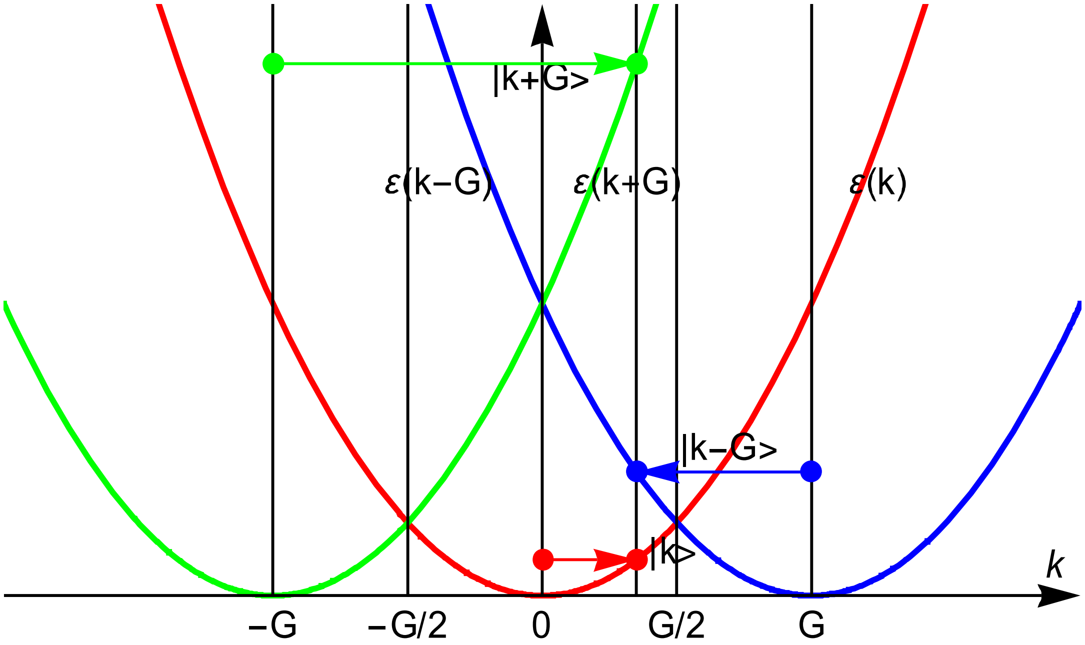
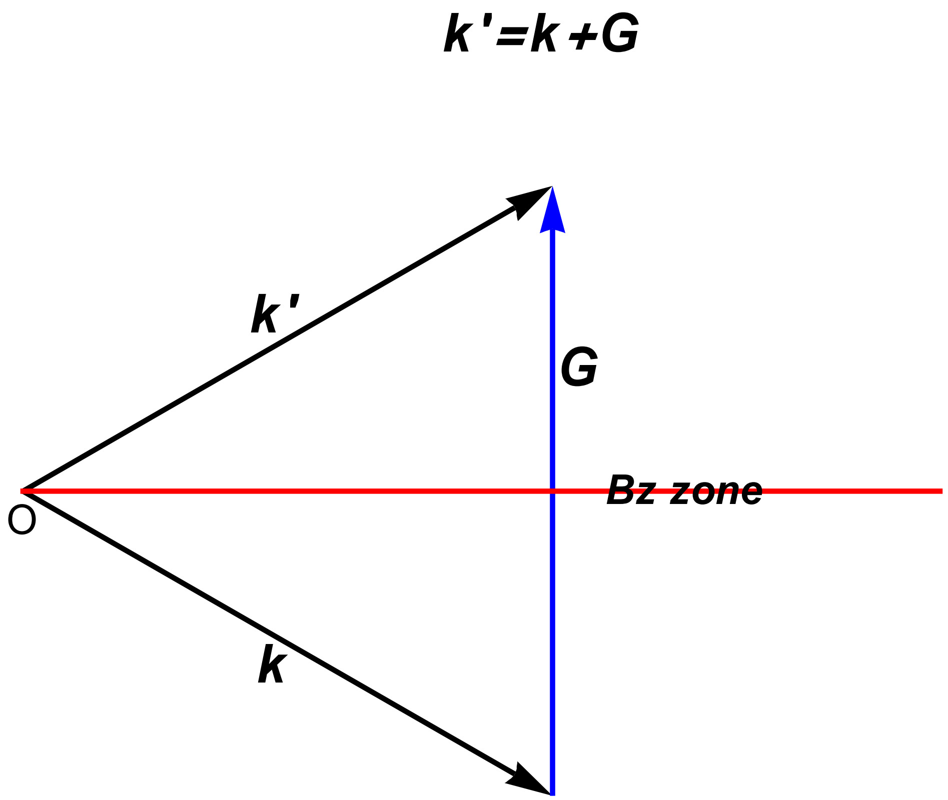
Nearly free electron model; perturbation

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
(Date: March 23, 2018)

In general, the wave function of conduction electrons can be expressed by a plane wave state $|\boldsymbol{k}\rangle$ with the wave function $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ in a periodic potential. Only when the Bragg condition $\boldsymbol{k}' = \boldsymbol{k} \pm \boldsymbol{G}$ is satisfied, the electron wave is reflected and changed into a reflected wave state $|\boldsymbol{k}'\rangle$ with the wave function $e^{i\boldsymbol{k}'\cdot\boldsymbol{r}}$, where G is the reciprocal lattice vector. The combination of the incident plane wave and the reflected plane wave leads to the standing wave. Here we consider a very simple model (nearly free electron model) in order to understand the fundamental property of the energy gap at the zone boundary. Here we consider a very simple model (nearly free electron model) in order to understand the fundamental property of the energy gap at the zone boundary.

1. Introduction





$$\boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{G}, \qquad |\boldsymbol{k}'| = |\boldsymbol{k}|$$

leading to the Bragg condition

$$\boldsymbol{G} \cdot (\boldsymbol{k} + \frac{\boldsymbol{G}}{2}) = 0 .$$

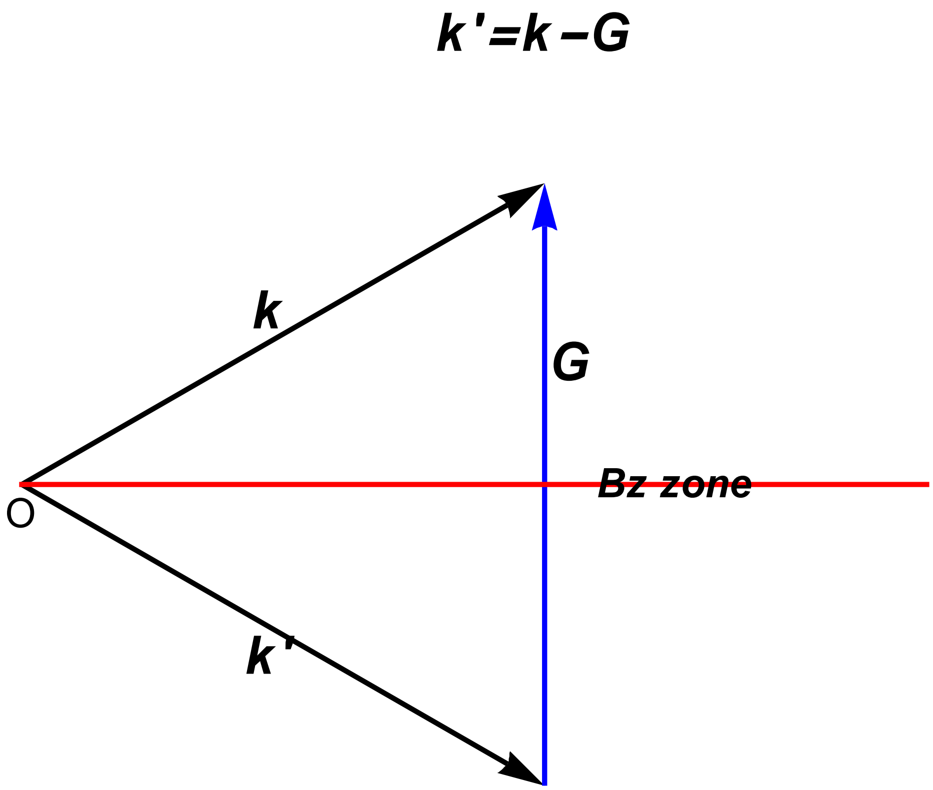


Fig. The energy dispersion curves for $\varepsilon_k^{(0)}$ and $\varepsilon_{k-G}^{(0)}$. (i) $k = \frac{G}{2}$ (denoted by green line), $\varepsilon_k^{(0)} = \varepsilon_{k-G}^{(0)}$ (degenerate case, independent states with the same energy). (ii) $k \neq \frac{G}{2}$ (denoted by blue line) $\varepsilon_k^{(0)} \neq \varepsilon_{k-G}^{(0)}$ (non-degenerate case).

$$\varepsilon_k^{(0)} = \frac{\hbar^2}{2m} k^2$$

G is the reciprocal lattice;

$$G = \frac{2\pi}{a}.$$

Here we assume a periodic potential (perturbation)

$$V = \sum_G V_G e^{iGx}$$

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

$|k\rangle$ with energy $\varepsilon_k^{(0)} = \frac{\hbar^2}{2m} k^2$

We consider

$|k - G\rangle$ with energy $\varepsilon_k^{(0)} = \frac{\hbar^2}{2m} (k - G)^2$

2. Non-degenerate case

For the non-degenerate case, there are two independent states with different energies. We apply the perturbation to the non-degenerate case. Thus we get the perturbed energy as

$$\varepsilon_k = \varepsilon_k^{(0)} + \langle k|V|k\rangle + \frac{\langle k-G|V|k\rangle}{\varepsilon_k^{(0)} - \varepsilon_{k-G}^{(0)}} + \frac{\langle k+G|V|k\rangle}{\varepsilon_k^{(0)} - \varepsilon_{k+G}^{(0)}} + \cdots$$

$$\varepsilon_{k-G} = \varepsilon_{k-G}^{(0)} + \langle k-G|V|k-G\rangle + \frac{\langle k|V|k-G\rangle}{\varepsilon_{k-G}^{(0)} - \varepsilon_k^{(0)}} + \frac{\langle k+G|V|k-G\rangle}{\varepsilon_{k-G}^{(0)} - \varepsilon_{k+G}^{(0)}} + \cdots$$

Here we note that

$$\langle k|V|k\rangle = V_0, \qquad \langle k-G|V|k-G\rangle = V_0$$

$$\langle k-G|V|k\rangle = V_G, \quad \langle k+G|V|k\rangle = V_{-G} = V_G{}^*$$

One of the eigen energies is

$$\begin{aligned}\varepsilon_k &= \varepsilon_k^{(0)} + V_0 + \frac{V_G}{\varepsilon_k^{(0)} - \varepsilon_{k-G}^{(0)}} + \frac{V_G{}^*}{\varepsilon_k^{(0)} - \varepsilon_{k+G}^{(0)}} + \cdots \\ &\approx \varepsilon_k^{(0)} + V_0 + \frac{V_G}{\varepsilon_k^{(0)} - \varepsilon_{k-G}^{(0)}}\end{aligned}$$

The corresponding eigenstate is

$$\begin{aligned}|\psi_k\rangle &= |k\rangle + \frac{1}{\varepsilon_k^{(0)} - \varepsilon_{k-G}^{(0)}} |k-G\rangle\langle k-G|V|k\rangle \\ &= |k\rangle + \frac{V_G}{\varepsilon_k^{(0)} - \varepsilon_{k-G}^{(0)}} |k-G\rangle\end{aligned}$$

Another eigen energy is

$$\varepsilon_{k-G} = \varepsilon_{k-G}^{(0)} + V_0 + \frac{V_G{}^*}{\varepsilon_{k-G}^{(0)} - \varepsilon_k^{(0)}} + \frac{V_{2G}{}^*}{\varepsilon_{k-G}^{(0)} - \varepsilon_{k+G}^{(0)}} + \cdots$$
$$\approx \varepsilon_{k-G}^{(0)} + V_0 + \frac{V_G{}^*}{\varepsilon_{k-G}^{(0)} - \varepsilon_k^{(0)}}$$

The corresponding eigen state is

$$|\psi_{k-G}\rangle = |k-G\rangle + \frac{1}{\varepsilon_{k-G}^{(0)} - \varepsilon_k^{(0)}} |k\rangle\langle k|V|k-G\rangle$$
$$= |k-G\rangle + \frac{V_G{}^*}{\varepsilon_{k-G}^{(0)} - \varepsilon_k^{(0)}} |k\rangle$$

3. Degenerate case

As indicated above, if $|\boldsymbol{k}\rangle$ and $|\boldsymbol{k}-\boldsymbol{G}\rangle$ are still independent states but degenerate in energy,

$$\varepsilon_{\boldsymbol{k}}^{(0)} - \varepsilon_{\boldsymbol{k}-\boldsymbol{G}}^{(0)} \approx 0$$

the expansion (non-degenerate case)mis no longer applicable. Note that the condition is expressed by

$$\varepsilon_{\boldsymbol{k}}^{(0)} - \varepsilon_{\boldsymbol{k}-\boldsymbol{G}}^{(0)} = 0$$

or

$$\boldsymbol{k}^2 = (\boldsymbol{k}-\boldsymbol{G})^2$$

which leads to the Bragg condition.

$$2\boldsymbol{k}\cdot\boldsymbol{G} = \boldsymbol{G}^2$$

We consider the two independent states with the same energy

$$|\boldsymbol{k}\rangle \text{ and } |\boldsymbol{k}-\boldsymbol{G}\rangle$$

with

$$\varepsilon_{\boldsymbol{k}}^{(0)} = \varepsilon_{\boldsymbol{k}-\boldsymbol{G}}^{(0)} = \varepsilon^0$$

The matrix element of the perturbation based on the two states $|\boldsymbol{k}\rangle$ and $|\boldsymbol{k}-\boldsymbol{G}\rangle$ is given by the 2 x 2 matrix

$$\hat{V} = \begin{pmatrix} \langle k|V|k\rangle & \langle k-G|V|k\rangle \\ \langle k|V|k-G\rangle & \langle k-G|V|k-G\rangle \end{pmatrix} = \begin{pmatrix} V_0 & V_G \\ {V_G}^* & V_0 \end{pmatrix}$$

Following the perturbation theory from quantum mechanics, we solve the eigenvalue problems as follows.

$$\hat{V}|\phi\rangle = \varepsilon^{(1)}|\phi\rangle$$

where

$$|\phi\rangle = C(k)|k\rangle + C(k-G)|k-G\rangle = \begin{pmatrix} C(k) \\ C(k-G) \end{pmatrix}$$

Thus we get

$$\begin{pmatrix} V_0 & V_G \\ {V_G}^* & V_0 \end{pmatrix}\begin{pmatrix} C(k) \\ C(k-G) \end{pmatrix} = \varepsilon^{(1)}\begin{pmatrix} C(k) \\ C(k-G) \end{pmatrix}$$

We assume that $V_G = -V$ with $V>0$ for simplicity, without losing any generality. The negative V_G means the attractive potential. We solve this problem using the Pauli matrix,

$$\begin{aligned} \hat{V} &= \begin{pmatrix} V_0 & -V \\ -V & V_0 \end{pmatrix} \\ &= V_0\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - V\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ &= V_0\hat{1} - V\hat{\sigma}_x \end{aligned}$$

We note that

$$\hat{\sigma}_x|+x\rangle = |+x\rangle. \qquad \hat{\sigma}_x|-+x\rangle = -|-x\rangle$$

where

$$|+x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}, \qquad |-x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Thus we get

$$\hat{V}|+x\rangle = \left(V_0\hat{1} - V\hat{\sigma}_x\right)|+x\rangle = (V_0 - V)|+x\rangle|$$

$$\hat{V}|-x\rangle = \left(V_0\hat{1} - V\hat{\sigma}_x\right)|-x\rangle = (V_0 + V)| - x\rangle|$$

So we have

(a) Lower energy eigenvalue: $\varepsilon^0 + V_0 - V$. eigenstate $|\phi_l\rangle = |+x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$

When $V_0 = 0$, the energy is lower than the energy of free electron because of the attractive potential.

(b)Higher energy eigenvalue: $\varepsilon^0 + V_0 + V$. eigenstate $|\phi_u\rangle = |-x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$

When $V_0 = 0$, the energy is higher than the energy of free electron.

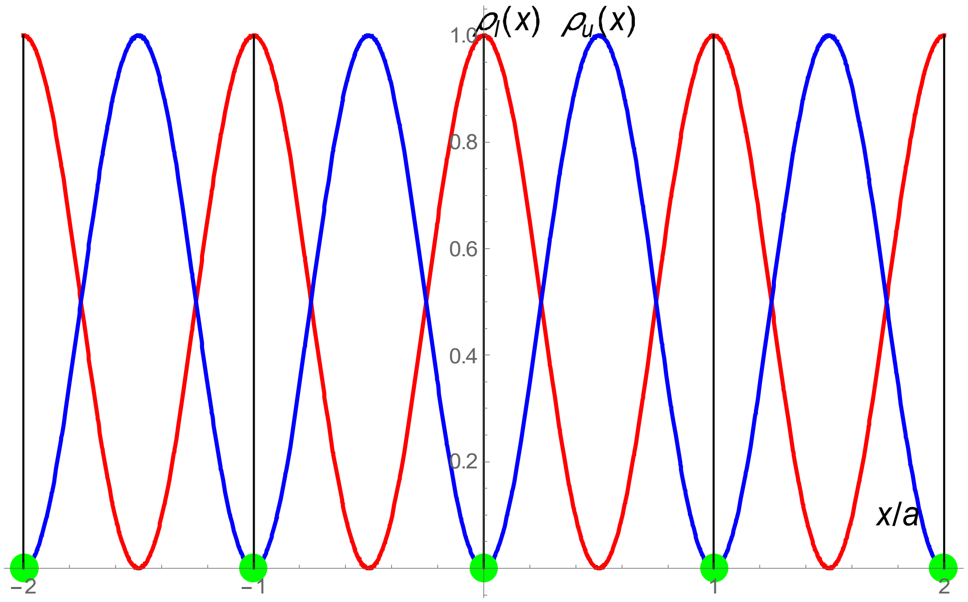
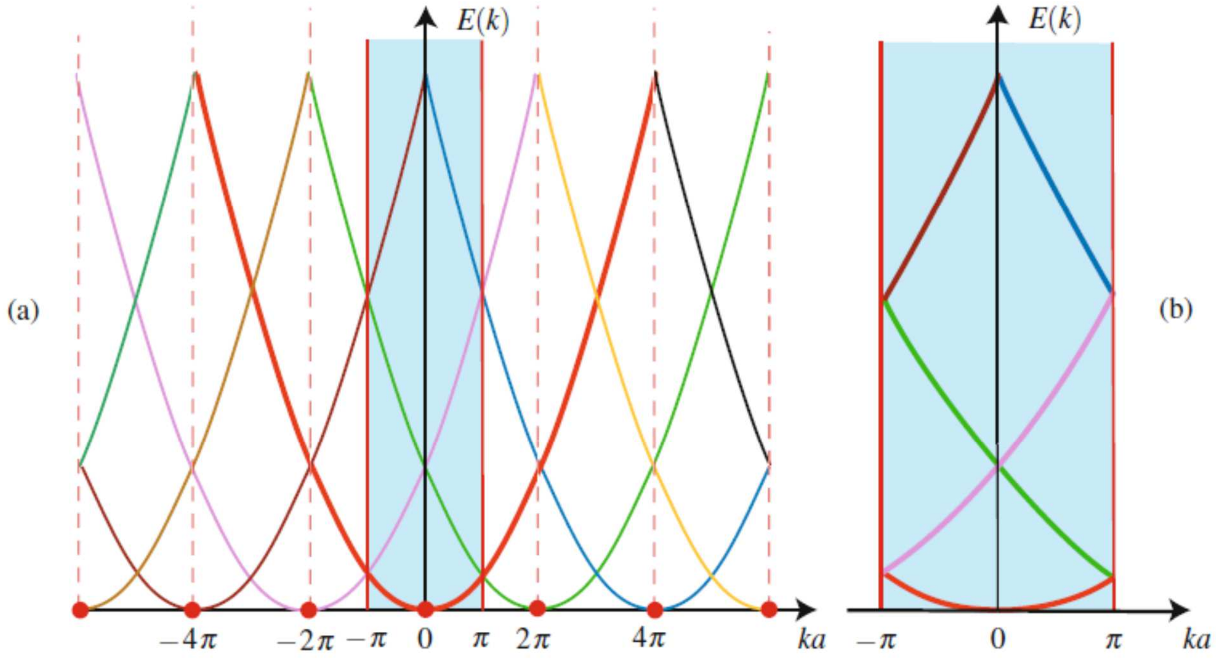


Fig. Probability of finding electrons in the lower band state (denoted by red, $\rho_l = |\psi_l|^2$) and upper band state (denoted by blue, $\rho_u = |\psi_u|^2$). Positive ions are located at $x/a = n$ (n: integers).



The energy gap appears between the upper energy level and the lower energy level as

$$\varepsilon_g = 2V = 2\lfloor V_G \rfloor$$

In other words, the two degenerate states are split by the energy gap which is two times larger that the absolute value of the Fourier component of the periodic potential. We have the wave functions for the lower band and upper band as

$$\phi_l(x) = \frac{1}{\sqrt{2}}\left[e^{ikx} + e^{i(k-G)x}\right] = \frac{1}{\sqrt{2}}\left(e^{i\frac{\pi}{a}x} + e^{-i\frac{\pi}{a}x}\right) = \frac{1}{\sqrt{2}} 2\cos\left(\frac{\pi}{a}x\right)$$

$$\phi_u(x) = \frac{1}{\sqrt{2}}\left[e^{ikx} - e^{i(k-G)x}\right] = \frac{1}{\sqrt{2}}\left(e^{i\frac{\pi}{a}x} - e^{-i\frac{\pi}{a}x}\right) = \frac{1}{\sqrt{2}} 2i\sin\left(\frac{\pi}{a}x\right)$$

where $k = \frac{\pi}{a}$, $G = \frac{2\pi}{a}$

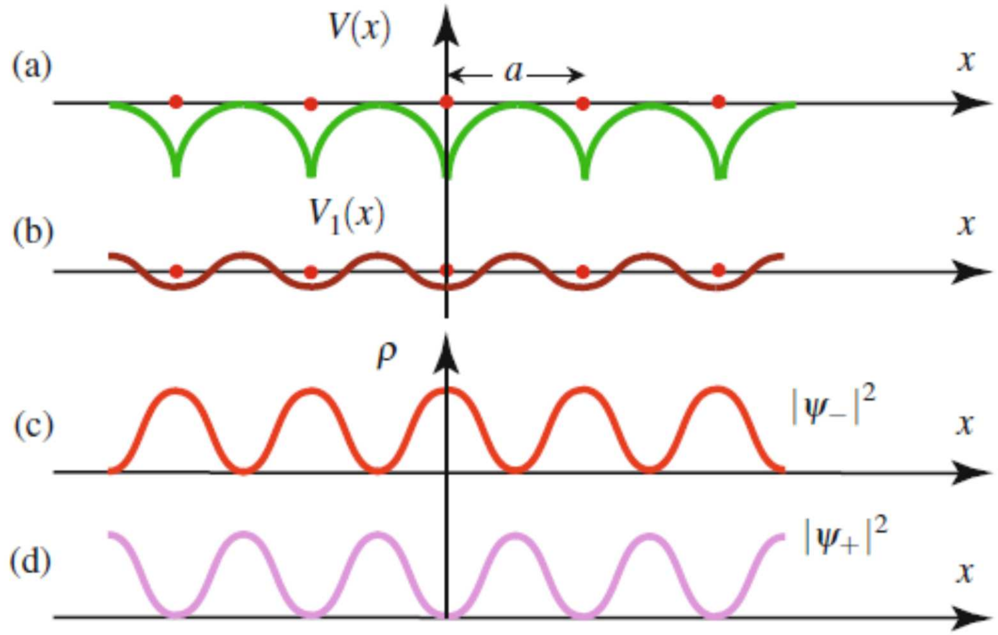


Fig. (a) Position dependence of the electrostatic potential energy of an electron subject to the Coulomb field of the ions in a linear chain of atoms. (b) Potential limited to its Fourier co-efficient obtained for $k = G$ (V_G) and $k = -G$ ($V_{-G} = V_G{}^*$). $G = 2\pi/a$. (c) and (d) Probability of finding the electron as a function of position for the state

4. Eigenvalue problem

(a) Two states with $|k\rangle,\ |k-G\rangle$

$$|\psi_a\rangle = C(k)|k\rangle + C(k-G)|k-G\rangle = \begin{pmatrix} C(k) \\ C(k-G) \end{pmatrix}$$

Eigenvalue problem

$$H|\psi\rangle = \begin{pmatrix} \varepsilon_k^{(0)} & V_G{}^* \\ V_G & \varepsilon_{k-G}^{(0)} \end{pmatrix} |\psi\rangle = \varepsilon|\psi\rangle$$

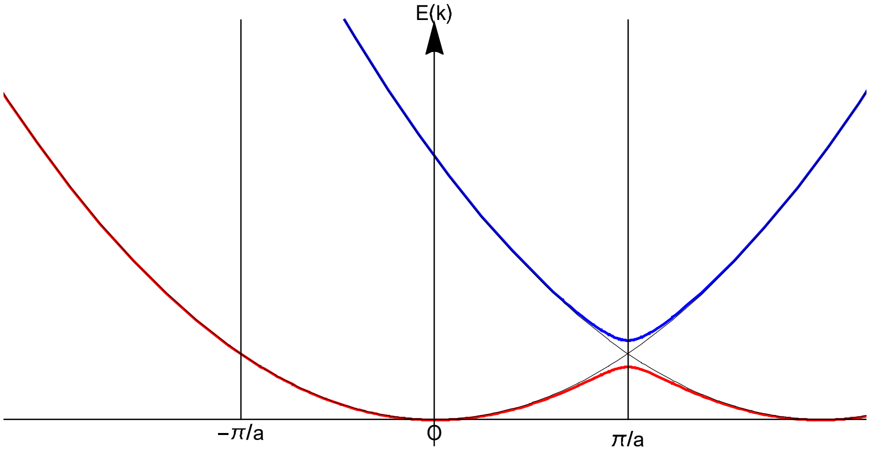
where

$$\varepsilon_k^{(0)} = \frac{\hbar^2}{2m} k^2$$

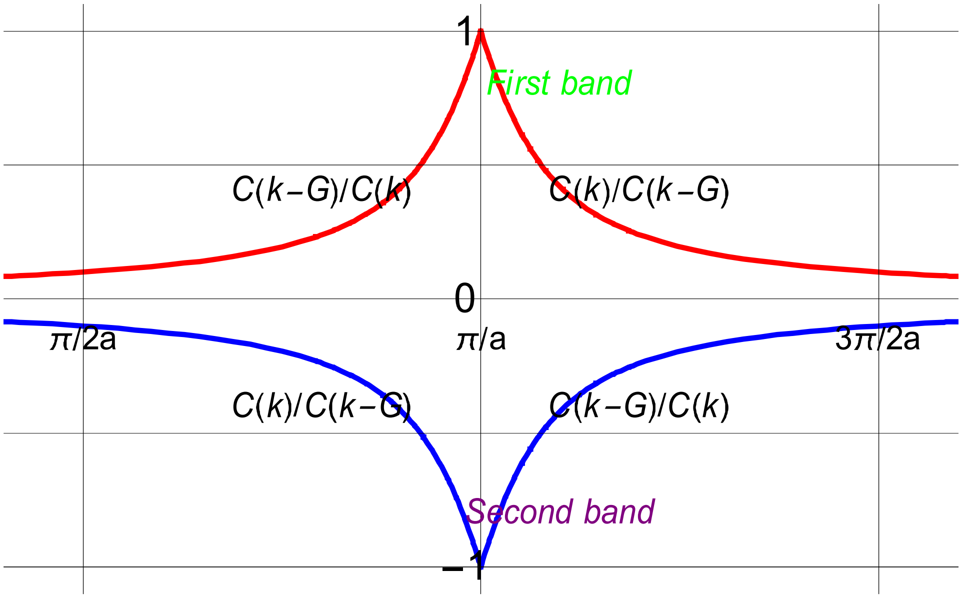
We solve this problem using the Mathematica. For simplicity we use

$$m \to 1, \hbar \to 1, a \to 1, V_G = -1$$

for the numerical calculation.



There is an energy gap at $k = \frac{\pi}{a}$.



(b) Two states with $|k\rangle$, $|k+G\rangle$

$$|\psi_b\rangle = C(k)|k\rangle + C(k+G)|k+G\rangle = \begin{pmatrix} C(k) \\ C(k+G) \end{pmatrix}$$

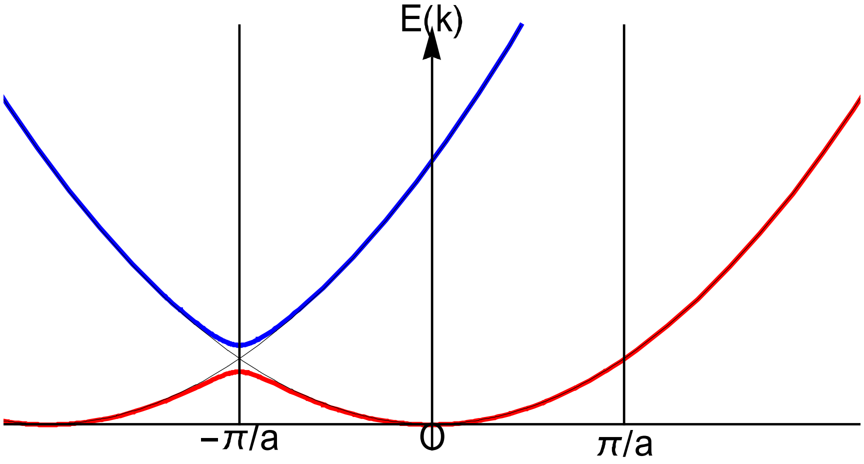
Eigenvalue problem

$$H|\psi\rangle = \begin{pmatrix} \varepsilon_k^{(0)} & V_G{}^* \\ V_G & \varepsilon_{k+G}^{(0)} \end{pmatrix} |\psi\rangle = \varepsilon|\psi\rangle$$

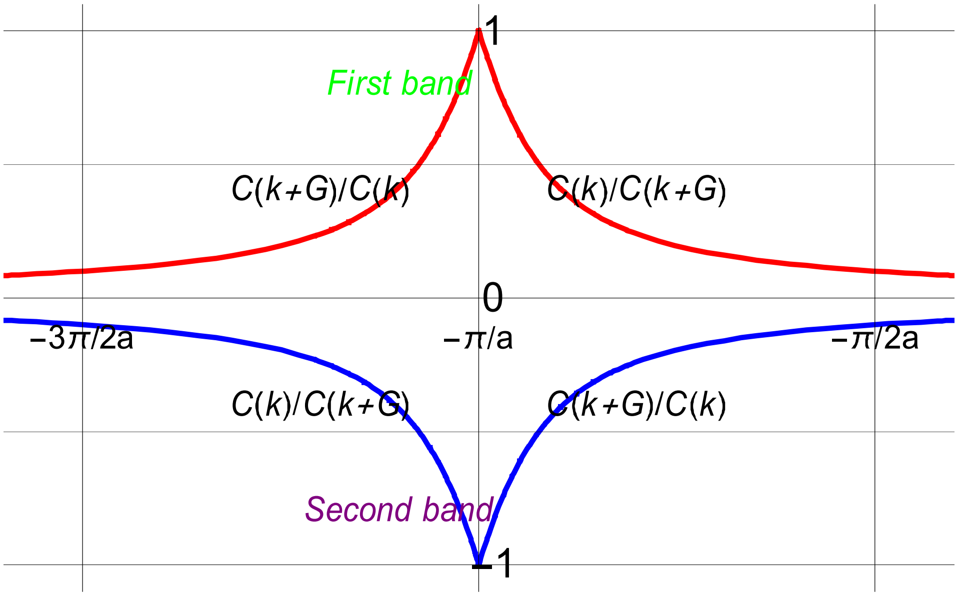
where

$$\varepsilon_k^{(0)} = \frac{\hbar^2}{2m} k^2$$

We solve this problem using the Mathematica



There is an energy gap at $k = -\frac{\pi}{a}$.



(c) Three states with $|k+G\rangle,\ |k\rangle,\ |k-G\rangle$

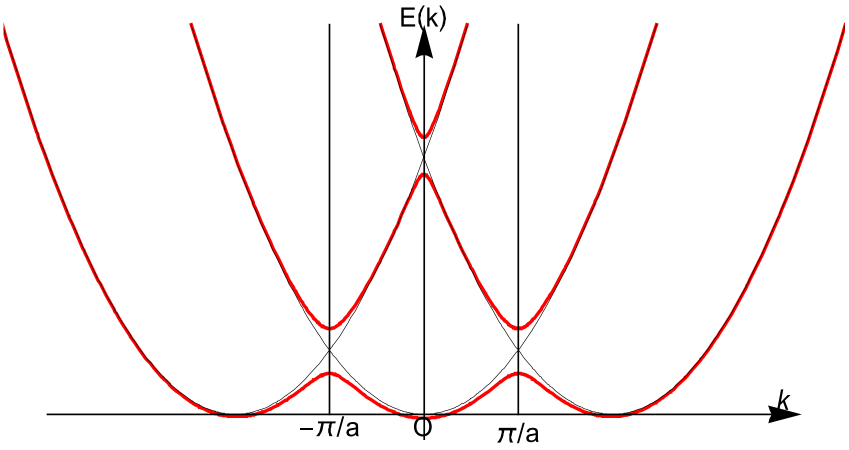
$$|\psi_a\rangle = C(k+G)|k+G\rangle + C(k)|k\rangle + C(k-G)|k-G\rangle$$
$$= \begin{pmatrix} C(k+G) \\ C(k) \\ C(k-G) \end{pmatrix}$$

Eigenvalue problem

$$H|\psi\rangle = \begin{pmatrix} \varepsilon_{k+G}^{(0)} & V_G^* & V_{2G}^* \\ V_G & \varepsilon_k^{(0)} & V_G^* \\ V_{2G} & V_G & \varepsilon_{k-G}^{(0)} \end{pmatrix} |\psi\rangle = \varepsilon|\psi\rangle$$

We use

$$V_G = -2,\ V_{2G} = 10,$$



There are three energy gaps at $k = -\frac{\pi}{a},\ 0,\ \frac{\pi}{a}$. The first energy gap (lower) at $k = -\frac{\pi}{a},\ \frac{\pi}{a}$. is given by $2|V_G|$ at $k = 0$, while the second energy gap is given by $2|V_{2G}|$.

5. 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.

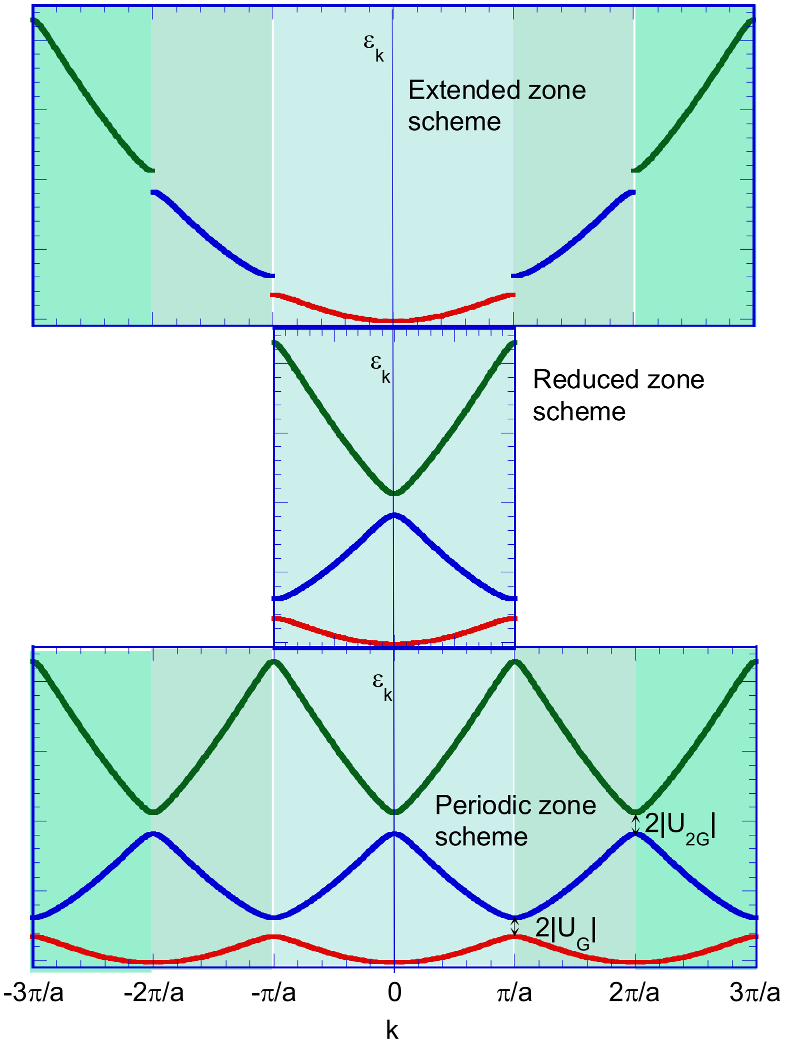


Fig. Three zone schemes for the 1D system. Extended zone scheme. Reduced zone scheme. Periodic zone scheme.

REFERENCE

H. Alloul, Introduction to the Physics of Electrons in Solids (Springer, 2007).

6. ((Example)) S.H. Simon problem 15-4

S.H. Simon, The Oxford Solid State Basis (Oxford, 2013).

Nearly free electrons in two dimensions

Consider the nearly free model for a square lattice with lattice constant *a*. Suppose the periodic potential is given by

$$\begin{aligned} V(x,y) &= 2V_{10}[\cos\left(\frac{2\pi x}{a}\right)+\cos\left(\frac{2\pi y}{a}\right)] \\ &+4V_{11}[\cos\left(\frac{2\pi x}{a}\right)\cos\left(\frac{2\pi y}{a}\right)] \\ &= V_{10}e^{i\boldsymbol{G}_{10}\cdot\boldsymbol{r}}+V_{10}e^{i\boldsymbol{G}_{01}\cdot\boldsymbol{r}}+V_{11}e^{i\boldsymbol{G}_{11}\cdot\boldsymbol{r}}+... \end{aligned}$$

(a) Use the nearly free electron model to find the energies of states at the wavevector $\boldsymbol{k}_a=\left(\frac{\pi}{a},0\right)$ (the boundary of the first Brillouin zone).

There are two degenerate states,

$$|\boldsymbol{k}\rangle,\ |\boldsymbol{k}-\boldsymbol{G}_{10}\rangle$$

with the same energy

$$\varepsilon_a=\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2=\frac{\hbar^2\pi^2}{2ma^2}$$

So the problem is reduced to solving using the time-independent perturbation for the degenerate case. We need to solve the eigenvalue problem of the Hamiltonian H' (2x2 matrix) under the basis of $\{|\boldsymbol{k}\rangle,\ |\boldsymbol{k}-\boldsymbol{G}\rangle\}$

$$H'=\begin{pmatrix}\varepsilon_a & V_{10}\\ V_{10} & \varepsilon_a\end{pmatrix}=\varepsilon_a\begin{pmatrix}1&0\\0&1\end{pmatrix}+V_{10}\begin{pmatrix}0&1\\1&0\end{pmatrix}=\varepsilon_a\hat{1}+V_{10}\hat{\sigma}_x$$

The Hamiltonian can be expressed by using the Pauli matrices. The eigenstates and the eigenvalues can be obtained as follows.

$$\hat{\sigma}_x|\pm x\rangle=\pm|\pm x\rangle$$

$$\begin{aligned} H'|\pm x\rangle &= (\varepsilon_a\hat{1}+V_{10}\hat{\sigma}_x)|\pm x\rangle \\ &= (\varepsilon_a\pm V_{10})|\pm x\rangle \end{aligned}$$

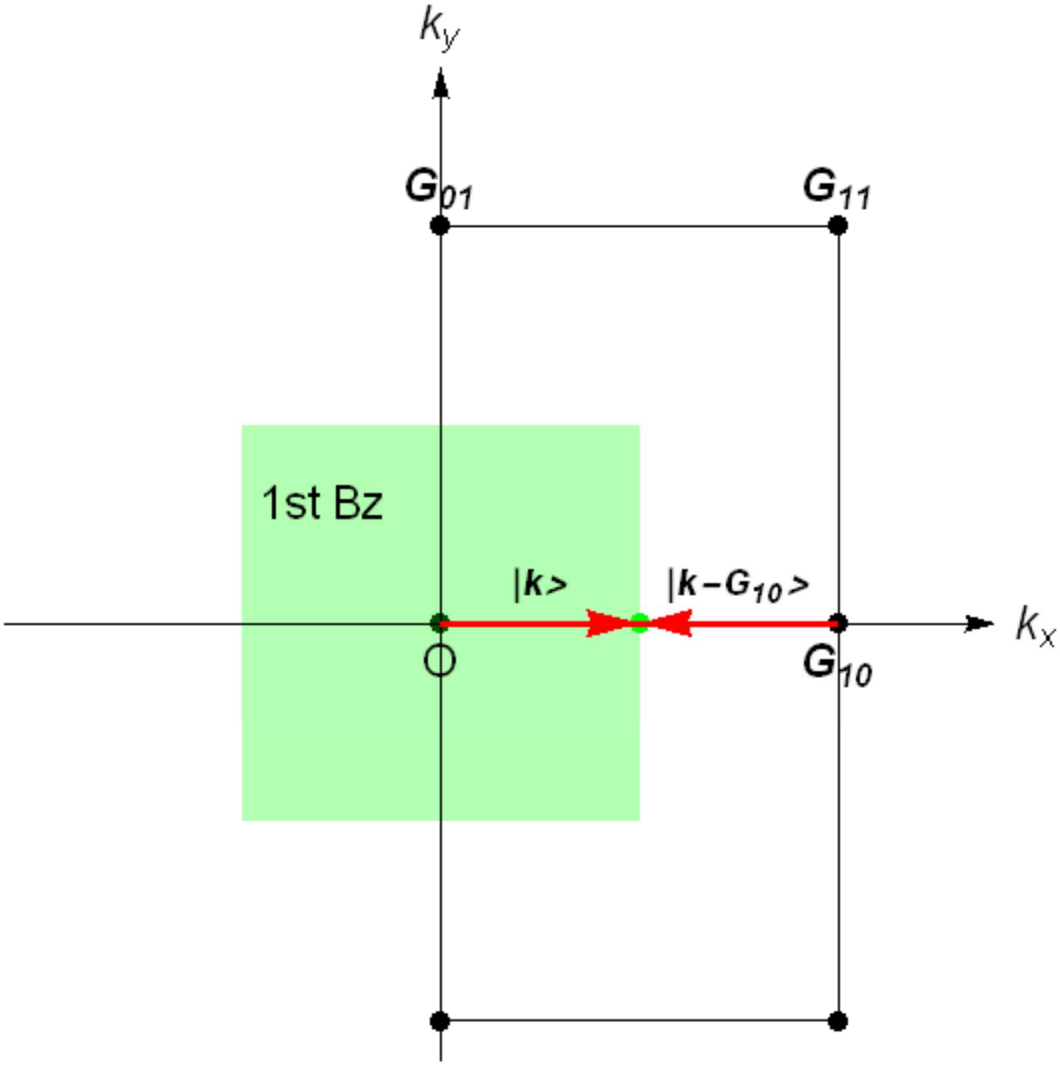
For the energy eigenvalue, ε_a+V_{10}, the eigenstate is

$$\left|+x\right\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} = \frac{1}{\sqrt{2}}[\left|\boldsymbol{k}\right\rangle + \left|\boldsymbol{k}-\boldsymbol{G}_{10}\right\rangle]$$

For the energy eigenvalue, $\varepsilon_a - V_{10}$, the eigenstate is

$$\left|-x\right\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} = \frac{1}{\sqrt{2}}[\left|\boldsymbol{k}\right\rangle - \left|\boldsymbol{k}-\boldsymbol{G}_{10}\right\rangle]$$

Note that for the attractive potential $V_{10}(<0)$ the energy $\varepsilon_a + V_{10}$ is lower tha the energy $\varepsilon_a - V_{10}$



(b) Calculate the energies of the states at wavevector $\boldsymbol{k}_b = \left(\frac{\pi}{a}, \frac{\pi}{a}\right)$ (the edge of the first Brillouin zone).

There are four degenerate states,

$$\left|\boldsymbol{k}\right\rangle,\ \left|\boldsymbol{k}-\boldsymbol{G}_{10}\right\rangle,\ \left|\boldsymbol{k}-\boldsymbol{G}_{11}\right\rangle,\ \left|\boldsymbol{k}-\boldsymbol{G}_{01}\right\rangle,$$

with the same energy

$$\varepsilon_b = \frac{\hbar^2}{2m}[\left(\frac{\pi}{a}\right)^2 + \left(\frac{\pi}{a}\right)^2] = \frac{\hbar^2\pi^2}{ma^2}$$

Using the time-independent perturbation for the degenerate case, we solve the eigenvalue problem of the 4x4 matrix based on the basis of $\{\left|\boldsymbol{k}\right\rangle,\ \left|\boldsymbol{k}-\boldsymbol{G}_{10}\right\rangle,\ \left|\boldsymbol{k}-\boldsymbol{G}_{11}\right\rangle,\ \left|\boldsymbol{k}-\boldsymbol{G}_{01}\right\rangle\}$ by using the Mathematica.

$$\begin{pmatrix} \varepsilon_b & V_{10} & V_{11} & V_{10} \\ V_{10} & \varepsilon_b & V_{10} & V_{11} \\ V_{11} & V_{10} & \varepsilon_b & V_{10} \\ V_{10} & V_{11} & V_{10} & \varepsilon_b \end{pmatrix}$$

$$\begin{aligned} \left|\psi\right\rangle &= C(\boldsymbol{k})\left|\boldsymbol{k}\right\rangle + C(\boldsymbol{k}-\boldsymbol{G}_{10})\left|\boldsymbol{k}-\boldsymbol{G}_{10}\right\rangle \\ &\quad + C(\boldsymbol{k}-\boldsymbol{G}_{11})\left|\boldsymbol{k}-\boldsymbol{G}_{11}\right\rangle + C(\boldsymbol{k}-\boldsymbol{G}_{01})\left|\boldsymbol{k}-\boldsymbol{G}_{01}\right\rangle \\ &= \begin{pmatrix} C(\boldsymbol{k}) \\ C(\boldsymbol{k}-\boldsymbol{G}_{10}) \\ C(\boldsymbol{k}-\boldsymbol{G}_{11}) \\ C(\boldsymbol{k}-\boldsymbol{G}_{01}) \end{pmatrix} \end{aligned}$$

For the energy eigenvalue, $\varepsilon_b - V_{11}$, the eigenstate is

$$\left|\psi_1\right\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ 0 \\ -1 \end{pmatrix}$$

For the energy eigenvalue, $\varepsilon_b - V_{11}$, the eigenstate is

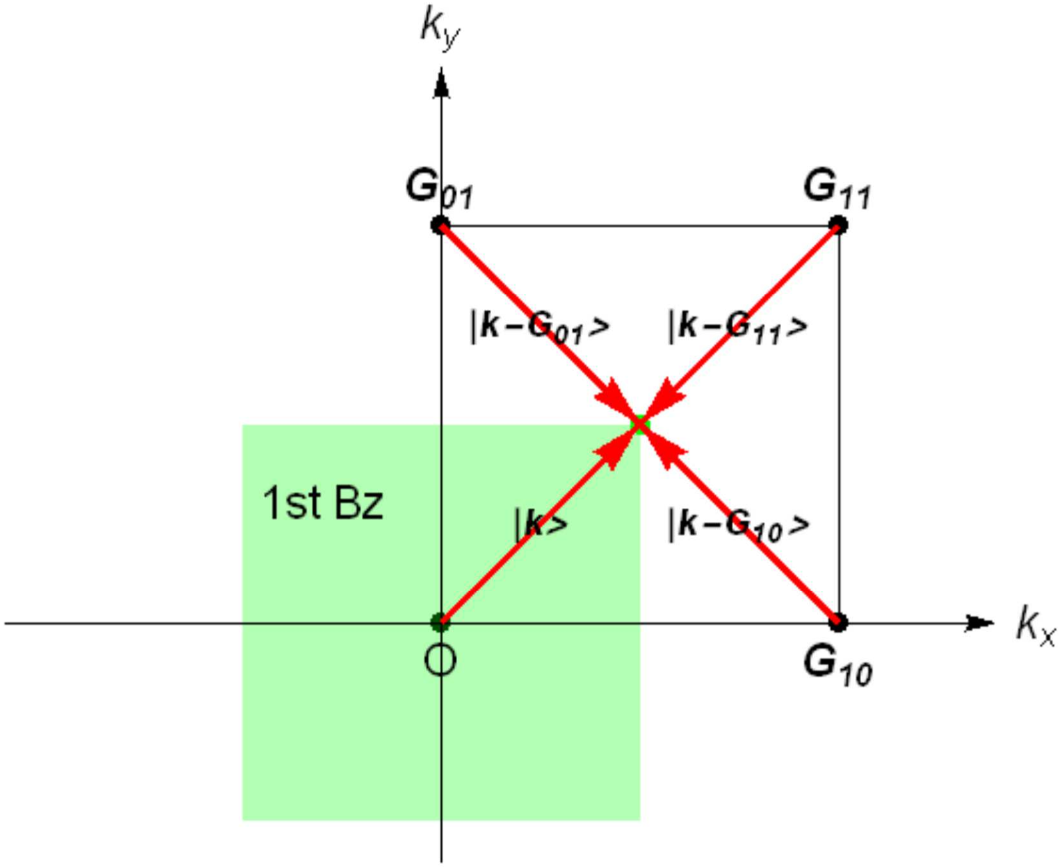
$$|\psi_2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \\ 0 \end{pmatrix}$$

For the energy eigenvaluse, $\varepsilon_b + V_{11} - 2V_{10}$, the eigenstate is

$$|\psi_2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \end{pmatrix}$$

For the energy eigenvalue, $\varepsilon_b + V_{11} + 2V_{10}$, the eigenstate is

$$|\psi_4\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$



((**Mathematica**))

```
Clear["Global`*"];
```

$$H1 = \begin{pmatrix} \epsilon & V10 & V11 & V10 \\ V10 & \epsilon & V10 & V11 \\ V11 & V10 & \epsilon & V10 \\ V10 & V11 & V10 & \epsilon \end{pmatrix};$$

```
eq1 = Eigensystem[H1]
```

```
{{-V11 + ∈, -V11 + ∈, -2 V10 + V11 + ∈, 2 V10 + V11 + ∈},
 {{0, -1, 0, 1}, {-1, 0, 1, 0},
  {-1, 1, -1, 1}, {1, 1, 1, 1}}}
```

```
ψ1 = -Normalize[eq1[[2, 1]]]
```

$$\left\{0, \frac{1}{\sqrt{2}}, 0, -\frac{1}{\sqrt{2}}\right\}$$

```
ψ2 = -Normalize[eq1[[2, 2]]]
```

$$\left\{\frac{1}{\sqrt{2}}, 0, -\frac{1}{\sqrt{2}}, 0\right\}$$

```
ψ3 = -Normalize[eq1[[2, 3]]]
```

$$\left\{\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\right\}$$

```
ψ4 = Normalize[eq1[[2, 4]]]
```

$$\left\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right\}$$

7. ((Example)) 2D energy band

Consider a two-dimensional (2D) square lattice with the lattice constant *a*.

(a) The kinetic energy of a free electron at a corner (M point) of the first Brillouin zone is larger than that of an electron at the midpoint (X point) of a side face of the zone by a factor of b. Calculate the value of b.

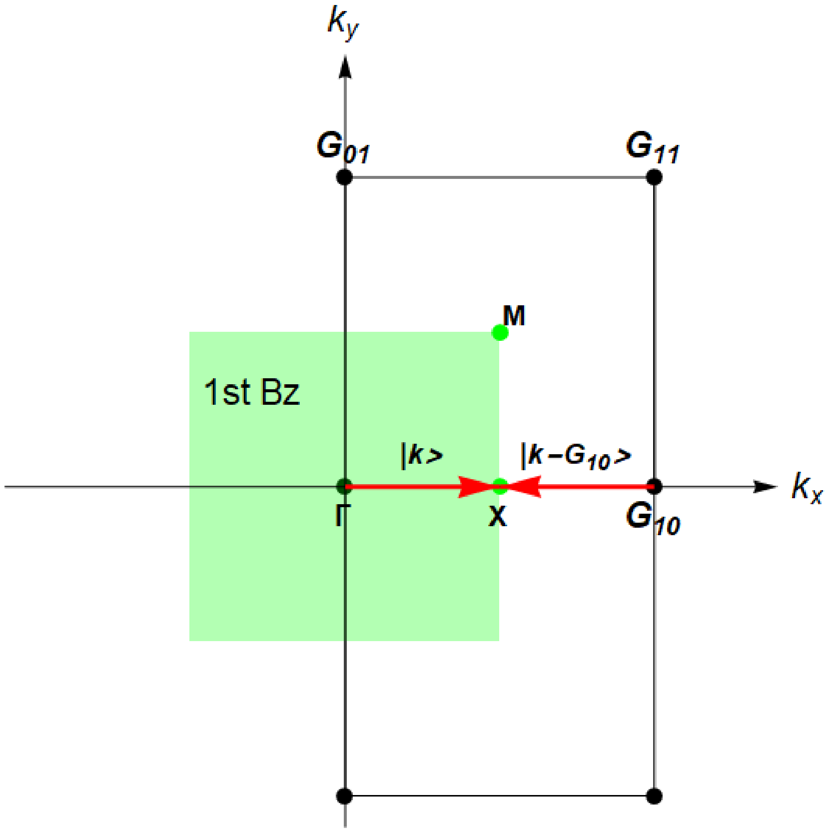


Fig. The first and second Brillouin zone for the 2D square lattice with lattice constant a. X point $:\left(\frac{\pi}{a},0\right)$ and M point $:\left(\frac{\pi}{a},\frac{\pi}{a}\right)$ in the reciprocal lattice. Reciprocal lattice points (denoted by red closed circles).

(b) The crystal potential of the corresponding material is

$$V(x,y)=-2V_0[\cos\left(\frac{2\pi x}{a}\right)+\cos\left(\frac{2\pi y}{a}\right)],$$

where V_0 (>0) is a constant and a is the lattice spacing. Find the energy at the midpoint of the zone face. Use the perturbation method for the degenerate states.

(c) When each atom of the 2D square lattice (lattice constant a) has one conduction electron (monovalent metal), what is the Fermi energy and the Fermi number?

(d) When each atom has two conduction electrons (divalent metal), what is the Fermi energy and the Fermi number? Hint: see the red circle in **Fig.**

(e) Assuming that your result in (b) is exact and that the system is divalent metal, what is the condition for the system to be metallic?

((**Solution**))

(a)

The energy of electron is expressed by

$$\varepsilon(k_x, k_y) = \frac{\hbar^2}{2m}(k_x{}^2 + k_y{}^2)$$

The energy at the point X [=$\left(\frac{\pi}{a}, 0\right)$]:

$$\varepsilon(X) = \frac{\hbar^2}{2m}(\frac{\pi^2}{a^2})$$

The energy at the point M [=$\left(\frac{\pi}{a}, \frac{\pi}{a}\right)$]:

$$\varepsilon(M) = 2\frac{\hbar^2}{2m}(\frac{\pi^2}{a^2}).$$

The factor b is the ratio defined by

$$b = \frac{\varepsilon(M)}{\varepsilon(X)} = 2.$$

(b)

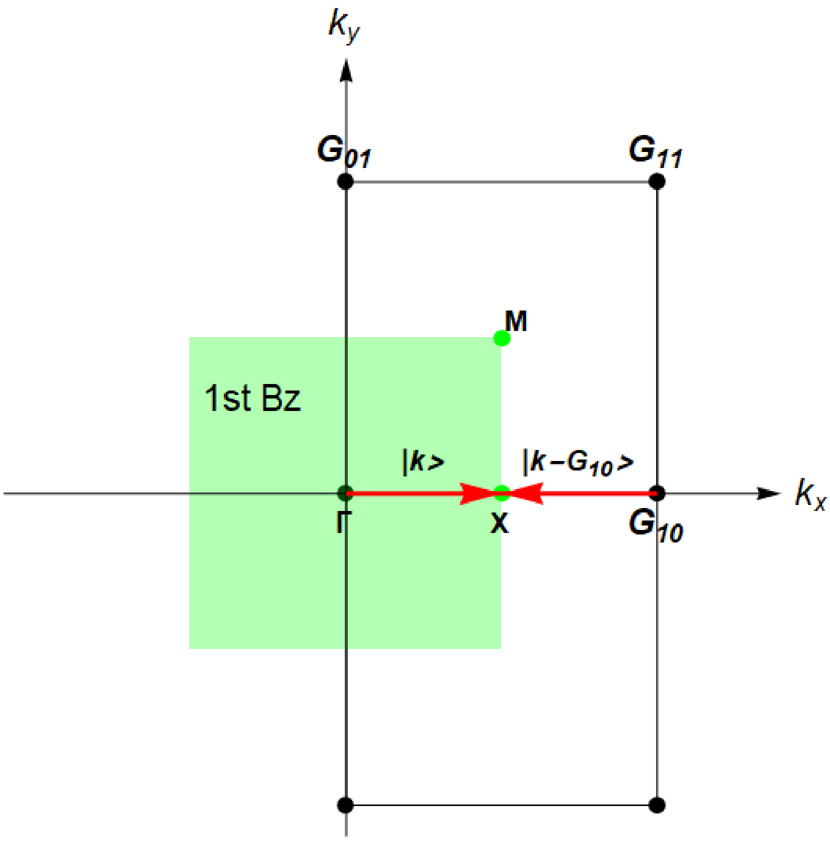
The potential energy is given by

$$V(x, y) = -V_0(e^{i\frac{2\pi x}{a}} + e^{-i\frac{2\pi x}{a}} + e^{i\frac{2\pi y}{a}} + e^{-i\frac{2\pi y}{a}}).$$

The reciprocal lattice vectors are defined by

$$\boldsymbol{G}(1,0) = (\frac{2\pi}{a}, 0), \qquad \boldsymbol{G}(0,1) = (0, \frac{2\pi}{a})$$

$$\boldsymbol{G}(-1,0)=(-\frac{2\pi}{a},0)\,, \qquad \boldsymbol{G}(0,-1)=(0,-\frac{2\pi}{a})$$



$$\langle \boldsymbol{k}|\hat{V}|\boldsymbol{k}\rangle = 0\,, \qquad \langle \boldsymbol{k}-\boldsymbol{G}_{10}|\hat{V}|\boldsymbol{k}-\boldsymbol{G}_{10}\rangle = 0\,,$$

$$\langle \boldsymbol{k}-\boldsymbol{G}_{10}|\hat{V}|\boldsymbol{k}\rangle = V_{-\boldsymbol{G}_{1,0}} = V_{\boldsymbol{G}_{-1,0}} = -V_0\,, \qquad \langle \boldsymbol{k}|\hat{V}|\boldsymbol{k}-\boldsymbol{G}_{10}\rangle = V_{\boldsymbol{G}_{1,0}} = -V_0\,.$$

At the point X, the states $|\boldsymbol{k}\rangle$ and $|\boldsymbol{k}-\boldsymbol{G}_{10}\rangle$ are degenerate under the unperturbed Hamiltonian [$\varepsilon(X)=\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2$]. When the perturbation Hamiltonian is applied, these two states are split.

$$\hat{V} = \begin{pmatrix} 0 & -V_0 \\ -V_0 & 0 \end{pmatrix} = -V_0\hat{\sigma}_x\,.$$

The energy eigenvalue:

$$\hat{V}|\pm x\rangle = -V_0\hat{\sigma}_x|\pm x\rangle = \mp V_0|\pm x\rangle .$$

Energy: $\varepsilon(X)+V_0$ Eigenstate $|-x\rangle = \frac{1}{\sqrt{2}}[|\boldsymbol{k}\rangle - |\boldsymbol{k}-\boldsymbol{G}\rangle]$

Energy: $\varepsilon(X)-V_0$ Eigenstate $|+x\rangle = \frac{1}{\sqrt{2}}[|\boldsymbol{k}\rangle + |\boldsymbol{k}-\boldsymbol{G}\rangle]$

The energy gap is $2V_0$.

(c)

At 0 K,

$$N = \frac{2A}{(2\pi)^2}2\pi\int kdk .$$

Note that

$$\varepsilon = \frac{\hbar^2}{2m}k^2 , \qquad \frac{m}{\hbar^2}d\varepsilon = kdk ,$$

$$n = \frac{N}{A} = \frac{2}{(2\pi)^2}2\pi\frac{m}{\hbar^2}\int_0^{\varepsilon_F} d\varepsilon = \frac{m}{\pi\hbar^2}\varepsilon_F .$$

(d)
For a divalent metal, there are two conduction electrons. The number density of conduction electrons:

$$n = \frac{2}{a^2} .$$

Then we have

$$n = \frac{2}{a^2} = \frac{m}{\pi\hbar^2}\varepsilon_F .$$

The Fermi energy is obtained as

$$\varepsilon_F = \frac{\pi\hbar^2}{m}\frac{2}{a^2} = \frac{\hbar^2}{2m}\frac{4\pi}{a^2} = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\left(\sqrt{\frac{4}{\pi}}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2(1.1284)^2 .$$

The Fermi wave number is

$$k_F = \left(\frac{\pi}{a}\right)(1.1284) .$$

(e)

The condition for the system to be metallic is that

$$\varepsilon(X) + V_0 = \frac{\hbar^2}{2m}\frac{\pi^2}{a^2} + V_0 < \varepsilon_F = \frac{\hbar^2}{2m}\frac{4\pi}{a^2} ,$$

or

$$V_0 = \frac{\hbar^2}{2m}\frac{3\pi}{a^2} ,$$

or

$$\varepsilon_F = \frac{\pi\hbar^2}{m}n .$$

Suppose that there is noe atom per square lattice ($a \times a$),

$$n = \frac{1}{a^2} .$$

leading to

$$\varepsilon_F = \frac{\pi\hbar^2}{ma^2} = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\frac{2}{\pi} = (0.61662)\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 .$$

$$k_F = \frac{\pi}{a}\sqrt{\frac{2}{\pi}} = (0.7979)\frac{\pi}{a} .$$

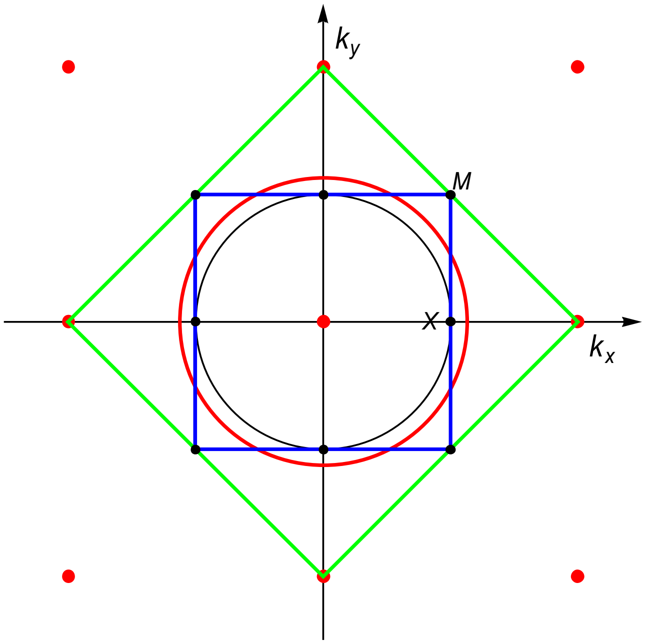
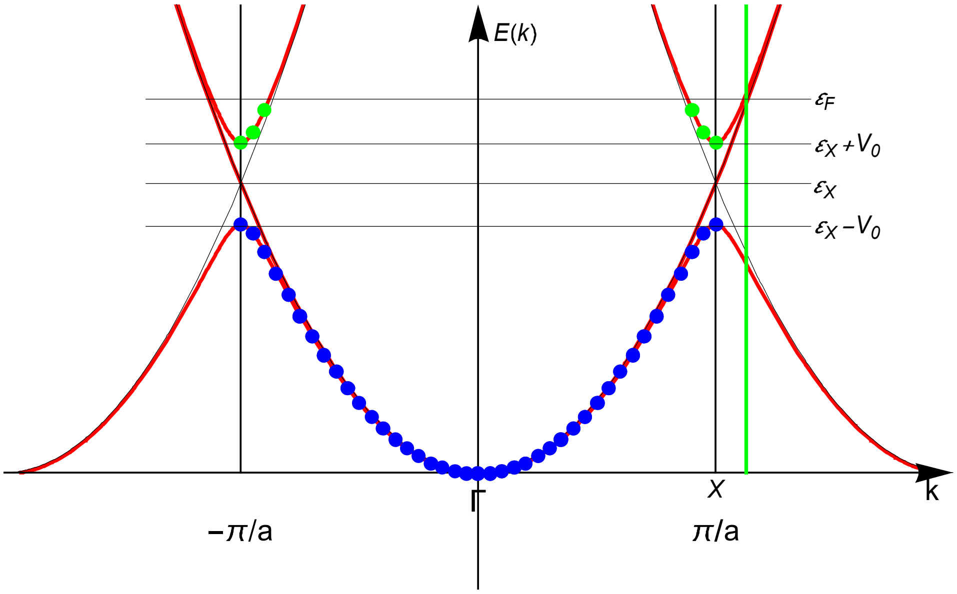
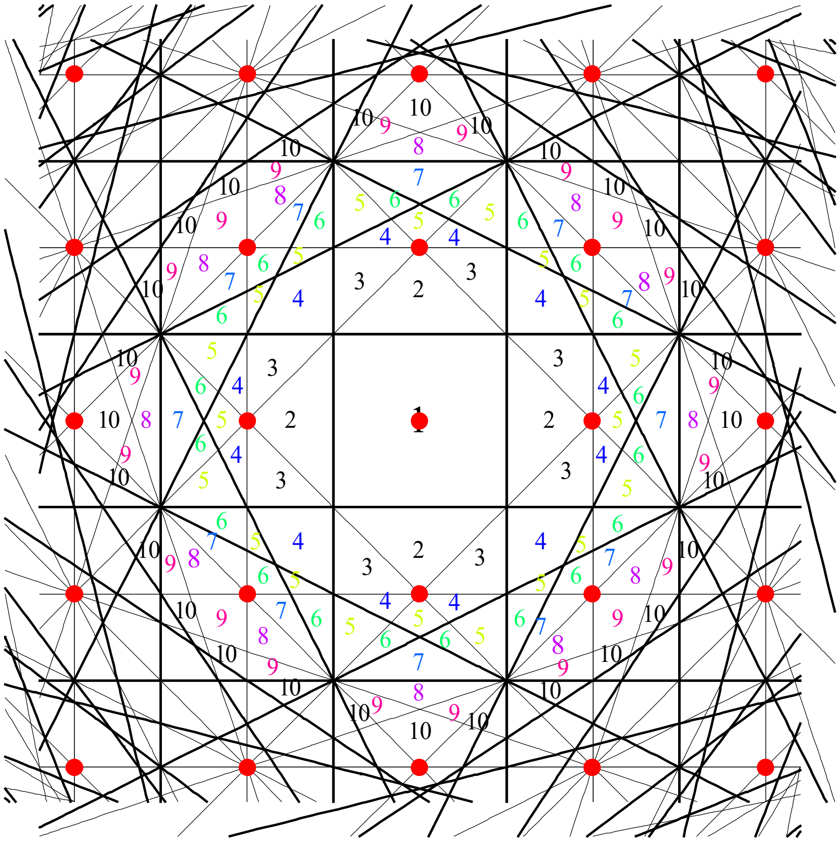


Fig. $\varepsilon(X) = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2$. The Fermi energy: $\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 (1.1284)^2$ for the divalent metal [red line].



((**Note**)) Brillouin zone of 2D square lattice



APPENDIX I Matrix element

$$\langle \boldsymbol{r} | \boldsymbol{k} \rangle = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}, \qquad \langle \boldsymbol{k} | \boldsymbol{r} \rangle = \frac{1}{\sqrt{V}} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}$$

$$V = \sum_{\boldsymbol{G}} V_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}}$$

The matrix element:

$$\begin{aligned}
\langle \boldsymbol{k}' | \hat{V} | \boldsymbol{k} \rangle &= \int d\boldsymbol{r} \langle \boldsymbol{k}' | \boldsymbol{r} \rangle V(\boldsymbol{r}) \langle \boldsymbol{r} | \boldsymbol{k} \rangle \\
&= \frac{1}{V} \sum_{\boldsymbol{G}} V_{\boldsymbol{G}} \int d\boldsymbol{r} e^{i(\boldsymbol{k}+\boldsymbol{G}-\boldsymbol{k}')\cdot\boldsymbol{r}} \\
&= \frac{1}{V} \sum_{\boldsymbol{G}} V_{\boldsymbol{G}} V \delta_{\boldsymbol{k}',\boldsymbol{k}+\boldsymbol{G}} \\
&= V_{\boldsymbol{G}} \delta_{\boldsymbol{k}',\boldsymbol{k}+\boldsymbol{G}}
\end{aligned}$$

leading to

$$\langle \boldsymbol{k}+\boldsymbol{G}|\hat{V}|\boldsymbol{k}\rangle = V_{\boldsymbol{G}}, \qquad \langle \boldsymbol{k}|\hat{V}|\boldsymbol{k}+\boldsymbol{G}\rangle = V_{-\boldsymbol{G}} = V_{\boldsymbol{G}}{}^{*}$$

Note that

$$V_{-G} = V_{G}{}^{*}$$

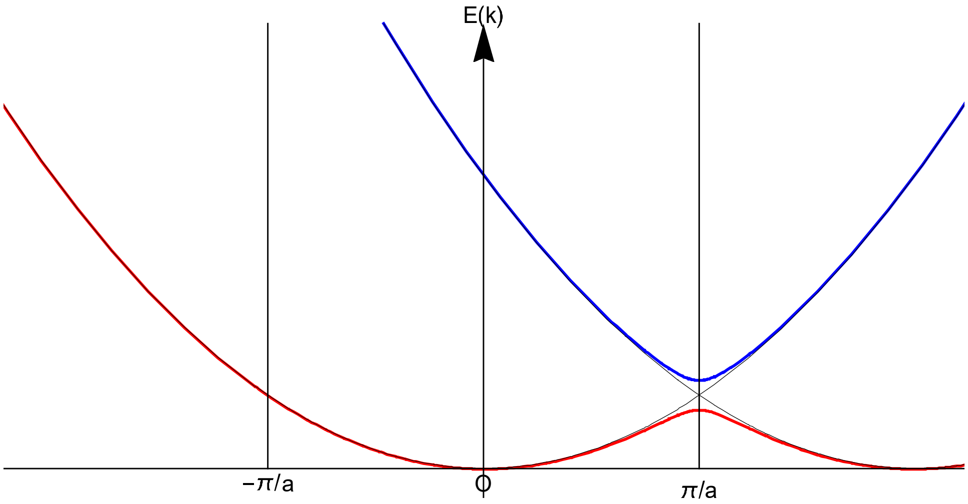
since

$$V(\boldsymbol{r}) = V^{*}(\boldsymbol{r}) \quad \text{(real)}$$

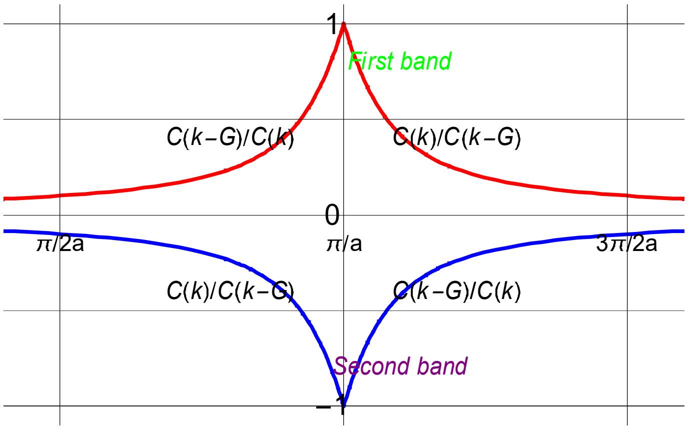
$$V(\boldsymbol{r}) = \sum_{\boldsymbol{G}} V_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}}, \quad V^{*}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} V_{\boldsymbol{G}}{}^{*} e^{-i\boldsymbol{G}\cdot\boldsymbol{r}} = \sum_{\boldsymbol{G}} V_{-\boldsymbol{G}}{}^{*} e^{i\boldsymbol{G}\cdot\boldsymbol{r}}$$

APPENDIX-II Mathematica

```
Clear["Global`*"];
        ℏ²
f[k_] = ── k²;
        2 m
M = {{f[k], Vk}, {Vk, f[k - K]}};
rule1 = {ℏ → 1, m → 1, K → 2 π, Vk → -1};
M1 = M /. rule1;
A = Eigenvalues[M1];
C1 = Eigensystem[M1];
                               k²   1
p1 = Plot[{A[[1]], A[[2]], ──, ─ (k - 2 π)²}, {k, -4 π, 4 π}, Axes → None,
                               2    2
  PlotStyle → {{Red, Thick}, {Blue, Thick}, {Black, Thin}, {Black, Thin}},
  PlotRange → {{-7, 7}, {-5, 30}}];
            C1[[2, 1]][[2]]   C1[[2, 2]][[1]]
p2 = Plot[{───────────────, ───────────────}, {k, 0.4 π, π}, Axes → None,
            C1[[2, 1]][[1]]   C1[[2, 2]] [[2]]
  PlotRange → {{-7, 7}, {-5, 30}}, PlotStyle → {{Red, Thick}, {Blue, Thick}}, PlotPoints → 30];
            C1[[2, 1]][[1]]   C1[[2, 2]][[2]]
p3 = Plot[{───────────────, ───────────────}, {k, π, 1.6 π}, Axes → None,
            C1[[2, 1]][[2]]   C1[[2, 2]] [[1]]
  PlotRange → {{-7, 7}, {-5, 30}}, PlotStyle → {{Red, Thick}, {Blue, Thick}}, PlotPoints → 30];
g2 = Graphics[{Black, Line[{{ π, 0}, { π, 30}}], Line[{{ -π, 0}, { -π, 30}}],
   Arrow[{{-4 π, 0}, { 4 π, 0}}], Arrow[{{0, -2}, {0, 30}}]}];
g3 = Graphics[{Text[Style["k", Black, Italic, 15], {12, 1}],
   Text[Style["E(k)", Black, 15], {0, 30.5}], Text[Style["π/a", Black, 15], {π, -1.5}],
   Text[Style["-π/a", Black, 15], {-π, -1.0}], Text[Style["O", Black, 15], {0, -1}]}];
Show[p1, g2, g3, PlotRange → {{-7, 7}, {-5, 35}}]
```

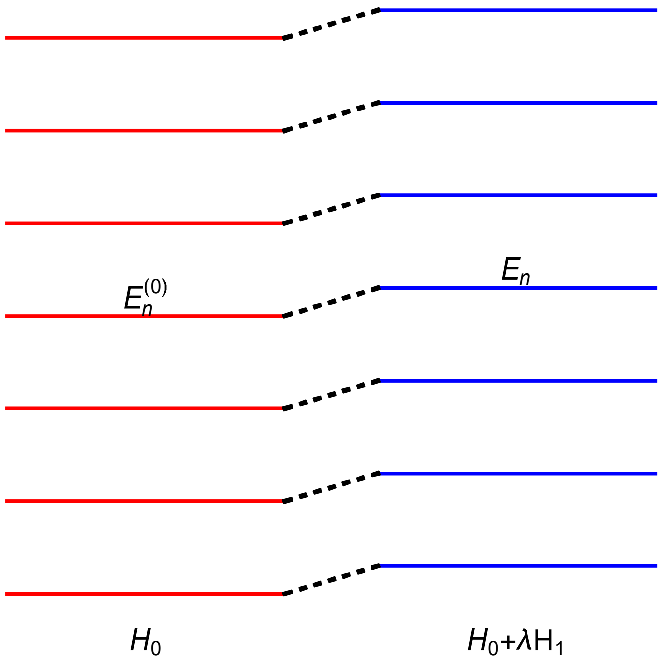


```
k1 = Graphics[{Black, Thin, Line[{{0.5 π, -1.1}, {0.5 π, 1.1}}],
   Line[{{1.5 π, -1.1}, {1.5 π, 1.1}}], Line[{{ π, -1.1}, { π, 1.1}}],
   Line[{{0.4 π, 0}, {1.6 π, 0}}], Line[{{0.4 π, -1}, {1.6 π, -1}}],
   Line[{{0.4 π, 1}, {1.6 π, 1}}] , Line[{{0.4 π, -1}, {1.6 π, -1}}],
   Line[{{0.4 π, 0.5}, {1.6 π, 0.5}}] , Line[{{0.4 π, -0.5}, {1.6 π, -0.5}}],
   Text[Style["1", Black, 15], {0.98 π, 1}], Text[Style["-1", Black, 15], {0.98 π, - 1}],
   Text[Style["0", Black, 15], {0.98 π, 0}], Text[Style["π/a", Black, 12], {π, -0.15}],
   Text[Style["3π/2a", Black, 12], {3 π / 2, -0.15}],
   Text[Style["π/2a", Black, 12], {π / 2, -0.15}],
   Text[Style["C(k)/C(k-G)", Black, Italic, 12], {1.2 π, 0.4}],
   Text[Style["C(k-G)/C(k)", Black, Italic, 12], {0.8 π, 0.4}],
   Text[Style["C(k-G)/C(k)", Black, Italic, 12], {1.2 π, -0.4}],
   Text[Style["C(k)/C(k-G)", Black, Italic, 12], {0.8 π, -0.4}] ,
   Text[Style["First band", Green, Italic, 12], {1.1 π, 0.8}],
   Text[Style["Second band", Purple, Italic, 12], {1.1 π, -0.8}] }];
Show[p2, p3, k1,  PlotRange → {{0.4 π, 1.6 π}, {-1.1, 1.1}}]
```



APPENDIX-III Time independent perturbation

1. Non-degenerate case



(a) Energy eigenvalue

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + O(\lambda^3)\,,$$

with

$$E_n^{(1)} = \left\langle \psi_n^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle,$$

$$E_n^{(2)} = \sum_{k\neq n} \frac{\left| \left\langle \psi_n^{(0)} \middle| \hat{H}_1 \middle| \psi_k^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_k^{(0)}}\,.$$

(b) Energy eigenstate

$$\left|\psi_n\right\rangle = \left|\psi_n^{(0)}\right\rangle + \lambda\left|\psi_n^{(1)}\right\rangle + \lambda^2\left|\psi_n^{(2)}\right\rangle + O(\lambda^3)\,,$$

with

$$\left|\psi_n^{(1)}\right\rangle = \sum_{k\neq n} \left|\psi_k^{(0)}\right\rangle \frac{\left\langle \psi_k^{(0)} \middle| \hat{H}_1 \middle| \psi_n^{(0)} \right\rangle}{E_n^{(0)} - E_k^{(0)}}\,,$$

and

$$\left|\psi_n^{(2)}\right\rangle = \sum_{k\neq n}\left|\psi_k^{(0)}\right\rangle [\sum_{l\neq n}\frac{\left\langle \psi_k^{(0)}\right|\hat{H}_1\left|\psi_l^{(0)}\right\rangle\left\langle \psi_l^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\rangle}{(E_n^{(0)}-E_k^{(0)})(E_n^{(0)}-E_l^{(0)})}$$

$$-\frac{\left\langle \psi_k^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\rangle\left\langle \psi_n^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\rangle}{(E_n^{(0)}-E_k^{(0)})^2}]$$

$$=\sum_{\substack{k\neq n\\ l\neq n}}\left|\psi_k^{(0)}\right\rangle\frac{\left\langle \psi_k^{(0)}\right|\hat{H}_1\left|\psi_l^{(0)}\right\rangle\left\langle \psi_l^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\rangle}{(E_n^{(0)}-E_k^{(0)})(E_n^{(0)}-E_l^{(0)})}$$

$$-\sum_{k\neq n}\frac{\left\langle \psi_k^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\rangle\left\langle \psi_n^{(0)}\right|\hat{H}_1\left|\psi_n^{(0)}\right\rangle}{(E_n^{(0)}-E_k^{(0)})^2}]$$

We note that $\left|\psi_n\right\rangle$ is not normalized, so an extra calculation must be performed in order to obtain the normalization factor.

2. Degenerate case: the first order

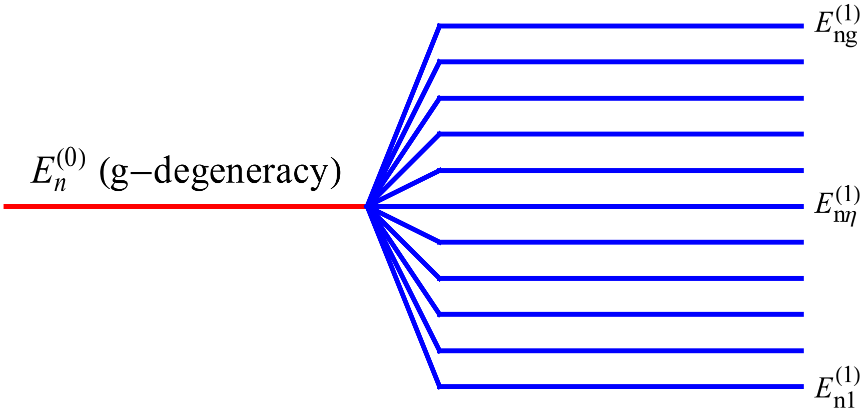
We have now *g*-degenerate states with

$$\left|\psi_n^{(0)}\right\rangle = \left|\varphi_{n,\mu}^{(0)}\right\rangle, \qquad (\mu = 1, 2, 3, ..., g)$$

where

$$\hat{H}_0\left|\varphi_{n,\mu}^{(0)}\right\rangle = E_n^{(0)}\left|\varphi_{n,\mu}^{(0)}\right\rangle.$$

$\left|\varphi_{n,\mu}^{(0)}\right\rangle$ is different state for different μ.



For the 1st-order terms in λ,

$$(\hat{H}_0 - E_n{}^{(0)})\left|\psi_n{}^{(1)}\right\rangle + (\hat{H}_1 - E_n{}^{(1)})\left|\psi_n{}^{(0)}\right\rangle = 0\,. \qquad (1)$$

By taking an inner product of $\left\langle \varphi_{n,\mu}{}^{(0)}\right|$ and Eq.(1), we get

$$\left\langle \varphi_{n,\mu}{}^{(0)}\right|(\hat{H}_0 - E_n{}^{(0)})\left|\psi_n{}^{(1)}\right\rangle + \left\langle \varphi_{n,\mu}{}^{(0)}\right|(\hat{H}_1 - E_n{}^{(1)})\left|\psi_n{}^{(0)}\right\rangle = 0\,,$$

or

$$\left\langle \varphi_{n,\mu}{}^{(0)}\right|\hat{H}_1\left|\psi_n{}^{(0)}\right\rangle = E_n{}^{(1)}\left\langle \varphi_{n,\mu}{}^{(0)}\middle|\psi_n{}^{(0)}\right\rangle.$$

Using the closure relation, we have

$$\sum_{\nu=1}^{g}\left\langle \varphi_{n,\mu}{}^{(0)}\right|\hat{H}_1\left|\varphi_{n,\nu}{}^{(0)}\right\rangle\left\langle \varphi_{n,\nu}{}^{(0)}\middle|\psi_n{}^{(0)}\right\rangle = E_n{}^{(1)}\left\langle \varphi_{n,\mu}{}^{(0)}\middle|\psi_n{}^{(0)}\right\rangle.$$

We need to calculate the matrix elements;

$$\left\langle \varphi_{n,\mu}{}^{(0)}\right|\hat{H}_1\left|\varphi_{n,\nu}{}^{(0)}\right\rangle.$$

Then we solve the eigenvalue problem

$$\sum_{\nu=1}^{g}[\left\langle \varphi_{n,\mu}{}^{(0)}\right|\hat{H}_1\left|\varphi_{n,\nu}{}^{(0)}\right\rangle - E_n{}^{(1)}\delta_{\mu\nu}]\left\langle \varphi_{n,\nu}{}^{(0)}\middle|\psi_n{}^{(0)}\right\rangle = 0\,,$$

where $\mu = 1, 2, ..., g$, and $\nu = 1, 2, ..., g$

or

$$\begin{pmatrix} H_{11} - E_n{}^{(1)} & H_{12} & H_{13} & . & . & . & H_{1g} \\ H_{21} & H_{22} - E_n{}^{(1)} & H_{23} & . & . & . & H_{2g} \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ H_{g1} & H_{g2} & H_{g3} & . & . & . & H_{gg} - E_n{}^{(1)} \end{pmatrix}\begin{pmatrix} \left\langle \varphi_{n,1}{}^{(0)}\middle|\psi_n{}^{(0)}\right\rangle \\ \left\langle \varphi_{n,2}{}^{(0)}\middle|\psi_n{}^{(0)}\right\rangle \\ . \\ . \\ . \\ . \\ \left\langle \varphi_{n,g}{}^{(0)}\middle|\psi_n{}^{(0)}\right\rangle \end{pmatrix} = 0$$

for the eigenvalue $E_n^{(1)}$. The Unitary transformation:

$$\left|\psi_{n,\mu}{}^{(0)}\right\rangle = \hat{U}\left|\varphi_{n,\mu}{}^{(0)}\right\rangle = \begin{pmatrix} U_{1\mu} \\ U_{2\mu} \\ . \\ . \\ U_{n\mu} \end{pmatrix}$$

where the Unitary operator is given by

$$\hat{U} = \begin{pmatrix} U_{11} & U_{12} & . & . & U_{1g} \\ U_{21} & U_{22} & . & . & . \\ . & . & . & . & . \\ . & . & . & . & . \\ U_{g1} & U_{g2} & . & . & U_{gg} \end{pmatrix}$$

and the matrix form of the bases are given by

$$\left|\varphi_{n,1}{}^{(0)}\right\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ . \\ . \\ . \\ 0 \end{pmatrix}, \left|\varphi_{n,2}{}^{(0)}\right\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ . \\ . \\ . \\ 0 \end{pmatrix}, \text{........................}, \left|\varphi_{n,g}{}^{(0)}\right\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ . \\ . \\ . \\ 1 \end{pmatrix}$$

Then we have the resultant energy as

$$E_n^{(0)} + E_{n,\mu}^{(1)} \qquad (\mu = 1, 2, 3, ..., g).$$

$$\left|\psi_{n,\mu}{}^{(0)}\right\rangle = \begin{pmatrix} U_{1\mu} \\ U_{2\mu} \\ . \\ . \\ . \\ . \\ . \\ U_{g\mu} \end{pmatrix}.$$