

# The Tight Binding Method for Band Structure Calculation

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The tight binding model is a powerful tool for calculating the band structure in solid-state physics. Using the Bloch theorem and the hypothesis of linear combination of atomic orbitals, the model allows us to efficiently calculate the energy of crystals. In this paper, we provide a brief introduction to the tight binding model and its applications to 2D square lattices and graphene.

## I. INTRODUCTION

A crystal is a solid material whose constituents (such as atoms, molecules, or ions) are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions. Often encountered are lattices under translational and rotational symmetry. These are called Bravais lattices, named after the French physicist Auguste Bravais who discovered the 14 possible Bravais lattices [1]. One can identify a Bravais lattice by its mathematical representation: a regular array of points  $\{\mathbf{R}\}$  in 3D which satisfies

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \quad (1)$$

where  $n_1, n_2, n_3$  are integers and  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$  are known as the primitive lattice vectors.

The knowledge of Bravais lattice allows us to represent system as a periodic Hamiltonian

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

which has eigenstates satisfying the lattice periodicity, known as Born-von Karman boundary condition [1]:

$$\psi(\mathbf{r} + N_i\mathbf{a}_i) = \psi(\mathbf{r}), \quad (3)$$

Thus, investigating the dynamics of an electron under the crystal Hamiltonian allows us to explain the electronic properties of crystals. However, this work is astonishingly difficult as our system size is  $\sim 10^{23}$  atoms, though the one atom problem is already known (and complicated).

This suggests us to look at the crystal in a more enlightening way. When an atom is placed in a crystal, its atomic orbital overlaps adjacent atomic sites. The overlap is typically small as electrons are tightly bound. Therefore, it is reasonable to make the assumption that the crystal wavefunction is constructed from a linear combination of individual atomic wavefunctions. This is an important assumption and, in chemistry, is widely known as LCAO (linear combination of atomic orbitals).

The true Hamiltonian of the system is hence equal to the single atom Hamiltonian plus small interatomic interaction matrix elements. In the tight binding model, this correction is assumed to contain only interaction terms (hoppings) between the central atom and its nearest neighbors.

## II. GENERAL FORMALISM

### A. Bloch's theorem

We begin with the Bloch's theorem, which states that in a periodic potential (lattice) like crystals, the solutions of (2) can be chosen as

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}), \quad (4)$$

where  $\mathbf{k}$  is the so-called crystal momentum vector and  $u_{\mathbf{k}}(\mathbf{r})$  is a periodic function satisfying the boundary conditions of the lattice, i.e.  $u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}(\mathbf{r})$ .

While the proof of Bloch's theorem [2] is omitted in this paper, we can intuitively see that this comes from the fact that the translation operator  $T_{\mathbf{R}}$ , defined by  $T_{\mathbf{R}}f(\mathbf{r}) = f(\mathbf{r} - \mathbf{R})$ , commutes with our periodic  $H$ . Therefore, they can have simultaneous eigenstates. In addition, the factor  $e^{i\mathbf{k}\mathbf{r}}$  comes from the representation  $T_x = e^{i\hat{p}x/\hbar}$  of the translation operator, thus the name "crystal momentum vector" of  $\mathbf{k}$ . An alternative form of Bloch's theorem that can be obtained directly from (4) is

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{\mathbf{k}}(\mathbf{r}), \quad (5)$$

where  $\mathbf{R}$  is a lattice vector.

Bloch wavefunction representation is a powerful tool that has tremendous applications in solid-state physics. Particularly, in the next section, we will use the Bloch wavefunction to implement the tight binding model.

### B. The tight binding model

Combining Bloch's theorem with the idea of LCAO introduced in section I, one expects to seek a solution to the full crystal Hamiltonian of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\phi(\mathbf{r} - \mathbf{R}), \quad (6)$$

where in the normalization factor  $N$  is the number of atoms in the crystal. One can easily verify (6) indeed satisfies the Bloch condition (5) noting that

$$\begin{aligned}
\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) &= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}'} e^{i\mathbf{k} \cdot \mathbf{R}'} \phi(\mathbf{r} + \mathbf{R} - \mathbf{R}') \\
&= \frac{1}{\sqrt{N}} e^{i\mathbf{k} \cdot \mathbf{R}} \left[ \sum_{\mathbf{R}'} e^{i\mathbf{k} \cdot (\mathbf{R}' - \mathbf{R})} \phi(\mathbf{r} - (\mathbf{R}' - \mathbf{R})) \right] \\
&= \frac{1}{\sqrt{N}} e^{i\mathbf{k} \cdot \mathbf{R}} \left[ \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \phi(\mathbf{r} - \mathbf{R}) \right] \\
&= e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{\mathbf{k}}(\mathbf{r}).
\end{aligned} \tag{7}$$

We can further simplify (6) by assuming that all atomic wavefunctions of the same element are in the same atomic level. This assumption turns out often the realistic case and, in fact, one can prove this assumption by writing each  $\phi(\mathbf{r} - \mathbf{R})$  as a linear combination of atomic orbitals and using the condition of small interatomic correction to conclude that the coefficients are approximately zero except for a specific orbital (we let the reader refer to [3]).

Thus, in (6) we can restrict  $\phi(\mathbf{r})$  to be an atomic eigenstate  $\phi_0(\mathbf{r})$  with energy  $E_0$  (for example, the  $s$ -orbital of copper). Consequently, the crystal energy  $\epsilon$  will be a deviation from  $E_0$  and will depend on the crystal momentum  $\mathbf{k}$ .

Now if we rewrite the Hamiltonian as the atomic Hamiltonian with an added small correction potential  $\Delta U(\mathbf{r})$  and multiply the crystal Schrödinger equation

$$H\psi_{\mathbf{k}}(\mathbf{r}) = (H_{\text{atom}} + \Delta U(\mathbf{r}))\psi_{\mathbf{k}}(\mathbf{r}) = \epsilon(\mathbf{k})\psi_{\mathbf{k}}(\mathbf{r}) \tag{8}$$

by the atomic wavefunction  $\phi_0^*(\mathbf{r})$ , integrate over all  $\mathbf{r}$ , using the fact that

$$\int d\mathbf{r} \phi_0^*(\mathbf{r}) H_{\text{atom}} \psi_{\mathbf{k}}(\mathbf{r}) = E_0 \int d\mathbf{r} \phi_0^*(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}), \tag{9}$$

we obtain

$$\epsilon(\mathbf{k}) = E_0 + \frac{\int d\mathbf{r} \phi_0^*(\mathbf{r}) \Delta U \psi_{\mathbf{k}}(\mathbf{r})}{\int d\mathbf{r} \phi_0^*(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r})} \tag{10}$$

Plugging (6) into (10) and separating the sums into terms with  $\mathbf{R} = 0$  (the central atom) and  $\mathbf{R} \neq 0$  (the neighbors) we get

$$\epsilon(\mathbf{k}) = E_0 + \frac{\beta + \sum_{\mathbf{R} \neq 0} \gamma(\mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}}}{1 + \sum_{\mathbf{R} \neq 0} \alpha(\mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}}}, \tag{11}$$

where

$$\beta = \int d\mathbf{r} |\phi_0(\mathbf{r})|^2 \Delta U, \tag{12}$$

$$\gamma(\mathbf{R}) = \int d\mathbf{r} \phi_0^*(\mathbf{r}) \Delta U \phi_0(\mathbf{r} - \mathbf{R}), \tag{13}$$

$$\alpha(\mathbf{R}) = \int d\mathbf{r} \phi_0^*(\mathbf{r}) \phi_0(\mathbf{r} - \mathbf{R}). \tag{14}$$

We are now ready to implement the assumptions of the tight binding method. First, all terms in the numerator of (11) are of first order correction. In addition, terms  $\alpha(\mathbf{R})$  in the denominator are also of first order, thus, up to first order approximation, we can drop them. Second, the tight binding method hypothesizes that the potential correction  $\Delta U$  contains only hopping terms between nearest neighbors (n.n.) so as the sum in the numerator is truncated accordingly. The tight binding energy is hence obtained as

$$\epsilon(\mathbf{k}) = E_0 + \sum_{n.n.} \int d\mathbf{r} \phi_0^*(\mathbf{r}) \Delta U \phi_0(\mathbf{r} - \mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}}, \tag{15}$$

Finally, we can convert (15) nicely into Dirac representation

$$\epsilon(\mathbf{k}) |\phi_0\rangle = E_0 |\phi_0\rangle + \Delta U |\phi_0\rangle \tag{16}$$

by setting

$$\Delta U = -t \sum_{n.n.} |\phi_{\text{neighbor}}\rangle \langle \phi_0|, \tag{17}$$

where

$$|\phi_{\text{neighbor}}\rangle = |\phi_0\rangle e^{i\mathbf{k} \cdot \mathbf{R}}, \tag{18}$$

and  $t$  is the interaction potential between neighboring atoms.

### III. 2D MONOATOMIC SQUARE LATTICES

To help us gain some insight about crystal lattice and the usage of the tight binding model, we consider a simple example of a 2D monoatomic square lattice as shown in Fig. 1

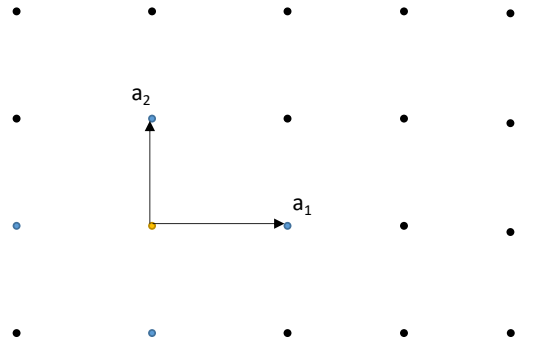


FIG. 1: A region of a 2D square lattice, with  $\mathbf{a}_1, \mathbf{a}_2$  being the primitive lattice vectors, i.e. the entire lattice can be spanned by these vectors. Each atom has 4 nearest neighbors. The lattice constant is  $|\mathbf{a}_1| = |\mathbf{a}_2| = a$ .

Let  $\phi_0$  and  $E_0$  be the ground state of each individual atom. Again, in the tight binding model, the interaction between atoms is given by (17).

To apply formula (16), we first pick a lattice point, say the yellow one, to be our central atom, i.e.  $\mathbf{R} = 0$ . So its 4 nearest neighbors are located at  $a(0, \pm 1)$  and  $a(\pm 1, 0)$  and (16) reads

$$\begin{aligned}\epsilon(\mathbf{k}) &= E_0 + \langle \phi_0 | \Delta U | \phi_0 \rangle \\ &= E_0 + \sum_{n.n.} e^{i\mathbf{k} \cdot \mathbf{R}} \langle \phi_0 | \Delta U | \phi_0 \rangle \\ &= E_0 - t \sum_{\text{nearest } \mathbf{R}_j} e^{i\mathbf{k} \cdot \mathbf{R}_j} \\ &= E_0 - 2t(\cos k_x a + \cos k_y a),\end{aligned}\quad (19)$$

where  $\mathbf{k} = (k_x, k_y)$ .

Clearly we have calculated the energy band of the 2D square lattice just by a few lines of calculation. The most important step in the tight binding method is to identify the Bravais lattice with its primitive vectors and then the nearest neighbors. Nevertheless, in most of the cases crystals are not merely a single Bravais lattice.

#### IV. GRAPHENE

Graphene is a two dimensional single atomic layer of carbon atoms arranged in a honeycomb lattice. (see Fig. 2)

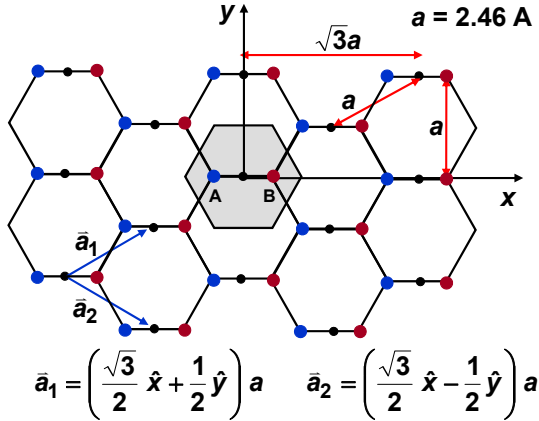


FIG. 2: Picture adapted from Professor Levitov's lecture slides [4]. Graphene, a honeycomb lattice that can be described by two triangular Bravais lattices relatively shifted to each other, corresponding to the red-atom and blue-atom lattices as depicted. Both lattices have  $\mathbf{a}_1 = (\sqrt{3}/2\hat{x} + 1/2\hat{y})a$  and  $\mathbf{a}_2 = (\sqrt{3}/2\hat{x} - 1/2\hat{y})a$  being the primitive lattice vectors.

Unlike the 2D monoatomic square lattice, honeycomb is not Bravais. Indeed, it is impossible to find two primitive vectors that could span the entire graphene lattice, yet we can describe the graphene with two triangular Bravais sublattices. As depicted in Fig. 2, we can choose one sublattice centered at atom  $A$  and spanned by two

vectors  $\mathbf{a}_1, \mathbf{a}_2$ , so as it consists of all “blue” atoms. The other sublattice is centered at atom  $B$  and also spanned by  $\mathbf{a}_1, \mathbf{a}_2$ , corresponding to the “red” atoms. These two sublattices indeed together span out our graphene. Interestingly, all the nearest neighbors of each atom are now in the other lattice that does not contain the atom.

As we know, carbon has four electrons in its open shell available for bonding. By  $sp^2$  hybridization, three of them are used for bonding in the hexagonal lattice. This leaves one electron, with non-degenerate energy  $E_0$ , per atom that determines the electronic properties of graphene. Again, we will use the tight binding model to analyze the electron energy:

$$\Delta U = -t \sum_{n.n.} |\phi_{\text{neighbor}}\rangle \langle \phi_0|. \quad (20)$$

For atom  $A$  in sublattice  $A$ , its 3 nearest neighbors are located at  $\mathbf{B}, \mathbf{B} - \mathbf{a}_1, \mathbf{B} - \mathbf{a}_2$ . Suppose the atom at  $\mathbf{B}$  is in the state

$$|\phi_1\rangle. \quad (21)$$

Using (5), we know the atoms at  $\mathbf{B} - \mathbf{a}_1$  and  $\mathbf{B} - \mathbf{a}_2$  are, respectively, in the states

$$|\phi_1\rangle e^{-i\mathbf{k} \cdot \mathbf{a}_1}, \quad (22)$$

$$|\phi_1\rangle e^{-i\mathbf{k} \cdot \mathbf{a}_2}. \quad (23)$$

Plugging (20), (21), (23) and (22) into (16) we get

$$(\epsilon(\mathbf{k}) - E_0) |\phi_0\rangle = -t (1 + e^{-i\mathbf{k} \cdot \mathbf{a}_1} + e^{-i\mathbf{k} \cdot \mathbf{a}_2}) |\phi_1\rangle. \quad (24)$$

Similarly, by considering the atom at  $\mathbf{B}$  with its 3 nearest neighbors at  $\mathbf{A}, \mathbf{A} + \mathbf{a}_1, \mathbf{A} + \mathbf{a}_2$ , we obtain

$$(\epsilon(\mathbf{k}) - E_0) |\phi_1\rangle = -t (1 + e^{i\mathbf{k} \cdot \mathbf{a}_1} + e^{i\mathbf{k} \cdot \mathbf{a}_2}) |\phi_0\rangle. \quad (25)$$

Combining (24) and (25) we obtain an eigenvalue equation

$$\epsilon(\mathbf{k}) \begin{pmatrix} \phi_0 \\ \phi_1 \end{pmatrix} = \begin{pmatrix} E_0 & -tf(\mathbf{k}) \\ -tf^*(\mathbf{k}) & E_0 \end{pmatrix} \begin{pmatrix} \phi_0 \\ \phi_1 \end{pmatrix}, \quad (26)$$

where  $f(\mathbf{k}) = 1 + e^{-i\mathbf{k} \cdot \mathbf{a}_1} + e^{-i\mathbf{k} \cdot \mathbf{a}_2}$  and the  $2 \times 2$  matrix on the right hand side can be interpreted as the effective Hamiltonian of the graphene lattice, with basis  $\{|\phi_0\rangle, |\phi_1\rangle\}$ , known as “pseudospin.”

Solving (26) we obtain the dispersion relation of graphene as

$$\epsilon(k) = E_0 \pm t |1 + e^{-i\mathbf{k} \cdot \mathbf{a}_1} + e^{-i\mathbf{k} \cdot \mathbf{a}_2}|. \quad (27)$$

We can now substitute  $\mathbf{a}_1 = a(\sqrt{3}/2, 1/2)$ ,  $\mathbf{a}_2 = a(\sqrt{3}/2, -1/2)$ ,  $\mathbf{k} = (k_x, k_y)$  into (27) and set the energy level  $E_0 = 0$  to get

$$\epsilon(\mathbf{k}) = \pm t \sqrt{3 + 2 \cos(k_y a) + 4 \cos(\sqrt{3} k_x a / 2) \cos(k_y a / 2)}. \quad (28)$$

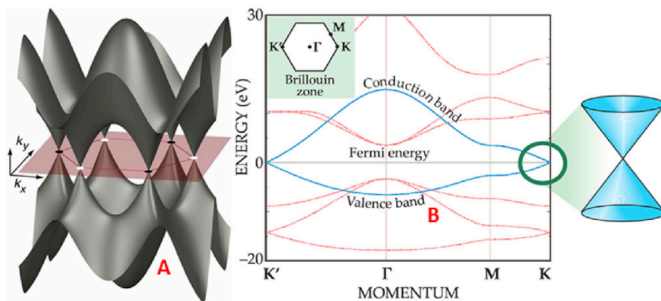


FIG. 3: Picture adapted from [5]. Left: 3D band structure of graphene by tight binding model. Right: 2D electronic band structure of graphene. The tight binding model gives two symmetrical energy bands. The lower band is completely filled, but the conduction band and valence band touch at the plane  $\epsilon = 0$  at the corners of the first Brillouin zone, making graphene a zero-gap semiconductor.

Shown in Fig. 3 is the 3D plot of (28). Clearly, with some simple calculation using the tight binding model, we have found two energy bands of graphene, which have reflectional symmetry through the  $\epsilon = 0$  plane. Furthermore, our model also predicts the zero band gap of graphene, which gives rise to many interesting physics. Using the band structure obtained from this model, one can also study many other topics related to graphene such as carbon nanotubes, which are formed by rolling

graphene along either the  $x$  or  $y$  axis. In such cases, the energy bands reduce to energy strips along  $k_x$  or  $k_y$  due to the periodicity of the tubes.

## V. DISCUSSION

This paper summarizes some aspects of the tight binding model and its applications for calculating the energy bands of crystals. We introduce the Bloch theorem, which relates electron wavefunction to crystal momentum, and then use it along with the hypothesis of nearest neighbor binding to derive the tight binding approximation for crystal energy. We also present some applications of the tight binding model, one of which is for graphene lattice, a typical example of the usage of the model. Via these examples, we find that the tight binding model provides a decent way to calculate the energy bands structure, which enables us to explain many interesting electronic physics emerged from crystals.

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- [1] N. Ashcroft and N. Mermin, *Solid State Physics*, ch. 4, pp. 64–83. Harcourt College Publishers, 1976.
  - [2] C. Kittel, *Introduction to Solid State Physics*, ch. 7, pp. 167,173. John Wiley Sons Inc., 2005.
  - [3] N. Ashcroft and N. Mermin, *Solid State Physics*, ch. 10, pp. 176–189. Harcourt College Publishers, 1976.
  - [4] *Theory of Solids I*. An MIT course taught by Prof. Leonid

Levitov.

- [5] J. Wang, X. Xu, X. Mu, F. Ma, and M. Sun, “Magnetics and spintronics on two-dimensional composite materials of graphene/hexagonal boron nitride,” *Materials Today*, vol. 3, pp. 93–117, 12 2017.