Electronic Structure of Calculations Based on Tight Binding Method

Mehmet Ergin

11.01.2010

Abstract: Different methods using to calculate electronic band structure, however tight binding method is used widely and it works in more different cases. In this report, introductory knowledge is given about band structure and tight binding method. Tight Binding’s 1D and 2D calculations also shown in this report.

Introduction:

Electronic band structure is the ranges of energy, which electrons is forbidden or allowed to have. Band structure determines optical and electronic properties of materials. Band gap is important topic in electronic band structure; it means, “the difference between the top of the highest occupied band and the bottom of the lowest unoccupied band” [1] In solids too many atom came together and the number of orbitals becomes large, because of that energy differences small and energy bands is discrete. Although, when some of the intervals of energy contain no orbital, it produced the band gaps.[2] Metals have so many band which is partly filled, so metals have high conductivity. Fully occupied band in insulator or semiconductor called the valance band. Valance band is the highest range of electron energies, the highest point of the valance band is called the valance band edge.

One another important subject is Fermi surface. Pauili exclusion principle said that maximum only one electron allowed per quantum state, so that number of bands may be partially filled. “In momentum space, these particles fill up a sphere of radius \( p_F \), the surface of which is called the Fermi surface.” [3]

Various techniques used for to calculate the band structure energy. Some of these methods are; Pseudopotentials, Green’s Function, Independent Electron Approximation, Muffin-Tin Potentials and Tight Binding.

Tight binding method is different from other methods, since it is suitable for more cases and directly suitable for any real solid.[4] Tight binding method is the easiest method for calculating band structures in not only conceptually but also computationally. This method also referred to as Linear Combination of Atomic Orbitals. [5] Tight binding method is based on Linear Combination of Atomic Orbitals (LCAO) approach used in molecular physics. Because of this situation, tight binding method is not only applied to crystalline but also applied to non-crystalline materials. “The approximation is quite good for the inner electron of atoms, but it is not often a good description of the conduction themselves.” [6]

One of the simplest and general case of in tight binding is an isolated s band. To calculate this case, we write Hamiltonian ‘H’ as;

\[
H_{\text{at}} \psi(n) = E_n \psi(n) \tag{1}
\]
\[ H = H_{at} + \Delta U(r) \] (2)

Where \( H_{at} \) containing the potential and kinetic energy of one ion. \( \Delta U(r) \) is the potential generated by other ions in the lattice. Schrödinger equation also satisfied by the eigenfunctions of the atomic problem

\[ H_{at} \phi_n(r) = E_n \phi_n(r) \] (3)

In here \( n \) means, collectively a full set of quantum numbers. Then if we will expand formulation (3) we get,

\[ \phi(r) = \sum_n b_n \phi_n(r) \] (4)

Than we make a combination of localized states with the symmetry of the lattice:

\[ \psi(r) = \sum_R e^{i \mathbf{k} \cdot \mathbf{R}} \phi(r-R) \] (5)

Bloch function can be written like Formulation (5), \( \phi \) in this formulation known as Wannier formulation.

1D Band Structure of a Periodic Linear Carbon Atom’s Chain

\[ \ldots o o o o o o o o o \ldots \to x \]

Distances between two atom is “a”, periodic chain consist of same atom.

Considering an atom inside the chain; there are 2 nearest neighbors.

\[ \varepsilon(k) = E_s - \beta \sum_{n,n} \gamma(\mathbf{R}) \cos(k \mathbf{a} \cdot \mathbf{R}) \] (6)

\[ \gamma(\mathbf{R}) = -\int d\mathbf{r} \phi(\mathbf{r}) \Delta u(\mathbf{r}) \phi(\mathbf{r} - \mathbf{R}) \] (7)

\[ \beta = -\int d\mathbf{r} |\mathbf{\Delta u}(\mathbf{r})| |\phi(\mathbf{r})|^2 \] (8)

\[ \mathbf{R} = \pm a \mathbf{x}\]

\[ \mathbf{k} \cdot \mathbf{R} = \pm a \mathbf{x} \cdot \mathbf{k} = \pm a \mathbf{k} \]

\[ \varepsilon(\mathbf{k}) = E_s - \beta - \gamma \cos(\mathbf{k} \cdot \mathbf{a}) + \gamma \cos(\mathbf{k} \cdot -\mathbf{a}) \] (9)

\[ \varepsilon(\mathbf{k}) = E_s - \beta - 2\gamma \cos(\mathbf{k} \cdot \mathbf{a}) \] (10)

\[ \varepsilon(\mathbf{k}) = E_s + 2\gamma(\cos(k_x a) + \cos(k_y a)) \] (11)

Limits: \( \mathbf{k} a \to 0; \cos(\mathbf{k} a) \to 1 - \frac{1}{2}(\mathbf{k} a)^2 \)

\[ \varepsilon(\mathbf{k}) = E_s - \beta - 2\gamma(ka)^2 \] (12) : Linear function having no dependence on \( \mathbf{k} \).

Tight Binding Method for 2D Square Lattices

Normally the energy structure of crystals depends on the interactions between orbitals in the lattice. However, the tight binding approximation neglects interactions between atoms separated by large distances, an approximation which greatly simplifies the analysis. In solid state physics, the tight binding model calculates the electronic band structure using an approximate set of wave functions based upon superposition of orbitals located at each individual atomic site. [7]

In a tight binding approximation including only first nearest neighbor s-orbital, the band structure is given by:

\[ \varepsilon(\mathbf{k}) = E_s + \sum_k \epsilon^{\mathbf{k}} \gamma(\mathbf{R}) \] (13)

Figure 2: 2D square lattice fragment.

Where \( \gamma \) is the overlap integral between s-orbitals, \( \mathbf{R} \) is the translation vector of the lattice, and \( \hbar \mathbf{k} \) is the "crystal momentum" the quantum number for periodic systems. The band structure for a simple cubic lattice can now be readily calculated. Assuming that the bond integrals couple only to the first four nearest neighbors with position vectors \( \mathbf{R} \) equal to \((\pm a, 0)\) and \((0, \pm a)\), gives

\[ \varepsilon(\mathbf{k}) = E_s + 2\gamma(\cos(k_x a) + \cos(k_y a)) \] (14)
Figure 3: Four nearest neighbors included in transfer, the first Brillouin zone.

Figure 4: Tight Binding band structure of 2D square lattice Carbon atom, 3D view.

Figure 5: Tight Binding band structure of 2D square lattice Carbon atom, 2D view.

**Tight Binding Band Structure of Graphene**

Graphene is a single sheet of carbon atoms, which is arranged in the honeycomb structure. Referring to figure, the lattice vectors can be written as:

\[ \vec{a}_1 = a_0 \sqrt{3} (1/2, \sqrt{3}/2), \]
\[ \vec{a}_2 = a_0 \sqrt{3} (-1/2, \sqrt{3}/2) \]

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\[ \vec{a}_2 = a_0 \sqrt{3} (-1/2, \sqrt{3}/2) \]

\[ \vec{a}_3 = a_0 \sqrt{3} (1/2, -\sqrt{3}/2) \]

\[ \vec{a}_4 = a_0 \sqrt{3} (-1/2, -\sqrt{3}/2) \]

\[ | \vec{a}_{(1,2)}^* | = a = \sqrt{3} a_0 \]

\[ \varphi_k = \sum_{R \in G} e^{ikr} \varphi (x - R) \] (15)

We have to think that there are two orbitals per unit-cell.

\[ \varphi(x) = b_1 \varphi_1(x) + b_2 \varphi_2(x) = \sum b_n \varphi_n \] (16)

Then, consider the Hamiltonian for a single electron in the atomic potential given by all the carbon atoms:

\[ H = \frac{\hat{p}^2}{2m} + \sum_{R \in G} (V_{at} (\vec{x} - \vec{x}_1 - \vec{R}) + V_{at} (\vec{x} - \vec{x}_2 - \vec{R})) \] (17)

\[ \vec{x}_{1,2} \] denote the position of the two carbon atoms within the unit-cell.

\[ H \varphi_1 = \epsilon_1 \varphi_1 + ( \sum_{R \neq 0} (V_{at} (\vec{x} - \vec{x}_1 - \vec{R}) + V_{at} (\vec{x} - \vec{x}_2 - \vec{R}))) \varphi_1 \] (18)

\[ \epsilon_1 \] is the eigenvalue for the atomic pz state.

\[ H \varphi_{1,2} = \epsilon_{1,2} + \Delta U_{1,2} \varphi_{1,2} \]

Let \( \epsilon_1 = \epsilon_2 \) and choose \( \epsilon_{1,2} = 0 \),

\[ H \varphi_1 = \Delta U_1 \varphi_1 \text{ and } H \varphi_2 = \Delta U_2 \varphi_2 \]

We should solve to Schrödinger equation:

\[ H \varphi_k = \epsilon(\vec{k}) \varphi_k, \quad \epsilon(\vec{k}) \varphi_j \mid \varphi > = \varphi_j \mid \Delta U_j \mid \varphi > \] (20)
We have two parameters; so two equations are required to solve this eigenvalue problem. Then assume that only nearest-neighbor overlap integrals have to be taken into account. For instance, $\langle \phi_1 | \phi_2 \rangle$ is non-zero as is $\int \phi_1^* (\vec{x}) \phi_2 (\vec{x} - \vec{a}_1) .
$

\begin{align}
\langle \phi_1 | \phi_2 \rangle &= b_1 + b_2 (\int \phi_1^* (\vec{x}) \phi_2 (1 + e^{-i\vec{k} \cdot \vec{a}_1} + e^{-i\vec{k} \cdot \vec{a}_2}) \\
&= b_1 + b_2 (\int \phi_2^* (\vec{x}) \phi_1 (1 + e^{i\vec{k} \cdot \vec{a}_1} + e^{i\vec{k} \cdot \vec{a}_2})
\end{align}

(21)

Overlap integral is real: $\gamma_0 = \int \phi_1^* \phi_2 \in R$ (23)

$\gamma_1 = \int \phi_1^* \Delta U_1 \phi_2 = \int \phi_2^* \Delta U_2 \phi_1$ (24)

$\langle \phi_1 | \Delta U_1 | \phi_2 \rangle = b_2 \gamma_1 (1 + e^{-i\vec{k} \cdot \vec{a}_1} + e^{-i\vec{k} \cdot \vec{a}_2})$ (25)

$\langle \phi_1 | \Delta U_1 | \phi_2 \rangle = b_1 \gamma_1 (1 + e^{i\vec{k} \cdot \vec{a}_1} + e^{i\vec{k} \cdot \vec{a}_2})$ (26)

Eigenvalue problem is formulated as:

$\alpha(k) = 1 + e^{-i\vec{k} \cdot \vec{a}_1} + e^{-i\vec{k} \cdot \vec{a}_2}$ (27)

$\begin{align}
\frac{\varepsilon(\vec{k})}{\varepsilon^*(\vec{k})} &= \frac{a(y_0 \varepsilon(\vec{k}) - \gamma_1)}{\varepsilon(\vec{k})} \\
&= \frac{b_1}{b_2} = (\frac{\gamma_0}{\gamma_1})
\end{align}$ (28)

$\varepsilon(\vec{k}) = \pm \gamma_1 \sqrt{3 + 2 \cos(\vec{k} \cdot \vec{a}_1) + 2 \cos(\vec{k} \cdot \vec{a}_2) + 2 \cos(\vec{k} \cdot (\vec{a}_2 - \vec{a}_1))}$ (29)

If we express this result in different form by using the (x,y) components.

$\varepsilon (k_x k_y) = \pm \gamma_1 \sqrt{1 + 4 \cos \left( \frac{\sqrt{3}}{2} k_x \right) \cos \left( \frac{\sqrt{3}}{2} k_y \right) + 4 \cos^2 \left( \frac{\sqrt{3}}{2} k_x \right)}$ (30)

$a$ is the lattice constant, $a = \sqrt{3} a_0$ [8]

Figure 7: Tight Binding band structure of graphene, 3D view.

Figure 8: Tight Binding band structure of graphene, 2D view.

Conclusion:

Tight binding approximation is the most practical method to calculate electronic band structure. It is used in theoretical solid state physics and material science. Tight binding method is worked in many different cases and easily to calculate band structure in conceptually and computationally.

1D linear carbon atom chain investigated and band energy is a cosine function. In 2D square carbon lattice and graphene also investigated, these systems band energy is equal to the cosine summation. In 2D systems electronic band structures figure was plotted by Matlab and especially in Graphenes plot, figure 7, band gap is easily seen.
References:


