§ 5.3 Tight binding approximation

In preceding section we considered the weak periodic potential acting on the non interacting electrons as a small perturbation of its free motion. This treatment is justified only if the electron kinetic energy is large as compared with the variations of its potential energy. Its follows from virial theorem that the average kinetic energy of an electron in atom, molecule or crystal should be of the order of its average potential energy. This situation is brought about, for example, when a crystal is irradiated by electrons of at least several hundred eV.

We used this approach only for qualitative but not quantitative demonstration that the weak periodic potential leads to appearance of the band gap in the energy spectrum of the free electrons. To quantitatively describe the property of electrons in real systems is needs to exactly solve corresponding Schrodinger equation by Hartree-Fock, DFT or by any other methods.



Vice versa for tight binding (TB) approximation we assume that the electrons tightly bound, have a good localization. It is clear that this approach is not quantitatively exact but more realistic than the approximation of weakly bonded electrons. This approximation can be applied for internal (bonded) electrons located on the deep of electrons spectrum ab useful from methodical point of view. This approximation suggest exist of analytical solution for Schrodinger equation so we can directly calculate some important parameters characterize the properties of electrons in real crystals.

Let's start from isolated atom. On Figure 15 you can see the stylized image of periodic 3D crystal. All atoms are numbered and located in corresponding lattice sites. Assume that the Schrodinger equation describing the properties of electron in s-state (ground state) is:

$$\left(-\frac{\hbar^2}{2m}\Delta + U_0\right)\varphi_0 = E_0\varphi_0 \tag{1}$$

Here U_0 is the potential energy of electrons for isolated atoms (solid line on Figure 15), R_n - gives the position of atom with number n (or vector of parallel translations), r- position of electron, ρ_n - position of the same electron with respect to atom with number n and φ_0 - the electron wave function for s-state of an isolated atom.

The combination of isolated atoms into a crystal lattice leads to the splitting of the energy levels E_0 due to the occurrence of interatomic interactions and, as a consequence, the change in U_0 (see 1). The corresponding Schrodinger equation for crystal lattice is:

$$\left(-\frac{\hbar^2}{2m}\Delta + V\right)\varphi = E\,\varphi\tag{2}$$

It is important to emphasize that potential V is a periodic function (dotted line in Figure 15) and satisfies the condition:

$$V(\vec{r}) = V(\vec{r} + \vec{R}_n) \tag{3}$$

It is clear that the potential energy of crystal is less than the corresponding potential energy for isolated atoms (crystal lattice is more stable than the set of non interacting atoms):

$$\sum_{n=0}^{N} U_o(\vec{r} + \vec{R}_n) > V(\vec{r})$$
(4)

What about the new wave function $\varphi(\vec{r})$? There is the Bloch's theorem [https://en.wikipedia.org/wiki/Bloch %27s_theorem] showing that in periodic structures the wave function of electrons can be represented in the following form:

$$\varphi(\vec{r}) = u(\vec{r})e^{i\vec{k}\vec{r}}$$
, here $u(\vec{r}) = u(\vec{r} + \vec{R}_n)$ is a periodic function (5)

This theorem has a clear physical basis. Due to the periodicity of the crystal lattice at T = 0, the function describing any physical property of the crystal must be periodic with the same period. In other words, all unit cells are equivalent not only in structural but also in physical properties. The square value of the wave function gives the probability density of finding a particle at the corresponding point inside the crystal and this function must be periodic. This probability can be calculated directly from (5):

$$|\varphi(\vec{r})|^2 = \varphi^* \cdot \varphi = u(\vec{r})e^{i\vec{k}\vec{r}}u^*(\vec{r})e^{-i\vec{k}\vec{r}} = |u(\vec{r})|^2 \text{ but last function must be periodical} = |u(\vec{r}+\vec{R}_n)|^2$$
(6)

In our case we can present the wave function of s-electron (internal electrons of atom) in the form:

$$\varphi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{n=0}^{N} \varphi_0(\vec{\rho}_n) e^{-i\vec{k}\cdot\vec{\rho}_n} = \sum_{n=0}^{N} \varphi_0(\vec{\rho}_n) e^{i\vec{k}\cdot\vec{R}_n}$$
(7)

Let us assume that the wave functions for isolated atoms are well localized and normalized to unity this means that:

$$\int_{-\infty}^{+\infty} \varphi_0(\vec{\rho}_n) \varphi(\vec{\rho}_m) dV = \delta_{n,m}$$
(8)

Now we are ready to start the calculation of electron energy in periodic lattice in tight binding approximation. Generally the corresponding equation we get from (2):

$$E = \frac{\int \varphi^* (-\frac{\hbar^2}{2m} \Delta + V) \varphi \, dV}{\int \varphi^* \varphi \, dV}$$
(9)

Start calculation with the lower integral.

$$\int \varphi^* \varphi dV => applying(7) => \int \sum_n \varphi_0^*(\rho_n) e^{-i\vec{k}\cdot\vec{R}_n} \cdot \sum_m \varphi_0(\rho_m) e^{i\vec{k}\cdot\vec{R}_m} dV =$$

$$= \sum_n \sum_m e^{-i\vec{k}\cdot\vec{R}_n} e^{i\vec{k}\cdot\vec{R}_m} \int \varphi_0^*(\rho_m) \varphi_0(\rho_n) dV =$$

$$= \sum_n \sum_m e^{-i\vec{k}\cdot(\vec{R}_m - \vec{R}_n)} \delta_{n,m} = N, \text{ here N is a total number of atoms in the lattice.}$$
(10)

The upper integral:

After using equation (1) (take the kinetic energy part) we have:

$$-\frac{\hbar^2}{2m}\Delta\varphi_0 = (E_0 - U_0)\varphi_0 \tag{12}$$

And after substitution to (11):

$$\sum_{n} \sum_{m} e^{i\vec{k}(\vec{R}_{m}-\vec{R}_{n})} [\int \varphi_{0}^{*}(\rho_{n})(E_{0}+V-U_{0})\varphi_{0}(\rho_{m})dv] =$$

$$=\sum_{n} \sum_{m} e^{i\vec{k}(\vec{R}_{m}-\vec{R}_{n})} [\int \varphi_{0}^{*}(\rho_{n})(E_{0}+V-U_{0})\varphi_{0}(\rho_{m})dv] =$$

$$=E_{0} \sum_{n} \sum_{m} e^{i\vec{k}(\vec{R}_{m}-\vec{R}_{n})} \int \varphi_{0}^{*}(\rho_{n})\varphi_{0}(\rho_{m})dv + \sum_{n} \sum_{m} e^{i\vec{k}(\vec{R}_{m}-\vec{R}_{n})} \int \varphi_{0}^{*}(\rho_{n})(V-U_{0})\varphi_{0}(\rho_{m})dv =$$

$$=N \cdot E_{0} + \sum_{n} \sum_{m} e^{i\vec{k}(\vec{R}_{m}-\vec{R}_{n})} \int \varphi_{0}^{*}(\rho_{n})(V-U_{0})\varphi_{0}(\rho_{m})dv$$
(13)

Let's now to simplify the second integral in (13). I write the members with n=m=0 and $n, m \neq 0$ separately. Due to periodicity property of crystal the summation can be simplified:

$$\sum_{n=0}^{N} \sum_{m=0}^{N} e^{i\vec{k}(\vec{R}_{m}-\vec{R}_{n})} \int \varphi_{0}^{*}(\rho_{n})(V-U_{0})\varphi_{0}(\rho_{m}) dv = \sum_{n=0}^{N} e^{i\vec{k}(\vec{R}_{n}-\vec{R}_{0})} \int \varphi_{0}^{*}(\rho_{n})(V-U_{0})\varphi_{0}(\rho_{0}) dv = N \int \varphi_{0}^{*}(\rho_{0})(V-U_{0})\varphi_{0}(\rho_{0}) dv + N \sum_{n\neq0} e^{i\vec{k}(\vec{R}_{n}-\vec{R}_{0})} \int \varphi_{0}^{*}(\rho_{n})(V-U_{0})\varphi_{0}(\rho_{0}) dv$$
(14)

If we take into the account the fact that $V \le U_0$ so we can define new variables:

$$\int \varphi_{0}^{*}(\rho_{0})(V-U_{0})\varphi_{0}(\rho_{0})dv = -C$$

$$\int \varphi_{0}^{*}(\rho_{n})(V-U_{0})\varphi_{0}(\rho_{0})dv = -A_{0,n}$$
(15)

With the new notation, the final result is look as follows:

$$E = E_0 - C - \sum_{n \neq 0} e^{i\vec{k}(\vec{R}_n - \vec{R}_0)} A_{0,n}$$
(16)



The values for electron wavevector projections k_x, k_y, k_z , must be takken from nonequvalent region $\left[-\frac{\pi}{2}, \frac{\pi}{2}\right]$

(see Figure 10). Important to understand that now the crystal is three dimensional and nonequivalent values for wavevector filling the cube with side length pi. This cube containing non equivalent wavevectors have the name Irreducible Brillouin Zone or just IBZ. The view of IBZ depends on the symmetry of the lattice and for different structures it can be found here [https://en.wikipedia.org/wiki/Brillouin_zone].

For cubic crystall IBZ is a cube and looks like this (see Figure 17):



Here Γ ,X,M,R – some standard symmetrical points and directions. Final result of energy calculations (16) is:

$$E(k_{x},k_{y},k_{z}) = E_{0} - C - 2A(\cos(k_{x}a) + \cos(k_{y}a) + \cos(k_{z}a))$$
(18)



Due to the 4-dimensionality of function (18), we cannot plot the entire function, but only some of its sections. In example the Γ -X direction was selected.

$$E(k_x, 0, 0) = E_0 - C - 2A(\cos(k_x a) + 2)$$
(19)

As you can see, the union of independent atoms into a crystal leads to:

1.) decrease in the energy of electrons by **C**

2.) the splitting of the s-state into an energy band (leads to the appearance of a band structure in the energy spectrum of electrons).

This process is shown in Figure 18 and the appeared zone has a width of 4A.

The same type of calculations can be done for 2p state. The results presented in Figure 19. The result is qualitatively the same as for the 1s state, but there is a slight difference.

The point is that the 2p state is three times degenerate. As you remember from the course of quantum mechanics the wave function for hydrogen-like atoms depends on three quantum numbers: n-principal, l-orbital, and mmagnetic. For 2p-state n=2, l=1 and m have three possible values +1,0,-1. Energy depends only on principle quantum number. The formation of crystals from independent atoms leads to the splitting of each state into a corresponding energy band (see Figure 19). Qualitatively this process for s and p-states is shown on Figure 20. It is clear that for more complicated (with large number of electrons) atoms it is needs to take into not only **s** and **p** states but **d** and **f** too. In this case, a more complex picture arises with a large number of crossing energy bands (see Figure 15).

Another important function that can be measured experimentally is the density of states function (5.1/25). For systems with a large number of electrons (and states that we must take into account), the density state function must be calculated separately for each energy band. It is practically impossible to do this analytically, but it can be done numerically. Programs that calculate the properties of a real system do this using the following formula:

$$G(E) = \sum_{n} \sum_{(k_x, k_y, k_z) \in 1\text{BZ}} \delta(E - E_n(k_x, k_y, k_z))$$
(20)

Results of this calculations for 1d example is presented on Figure 21. The Fermi energy can be calculated for T=0 from equation:

$$2N = \int_{0}^{E_{F}} G(E) dE$$
(21)

Chemical potential can be calculated in case T > 0 from expression:

$$2N = \int_{0}^{\infty} G(E)f(E,T)dE$$
(22)