

# ENERGY DISPERSION USING TIGHT BINDING THEORY (GRAPHENE)

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## 1 INTRODUCTION

## 2 THEORY

- Crystal Structures
- Lattice Translation Vector
- Types of Lattices
- Reciprocal Lattice
- Brillouin Zone
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- Bloch Theorem
- Tight Binding
- Schrodinger Equation
- Hamiltonian

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## 5 SUMMARY

# TIGHT BINDING

## INTRODUCTION

- The Tight Binding or Linear Combination of Atomic Orbitals (LCAO) method is primarily used to calculate the band gap and single-particle Bloch states of a material.
- This band gap is calculated by applying the Bloch Theorem and getting the crystal wave function.
- This crystal wave function is now applied to the Schrodinger equation and we get the energy by calculating the eigen values of the hamiltonian matrix.
- But before all this we have to change our direct lattice vectors to the Reciprocal Lattice vectors, which we will discuss further in the presentation.
- This method is usually used in calculations of very large systems, with more than around a few thousand atoms in the unit cell. This method is simple and computationally very fast.

# SOME THEORETICAL CONCEPTS

## CRYSTAL STRUCTURES

- Crystals are composed of a periodic array of atoms. An ideal crystal is composed of identical structural units in space. The structure of all crystals can be described in terms of a lattice, with a group of atoms attached to every lattice point. The group of atoms is called the basis and when repeated in space it forms the crystal

# SOME THEORETICAL CONCEPTS

## LATTICE TRANSLATION VECTOR

- The lattice is defined by three fundamental translation vectors such that the atomic arrangement looks the same in every respect when viewed from a point  $r$ .

$$r' = r + u_1 a_1 + u_2 a_2 + u_3 a_3 \quad (1)$$

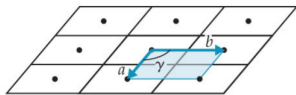
- $a_1, a_2, a_3$  are translation vectors, and  $u_1, u_2, u_3$  are arbitrary integers and  $r$  defines a set of lattice points together they define a lattice.

$$\text{lattice} + \text{basis} = \text{crystal} \quad (2)$$

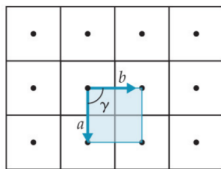
# SOME THEORETICAL CONCEPTS

## TYPES OF LATTICES

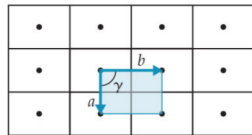
Oblique lattice and 4 special types of lattices possible in 2 dimensions and 13 special lattices with general triclinic lattice in three dimensions.



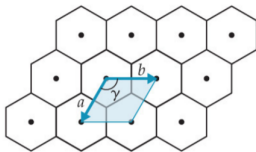
Oblique lattice ( $a \neq b$ ,  $\gamma = \text{arbitrary}$ )



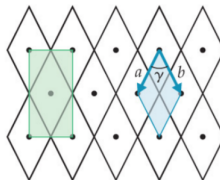
Square lattice ( $a = b$ ,  $\gamma = 90^\circ$ )



Rectangular lattice ( $a \neq b$ ,  $\gamma = 90^\circ$ )



Hexagonal lattice ( $a = b$ ,  $\gamma = 120^\circ$ )



Rhombic lattice ( $a = b$ ,  $\gamma = \text{arbitrary}$ )  
Centered rectangular lattice

# SOME THEORETICAL CONCEPTS

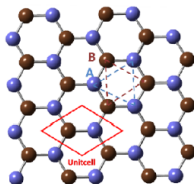


FIGURE: Graphene lattice

# SOME THEORETICAL CONCEPTS

## RECIPROCAL LATTICE

- Every crystal has two lattices associated with it, the direct lattice and the reciprocal lattice.

Reciprocal lattice provides a simple geometrical basis for understanding:

- 1 All things of "wave nature" (like the behavior of electron and lattice vibrations in crystals).
- 2 The geometry of x-ray and electron diffraction patterns. The vectors of direct lattice have dimensions as [length] while that of the reciprocal lattice is [1/length]
- 3 The reciprocal lattice is defined by reciprocal lattice vectors  $\vec{K}_1$ ,  $\vec{K}_2$  and  $\vec{K}_3$  related to direct lattice vectors as



# SOME THEORETICAL CONCEPTS

$$\vec{K}_1 = \frac{2\pi(\vec{b} \times \vec{c})}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{K}_2 = \frac{2\pi(\vec{c} \times \vec{a})}{\vec{b} \cdot (\vec{c} \times \vec{a})} \quad (3)$$

$$\vec{K}_3 = \frac{2\pi(\vec{a} \times \vec{b})}{\vec{c} \cdot (\vec{a} \times \vec{b})}$$

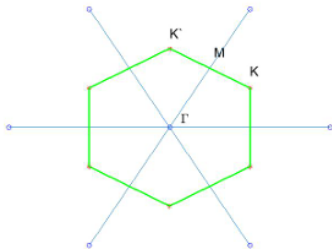
# SOME THEORETICAL CONCEPTS

## BRILLOUIN ZONE

- A Brillouin zone is defined as a Weigner-Seitz primitive cell in the reciprocal lattice. The Brillouin zone represents all the wave vectors which can be Bragg reflected by the crystal.
- The set of planes that are perpendicular bisectors of the reciprocal lattice vectors is of general importance in the theory of wave propagation in crystals. A wave whose wave vector drawn from the origin terminates on any of these planes will satisfy the condition for diffraction.
- These planes divide the Fourier space of the crystal into fragments.
- The first Brillouin zone:  
The first Brillouin zone is the smallest volume entirely enclosed by the planes that are perpendicular bisectors of the lattice vectors.  
The first Brillouin zone of graphene is hexagonal in shape as shown in the fig.

# SOME THEORETICAL CONCEPTS

## BRILLOUIN ZONE



Brillouin Zone

# SOME THEORETICAL CONCEPTS

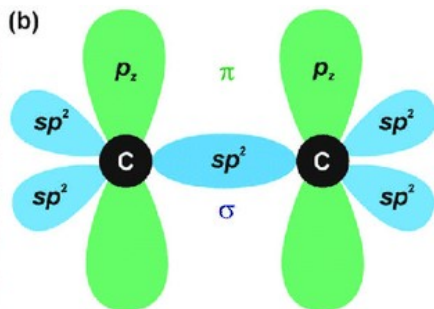
## HYBRIDIZATION

- Intermixing of orbitals and rearrangement of energies is called hybridization. The hybridization of orbitals results in orbitals that are more directional, and have greater overlap when forming bonds, therefore the bonds formed are stronger. The compounds are more stable.

# SOME THEORETICAL CONCEPTS

## SP<sup>2</sup> HYBRIDIZATION

*Sp*<sup>2</sup> hybridization can explain the Trigonal-planar structure of molecules. In it, the 2s orbitals and two of the 2p orbitals hybridize to form three *sp* orbitals, each consisting of 67% p and 33% s character. The frontal lobes align themselves in the Trigonal-planar structure, pointing to the corners of a triangle in order to minimize electron repulsion and improve overlap. The remaining p orbital remains unchanged and is perpendicular to the plane of the three *sp*<sup>2</sup> orbitals



# SOME THEORETICAL CONCEPTS

## BLOCH THEOREM

- It is defined as the most general form of the one-electron crystal wave function. It works on the principle of periodic potentials of the lattice, which can be replicated throughout the solid.
- The wave functions for electrons in a crystal, with a periodic potential can be written in the form:

$$\psi(r) = e^{ik \cdot r} u_k(r) \quad (4)$$

where  $U_k(r)$  is a periodic potential with the same periodicity as the lattice.

# SOME THEORETICAL CONCEPTS

## TIGHT BINDING

- Tight Binding Theory or also called Tight Binding approximation is an approach to calculate the Energy gap.
- When two neighbouring isolated atoms who have their own individual wave function comes closer, they superimpose and gives a resultant Wave function which is called a Crystal wave function, and that wave function is used to calculate the Energy gap.

$$\psi(r) = e^{ik \cdot r} \phi_k(r - X_j) \quad (5)$$

Here  $\psi(r)$  is the Crystal wave function we have to calculate,  $e^{ik \cdot r}$  comes from the Bloch theorem,  $\phi_k$  is the atomic wave function and  $(r - X_j)$  gives the position vector of the  $j^{th}$  atom.

# SOME THEORETICAL CONCEPTS

## SCHRODINGER EQUATION

- The Schrodinger equation implies that when a Hamiltonian operates on a wave function  $\psi$ , the result would be proportional to the same wave function, and the proportionality constant  $E$  is the energy of the wave function.

$$\hat{H}\psi = E\psi \quad (6)$$

In this case,  $\psi$  is Crsytal wave function,  $E$  is eigen values which gives the Energy , and  $\hat{H}$  is the Hamiltonian operator.

- By solving the single-particle Schrodinger equation for the states in a crystal by expanding the Bloch states in terms of a linear combination of atomic orbitals (LCAO) and with the Hamiltonian formed we can obtain the Eigenvalues  $E_\alpha$  and eigenvectors  $\alpha$  with respect to the wave vector ( $k$ ).

$$E\{\phi_o\} = [h(\vec{k})]\{\phi_o\} \quad (7)$$



# SOME THEORETICAL CONCEPTS

## HAMILTONIAN

- Hamiltonian is an operator for the total energy of a system in quantum mechanics. It tells about kinetic and potential energy for a particular system.
- The off-diagonal elements of the Hamiltonian are indicative of the coupling between the two energy states.
- If they are zero, there is zero probability of a transition. However, Since here they are non-zero in this case, there is a non-zero probability of the transition. And diagonal elements represent the energy of the states. i.e.  $H(0, 0)$  and  $H(1, 1)$ .

# HAMILTONIAN

## HAMILTONIAN FOR SP<sup>2</sup> HYBRIDIZATION IN THE CASE OF GRAPHENE

- Using the tight binding and Bloch theorem for Graphene, we obtain the dispersion relation with respect to K vectors and R vectors.
- If  $R_1$ ,  $R_2$ , and  $R_3$  are the vectors connecting the nearest carbon atoms, and only the  $p_z$  orbitals of graphene are considered, the Hamiltonian changes from the general expression to,

$$H = \begin{pmatrix} \epsilon_\pi & V_{pp\pi}(e^{(ik.R1)} + e^{(ik.R2)} + e^{(ik.R3)}) \\ V_{pp\pi}(e^{(-ik.R1)} + e^{(-ik.R2)} + e^{(-ik.R3)}) & \epsilon_\pi \end{pmatrix}$$

- where  $V_{pp\pi}$  is the potential of the  $\pi$  bond,  $\epsilon_\pi = 0$  for the case we are doing,  $R_1$ ,  $R_2$  and  $R_3$  are the position vectors and  $k$  is the wave vector.

# METHODOLOGY

- Imported the required modules, like
  - 1 Numpy:- to help define special functions and perform mathematical operations.
  - 2 Matplotlib:- to plot the energy levels.
  - 3 Scipy (Linalg):- to get the Eigenvalues of the Hamiltonian.  
(Hence getting energies for bonding and anti-bonding orbitals in respective directions)
  - 4 Pandas:- to create the tables.
- We started by defining the parameters like the potential of the pi bond, Empty Hamiltonian, K-vectors, energies for bonding and anti-bonding orbitals in respective directions, position vectors, and diagonal elements of the Hamiltonian.
- Identified the type of lattice and lattice vectors in our case lattice had a honey-comb structure with lattice vectors  $a_1$  and  $a_2$ :

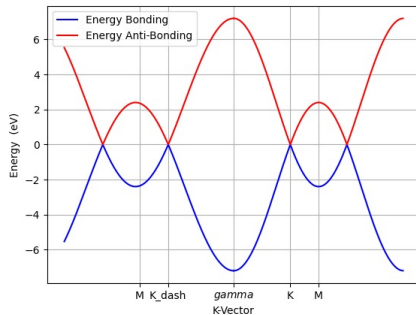
$$a_1 = \frac{a}{2}(3, 3) ; a_2 = \frac{a}{2}(3, 3)$$

and position vectors of neighboring atoms:

$$R_1 = \frac{a}{2}(1, \sqrt{3}) ; R_2 = \frac{a}{2}(1, -\sqrt{3}) ; R_3 = -a(1, 0)$$

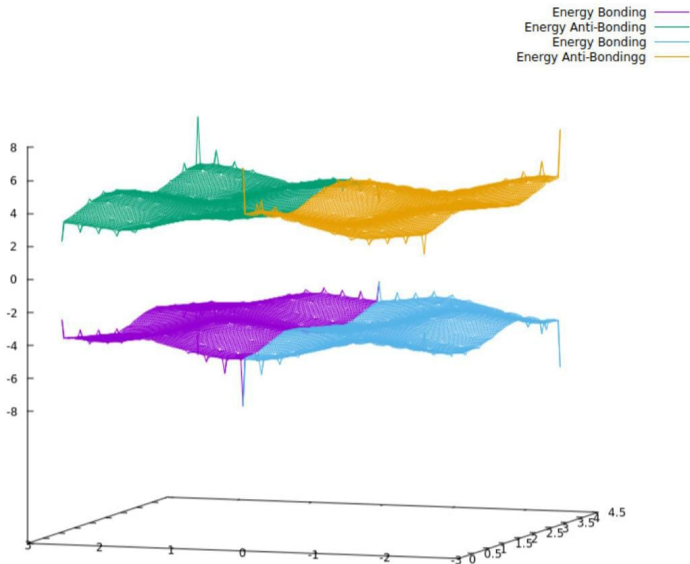
- Calculated K-vectors, reciprocal lattice vectors using  $a_1$  and  $a_2$  as  $K_1$  and  $K_2$  using the formulas shared above.
- Also identified  $\Gamma$  (Center of symmetry) and M (Midpoint between K and  $K'$ ).
- Made  $2 \times 2$  hamiltonian for carbon-carbon pi bond for graphene and solved for the eigenvalues i.e. Energies of bonding and antibonding orbitals.
- Plotting energies with  $|K|$  in gamma-k and gamma- $k'$  direction.

# ANALYSIS OF RESULT

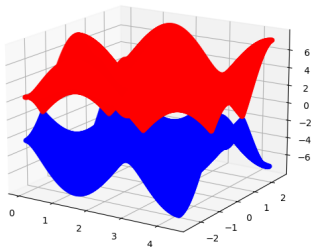
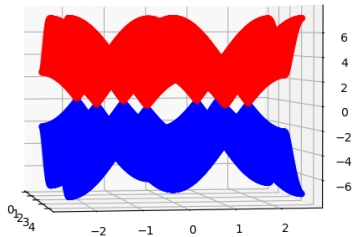


We have obtained this 2d plot from our python result. It shows, both the Bonding and Anti-Bonding meet at the ground state. The points where we can see the minimum energy gap are the K and K' points.  $\Gamma$  is the center of symmetry where we have the absolute maxima.

# ANALYSIS OF RESULT



# ANALYSIS OF RESULT



## ANALYSIS OF RESULT

Similarly, In these 3D Graphs, we have plotted the Energy Dispersion in the Z axis and the  $|K|$  in the X and Y axis. The upper part is the Energy of the Anti-Bonding orbital, and the lower part is the Energy of the Bonding Orbital. The first graph is obtained from GNU and the rest two are from Python. The points where we can see the minimum energy gap at certain points only are known as the Dirac points of K-points.  $\Gamma$  is the center of symmetry where we have the absolute maxima. This trend is repeated throughout the lattice. This trend is repeated throughout the lattice.



# SUMMARY

- In this report, we explained and implemented the Tight-Binding Model in an attempt to understand the bandgaps in 2D semiconductors, in our case Monolayer Graphene sheet.
- We started off by studying the structure and electronic properties of graphene to give us an idea of what to expect from our results. Then, we moved from the direct lattice to the Reciprocal Lattice.
- Using the position vectors of the neighboring atoms and applying the Bloch theorem to the Schrodinger equation on the wave function, we got the dispersion relation
- Using the Hamiltonian Matrix calculated the Energy from the eigenvalues using the inbuilt PYTHON function.

- We obtain the Energies for Bonding and Anti-Bonding orbital for the carbon-carbon  $\pi$  bond, On plotting the energies with  $|K|$ , we noticed to have energy gap  $< 0.5eV$  and hence very close to zero.