From Quantum Mechanics to Condensed Matter: Semi-Metallic Properties of Monolayer Graphene via Tight-Binding and LCAO

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Abstract:

This literature review examines the semi-metallic properties of monolayer graphene through the theoretical approach of the Tight-Binding Model coupled with the Linear Combination of Atomic Orbitals (LCAO) method. Beyond its implications for electronics, graphene's exceptional mechanical strength, thermal conductivity, and chemical stability have positioned it as a transformative material in fields such as nanomedicine, renewable energy storage, filtration systems, and advanced composite materials. Sources from foundational quantum mechanics to contemporary condensed matter research are synthesized to trace the conceptual and mathematical bridge between atomic-scale physics to determine the electronic band structure of graphene. The analysis begins with the derivation of graphene's lattice geometry and reciprocal space, followed by a review of the formalism underlying the Tight-binding Hamiltonian. The role of LCAO in describing electron wavefunctions is explored when approximating the scaling energy factor between the energy bands in graphene, with emphasis on the presence of Dirac cones and zero bandgap behavior at the K and K′ points of the Brillouin zone, ultimately leading to the peculiar properties of graphene.

Introduction (Prerequisites):

Why is it that graphene itself exhibits semimetal properties and half-integer spins on its edges [1], but when twisted 1.1 degrees, is a topological superconductor [2], and when triple-stacked, becomes a semiconductor?[3] You have probably heard about graphene sometime in your life. Graphene is such a simple structure of a hexagonal lattice of carbon atoms, yet it proves so relevant in the advancement of technology and quantum science today. This paper promises to provide insights into why such phenomena occur, as well as how the contribution of its orbitals determines the properties of graphene. It also provides an insight into condensed matter physics for beginners, as well as how materials are studied in the realm of the quantum world.

As seen in Ref[4], ever since the rise of quantum theory in the early 20th century, many mysteries of how materials work have been unveiled. We will show how using the Schrodinger equation, the wavefunctions of electrons within the crystal are derived, and how energy states of the material band structure determine the electrical properties of graphene.

You are probably familiar with classical physics, in which objects behave as fixed particles. However, in the realm of the quantum world, these properties seem to change. Electrons in the atom no longer seem to carry their energy as particles with definite position, but rather as waves, in which there are regions the electrons are more probable to be in. The function that describes this distribution is known as the wavefunction, and this is considered to be an innate property of how quantum particles seem to behave, exhibiting both wave-like and particle-like properties.

The Basics Of Quantum Systems and the Schrodinger Equation

According to Schrodinger's theory in 1926, the wavefunction, Ψ is an abstract quantity that is responsible for determining the probability distribution of electrons in a given space. For instance, if we have a wavefunction that is sinusoidal, then the electron would be more likely to end up in places where the wavefunction has a higher value of $|\Psi|$^2. Think of it this way: If there is a cake on one side of the room, and fruits on the other, and a kid was in the room, you would expect that the probability is higher that the kid is staring at the cake (Figure 1). Electrons work the same way, only they tend to shift to places of lower potential energy in the crystal, which results in this so-called "probability density distribution."

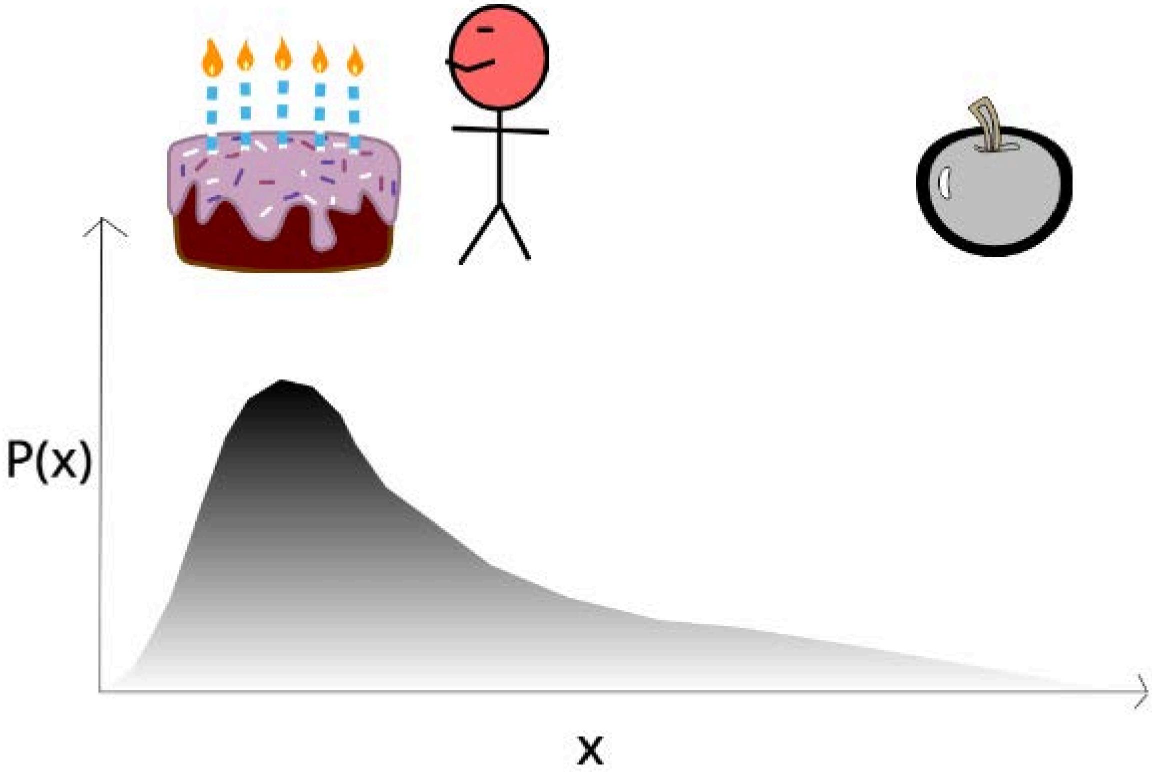


Figure 1 - There is a higher probability that the kid is closer to the cake, so the probability density function of the kid is closer to the cake than the apple.

Another property of the wavefunction that Schrodinger had to assume in his theory was that it was a continuous value. This is why electrons in the atom occupy discrete “energy levels” as you may have heard in chemistry class, because these are the only wave functions that have frequencies continuous across a single revolution (whole-number of waves per revolution). This is why in singular atoms, the s-orbital (1 wave per revolution), the p-orbital (2 waves per revolution), d-orbitals (4 waves per revolution), and so on are the probability distributions that electrons take in atoms (Figure 2). As you can probably imagine, the functions with more waves per cycle have more energy. But to prove this, let’s look at a prominent example of why: The potential well problem.

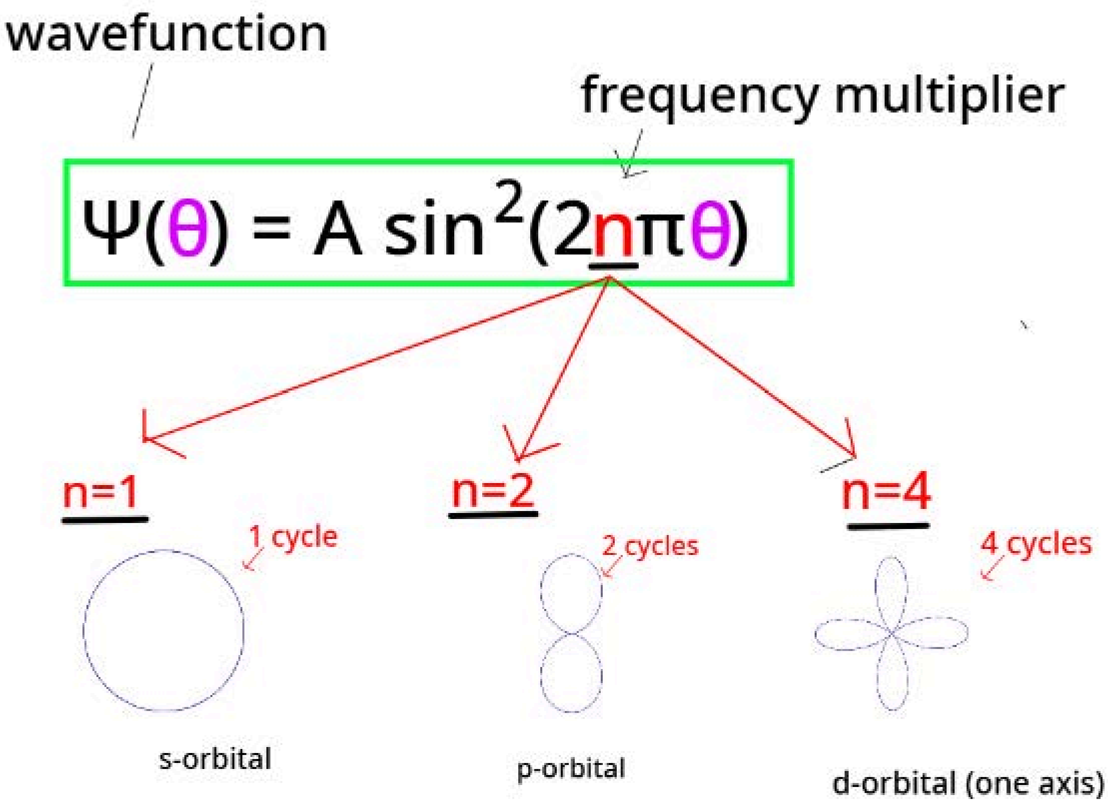


Figure 2 - Electrons in the atom take on wavefunctions that form a continuous loop. These are the fixed orbitals that are present in the atom.

Earlier, we learned that electrons are more keen to move to places with lower potentials, so suppose we were to place an electron in a box, where the potential is zero throughout, but is infinity beyond its walls (Figure 3). As we learned earlier, wavefunctions can only take continuous forms, so we end up getting a base wave, with several harmonics (or higher frequencies of waves that are multiples of the original wave).

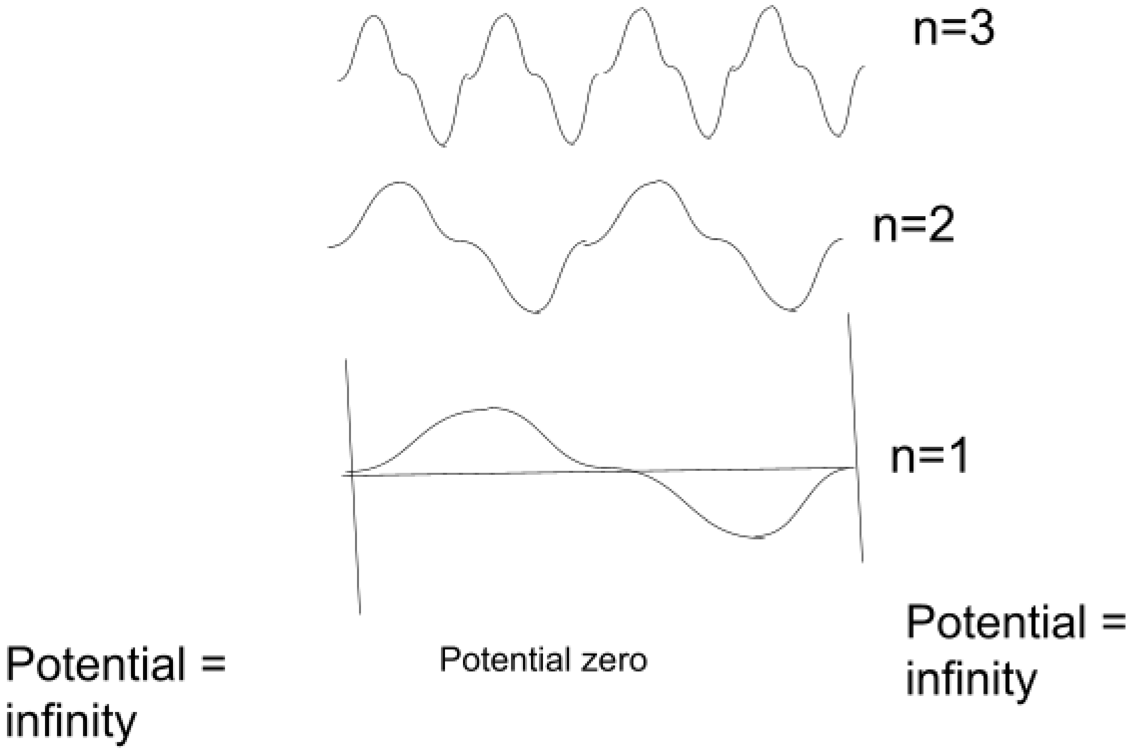


Figure 3 - Only the base wave and its harmonics can exist within the box. Not shown in the picture, but the base wave's length is twice the length of the box.

Since the potential is 0, we make the assumption that the particle's energy is entirely kinetic. We can utilize de Broglie's formula to relate the corresponding "wavelength" of the massive particle to its momentum ($\lambda = h/p$), as well as the notion that the particle energy is (½)mv^2, to derive so-called "energy" states of the system (Figure 4). For more simplified results, we define a new variable, one that we will call the wavevector k (equivalent to $2\pi/\lambda$), which will prove its importance later when we analyze the energy states of graphene.

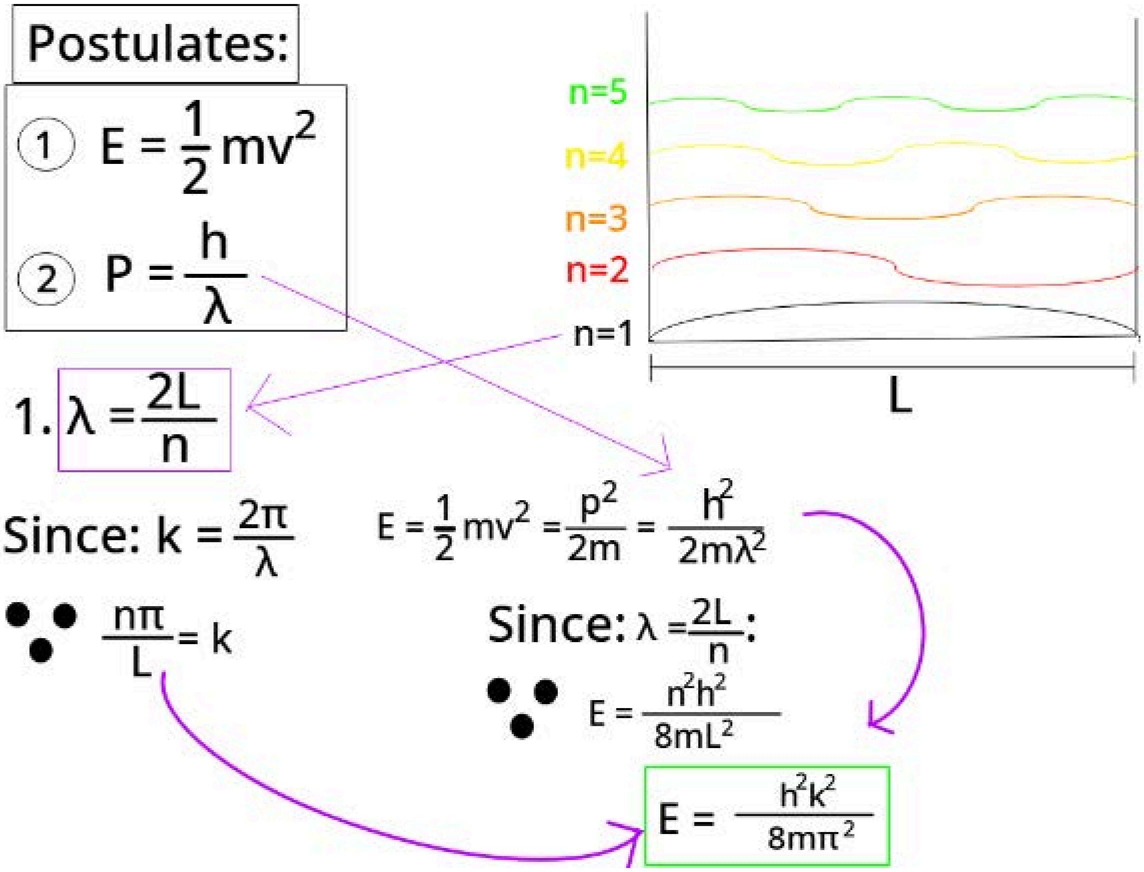


Figure 4 - The base wave (n=1), has a wavelength of twice the box length L, and every other wave is smaller by a multiple of n. Substituting the wavevector k at the end of the calculation yields a result where the energy is proportional to k^2. This is known as a quadratic dispersion relation.

As we can see from this example, electron energies in regions of constant potential tend to have a squared (thus parabolic) relation with the wavevector k. In contrast, by Planck's Law (E = hf), we can see the energy dependence for photons is instead proportional to the first order of k, known as **linear dispersion** (Figure 5).

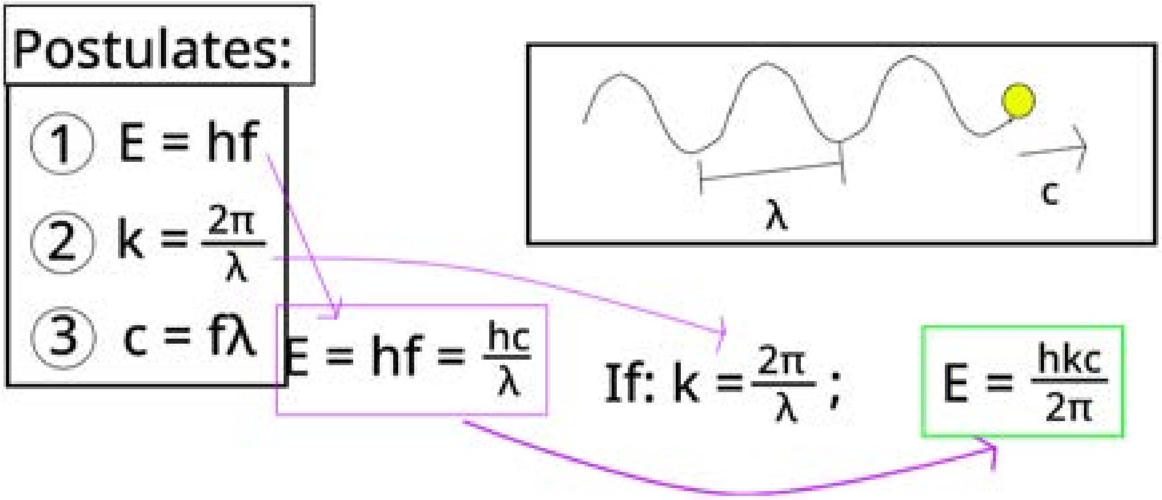


Figure 5 - Linear dispersion of photons, since the energy is proportional to the first order of k. This is because its energy is also proportional to its frequency by Planck’s Law.

In the case of quantum materials, one can visualize a comparison with these so-called “energy levels” of the box with the orbitals we have previously seen in the atom. In special cases, the material can manipulate its arrangement of atoms, such that the orbital wave functions overlap and cancel out, leading to linear dispersion. Essentially, this causes electrons in the solid to behave similarly to light, exhibiting relativistic and massless properties. Ultimately, it is this principle in which the peculiar properties of monolayer graphene are founded upon, and this paper will provide a comprehensive derivation of the overlap of electron wavefunctions in the crystal used to approximate the electrical properties of Graphene.

Shown in Figure 6 is the energy relation of particles on the quantum scale that Austrian physicist Erwin Schrodinger derived in 1926. For the sake of simplicity, this paper will not go into how it was derived, but the basics of this equation will still need to be known.

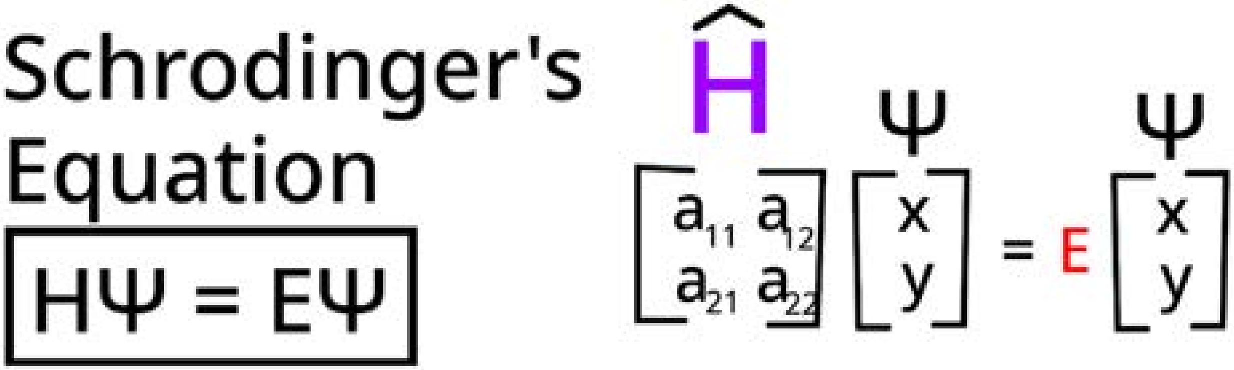


Figure 6 - Incorporating variables such as the wavefunction that suggest a wavelike nature, it attempts to describe the state of particles at the quantum scale in non-relativistic scenarios.

Psi is the wavefunction, H is the Hamiltonian operator, and E are the energy eigenstates. The Hamiltonian is the matrix operator containing the total energy of a quantum system, while the energy eigenstates are the allowed energy states the particle can occupy in the system. Since the Hamiltonian operator and the wavefunction aren't single numbers, but a matrix and a vector, respectively. While each element of the Hamiltonian square matrix holds information about each interaction of orbitals between atoms of different sublattices in graphene, the vector wavefunction describes the coefficients of each of the element bases in the Hamiltonian matrix. Applying the Hamiltonian matrix on the wavefunction, we get a product of the coefficient E times the wavefunction. The multiple possible solutions E in the case of a specific energy system are the solutions to the energy values of the system, or eigenstates. For more information about Schrodinger's equation, check the fifth in-text citation [5]. When determining the band structure of Graphene, we will be solving for the solutions to these eigenstates.

The Mathematical Nature of Crystalline Lattices

Atoms arranged in uniform patterns are known as crystals. If the repeating placements of atoms in a crystal can be described by a singular mathematical transformation, the crystal is known to be a Bravais lattice.

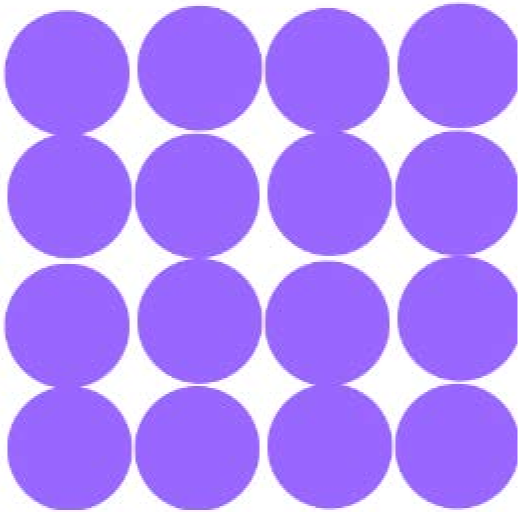


Figure 7 - A square Bravais Lattice

For instance, if we have the 2D square lattice shown in figure 6, we might describe the placements of every atom with the single transformation: V(x, y) = V(x + Na, y + Na), where N is any integer, and a is the unit cell length or interatomic distance between lattice points. It is generally understood that there are only 14 3D and 5 2D Bravais lattices, and describing the placement of the atoms in other crystals may require multiple mathematical transformations, each describing distinct, inferior sublattices of the crystal.

Having a baseline understanding of the placement of atoms in a crystal is crucial for determining the band structure (a graph of the energy states of the system with respect to wavevector dimensions in the crystal), and thus the material properties of the crystal, since the hopping distance from atom to atom in each sublattice determines the scaling factor of each Hamiltonian element. This scaling factor, as we'll see later, comes as a result of the exponential nature of the decay of the electronic wavefunctions with respect to distance.

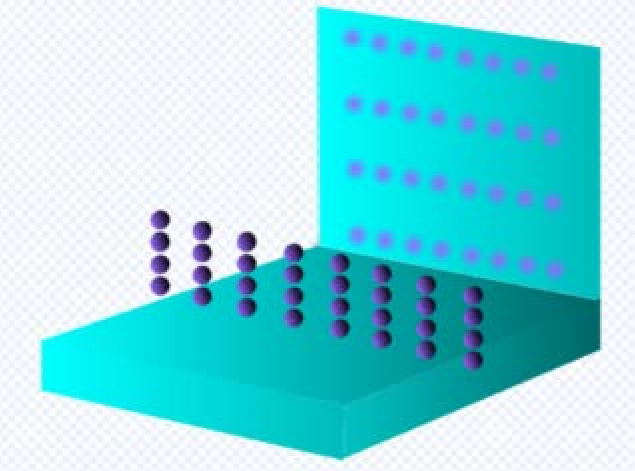
$$H_{nm}(\mathbf{k}) = \sum_{\mathbf{R}} \boxed{e^{i\mathbf{k}\cdot\mathbf{R}}} H_{nm}(\mathbf{R})$$

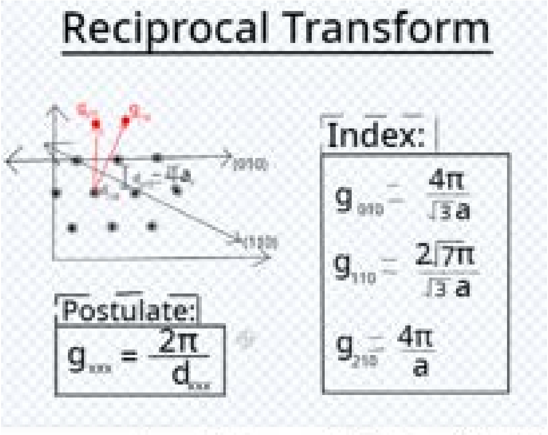
Figure 8 - Formula for the Hamiltonian matrix elements with respect to the wavevector k. R represents the distance between the orbital pair comprising each element. As the distance between hopping orbitals increases, the smaller the elements corresponding to the electron hopping between those two orbitals.

Reciprocal Lattices

Since it's convenient to express the wavefunctions and energy values in terms of k (which hold reciprocal length units), we must also use reciprocal lattice vectors to describe the placements of atoms in the crystal when determining the electronic properties in certain areas of the crystal.

To find the reciprocal of a rectangular lattice, simply find the reciprocal of the vertical and horizontal distances (bottom left).or more complex crystal systems, a more technical approach must be taken (bottom right).





$$V(x,y) = V\left(x + \frac{2N_x\pi}{a}, y + \frac{2}{\sqrt{3}}\left(\frac{N_x\pi}{a} + \frac{2N_y\pi}{a}\right)\right)$$

Figure 9- Passing X-rays through a rectangular lattice will the reciprocal lattice: shorter distances in the direct lattice correspond to longer distances in the reciprocal lattice, and vice versa.

Figure 10- Reciprocal LatticeTransformation produce various crystallographic planes.

In this approach, crystallographic planes with coordinates [0 1 0] to [X 1 0] are drawn through the lattice with respect to an origin (chosen to be the second atom left to the middle row). The X component is any real number, and is the number of unit cells the plane slopes downward per horizontal unit cell distance. Then, we take the reciprocal of the perpendicular distance from the origin to each distinct plane (dxxx, where xxx is the coordinates of the plane) and multiply it by 2π. Next, we repeat this process for a variety of different plane coordinates (not just [X 1 0]) and the reciprocal pattern is revealed (below).

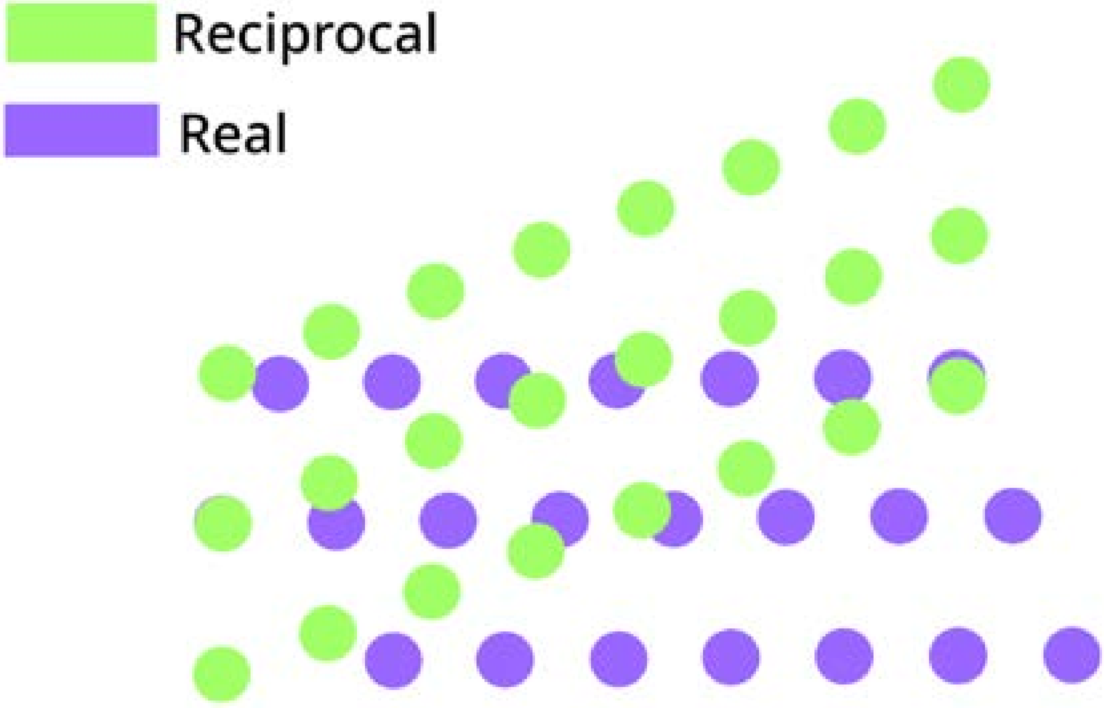


Figure 11 - The more crystallographic planes to transform the orthogonal vectors, the more reciprocal lattice points are revealed.

In the case of Graphene, which doesn't have rectangular unit cells, understanding this method will be important for determining the reciprocal lattice transformation in order to describe the electrical properties in different areas of the crystal.

Body:

Part 1: The Periodic Potential and the Bloch Wavefunction

As crystals that exhibit a repeating structure of atoms, we should expect the potential and thus wavefunction to be periodic over the unit cell. The periodic nature of this wavefunction is known as a Bloch function. This one assumption drives our first postulate, which we will normalize with our previous orbital wavefunctions in order to create one that describes both the repetition of the lattice as well as the nature of its orbitals.

LCAO

$$\Psi_n(\mathbf{x}) = \sum_{R} c(\boldsymbol{R})\varphi_{n\boldsymbol{R}}(\mathbf{x})$$

Bloch's Function

$$\Psi_{n\mathbf{k}}(\mathbf{x}) = u_{n\mathbf{k}}(\mathbf{x})e^{i\mathbf{k}\cdot\mathbf{x}}$$

Figure 12 - Since the Linear Combinations of the atomic orbitals of the crystal must be periodic over each unit cell, we can solve the variable parts of each equation to uncover more information about the composite wavefunction states.

The “LCAO” (Linear Combination of Atomic Orbitals) function on the left incorporates orbital wavefunction properties. The function c(r) represents the probability “weighting” coefficient associated with the specific distance R from the center of the orbital. While phi(x) represents the angular dependence on this weightage. Then, this value is summed over all orbitals at this specific point R in order to find the composite wavefunction of all the orbitals. Therefore, this must match the Bloch function on the right, since it must be periodic over every cell of repeating atomic arrangements.

In Block’s Function, the value u(x) holds information about the repeating nature of the lattice, while e^ikx represents the plane wave characteristic of the function, where k is the wavector (refer to figure 12). u(x) represents the amplitude of this periodic cell, and Felix Bloch (1905-1983) derived this important equation in his thesis. As we move onto describing the wavefunctions in crystals, the only change is that the wavelength of the functions take integer multiples of the unit cell size (referred to as “a,” rather than integer divisors of the size of a box. Therefore, k now represents integer multiples of 2π divided by a.

To properly model the electronic behavior of a solid, we need to represent the wavefunction for a reciprocal lattice, since, as we determined earlier, the energy of an electron depends on its wavevector k, which has reciprocal dimensions of normal space (the wavelength). This is why converting the periodic potential and wave function equations to reciprocal space is the easiest way to determine the electronic structure of the properties, since it’s in reciprocal dimensions. In the same way a Fourier transform separates a wave function into its constituent frequencies, we can apply this to the pattern of wavefunctions that arise from the different multiples of the periodic spacing of lattice points. All of these frequencies are then added up, hence the summation of the Fourier Transform:

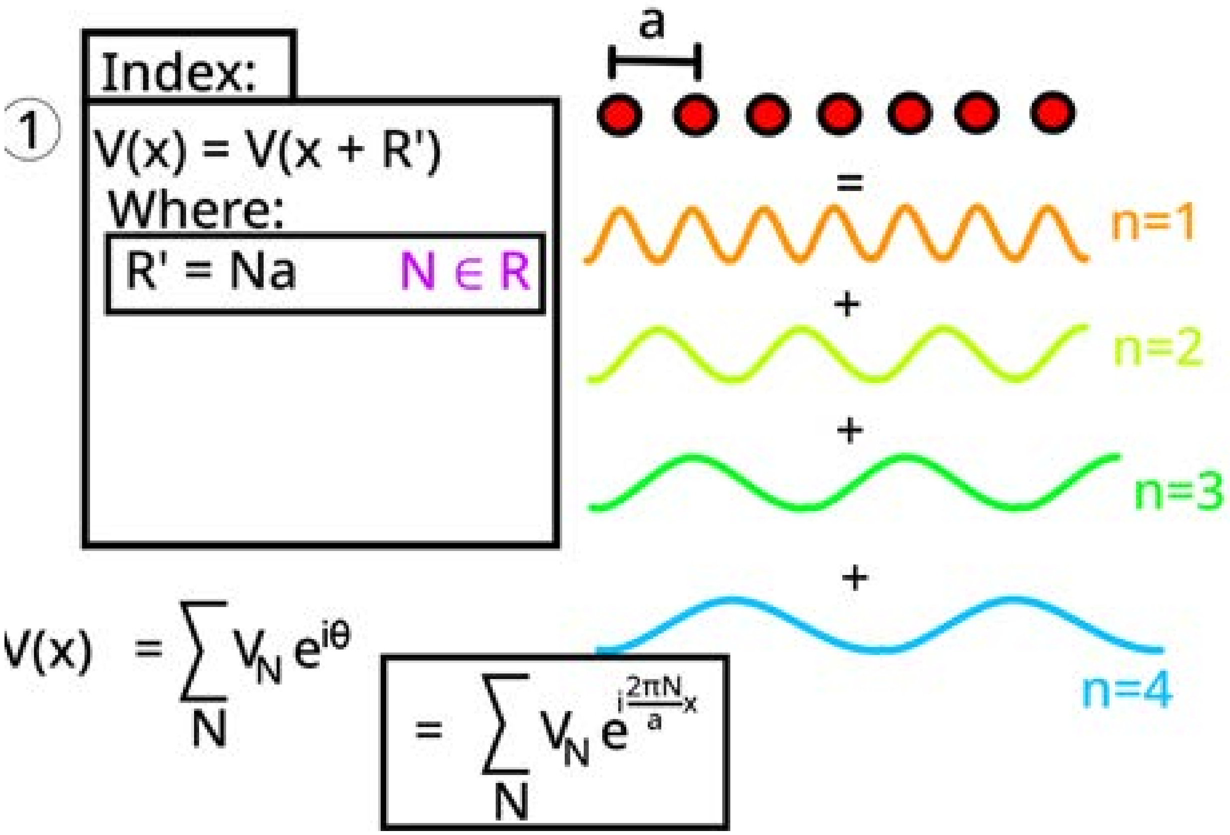
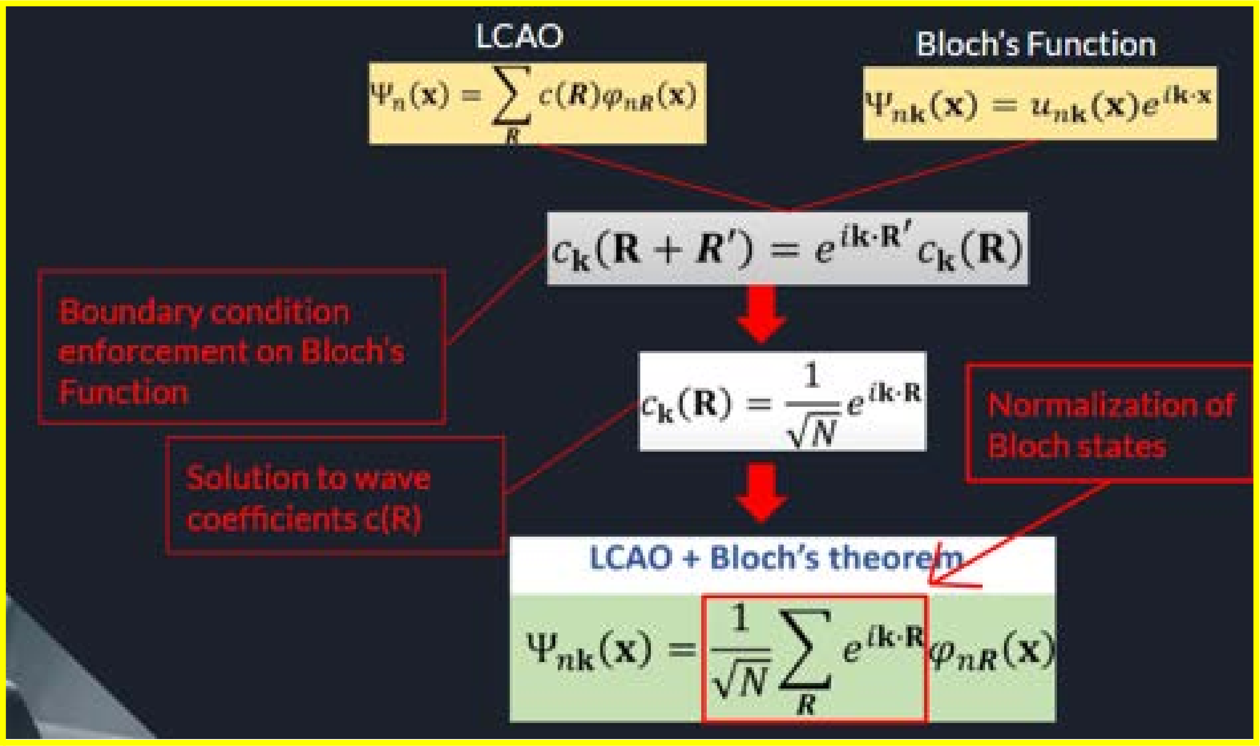


Figure 13 - Splitting the periodic wave function into its constituent wavelengths, the Fourier transform of the periodic potential is effectively the sum of all amplitudes of said component wavefunctions.

In order to make use of both orbital overlaps and wave function periodicity in the model, we need to combine them into one function to obtain the perks of both functions.



LCAO

$\Psi_n(\mathbf{x}) = \sum_R c(R)\varphi_{nR}(\mathbf{x})$

Bloch's Function

$\Psi_{n\mathbf{k}}(\mathbf{x}) = u_{n\mathbf{k}}(\mathbf{x})e^{i\mathbf{k}\cdot\mathbf{x}}$

$c_{\mathbf{k}}(\mathbf{R} + R') = e^{i\mathbf{k}\cdot\mathbf{R}'}c_{\mathbf{k}}(\mathbf{R})$

Boundary condition enforcement on Bloch's Function

$c_{\mathbf{k}}(\mathbf{R}) = \frac{1}{\sqrt{N}}e^{i\mathbf{k}\cdot\mathbf{R}}$

Normalization of Bloch states

Solution to wave coefficients c(R)

LCAO + Bloch's theorem

$\Psi_{n\mathbf{k}}(\mathbf{x}) = \boxed{\frac{1}{\sqrt{N}}\sum_R e^{i\mathbf{k}\cdot\mathbf{R}}}\varphi_{nR}(\mathbf{x})$

Figure 14 - In this figure, we normalize the Bloch and LCAO function to uncover information about the composite wavefunction. The appearance of the 1/sqrt(N) normalizing factor present in the last two lines is explained in Figure 9.

As seen by figure 14, if we were to translate composite wave function (psi_n(x)) by a distance R', we can see that the phi(x) factor of the LCAO wave function (top left) would be independent of R', dependent only on the distance relative to the center of the orbital. The only variable factor is c_k(R).

Translating the composite wavefunction in Bloch form (top right) also by a distance R', would only change the e^ik*R' factor of the equation.

Therefore, translating the function by R' changes only the weighting constant c_k(R), which has the added result of multiplying e^ik*R'(2nd row of figure 14). Since the periodicity of both functions must be the same, we can conclude that if they repeat over an atomic distance R', we must get the equation above, linking the coefficient c(R) with periodicity-dependent coefficients on the right (3rd row of figure #).

Due to the Normalization of Composite Wavefunctions:

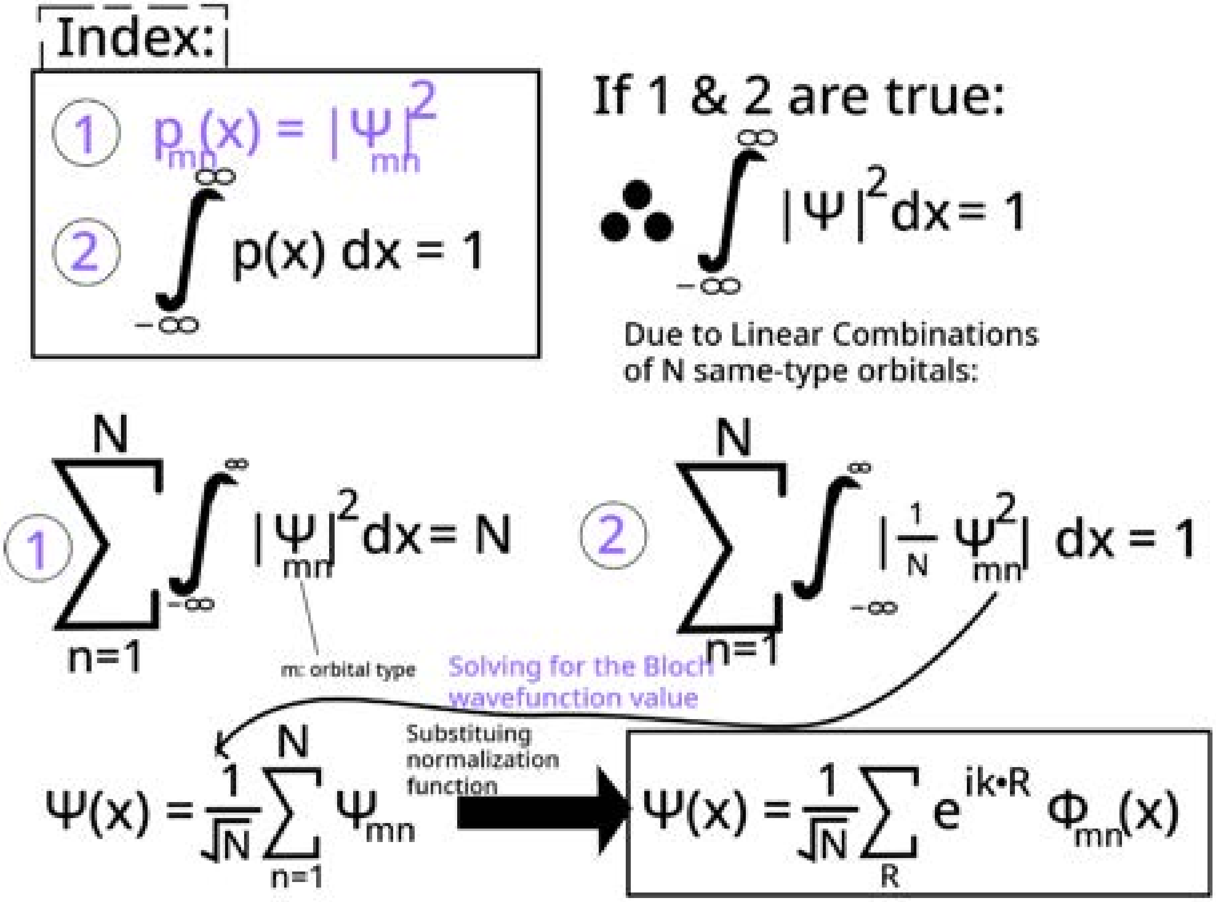


Figure 15 - In this figure, we derive the normalizing factor (1/sqrt(N)) present in the final form of the composite wavefunction.

Since the integral of each orbital probability density function over all space must add up to 1, and we defined the probability density function earlier as being the square modulus of each orbital wave function, we can conclude that a composite wave function of N number of orbitals must have an integral of N over all space.

Dividing by N, we find that the composite wave function must be a factor of 1/sqrt(N) of the sum of all the same orbital-type wavefunctions, thus reaching the equation we see in figure 8.

Part 2: Utilizing the LCAO Function Predict the Energy States of Monolayer Graphene

Applying these principles to Graphene, we can use them to predict its electronic states. Since Graphene isn't a Bravais Lattice (a crystal lattice in which every point of the crystal can be described by a mathematical equation), we must divide Graphene into two sublattices in order to apply the principles that we talked about earlier. Each unit cell has one of each point from the two sublattices, and we will use the wave vectors a1 and a2 (both one unit cell (a) in magnitude). The unit cell distance a is about √3 times the distance between two adjacent Carbon atoms.

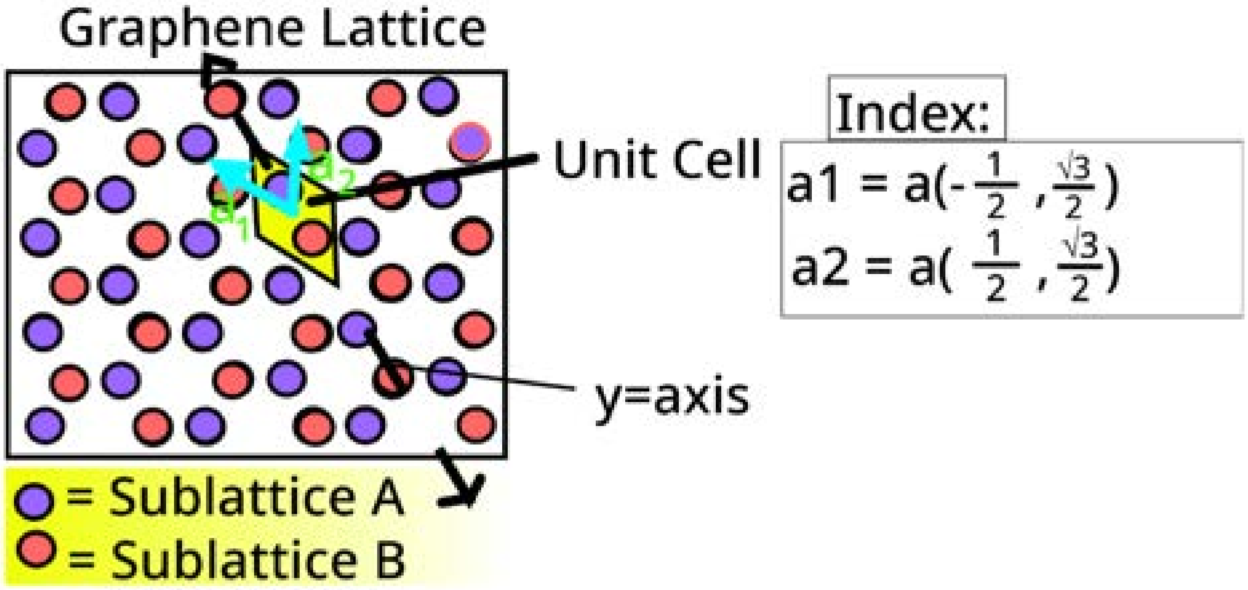


Figure 16 - Since Graphene is not a Bravais lattice, we must distinguish two separate hexagonal sublattices that constitute the overall structure. Defining the wavevectors a1 and a2 will be necessary in our procedures to calculate the Hamiltonian matrix of the Schrodinger equation.

Although we've already defined the unit cell structure of Graphene and its lattice nature, we still need one last piece of information to calculate the electron hopping energies between atoms. Defining the placement of the nearest neighboring atoms of each sublattice helps us accurately determine the perturbations due to the electric potential in the crystal.

Part 3: Applying The Tight-Binding Method

Along with the precise details of the electronic orbital overlaps and scaling factors (which we talked about earlier) present in what is known as the Tight-Binding Method for calculating the relative size of each of the terms of the Hamiltonian Matrix, we can compute the precise values of the electron energy hopping values in graphene, which we can then analyze to determine its material properties.

Recalling the nature of matrices from linear algebra, we know that the solutions for the coefficients required to scale a vector that results in the product of a particular matrix with that vector are known as eigenvalues. In the Schrodinger equation, the eigenvalues of the Hamiltonian Matrix correspond to the solutions to the energy states of the system.

$$\overset{\hat{H}}{\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix}} \overset{\Psi}{\begin{bmatrix} x \\ y \end{bmatrix}} = \overset{\text{Eigenvalue}}{\lambda} \overset{\Psi}{\begin{bmatrix} x \\ y \end{bmatrix}}$$

① $\hat{H}\Psi = \lambda\Psi$
② $\hat{H}\Psi - \lambda\Psi = 0$
③ $\hat{H}\Psi - \lambda I\Psi = 0$

Factor Ψ

④ $(\hat{H} - \lambda I)\Psi = 0$

Figure 17 - Moving the right side of the equation to the left, and adding identity matrix I to match the dimensions of the Hamiltonian matrix, we get the final expression for the combination of terms that makes the equation equal to zero.

Additionally, if we move the eigenvalue side of the equation to the left, and then multiply it by identity matrix I which has the same dimensions as the matrix operator, we find that the combined matrix operator can't be invertible, since doing so would result in the value of the vector being zero. By the nature of square matrices, this is only possible if the determinant of the matrix is 0.

If: $(\hat{H} - \lambda I)^{-1}(\hat{H} - \lambda I)\Psi = (H - \lambda I)^{-1}\,0$

①

Since: $\Psi \neq 0$, $\det(\hat{H} - \lambda I) = 0$

$$\therefore \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} - \lambda \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \begin{bmatrix} a_{11} - \lambda & a_{12} \\ a_{21} & a_{22} - \lambda \end{bmatrix} = 0$$

$$\text{Since:} \det \begin{bmatrix} a_{11} - \lambda & a_{12} \\ a_{21} & a_{22} - \lambda \end{bmatrix} = (a_{11} - \lambda)(a_{22} - \lambda) - (a_{21}a_{12}) = 0$$

$$\boxed{\therefore \; \lambda = \frac{a_{11} + a_{22} \pm \sqrt{a_{22}^2 - 2a_{11}a_{22} + 4a_{21}a_{12} + a_{11}^2}}{2}}$$

Figure 18 - Solving for the determinant of the matrix and setting it to zero, we get the final expression for the eigenvalue solutions of the Hamiltonian matrix H_hat.

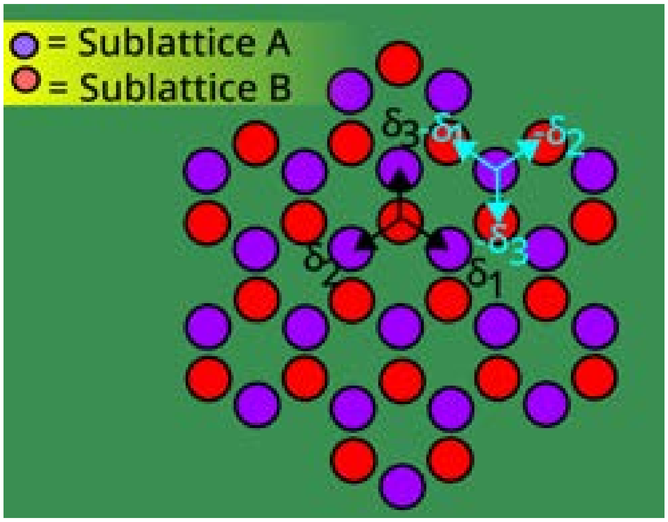
Solving for the eigenstates of the matrix, we get the result shown above. This derivation will prove crucial when diagonalizing the square Hamiltonian matrix of the orbital overlaps of Graphene.

Shown below is the simplified Tight-Binding Equation for the Hamiltonian matrix elements of the electron hopping between sublattices a and b.

$$H = -t \sum_{\langle i,j \rangle} a_{\sigma,i}^{\dagger} b_{\sigma,j} + H.c$$

Figure 19 - Given above is the general structure of the Tight-Binding Hamiltonian, with the summation adding the hopping scaling factors between sublattice i and j in a particular orbital combination. Substituting different orbital types (s, px, py, and Pz) for a and b results in the element corresponding to that interaction of the total matrix.

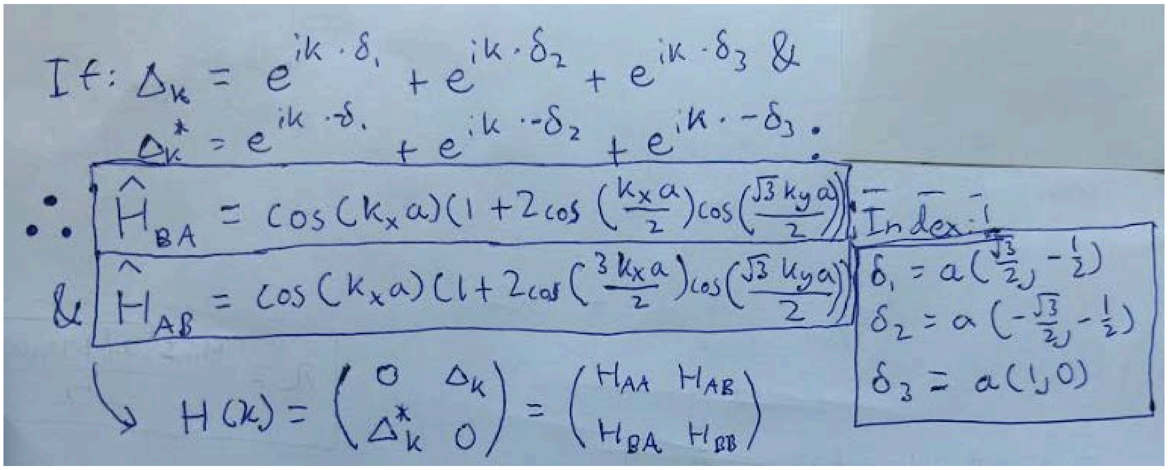
Lowercase t represents the hopping parameter which is determined by the integral of the scalar product of two orbitals using the LCAO method (as we'll see later), and the "a" with the dagger symbol represents the creation operator, which places an electron in a certain orbital state in sublattice a. Lowercase "b" represents the annihilation operator, or the removal of an electron at a certain site in sublattice b. Together, this process simulates electrons hopping back and forth. Finally, "H.c" (stands for Hermitian Conjugate) reverses the action by removing the electron from sublattice a and placing it back in sublattice b.



$$\boxed{\hat{H} = \left(\sum c_a^{\dagger} c_b \left(e^{ik\cdot\delta_1} \quad e^{ik\cdot\delta_2} \quad e^{ik\cdot\delta_3} \right) + \sum c_b^{\dagger} c_a \left(e^{ik\cdot-\delta_1} \quad e^{ik\cdot-\delta_2} \quad e^{ik\cdot-\delta_3} \right) \right) (-t)}$$

Figure 20 - Substituting in the coordinates for the inter sublattice points, we get the total Hamiltonian expression (shown at the bottom).

Substituting all hopping coefficients by inventing a new variable delta(k), we find that by inserting the precise hopping vectors between the sublattices of graphene, that the hopping from A to B happens to be the Hermitian Conjugate of B to A. We can also remove the imaginary part of these coefficients, converting the exponential imaginary elements into cosine elements (using Euler's formula).



If: $\Delta_k = e^{ik\cdot\delta_1} + e^{ik\cdot\delta_2} + e^{ik\cdot\delta_3}$ &

$\Delta_k^* = e^{ik\cdot-\delta_1} + e^{ik\cdot-\delta_2} + e^{ik\cdot-\delta_3}$.

$$\therefore \boxed{\hat{H}_{BA} = \cos(k_x a)\left(1 + 2\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{\sqrt{3}k_y a}{2}\right)\right)}$$

$$\& \boxed{\hat{H}_{AB} = \cos(k_x a)\left(1 + 2\cos\left(\frac{3k_x a}{2}\right)\cos\left(\frac{\sqrt{3}k_y a}{2}\right)\right)}$$

Index:

$\delta_1 = a\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)$

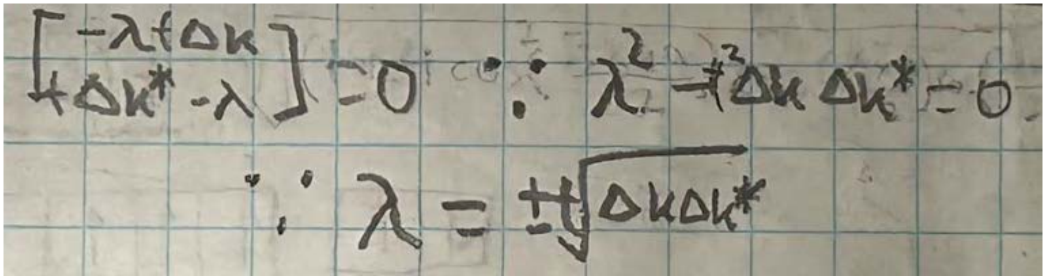
$\delta_2 = a\left(-\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)$

$\delta_3 = a(1, 0)$

$$\hookrightarrow H(k) = \begin{pmatrix} 0 & \Delta_k \\ \Delta_k^* & 0 \end{pmatrix} = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}$$

Figure 21 - Relative solutions of the Hamiltonian matrix elements for the sublattice hopping between A to B and B to A. By assuming the determinant to be zero, we’ll be using the same principles as earlier to derive the energy eigenstates of the system.

Implementing the principles of matrices we discovered earlier, we can derive the relative eigenstate solutions without solving for the amplitude t yet.

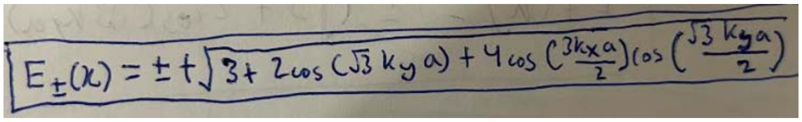


$$\begin{bmatrix} -\lambda & t\Delta k \\ t\Delta k^* & -\lambda \end{bmatrix} = 0 \therefore \lambda^2 - t^2 \Delta k \Delta k^* = 0$$

$$\therefore \lambda = \pm t\sqrt{\Delta k \Delta k^*}$$

Figure 22 - Solution to the energy eigenstates in terms of variables t, delta k, and delta k asterisk.

Without knowing the amplitude t, it is now possible to plot the shape of the relative band structure:



$$\boxed{E_\pm(k) = \pm t\sqrt{3 + 2\cos(\sqrt{3}k_y a) + 4\cos\left(\frac{3k_x a}{2}\right)\cos\left(\frac{\sqrt{3}k_y a}{2}\right)}}$$

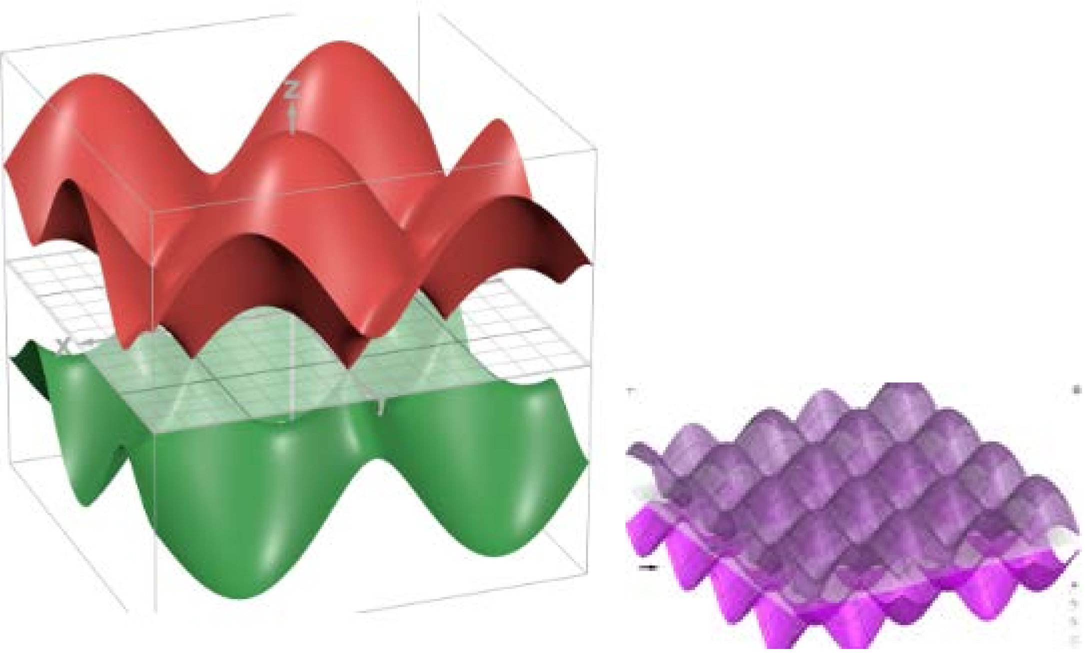


Figure 23 - A graph of the relative band structure plotted on Geogebra 3D Graphing Calculator. Expanding the variables delta k and delta k asterisk back into their sinusoidal components, we solve for the general shape of the energy states of Graphene.

However, our work here is not finished, since determining the magnitude of the hopping parameter t is essential for analyzing the delocalization of electrons, thereby affecting the material's conductivity.

Out of four different types of orbitals present in the Carbon atoms of Graphene (s, px, py, and Pz), we will be calculating the hopping energy of the Pz to Pz orbital overlap, since this interaction in particular results in the peculiar properties of Graphene.

Referring to a table of hopping parameters between different orbital types, we find the value of the hopping energy between two Pz orbitals of a π bond to be ~ 2.7 electron volts (or around 2.7 times the energy value of a singular electron accelerated through a 1 Volt potential). For more information on the derivation of this hopping parameter, readers are encouraged to refer to Appendix A.

Energy Bands of Graphene

Plotting the band structure values over every single area in Graphene's unit cell will be time consuming and ineffective, so we have chosen a few, highly symmetric points throughout the crystal to which we will set the path to map the band structure along. Precisely, this will be from Γ -> M -> K - T or yellow to red to orange in the figure below, and the hexagonal area surrounding the central atom is known as the Brillouin zone.

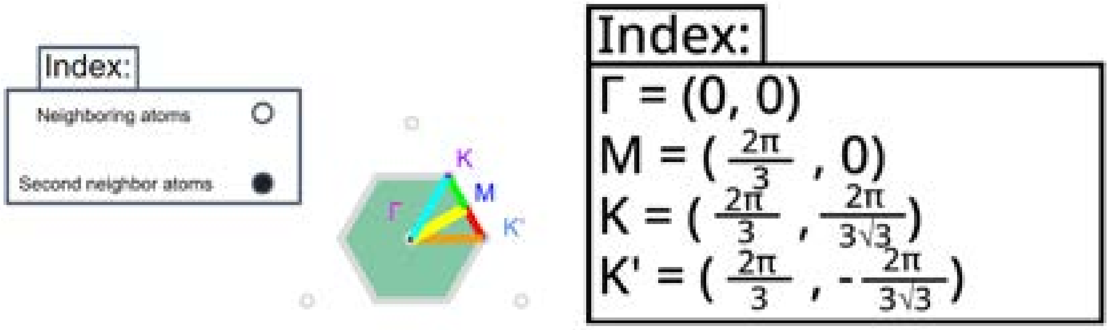


Fig 24- Above shows a B-type Graphene atom with its three nearest neighbors. In order to capture the essence of the band structure, we probe over 3 different points that each have commonly repeating potentials throughout the Brillouin zone.

Since our equations are in units of inverse distance (hence the kx and ky wavevector units), we will need to describe this path using reciprocal lattice vectors. This is done by transforming the coordinates of the direct space vectors into reciprocal space. The final band structure is shown below.

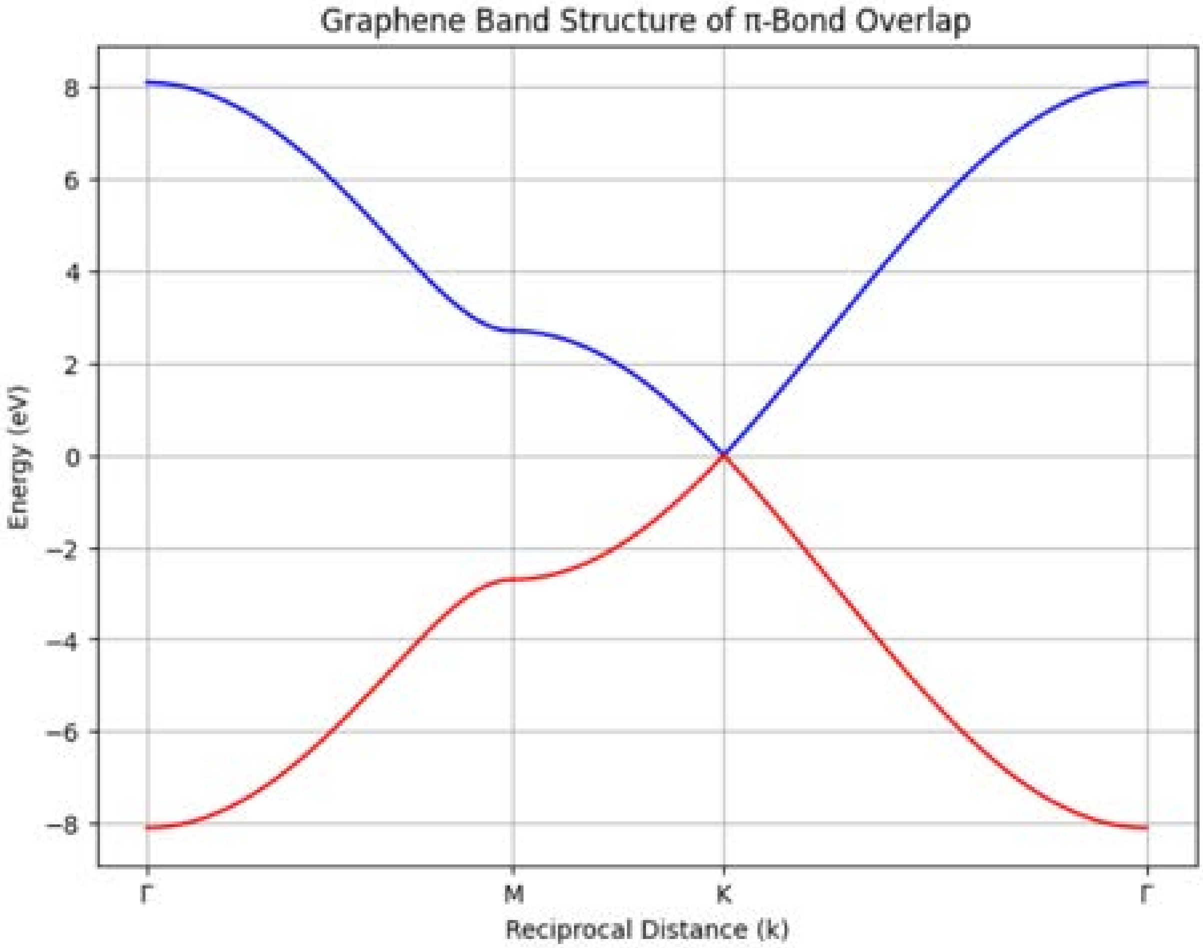


Fig 25 - A plot of the Graphene's band structure over the three highly symmetric lattice points across the Brillouin Zone above. This was done by manipulating kx and ky into four different piecewise functions that described the band structure over the given paths connecting lattice points.

Discussion:

Electronic Properties of Graphene:

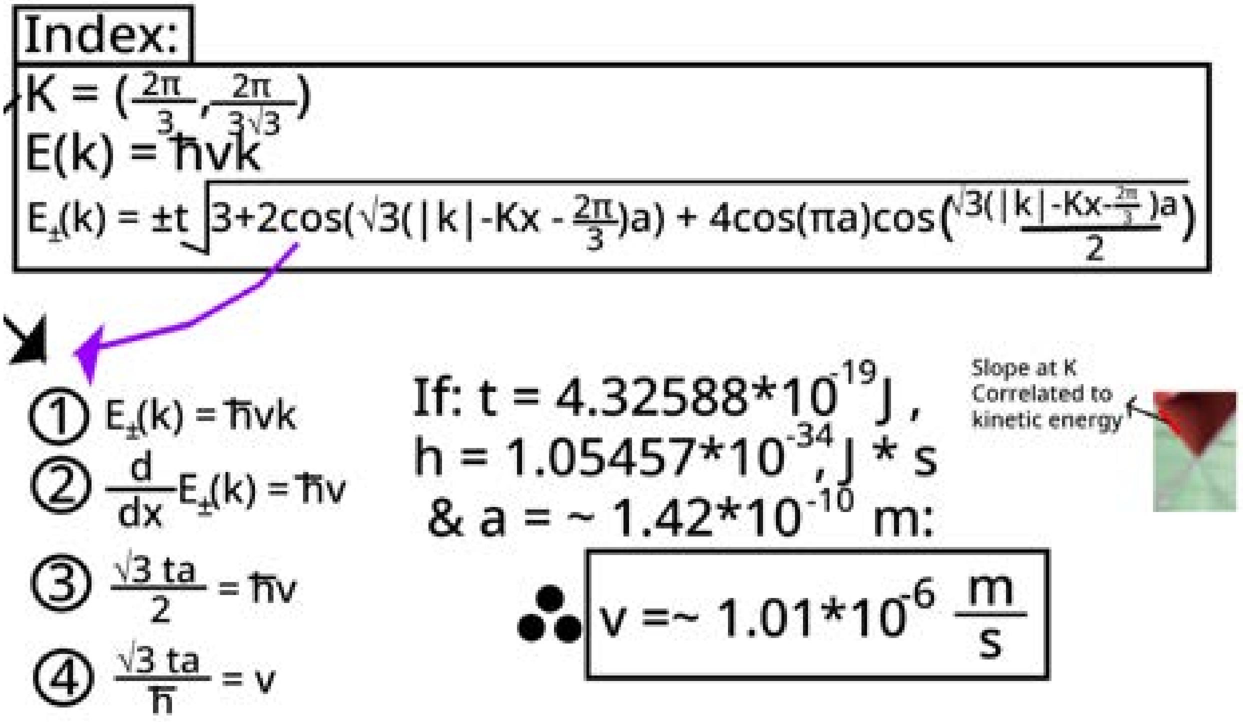
Now that we have derived the energy states of Graphene, let's show how this reveals its extraordinary material properties. As we can see, the energy bands intersect at point K with a seemingly linear behavior[5]. The bands touch at the energy value of zero, known as the Fermi energy of the material (or the highest occupied state of electrons in the material at a temperature of absolute zero). For more information on the code to produce this plot, readers should refer to Appendix B.

Since the second band is above the Fermi energy, this means it's in the conductive state, where electrons propagate freely throughout the material. Since this band gap touches the energy band below the Fermi level (which is filled up by electrons), it allows them to freely flow into the conduction state, since the hopping energy at the point K is effectively zero. Since the bands at this point are very close in energy, Graphene can be classified as a semimetal, a subclass of materials in solid-state physics sharing both metallic and nonmetallic properties. This perfectly explains the properties of graphene, since it has the ability to conduct electricity like metals, but lacks malleability like most nonmetals[6].

If we recall the nature of massless particles such as photons from the introductory prerequisites of this analysis, when the energy of particles in a system is directly proportional to the wavevector k, it arises in photon-like properties of the electrons present at lattice point K, since the dispersion correlation is roughly linear at that point. Points in the crystal which exhibit linear dispersion are known as Dirac points. Therefore, Graphene effectively exhibits massless Dirac fermions at K [7]. Therefore, the electrons move at extremely fast speeds with very little resistance, enabling its groundbreaking potential in the field of high-speed electronic devices, such as Terahertz-band circuits.

Calculating the Fermi Velocity of Graphene

Additionally, we can even calculate the velocity of these electrons, utilizing the same energy to wavevector correlation we derived from photons. The slope of the Dirac Cone near the K point must be equal to the constants relative to the wavevector k to energy in our equation.



Index:

$$K = \left(\frac{2\pi}{3}, \frac{2\pi}{3\sqrt{3}}\right)$$

$$E(k) = \hbar vk$$

$$E_{\pm}(k) = \pm t\sqrt{3+2\cos\left(\sqrt{3}\left(|k|-Kx-\frac{2\pi}{3}\right)a\right) + 4\cos(\pi a)\cos\left(\frac{\sqrt{3}\left(|k|-Kx-\frac{2\pi}{3}\right)a}{2}\right)}$$

① $E_{\pm}(k) = \hbar vk$

② $\frac{d}{dx}E_{\pm}(k) = \hbar v$

③ $\frac{\sqrt{3}\,ta}{2} = \hbar v$

④ $\frac{\sqrt{3}\,ta}{\hbar} = v$

If: $t = 4.32588*10^{-19}$ J,
$h = 1.05457*10^{-34}$ J * s
& $a = \sim 1.42*10^{-10}$ m:

$$\therefore \boxed{v =\sim 1.01*10^{-6}\ \frac{m}{s}}$$

Fig 26 - Derivation of the velocity of electrons near the Dirac point.

Therefore, by finding the derivative of the relative eigenstate equation at a minute distance k away, we can cancel out all insignificant higher-order terms of k, and include only the linear one [8].

Since the speed of electrons in graphene is about a 300th the speed of light, this furthermore bolsters the idea that the semimetal has potential applications for high-speed electronics, such as those used in satellite communication, radar systems, and medical devices, since they demand fast data processing and transmission.

Conclusion:

As quantum field theory advances, improvements in computational models will lead to the discovery of new materials with interesting properties, which will in turn lead to advancements in technology, such as the quantum computing field. A new type of material, known as topological insulators in particular, exhibits conductivity on its surfaces but insulating properties in its bulk, allowing for the protection of the superposition of qubits in quantum computers. The superposition of the thousands of states present in qubits leads to astronomical efficiency, far better than the classical bits, which can only store zeros and ones.

This paper is merely an introduction for the amateur quantum theorist to the vast expanse of the various subfields in condensed matter physics through a very basic example of the application of quantum theory in determining the precise electrical properties of solids. Determining such electrical properties in other materials may not prove to be as simple and may require a much deeper understanding of quantum theory.

To those curious in continuing to pursue the field of condensed matter physics, I recommend exploring different, more accurate computation models than the Tight-Binding Model, such as Density Functional Theory, or the calculations and band structure predictions of different types of solids, such as insulators, semiconductors, metals, superconductors, topological insulators, and other subgroups of materials in solid-state physics.

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- **Text Citations:**

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Appendix A:

In quantum mechanics, the inner product between two vectors is defined as the sum of constituent products between each element of the same number placement in each vector.

Given:

$$\Psi_A = \begin{bmatrix} A1 \\ A2 \\ A3 \\ \vdots \end{bmatrix} \quad \Psi_B = \begin{bmatrix} B1 \\ B2 \\ B3 \\ \vdots \end{bmatrix}$$

$$\langle \Psi_A | \Psi_B \rangle = A1 \cdot B1 + A2 \cdot B2 + \ldots + AN \cdot BN$$

According to the LCAO model, the hopping energy is simply the scalar (or inner) product of the two orbitals times the kinetic energy operator -((h_bar)^2)/2m. We can use the Gaussian approximation for wavefunction decay to solve for the hopping integral.

$$t = \langle \phi_i | \hat{H} | \phi_j \rangle$$

$$\phi_{p_z}^{A}(\mathbf{r}) = N(z - z_A) e^{-\alpha |\mathbf{r} - \mathbf{R}_A|^2}$$

Since the square modulus of the orbital wavefunction must be equal to 1 over all of space, we solve for the normalization coefficient as shown below.

$$\boxed{N = \left(\frac{128\alpha^5}{\pi^3} \right)^{1/4}}$$

Solving for the hopping integral, we find the value of the hopping energy between two Pz orbitals to be ~ 2.7 electron volts (or around 2.7 times the energy value of a singular electron accelerated through a 1 Volt potential).

Appendix B:
Python Code:
https://github.com/Chalcopyrite-obesity/The-Band-Structure-of-Graphene-Plot

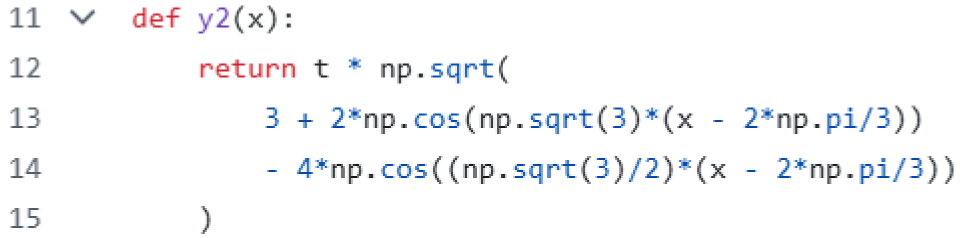
Elaboration on Code: In order to probe the band structure along the three points of the Brillouin Zone, we split up the code into three different equations and connect them together. In order to get from the center Γ to M, we have to replace all y values of the equation with zero, leading to the formula below:

$$E = + t\sqrt{5 + 4\cos(\tfrac{3x}{2})} \;;\; x : [0, \tfrac{2\pi}{3})$$

This will be the first equation we define in our Python code.

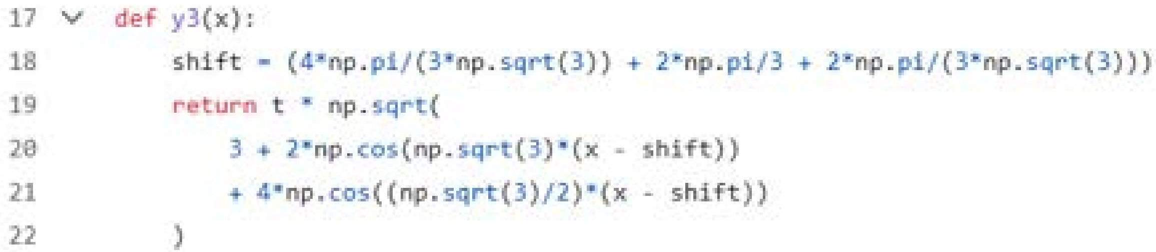
```
def y1(x):
    return t * np.sqrt(5 + 4*np.cos(3*x/2))
```

Since the next part of the path (M -> K) is orthogonal to the first, we can instead substitute all Xs to zero, and then replace all Ys with Xs to plot along the same graph.



```
def y2(x):
    return t * np.sqrt(
        3 + 2*np.cos(np.sqrt(3)*(x - 2*np.pi/3))
        - 4*np.cos((np.sqrt(3)/2)*(x - 2*np.pi/3))
    )
```

However, since the path K -> Γ is diagonal across the function, we can't use these tactics to probe the final vector. But we can see that the path along this diagonal follows the exact same pattern as the portion of the function along the y direction due to the symmetry of hexagons. Therefore, flipping the functions and doing several transformations, we get the final function below.



```
def y3(x):
    shift = (4*np.pi/(3*np.sqrt(3)) + 2*np.pi/3 + 2*np.pi/(3*np.sqrt(3)))
    return t * np.sqrt(
        3 + 2*np.cos(np.sqrt(3)*(x - shift))
        + 4*np.cos((np.sqrt(3)/2)*(x - shift))
    )
```

Plotting these functions in sequence, we derive the final band structure of monolayer graphene across these symmetrical paths of the Brillouin Zone.