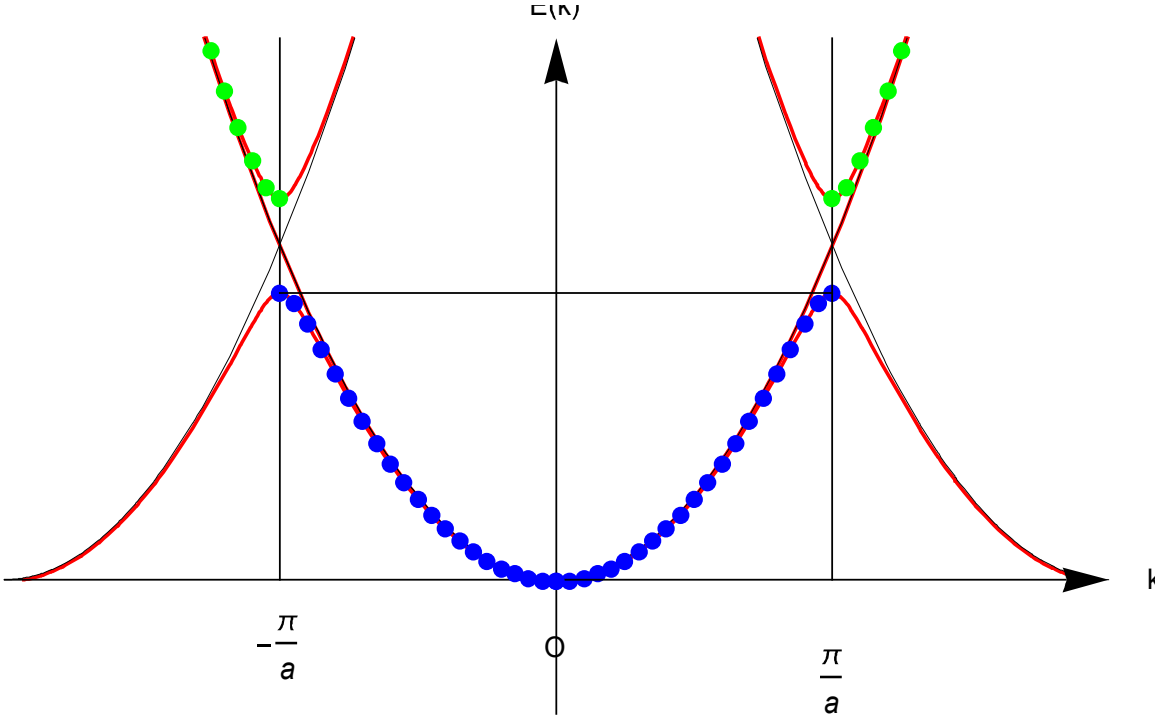


Fig. Energy band with $2N$ filled states (full filled state) in the first Brillouin zone. The $2N$ states are allowed in the first Brillouin zone. The energy gap is associated with the Bragg reflection at the boundary of the first Brillouin zone $k = \pm\frac{\pi}{a}$.

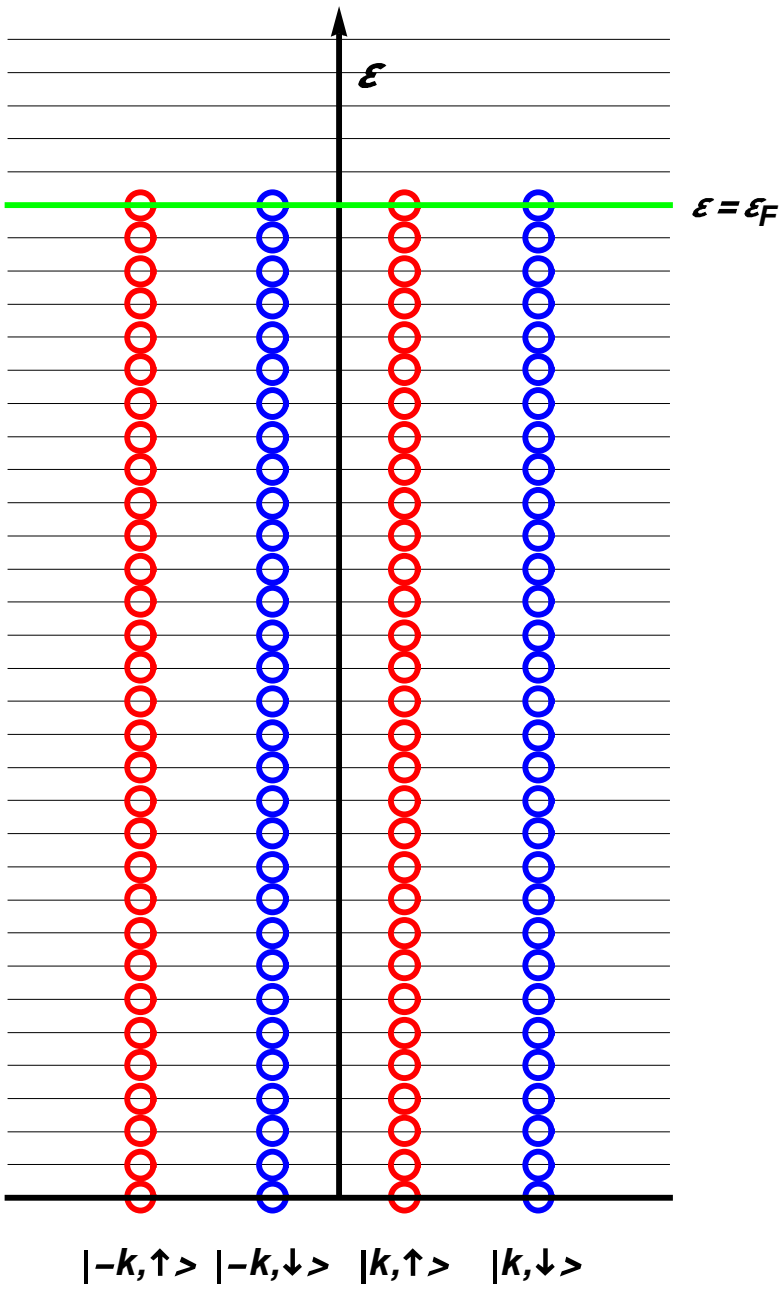


Fig. Occupation of energy states below the Fermi energy.

7. Metal and insulator

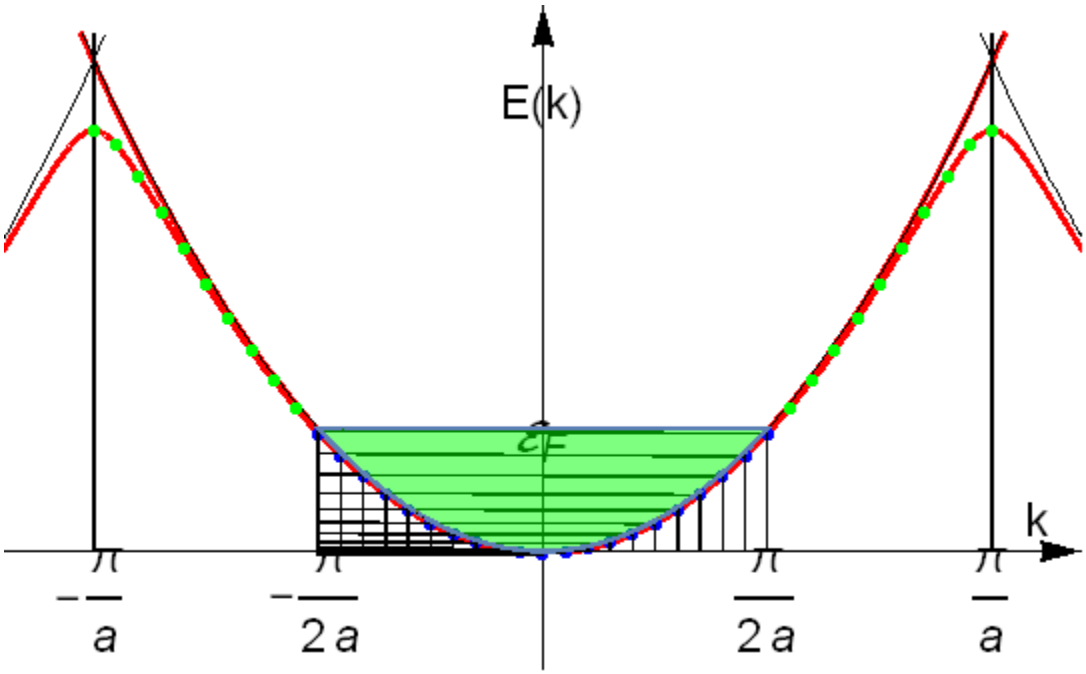
N is the number of unit cell. The size of the system is $L = Na$, where a is the lattice constant. The number of states in the Brillouin zone is equal to 2N, where the factor 2 comes from the spin 1/2.

Suppose that there is one conduction electron per atom. In this case there are N electrons. Since there are $2N$ states in the first Brillouin zone, a half of states in the Brillouin zone are occupied.

When there is one conduction electron per atom. In this case there are N electrons. Since there are $2N$ states in the first Brillouin zone, a half of states in the Brillouin zone are occupied. So the system is metallic.

When there are two conduction electrons per atom. In this case there are $2N$ electrons. Since there are $2N$ states in the first Brillouin zone, all states in the first Brillouin zone are occupied. The system is insulator.

When there are three conduction electrons per atom. In this case there are $3N$ electrons. Since there are $2N$ states in the first Brillouin zone, all states in the first band are occupied. A half of the states in the second band are occupied by the remaining electrons. The system is metallic.



8. Charge density wave: Peierls Instability

(a) Regular lattice

Suppose that the system consists of N atoms, forming a linear chain along the x direction. They are periodically arranged such that the distance between the nearest neighbor atoms is a. The size of the system is $L = Na$.

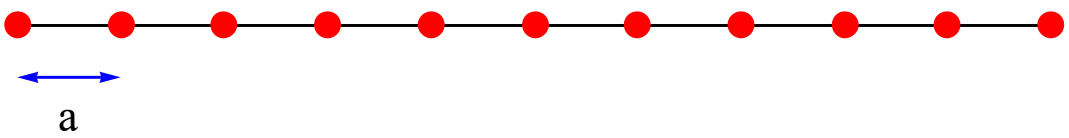


Fig. One dimensional chain of atoms where the nearest neighbor distance is a.

The energy gap appears at the Brillouin zone boundary ($k = \pm\frac{\pi}{a}$). The energy gap is fixed at this reciprocal lattice point. In this case there are $2N$ states for the first Brillouin zone ($|k| \le \frac{\pi}{a}$). The factor 2 comes from the spin of electrons. When each atom has two electrons, there are $2N$ electrons in the system. Then the band is filled up to the Brillouin zone (insulator). When each atom has one electrons, there are N electrons in the system. Then the band is half-filled in the energy band (metal).

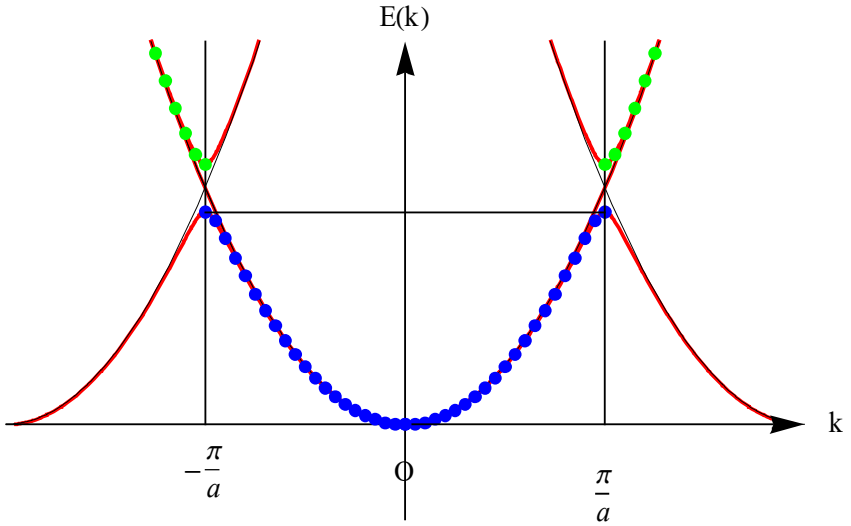


Fig. Energy band for the system where there are two electrons per atom. All states are occupied up to the zone of the Brillouin zone (insulator)

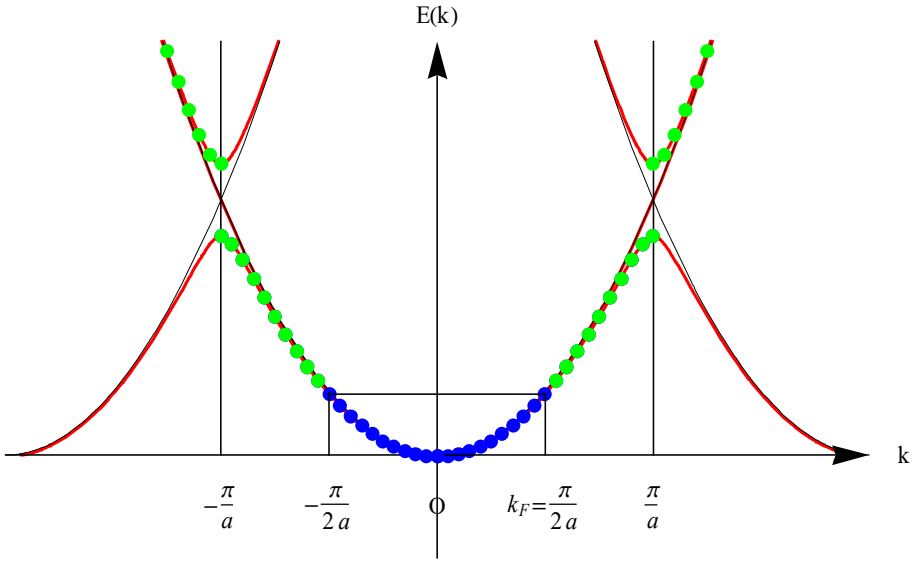


Fig. Energy band for the system with one electron per atom. All states are occupied for $|k|<k_F$ ($= \pi/a$) in the Brillouin zone (metal)

(b) Effect of lattice distortion

We still assume that there is one electron per atom in the linear chain. Now let us displace every second atom by a small distance δ.

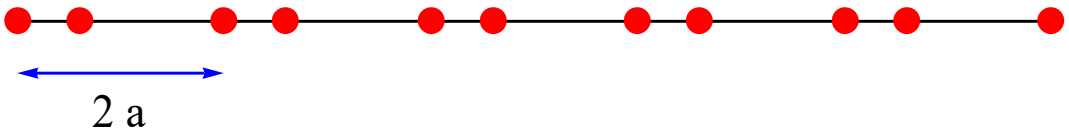


Fig. Lattice constant changes from a to $2a$ due the lattice distortion.

This reduces the symmetry to that of a chain with spacing $2a$, and the potential acquires a Fourier component of wave number π/a which in this case is equal to $2k_F$. This results in an energy gap at $k = k_F = \pi/2a$, in accordance with the change in the periodicity from a to 2a. In this case, all states raised by the change are empty, and all states lowered are occupied, so the system becomes insulator.

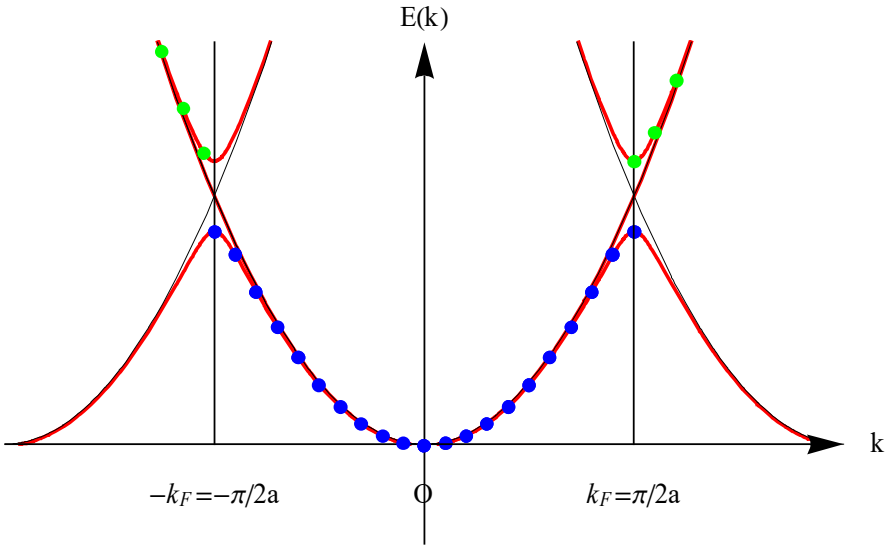


Fig. Energy band for the system with one electron per atom, after the lattice distortion. The energy gap appears at $k=k_F = \pm\pi/2a$. The system changes from metal to insulator (Peierls instability).

REFERENCES

S.L. Altman, Band Theory of Metals (Pergamon, 1970)

C. Kittel, Introduction to Solid State Physics 8-th edition (John Wiley and Sons, 2005).