**Tight binding approximation**
Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
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The tight-binding model is opposite limit to the nearly free electron model. The potential is so large that the electrons spend most of their lives near ionic cores, only occasionally shift to nearest core atom quantum mechanically.

The nearly free electron method looks at the wave-functions outside the atomic cores, where they look very like **plane waves**. Within the cores they look like **atomic orbitals**. This suggests an entirely different scheme for the construction of electron wave-functions: we try to combine atomic orbitals, each localized on a particular atom, to represent a state running throughout the crystal.
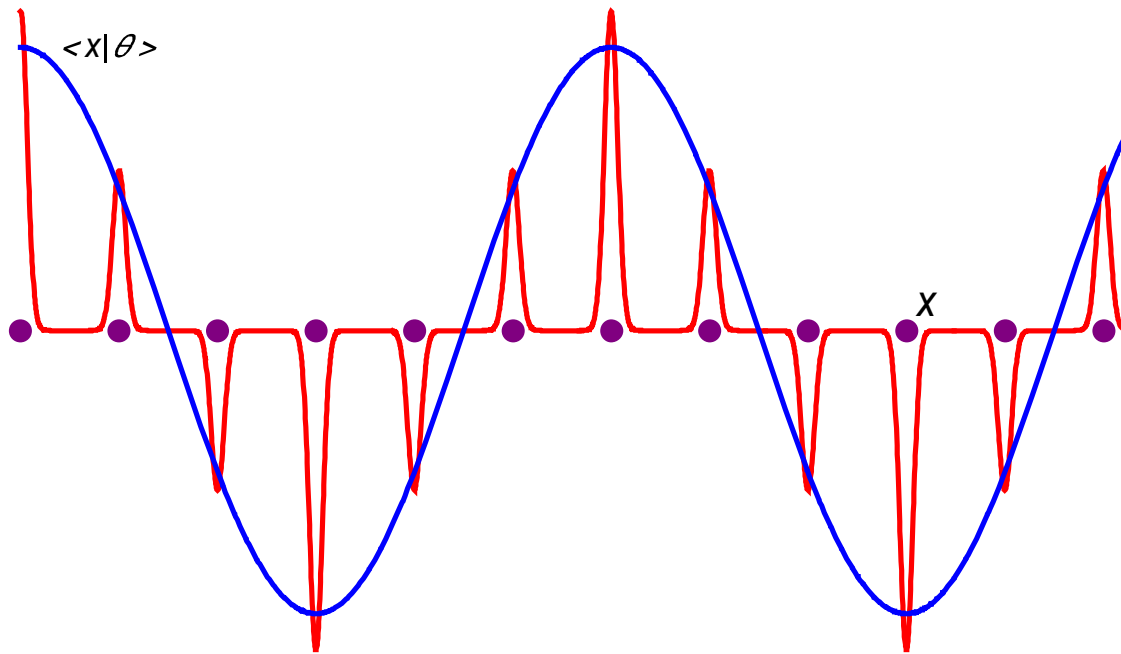
1.   One dimensional case: Bloch theorem

Suppose that the electrons are tightly bound to the nuclei. Thewavefunction would coincide within the n cell, with an atomic eigenfunction ϕ_a (such as 1s, 2s, 2p,). Then the wavefunction of the system may be expressed by a linear combination of atomic orbital (LCAO) function,

$$\psi_k(x) = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} C_n \phi_a(x - na).$$

The coefficient C_n can be determined as

$$C_n = e^{ikna},$$

from the requirement that $\psi_k(x)$ should be the Bloch wave function;

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

((Proof))
Since

$$\psi_k(x+a) = \frac{1}{\sqrt{N}}\sum_{n=1}^{N} C_n\phi_a(x+a-na) = \frac{1}{\sqrt{N}}\sum_{j=1}^{N} C_{j+1}\phi_a(x-ja),$$

$$e^{ika}\psi_k(x) = \frac{1}{\sqrt{N}}e^{ika}\sum_{j=1}^{N} C_j\phi_a(x-ja),$$

we get the relation

$$C_{j+1} = e^{ika}C_j.$$

When $C_1 = e^{ika}$, C_n is obtained as

$$C_n = e^{ikna}.$$

Then we have the Bloch wave as

$$\psi_k(x) = \frac{1}{\sqrt{N}}\sum_{n=1}^{N} e^{ikna}\phi_a(x-na).$$

((Note)) It is also clear that this form of $\psi_k(x)$ satisfies the Bloch theorem,

$$\psi_k(x) = \frac{1}{\sqrt{N}}e^{ikx}\sum_{n=1}^{N} e^{-ik(x-na)}\phi_a(x-na) = e^{ikx}u_k(x),$$

where

$$u_k(x) = \sum_{n=1}^{N} e^{-ik(x-na)}\phi_a(x-na).$$

$u_k(x)$ is a periodic function with a lattice period a,

$$u_k(x+a) = \sum_{n=1}^{N} e^{-ik[x-(n-1)a]} \phi_a[x-(n-1)a] = u_k(x).$$

It can be easily shown that $\psi_k(x)$ possesses all the required properties of the Bloch waves,

$$\psi_{k+G}(x) = \sum_{n=1}^{N} e^{ikna} e^{iGna} \phi_a(x-na) = \sum_{n=1}^{N} e^{ikna} \phi_a(x-na) = \psi_k(x).$$

((Note))   Validity of the choice of above wave function

From the Bloch theorem, we have

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

We choose $u_k(x)$ as

$$u_k(x) = \sum_n \phi_a(x-na)$$

we note that $\phi(x-na)$ is a wave function localized at $x = na$ [like a Dirac delta function $\delta(x-na)$]. It is clear that $u_k(x)$ is periodic such that

$$u_k(x+a) = \sum_n \phi_a(x+a-na) = \sum_n \phi_a[x-(n-1)a] = u_k(x)$$

We note that

$$\psi_k(x) = e^{ikx} u_k(x)$$
$$= \sum_n e^{ikx} \phi_a(x-na)$$
$$\approx \sum_n e^{ikna} \phi_a(x-na)$$

In general case (3D system)

$$\psi_k(r) = e^{ik \cdot r} u_k(r)$$
$$= \sum_l e^{ik \cdot r} \phi_a(r-R_l)$$
$$\approx \sum_l e^{ik \cdot R_l} \phi_a(r-R_l)$$

2. Three dimensional case

According to the Bloch theorem, we consider the wavefunction given by

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} e^{i\mathbf{k}\cdot\mathbf{R}_j} \phi_a(\mathbf{r} - \mathbf{R}_j),$$

where we assume that there is one atom per unit cell. The number of atoms is N.

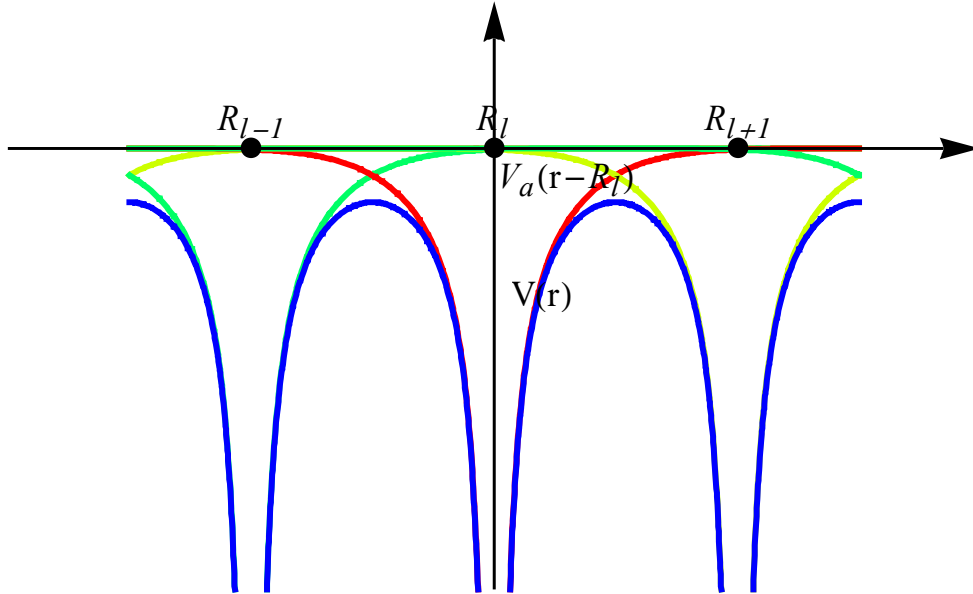$$\int d\mathbf{r} \phi_a^*(\mathbf{r} - \mathbf{R}_j)\phi_a(\mathbf{r} - \mathbf{R}_l) = \delta_{jl}.$$

The wavefunction $\psi_k(\mathbf{r})$ is normalized as follows.

$$\int d\mathbf{r} \psi_k^*(\mathbf{r})\psi_k(\mathbf{r}) = \frac{1}{N}\sum_{j,l}^{N} e^{-i\mathbf{k}\cdot\mathbf{R}_j} e^{i\mathbf{k}\cdot\mathbf{R}_l} \int d\mathbf{r}\phi_a^*(\mathbf{r} - \mathbf{R}_j)\phi_a(\mathbf{r} - \mathbf{R}_l)$$

$$= \frac{1}{N}\sum_{j,l}^{N} e^{-i\mathbf{k}\cdot\mathbf{R}_j} e^{i\mathbf{k}\cdot\mathbf{R}_l} \delta_{jl}$$

$$= 1$$

The Hamiltonian H is defined by

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}),$$

where $V(\mathbf{r})$ is the periodic potential of the present system.

Fig. Potential in the tight binding approximation. The potential $V_a(r - R_l)$ is the potential from the isolated atom at R_l. $\tilde{V}(r) = \sum_{j=1}^{N} V_a(r - r_j)$. $V(r)$ is a periodic potential of the system: $V(r) < \tilde{V}(r)$.

Here $V_a(r - R_l)$ is the potential of the atom isolated at the position vector R_l. The wavefunction $\phi_a(r - R_l)$ satisfies the Schrödinger equation,

$$[-\frac{\hbar^2}{2m}\nabla^2 + V_a(r - R_l)]\phi_a(r - R_l) = \varepsilon_a^{(0)}\phi_a(r - R_l),$$

where $\varepsilon_a^{(0)}$ is the energy eigenvalue of the isolated atom. The Hamiltonian of the system is given by

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

where $V(r)$ is the periodic potential of the system. It is different from the potential $\tilde{V}(r)$ which is defined by

$$\tilde{V}(r) = \sum_{j=1}^{N} V_a(r - r_j)$$

and

$$V(r + R_l) = V(r), \qquad \tilde{V}(r + R_l) = \tilde{V}(r)$$

We start with the eigenvalue problem with the Schrödinger equation for the Hamiltonian,

$$H\psi_k(r) = \varepsilon_k\psi_k(r),$$

Noting that

$$\tilde{V}(r)\phi_a(r - R_l) = \sum_{j=1}^{N} V_a(r - r_j)\phi_a(r - R_l)$$
$$= V_a(r - r_l)\phi_a(r - R_l)$$

we get

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$$[-\frac{\hbar^2}{2m}\nabla^2 + V(r)]\psi_k(r) = \frac{1}{\sqrt{N}}\sum_{l=1}^{N} e^{ik\cdot R_l}[-\frac{\hbar^2}{2m}\nabla^2 + V(r)]\phi_a(r - R_l)$$

$$= \frac{1}{\sqrt{N}}\sum_{l=1}^{N} e^{ik\cdot R_l}\{-\frac{\hbar^2}{2m}\nabla^2 + \tilde{V}(r) + [V(r) - \tilde{V}(r)]\}\phi_a(r - R_l)$$

$$= \frac{1}{\sqrt{N}}\sum_{l=1}^{N} e^{ik\cdot R_l}[-\frac{\hbar^2}{2m}\nabla^2 + V_a(r - R_l)]\phi_a(r - R_l)$$

$$+ \frac{1}{\sqrt{N}}\sum_{l=1}^{N} e^{ik\cdot R_l}[V(r) - \tilde{V}(r)]\phi_a(r - R_l)$$

Thus we have

$$[-\frac{\hbar^2}{2m}\nabla^2 + V(r)]\psi_k(r) = \varepsilon_a^{(0)}\frac{1}{\sqrt{N}}\sum_{l=1}^{N} e^{ik\cdot R_l}\phi_a(r - R_l)$$

$$+ \frac{1}{\sqrt{N}}\sum_{l=1}^{N} e^{ik\cdot R_l}[V(r) - \tilde{V}(r)]\phi_a(r - R_l)$$

$$= \varepsilon_k \frac{1}{\sqrt{N}}\sum_{l=1}^{N} e^{ik\cdot R_l}\phi_a(r - R_l)$$

By multiplying both sides of this equation by $\phi_a^*(r - R_{l'})$ and integrating over all the space, we have

$$(\varepsilon_k - \varepsilon_a^{(0)})\sum_{l=1}^{N} e^{ik\cdot R_l}\int dr \phi_a^*(r - R_{l'})\phi_a(r - R_l)$$

$$= \sum_{l=1}^{N} e^{ik\cdot R_l}\int dr \phi_a^*(r - R_{l'})[V(r) - \tilde{V}(r)]\phi_a(r - R_l)$$

We note that

$$\int dr \phi_a^*(r - R_{l'})\phi_a(r - R_l) = \delta_{l,l'}$$

(orthogonality of the wave function)

Thus we get

$$(\varepsilon_k - \varepsilon_a^{(0)})\sum_{l=1}^{N} e^{ik\cdot R_l}\delta_{l,l'} = \sum_{l=1}^{N} e^{ik\cdot R_l}\int dr \phi_a^*(r - R_{l'})[V(r) - \tilde{V}(r)]\phi_a(r - R_l)$$

or

$$(\varepsilon_k - \varepsilon_a^{(0)})e^{i\mathbf{k}\cdot\mathbf{R}_{l'}} = \sum_{l=1}^{N} e^{i\mathbf{k}\cdot\mathbf{R}_l} \int d\mathbf{r} \phi_a^*(\mathbf{r} - \mathbf{R}_{l'})[V(\mathbf{r}) - \tilde{V}(\mathbf{r})]\phi_a(\mathbf{r} - \mathbf{R}_j)$$

When we define the potential difference by

$$\Delta V(\mathbf{r}) = V(\mathbf{r}) - \tilde{V}(\mathbf{r})$$
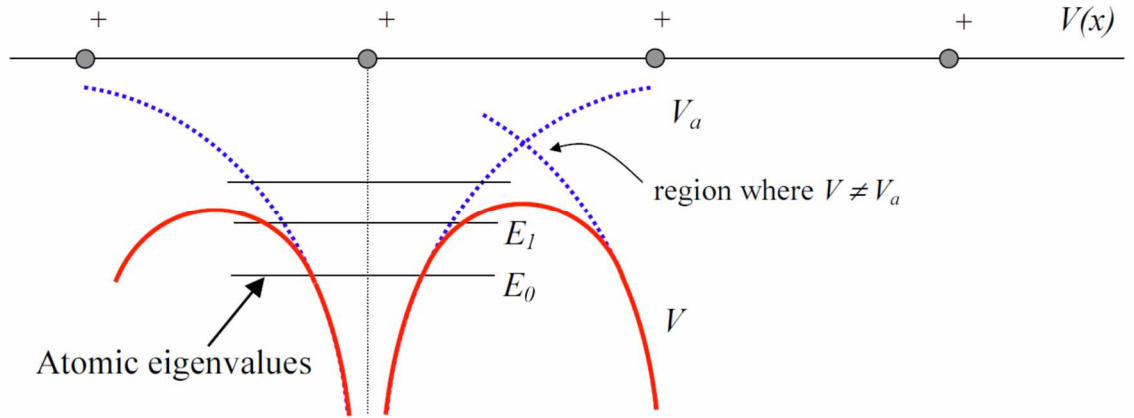
which is negative, we get

$$\varepsilon_k - \varepsilon_a^{(0)} = \sum_{l=1}^{N} e^{i\mathbf{k}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})} \int d\mathbf{r} \phi_a^*(\mathbf{r} - \mathbf{R}_{l'})\Delta V(\mathbf{r})\phi_a(\mathbf{r} - \mathbf{R}_l)$$

Note that this integral remains unchanged when the variable of the integral is changed from $\mathbf{r} - \mathbf{R}_l$ to $\mathbf{r}$, since

$$\Delta V(\mathbf{r} - \mathbf{R}_l) = \Delta V(\mathbf{r}).$$

Here we put

$$\mathbf{R}_l - \mathbf{R}_{l'} = \mathbf{R}_h,$$

Fig. Schematic form of the potential energy for tightly bound electrons, alng a given direction in the crystal. (Rigamonti and Carretta, Structure of Matter, Springer, 2007).

Then we have

$$\varepsilon_k - \varepsilon_a^{(0)} = \sum_{h=1}^{N} e^{i\mathbf{k}\cdot\mathbf{R}_h} \int d\mathbf{r}\, \phi_a^*(\mathbf{r}+\mathbf{R}_h)\Delta V(\mathbf{r})\phi_a(\mathbf{r})$$

When the matrix element t_h is defined by

$$t_h = \int d\mathbf{r}\, \phi_a^*(\mathbf{r}+\mathbf{R}_h)\Delta V(\mathbf{r})\phi_a(\mathbf{r}),$$
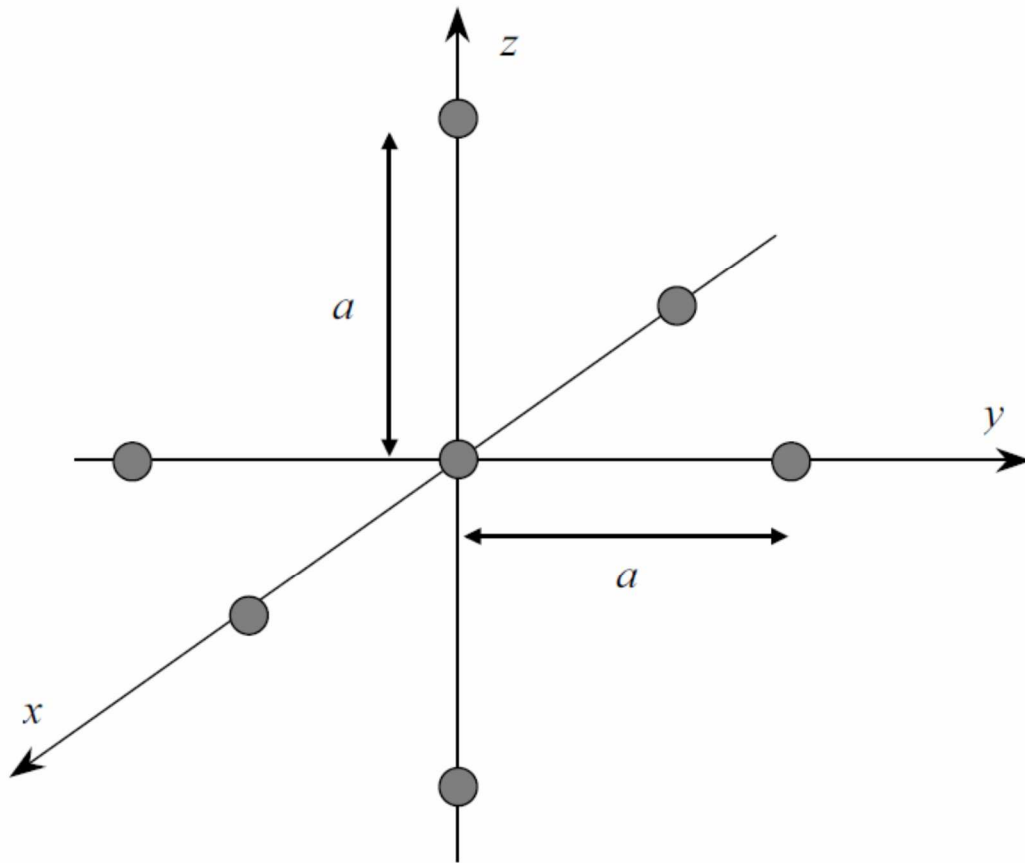
the energy eigenvalue is approximated by

$$\begin{aligned}
\varepsilon_k &= \varepsilon_a^{(0)} + \sum_h t_h e^{i\mathbf{k}\cdot\mathbf{R}_h} \\
&\approx \varepsilon_a^{(0)} - \alpha - \sum_{n.n.} t_{n.n.} e^{i\mathbf{k}\cdot\mathbf{R}_h} \quad . \\
&\approx \varepsilon_a^{(0)} - \alpha - \gamma \sum_{n.n.} e^{i\mathbf{k}\cdot\mathbf{R}_h}
\end{aligned}$$

The sum over $\mathbf{R}_h$ includes only values for which R_l denotes a nearest neighbor of R_j. In the present case, both α and γ are positive since ΔV is negative. Note that the n.n denotes the nearest neighbor pairs.
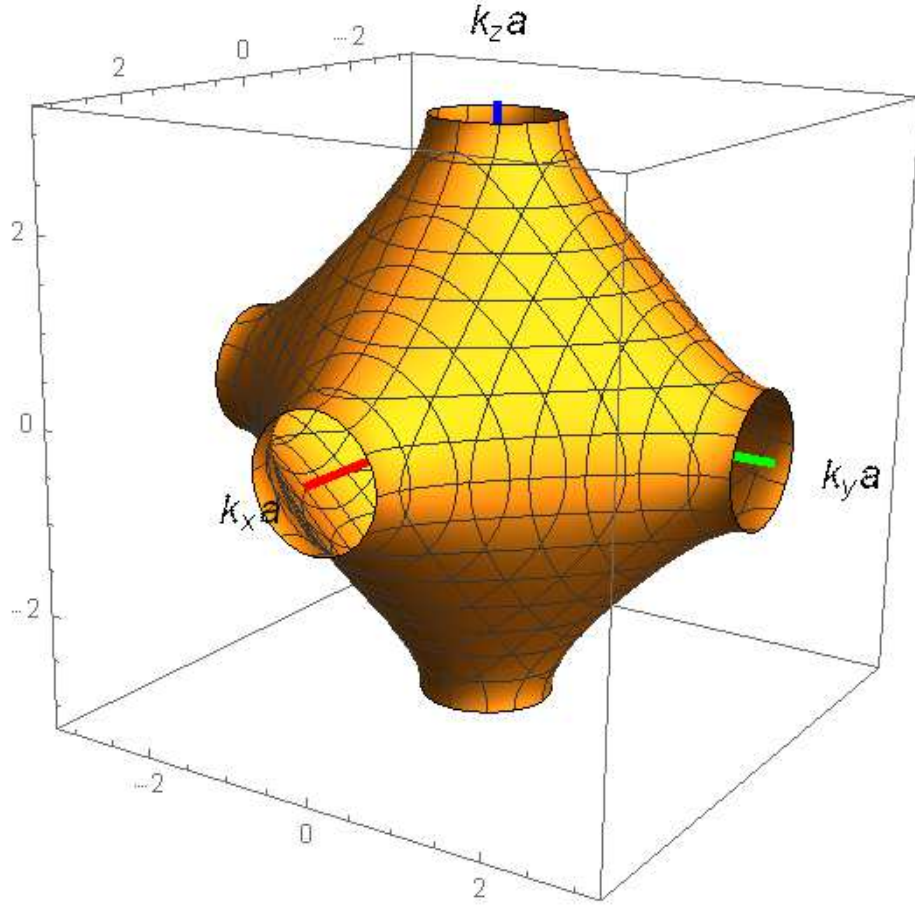
3.   **3D systems: scc, fcc, and bcc**
(a)   **Simple cubic**

For the simple cubic lattice with the lattice constant a,

$$\varepsilon_k = \varepsilon_a^{(0)} - \alpha - 2\gamma(\cos k_x a + \cos k_y a + \cos k_z a),$$

Fig.   ContourPlot for the constant energy surface in the reciprocal lattice space. $\cos k_x a + \cos k_y a + \cos k_z a = 0.75$.

When $|k_x a| << 1$, $|k_y a| << 1$, and $|k_z a| << 1$, we get
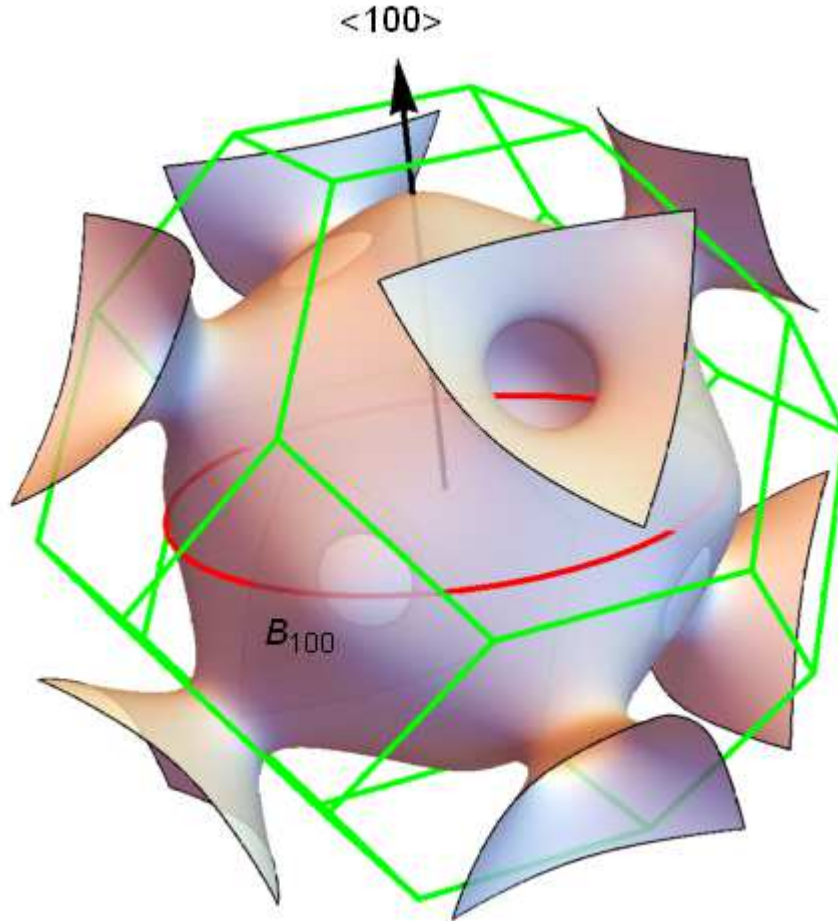
$$\varepsilon_k = \varepsilon_a^{(0)} - \alpha - 6\gamma + \gamma a^2 (k_x^2 + k_y^2 + k_z^2).$$

(b)   fcc

There are twelve nearest neighbor atoms in the fcc lattice;

$$\boldsymbol{a}_1 = \frac{a}{2}(0,1,1) \ , \quad \boldsymbol{a}_2 = \frac{a}{2}(-1,0,1) \ , \quad \boldsymbol{a}_3 = \frac{a}{2}(-1,1,0) \ , \quad \boldsymbol{a}_4 = \frac{a}{2}(1,0,1) \ , \quad \boldsymbol{a}_5 = \frac{a}{2}(0,-1,1) \ ,$$

$$\boldsymbol{a}_6 = \frac{a}{2}(1,1,0), \quad \boldsymbol{a}_7 = \frac{a}{2}(-1,-1,0), \quad \boldsymbol{a}_8 = \frac{a}{2}(0,1,-1), \quad \boldsymbol{a}_9 = \frac{a}{2}(-1,0,-1), \quad \boldsymbol{a}_{10} = \frac{a}{2}(1,-1,0),$$

$$\boldsymbol{a}_{11} = \frac{a}{2}(1,0,-1) \ , \quad \boldsymbol{a}_{12} = \frac{a}{2}(0,-1,-1)$$

$$\varepsilon_k = \varepsilon_a^{(0)} - \alpha - 4\gamma[\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_y a}{2}\right)\cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_z a}{2}\right)\cos\left(\frac{k_x a}{2}\right)]$$

.

Fig. ContourPlot for the Fermi surface of Copper (M. Suzuki and I.S. Suzuki).

https://www.researchgate.net/publication/322027719_Understanding_of_open_orbits_in_copper_Fermi_surface_with_the_use_of_Mathematica

(c)   bcc
There are eight nearest neighbor atoms in the fcc lattice;

$$\boldsymbol{a}_1 = \frac{a}{2}(1,1,1) \ , \ \boldsymbol{a}_2 = \frac{a}{2}(-1,1,1) \ , \ \boldsymbol{a}_3 = \frac{a}{2}(1,-1,1) \ , \ \boldsymbol{a}_4 = \frac{a}{2}(1,1,-1) \ , \ \boldsymbol{a}_5 = \frac{a}{2}(-1,-1,1) \ ,$$

$$\boldsymbol{a}_6 = \frac{a}{2}(-1,1,-1), \ \boldsymbol{a}_7 = \frac{a}{2}(1,-1,-1), \ \boldsymbol{a}_8 = \frac{a}{2}(-1,-1,-1),$$

$$\varepsilon_k = \varepsilon_a^{(0)} - \alpha - 8\gamma \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right).$$

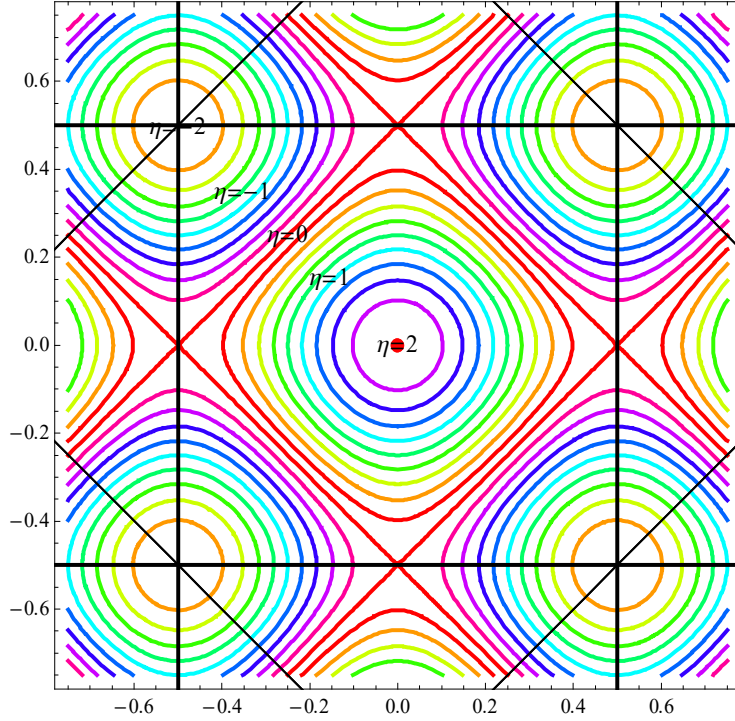((Mathematica program for the derivation of the energy dispersion in the Appendix)).

4.   2D system

For the 2D square lattice, we get

$$\varepsilon_k = \varepsilon_a^{(0)} - \alpha - 2\gamma(\cos k_x a + \cos k_y a)$$
$$= \varepsilon_a^{(0)} - \alpha - 2\gamma\eta$$

where η changes between -2 and 2,

$$\eta = \cos k_x a + \cos k_y a .$$

Fig.   ContourPlot of ε_k = constant in the tight binding approximation for the 2D square lattice (the first Brillouin zone). ($k_x a/2\pi$ - $k_y a/2\pi$). For the low energy, the ContourPlot shows a circle. ContourPlot of $\cos(2\pi x)+\cos(2\pi y$)= η, where η = -2, to 2 ($\Delta\eta$ = 0.1). The first Brillouin zone is denoted by the black thick line.

Near the origin of the k-space ($|k_x a| << 1$ and $|k_y a| << 1$), we get

$$\varepsilon_k = \varepsilon_a^{(0)} - \alpha - 4\gamma + \gamma a^2 (k_x^2 + k_y^2). \quad \text{(electron-like)}$$

The effective mass m^* is defined as

$$m^* = \frac{\hbar^2}{2\gamma a^2}.$$

Near the zone edge ($k_x a \approx \pi$ and $k_y a = \pi$), we get

$$\varepsilon_k = \varepsilon_a^{(0)} - \alpha - \gamma[(k_x a - \pi)^2 + (k_y a - \pi)^2]. \quad \text{(hole-lik)}$$

For the 1D lattice, we get

$$\varepsilon_k = \varepsilon_a^{(0)} - \alpha - 2\gamma \cos k_x a.$$

When $|ka| << 1$, we get

$$\varepsilon_k = \varepsilon_a^{(0)} - \alpha - 2\gamma + \gamma a^2 k^2.$$

The effective mass m^* is defined as
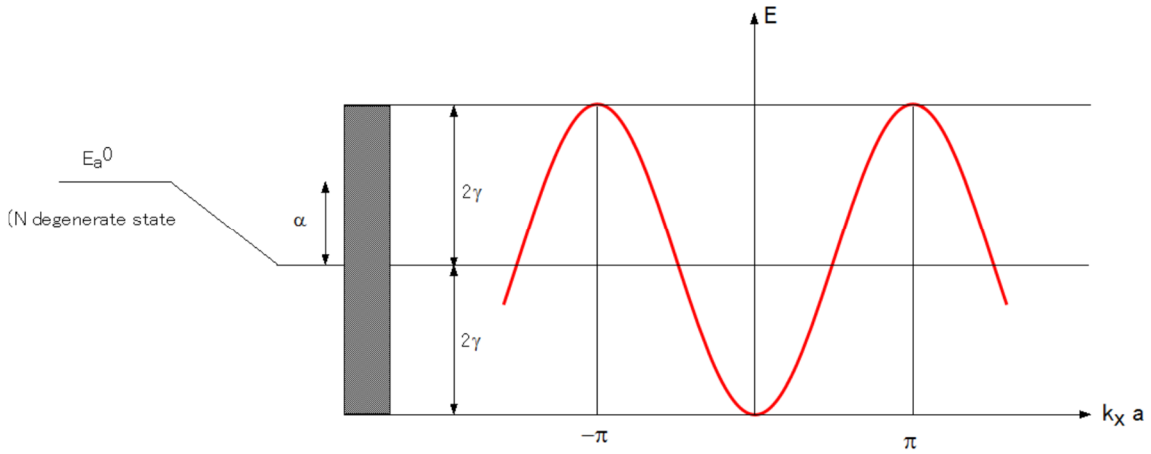
$$m^* = \frac{\hbar^2}{2\gamma a^2}.$$

Fig.   Formation of the energy band in the tight binding approximation

3. Summary
The following interesting conclusions may be derived from the above figures.
(a) The energy spectrum of the electrons consists of a number of allowed energy bands separated by energy gaps.
(b) The discontinuities in the energy spectrum, occur for the zone boundaries.

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APPENDIX

((**Mathematica**))
Program to find the form of energy dispersion for the tight binding approximation for the fcc and bcc

(a)   fcc lattice

```
Clear["Global`*"]; a1 = 2; A1 = a1/2 {0, 1, 1};

A2 = a1/2 {1, 0, 1}; A3 = a1/2 {1, 1, 0};
R1[h1_, h2_, h3_] := h1 A1 + h2 A2 + h3 A3;
Rmag = R1[h1, h2, h3].R1[h1, h2, h3];
list1 =
 Table[{Rmag, R1[h1, h2, h3]}, {h1, -1, 1, 1},
    {h2, -1, 1, 1}, {h3, -1, 1, 1}] //
   Flatten[#, 2] &;
list2 = Sort[list1, #1[[1]] < #2[[1]] &];
eq1 = Select[list2, (1 < #[[1]] < 3) &];
L1 = Length[eq1]; X[i_] := eq1[[i, 2]];
k = {kx, ky, kz};
f1 = Sum[Exp[i a/2 (k.X[i])], {i, 1, L1}] //

    ExpToTrig // FullSimplify
```

$$4 \left(\cos\left[\frac{a\,ky}{2}\right] \cos\left[\frac{a\,kz}{2}\right] + \cos\left[\frac{a\,kx}{2}\right] \left(\cos\left[\frac{a\,ky}{2}\right] + \cos\left[\frac{a\,kz}{2}\right] \right) \right)$$

(b)   bcc lattice

```
Clear["Global`*"]; a1 = 2; A1 = a1/2 {-1, 1, 1};

A2 = a1/2 {1, -1, 1}; A3 = a1/2 {1, 1, -1};
R1[h1_, h2_, h3_] := h1 A1 + h2 A2 + h3 A3;
Rmag = R1[h1, h2, h3].R1[h1, h2, h3];
list1 =
 Table[{Rmag, R1[h1, h2, h3]}, {h1, -2, 2, 1},
    {h2, -2, 2, 1}, {h3, -2, 2, 1}] //
   Flatten[#, 2] &;
list2 = Sort[list1, #1[[1]] < #2[[1]] &];
eq1 = Select[list2, (2 < #[[1]] < 4) &];
L1 = Length[eq1]; X[i_] := eq1[[i, 2]];
k = {kx, ky, kz};
f1 = Sum[Exp[i a/2 (k . X[i])], {i, 1, L1}] //

   ExpToTrig // FullSimplify
```

$$8 \cos\left[\frac{a\, kx}{2}\right] \cos\left[\frac{a\, ky}{2}\right] \cos\left[\frac{a\, kz}{2}\right]$$