

# The Tight Binding Model

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## Abstract

This document is intended as a detailed review of covalent bonding and the Tight Binding (LCAO) model in preparation for study of monolayer and bilayer graphene.

## 1 Covalent Bonding

Graphene is composed of hexagonally-shaped links of carbon atoms, each of which is linked to three other carbon atoms when the hexagons are tiled. These carbon atoms are linked together by covalent bonds. The purpose of this section is to review the fundamental concepts of covalent bonding, as well as the properties of the carbon atom itself.

Carbon is the chemical element with atomic number 6 - that is, there are six protons found in the nucleus of a Carbon atom. The ground-state electron configuration of Carbon is  $1s^2 2s^2 2p^2$ . However, when in the presence of other atoms, it is sometimes energetically favorable to promote one electron into the  $2p$  orbital - the energy cost of moving into this excited state is offset by the energy gained from covalent bonding.

In the case of graphene, carbon atoms exhibit  $sp^2$  hybridization wherein two  $2p$  orbitals, conventionally chosen as  $2p_x$  and  $2p_y$ , form a superposition with the  $2s$  orbital. The result is three coplanar orbitals separated by  $120^\circ$ . The remaining  $2p_z$  orbital lies perpendicular to the coplanar hybridized orbitals. Sheets of graphene are formed by planes of carbon atoms bonding via the hybridized orbitals, but this leaves the perpendicular  $2p_z$  orbital free.

We now turn our attention to the nature of covalent bonding in graphene. What follows is a description of covalent bonding that closely follows that presented in [1]. As a simple model, we can demonstrate the energetically favorable effects produced by covalent bonding if we imagine an atom as a potential well for an electron - specifically, we model an atom as an infinite square well. The ground state energy for a single electron in the infinite square well is given by:

$$E = \frac{\pi^2 \hbar^2}{2mL^2}$$

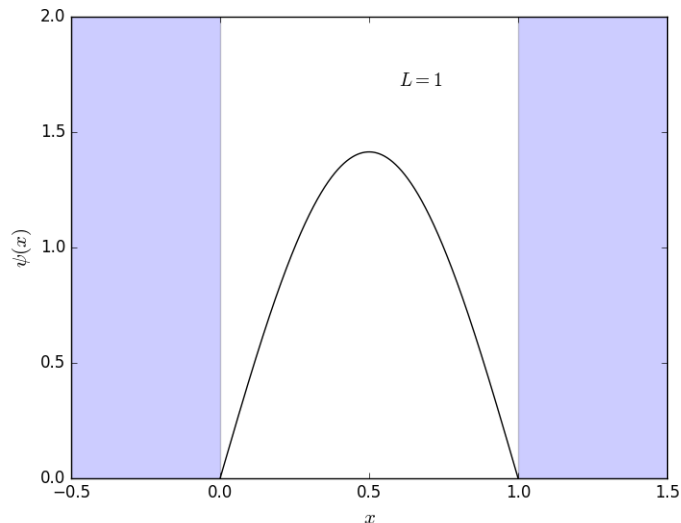


Figure 1: The ground state  $\psi(x)$  for the case  $L = 1$ .

and the ground state solution is

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

If we have two such atoms and we bring them close enough together, a single electron can be found in the shared space produced by doubling the well width. If the well width is doubled to  $2L$ , then the ground state energy becomes

$$E = \frac{\pi^2 \hbar^2}{2m(2L)^2}$$

Therefore, doubling the well width decreases the ground state energy by a factor of 4.

This simple model demonstrates the motivation for covalent bonding: delocalizing the electron is energetically favorable because the new ground state (the *bonding* orbital) is lower in energy than the original ground state. This principle holds even when considering one electron on each of the two atoms – both electrons can occupy the new lower-energy bonding orbital if they have opposite spin states. However, covalent bonding is not energetically favorable in every situation – *antibonding* orbitals can be produced that offset the decrease in energy due to the bonding orbital.

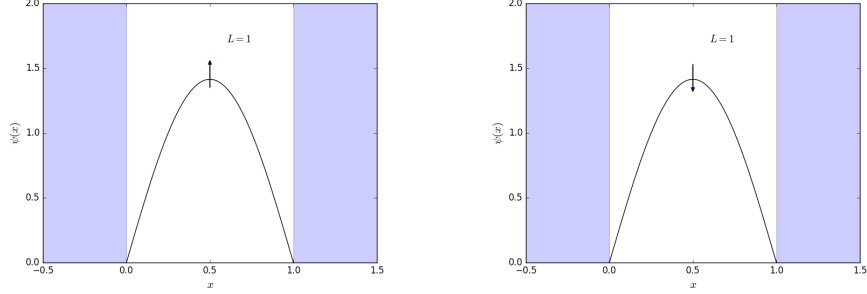


Figure 2: The individual ground state  $\psi(x)$  for the case  $L = 1$  shown for each atom - one with electron spin up and the other with spin down.

## 2 Tight Binding Model

### 2.1 Introduction: Two Hydrogen Atoms

We begin our discussion of the tight binding model by considering a simple system of two hydrogen atoms. Each hydrogen atom has a single electron orbiting its nucleus. Individually, the ground state of an electron orbiting a hydrogen nucleus has the form

$$\psi(r) = \frac{1}{\sqrt{\pi}a_0^{3/2}} e^{-r/a_0}$$

and exhibits the following radial probability density, plotted in Figure 4 with  $a_0 = 1$ .

$$P(r) = \int_V |\psi(r)|^2 r \sin(\theta) dr d\theta d\phi = \left( \frac{4r^2}{a_0^3} \right) e^{-2r/a_0}$$

In the region  $0 \leq r \leq 2a_0$ , this probability distribution is roughly equivalent to the infinite square well probability distribution, also shown in Figure 4. So, we can clearly model the hydrogen atom as a square potential well.

Now, when we bring the two hydrogen atoms close to one another, the well width doubles and the individual wave functions overlap as shown in Figure 5 (TO DO: finish potential well explanation.).

Our goal now is to establish a description of the covalently bonded system through the use of a linear combination of ground state orbitals. Let  $|\psi_{0,1}\rangle$  and  $|\psi_{0,2}\rangle$  be the ground states of the first and second hydrogen atom, respectively. Then,  $|\psi_{0,1}\rangle$  and  $|\psi_{0,2}\rangle$  are clearly solutions to the Schrodinger equations

$$H |\psi_{0,1}\rangle = (K + V_1) |\psi_{0,1}\rangle = E_0 |\psi_{0,1}\rangle$$

$$H |\psi_{0,2}\rangle = (K + V_2) |\psi_{0,2}\rangle = E_0 |\psi_{0,2}\rangle$$

where  $K$  is the kinetic energy of the electron, and  $V_i$  is the nuclear potential from site  $i$ . We will describe the ground state of a single electron orbiting the two

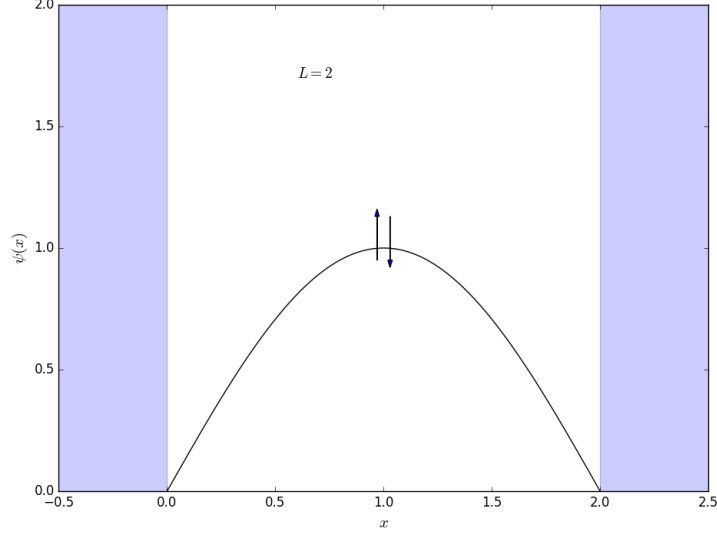


Figure 3: The new ground state  $\psi(x)$  for the case  $L = 2$  with two spin states.

hydrogen neighbors as a linear combination of these individual ground states. That is,

$$|\psi_0\rangle = c_1 |\psi_{0,1}\rangle + c_2 |\psi_{0,2}\rangle$$

We can roughly approximate  $|\psi_{0,1}\rangle$  and  $|\psi_{0,2}\rangle$  to be orthogonal. As shown in Figure 5 (TO BE ADDED), the individual ground states are localized to either side of the potential well and there is little overlap between the states given that the internucleic distance is not too short. This approximation allows us to establish the following orthogonality condition.

$$\langle \psi_{0,i} | \psi_{0,j} \rangle = \delta_{ij}$$

. Now we will attempt to solve the Schroedinger equation to find the new ground state energy of the bonded system. The Schroedinger Equation is simply

$$H |\psi_0\rangle = E |\psi_0\rangle$$

We have not yet established the form of the Hamiltonian, but we can make two observations. The first is that the Hamiltonian can be written as the sum of the kinetic energy of the electron, as well as the potential energy contributions from each of the hydrogen nuclei. That is,

$$H = K + V_1 + V_2$$

The second observation is that the Schroedinger equation can be written in a more explicit form. In this case, the new bonding ground state is a linear

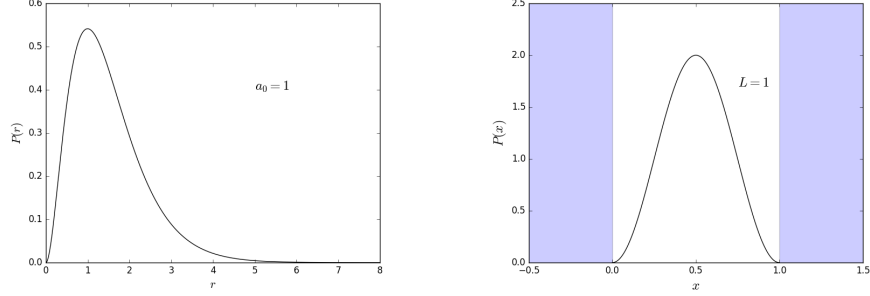


Figure 4: The radial probability distribution for the ground state of hydrogen. The radius of highest probability corresponds to the bohr radius  $a_0$ , which is set to 1 here. Also shown is the positional probability distribution of the infinite square well of length  $L = 1$ .

combination of two ground state orbitals - therefore, the Hamiltonian is a  $2 \times 2$  matrix.

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

This yields the following system of equations

$$\sum_j H_{ij} c_j = E a_i$$

where

$$H_{ij} = \langle \psi_{0,i} | H | \psi_{0,j} \rangle = \langle \psi_{0,i} | K + V_1 + V_2 | \psi_{0,j} \rangle$$

This allows us to examine the components of the Hamiltonian matrix.

$$H_{11} = \langle \psi_{0,1} | K + V_1 | \psi_{0,1} \rangle + \langle \psi_{0,1} | V_2 | \psi_{0,1} \rangle = E_0 + V_{cross}$$

$$H_{22} = \langle \psi_{0,2} | K + V_2 | \psi_{0,2} \rangle + \langle \psi_{0,2} | V_1 | \psi_{0,2} \rangle = E_0 + V_{cross}$$

$$H_{12} = \langle \psi_{0,1} | K + V_2 | \psi_{0,2} \rangle + \langle \psi_{0,1} | V_1 | \psi_{0,2} \rangle = -t$$

$$H_{21} = \langle \psi_{0,2} | K + V_2 | \psi_{0,1} \rangle + \langle \psi_{0,2} | V_1 | \psi_{0,1} \rangle = -t^*$$

where we have defined  $V_{cross} = \langle \psi_{0,2} | V_1 | \psi_{0,2} \rangle = \langle \psi_{0,1} | V_2 | \psi_{0,1} \rangle$  and the *hopping* term  $-t = \langle \psi_{0,1} | V_1 | \psi_{0,2} \rangle$ . The  $V_{cross}$  term represents the Coulomb potential due to neighboring sites (i.e. the *other* hydrogen nucleus). The hopping element  $t$  represents the mechanism by which the electron can move from one orbital to another. To obtain the eigenenergies, we can diagonalize this Hamiltonian as follows.

$$\det(H - EI) = \begin{vmatrix} E_0 + V_{cross} - E & -t \\ -t^* & E_0 + V_{cross} - E \end{vmatrix} = 0$$

From which we obtain

$$(E_0 + V_{cross} - E)^2 - |t|^2 = 0$$

$$E^2 - 2E(E_0 + V_{cross}) + (E_0 + V_{cross})^2 - |t|^2 = 0$$

Using the quadratic equation, we obtain the solution

$$E_{\pm} = E_0 + V_{cross} \pm |t|$$

Now, we will find the eigenstates associated with the new ground state energies. The Schroedinger equation, again, is

$$\begin{bmatrix} E_0 + V_{cross} & -t \\ -t^* & E_0 + V_{cross} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E_{\pm} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix}$$

which gives us the following system of equations to solve for  $c_1$  and  $c_2$

$$(E_0 + V_{cross})c_1 - tc_2 = E_{\pm}c_1$$

$$(E_0 + V_{cross})c_2 - t^*c_1 = E_{\pm}c_2$$

Our associated normalized eigenvectors are therefore

$$|\psi_+\rangle = \frac{1}{\sqrt{2}} |\psi_{0,1}\rangle - \frac{1}{\sqrt{2}} |\psi_{0,2}\rangle$$

$$|\psi_-\rangle = \frac{1}{\sqrt{2}} |\psi_{0,1}\rangle + \frac{1}{\sqrt{2}} |\psi_{0,2}\rangle$$

The first thing to notice here is that while the individual hydrogen atoms have a single ground state orbital, when the atoms are brought close together, the delocalized ground state orbital actually splits into two levels. The lower energy level (with energy  $E_-$ ) is called the *bonding* orbital because it promotes bonding by lowering the ground state energy. The higher energy orbital (associated with  $E_+$ ) is called the *antibonding* orbital. This is somewhat easier to understand if we factor in Coulomb repulsion between the neighboring nuclei and allow the  $V_{cross}$  term to vanish. In that case, we have

$$E_{\pm} = E_0 \pm |t|$$

So clearly, the bonding orbital has an energy lower than the original ground state energy and the antibonding orbital is associated with an energy higher than the original ground state energy. It is also worth noting that the difference between the bonding and antibonding energy levels is proportional to the hopping term. In the limit that the hopping term vanishes, indicating that there is no possibility to hop between sites, the ground state energies converge back to the original ground state energy of hydrogen.

## 2.2 Next Steps: One Dimensional Chain of Atomic Sites

We will now generalize our model a bit by considering a one-dimensional chain of  $N$  sites, as opposed to two. First, we establish some properties of our chain:

- There is a single orbital on each atomic site - we will denote the orbital on site  $i$  as  $|i\rangle$ .
- Periodic boundary conditions are enforced. That is, site  $N + 1$  is site 1.
- Orbitals are taken to be orthogonal to one another. Therefore,  $\langle i|j\rangle = \delta_{ij}$ .
- The interatomic spacing - distance between sites - is denoted  $a$ .

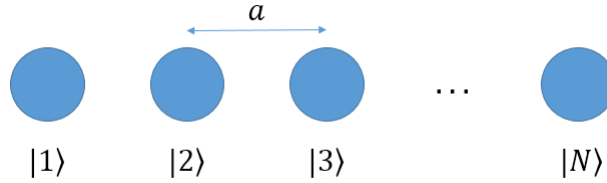


Figure 5: One dimensional chain of atomic sites. There is a single orbital at each site, denoted by  $|i\rangle$ . Interatomic spacing is  $a$ .

As before, we will consider a single electron moving around the chain of sites. The wavefunction for the electron is a linear combination of the atomic orbitals.

$$|\psi\rangle = \sum_{n=1}^N c_n |n\rangle$$

As before, we will use the Schrodinger equation to establish the eigenenergies and eigenstates of the system.

$$H |\psi\rangle = E |\psi\rangle$$

We observe the following about the Hamiltonian  $H$ :

$$H = K + \sum_j V_j$$

$$H_{nm} = \langle n| H |m\rangle$$

where, as before,  $K$  is the kinetic energy of the electron and  $V_j$  is the Coulomb interaction due to site  $j$ . We can derive the elements of the Hamiltonian matrix,  $H_{nm}$ , as follows:

$$H |m\rangle = (K + \sum_j V_j) |m\rangle$$

$$\begin{aligned}
&= (K + V_m) |m\rangle + \sum_{j \neq m} V_j |m\rangle \\
&= E_0 |m\rangle + \sum_{j \neq m} V_j |m\rangle
\end{aligned}$$

where  $E_0$  here is meant to be the energy associated with the orbital on a single atomic site. Therefore,

$$\begin{aligned}
\langle n | H | m \rangle &= E_0 \langle n | m \rangle + \sum_{j \neq m} \langle n | V_j | m \rangle \\
&= \delta_{nm} + \sum_{j \neq m} \langle n | V_j | m \rangle
\end{aligned}$$

The last term can be summarized in the following way:

$$\sum_{j \neq m} \langle n | V_j | m \rangle = \begin{cases} V_0 & n = m \\ -t & n = m \pm 1 \\ 0 & \text{otherwise} \end{cases}$$

The idea is the following:

- In the case  $n = m$ ,  $V_0$  represents a sum of all  $V_{cross}$  terms over the lattice. That is, it is the shift in the site energy due to Coulomb interactions with other sites.
- When  $n = m \pm 1$ , then  $|n\rangle$  and  $|m\rangle$  are nearest neighbors. In that case,  $\langle n | V_n | m \rangle$  is defined to be  $-t$ , the hopping term that takes the electron from site  $m$  to site  $n$ . All other contributions in the sum vanish – that is, we only consider nearest neighbor hopping (right?).

Therefore, the elements of the Hamiltonian are given by

$$\langle n | H | m \rangle = (E_0 + V_0) \delta_{nm} - t(\delta_{n+1,m} + \delta_{n-1,m})$$

The Ansatz solution for the eigenstate is given (in component form) as:

$$c_n = \frac{e^{-ikna}}{\sqrt{N}}$$

where  $c_n$  is the probability amplitude of the state  $|n\rangle$ ,  $k$  is the wavevector of the electron, and the  $1/\sqrt{N}$  term normalizes the wavefunction. TODO: Periodicity and boundary conditions. The periodicity of the solution can be examined by observing that  $e^{-i2n\pi} = 1$  for arbitrary integer  $n$  and writing

$$\begin{aligned}
c_n &= \frac{e^{-ikna}}{\sqrt{N}} = \frac{e^{-ikna}}{\sqrt{N}} e^{-i2n\pi} \\
&= \frac{e^{-i(kna+2n\pi)}}{\sqrt{N}} = \frac{e^{-i(k+2\pi/a)na}}{\sqrt{N}}
\end{aligned}$$



Therefore the solution for  $k$  is identical to the solution for  $k + 2\pi/a$ . When we enforce the periodic boundary conditions that site  $n = 1$  is equivalent to site  $n = N + 1$ , we find that  $k$  is quantized in units of  $2\pi/Na$ . Explicitly,

$$\begin{aligned} c_1 &= c_{N+1} \\ \frac{e^{-ika}}{\sqrt{N}} &= \frac{e^{-ik(N+1)a}}{\sqrt{N}} \\ 1 &= e^{-ikNa} \end{aligned}$$

The above equation can only be true if  $k$  is an integer multiple of  $2\pi/Na$ .

Now, if we plug our ansatz into the system of equations produced by the Schroedinger equation,

$$\begin{aligned} \sum_m H_{nm} c_m &= E c_n \\ \sum_m H_{nm} \frac{e^{-ikma}}{\sqrt{N}} &= E \frac{e^{-ikna}}{\sqrt{N}} \\ \sum_m [(E_0 + V_0)\delta_{nm} - t(\delta_{n+1,m} + \delta_{n-1,m})] \frac{e^{-ikma}}{\sqrt{N}} &= E \frac{e^{-ikna}}{\sqrt{N}} \\ (E_0 + V_0) \frac{e^{-ikna}}{\sqrt{N}} - t \left( \frac{e^{-ik(n+1)a}}{\sqrt{N}} + \frac{e^{-ik(n-1)a}}{\sqrt{N}} \right) &= E \frac{e^{-ikna}}{\sqrt{N}} \\ (E_0 + V_0) \frac{e^{-ikna}}{\sqrt{N}} - t \frac{e^{-ikna}}{\sqrt{N}} 2\cos(ka) &= E \frac{e^{-ikna}}{\sqrt{N}} \\ (E_0 + V_0) - t2\cos(ka) &= E \end{aligned}$$

The last equation is our dispersion relation  $E(k)$ , which describes the range of allowed energies for an electron floating through the lattice. The dispersion relation is plotted in Figure 7. There are a few observations we can make from the plot of the dispersion relation. The first is that the width of the allowed energies is a function of the hopping element  $t$ . There is at least one  $k$ -state that has an energy in this band. The allowed values for  $ka$  are functions of  $N$  such that

$$ka = \frac{2\pi}{N} m$$

where  $m$  is some integer. Therefore, when  $N = 1$  (the one site limit),  $k$  can only take on values  $0, 2\pi, 4\pi$ , etc. - all of which map to the same energy so only a single energy is allowed. As  $N$  grows, we increase the number of allowed  $ka$  values within a  $2\pi$  range and, therefore, increase the number of discrete energy levels until the band is saturated in the  $N \rightarrow \infty$  limit.

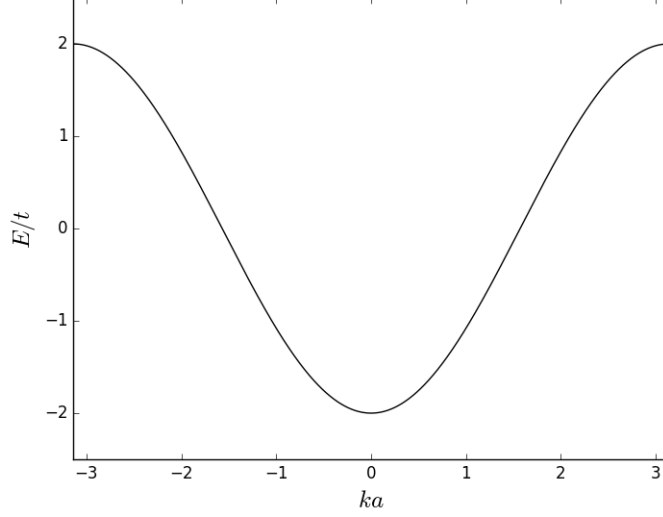


Figure 6: Dispersion relation for one-dimensional monoatomic chain with inter-atomic distance  $a$ . Dispersion relation is plotted in units of  $t$ , as a function of  $ka$ , allowing  $(E_0 + V_0)$  to vanish.

### 2.3 Arbitrary Crystal Structure

Now, we shift our focus to applying the tight binding model to an arbitrary crystal structure with multiple orbitals per site. Our discussion will closely follow that found in [2]. In the general case, we have  $N$  identical atomic sites with  $M$  orbitals per site. For each of the  $M$  orbitals, we can write down a Bloch state which represents the wavefunction of the electron in the periodically repeating lattice.

$$\Phi_m = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{i\vec{k} \cdot \vec{R}_{m,n}} \phi_m \vec{r} - \vec{R}_{m,n}$$

where  $\phi_m$  is the  $m$ th orbital and  $\vec{R}_{m,n}$  is the corresponding position of this orbital on the  $n$ th site. We should notice that these Bloch states are simply generalizations of the one-dimensional, single orbital solution. The full electronic wave function is a sum over the  $M$  Bloch states and is given by

$$\psi = \sum_{m=1}^M c_m \Phi_m$$

where  $c_m$  are the coefficients of linear superposition. To determine these coefficients, we can plug our expression for  $\psi$  into the Schrodinger equation.

### 2.3.1 One dimensional chain of atomic sites revisited

To see the effect of multiple orbitals per site, we will consider an extension of the one-dimensional chain where each atomic site has two orbitals. TODO: Finish section.

## 3 Monolayer Graphene

We now use the tight binding model to analyze the band structure of a single layer of graphene. Graphene can be thought of as a lattice where each site contains the unit cell shown in Figure 8. That is, each site in the lattice contains two carbon atoms, which we will label  $A$  and  $B$ . From each carbon atom, we only consider a single  $2p_z$  orbital. As described in the first section, the remaining valence electrons are tied up in  $\sigma$  bonds via  $sp^2$  hybridization. Let's begin by writing down the very general electronic wavefunction.

$$\psi_k = \sum_{m=1}^M c_m \Phi_m$$

where  $\Phi_m$  is the Bloch state defined by

$$\Phi_m = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{i\vec{k} \cdot \vec{R}_n} \phi_m(\vec{r} - \vec{R}_n)$$

The vector  $\vec{R}_n$  represents the position of the  $n$ th unit cell over a total of  $N$  unit cells. In our case, the index  $m$  will only sum over the sites  $A$  and  $B$  within the unit cell. Therefore, in the case of monolayer graphene, we can explicitly write

$$\psi_k = \frac{1}{\sqrt{N}} (c_A \sum_n e^{i\vec{k} \cdot \vec{R}_n} \phi_A + c_B \sum_n e^{i\vec{k} \cdot \vec{R}_n} \phi_B)$$

where  $\phi_A$  and  $\phi_B$  are the  $2p_z$  wavefunctions for sites  $A$  and  $B$ , respectively. The Hamiltonian is directly analogous to the one-dimensional chain example:

$$H = K + \sum_n V_A + V_B$$

where

$$V_A = V(\vec{r} - \vec{r}_A - \vec{R}_n)$$

$$V_B = V(\vec{r} - \vec{r}_B - \vec{R}_n)$$

If we apply the Hamiltonian to the  $\phi_A$  orbital, for example, we obtain the following:

$$\begin{aligned} H\phi_A &= (K + \sum_n V_A + V_B)\phi_A \\ &= E_A + [(\sum_{n, \vec{R}_n \neq 0} V_A + V_B) + V(\vec{r} - \vec{r}_B)]\phi_A \end{aligned}$$

where  $E_A = E_B$  is the energy of  $2p_z$  orbital. We will simplify a bit by allowing  $E_A = E_B = 0$ . Therefore, we obtain the two equations

$$H\phi_{A,B} = [(\sum_{n, \vec{R}_n \neq 0} V_A + V_B) + V(\vec{r} - \vec{r}_{B,A})]\phi_{A,B} = \Delta U_{A,B}\phi_{A,B}$$

where we have defined  $\Delta U$  as the potential energy term of the Hamiltonian.

Now, we will apply the Hamiltonian to the electronic wavefunction  $\psi_k$ :

$$H\psi_k = E(\vec{k})\psi_k$$

From here, it is easy to see

$$\langle \phi_{A,B} | H | \psi_k \rangle = \langle \phi_{A,B} | E(\vec{k}) | \psi_k \rangle$$

From which we obtain

$$E(\vec{k}) = \frac{\langle \phi_{A,B} | \Delta U_{A,B} | \psi_k \rangle}{\langle \phi_{A,B} | \psi_k \rangle}$$

We begin by calculating the denominator terms. In the following, we take only nearest neighbor overlap terms into account. That is,

$$\sum_n e^{i\vec{k} \cdot \vec{R}_n} \langle \phi_A | \phi_A \rangle = \langle \phi_A | \phi_A \rangle = 1$$

$$\sum_n e^{i\vec{k} \cdot \vec{R}_n} \langle \phi_A | \phi_B \rangle = \langle \phi_A | \phi_B \rangle (1 + e^{i\vec{k} \cdot -\vec{a}_1} + e^{i\vec{k} \cdot \vec{a}_2})$$

Now, we get, dropping the normalization factor,

$$\langle \phi_A | \psi_k \rangle = c_A + c_B \langle \phi_A | \phi_B \rangle (1 + e^{i\vec{k} \cdot -\vec{a}_1} + e^{i\vec{k} \cdot \vec{a}_2})$$

$$\langle \phi_B | \psi_k \rangle = c_B + c_A \langle \phi_B | \phi_A \rangle (1 + e^{i\vec{k} \cdot \vec{a}_1} + e^{i\vec{k} \cdot -\vec{a}_2})$$

Evaluating the numerator gives us

$$\langle \phi_A | \Delta U_A | \psi_k \rangle =$$

$$\langle \phi_B | \Delta U_B | \psi_k \rangle =$$

## References

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