Electronic Structure

Exploration of the Tight Binding model for Graphene and the Anderson Model

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Introduction

Electronic Band structures describe the allowed energy ranges that an electron may have in a solid. To demonstrate Band Structure and how exactly it can be provide useful information to Solid-State physics, I will show a few well known models. The Tight Binding model is a well known model used to calculate band structures using sets of superpositioned wave functions for isolated atoms at each site in a lattice. As its name suggests, its a quantum mechanical model describing the properties of tightly bound electrons. To formulate the Tight Binding calculations, we must exploit the method of LCAO (Linear Combination of Atomic Orbitals) which will give us approximate solutions to the time-independent Schrodinger equations. However, the periodicity of the lattice tells us that the wave function can only change by a phase factor, therefore the LCAO approximation can be represented by the familiar Bloch wave.

$$\psi(r + R_\ell) = e^{i\mathbf{k} \cdot \mathbf{R}_\ell} \psi(r)$$

The Bloch wave function is essentially where all of tight binding comes from, this will be shown in the first example of tight binding: Graphene. We will also demonstrate the tight binding model in the Anderson Model.

Graphene

Graphene is a very interesting case of tight binding to study, this is due to its abstract shape. Graphene is actually a material which just recently has collected a lot of attention, as it has defied previously thought laws of thermodynamics. We will be demonstrating with a honeycomb hexagonal shaped lattice of carbon atoms which means there will be two atoms per unit cell. This of course changes the approximation made from LCAO and thus the Bloch wave formulation. Generalized for two atoms per unit cell, Graphene’s wave function can be modeled as follows:

$$\Psi^k_1(\mathbf{r}) = c^A_1(\mathbf{k}) \Psi^A_1(\mathbf{r}) + c^B_1(\mathbf{k}) \Psi^B_1(\mathbf{r})$$

$$= \frac{1}{\sqrt{N}} \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} [c^A_1(\mathbf{k}) \phi(\mathbf{r} - \mathbf{R}_j^A) + c^B_1(\mathbf{k}) \phi(\mathbf{r} - \mathbf{R}_j^B)],$$

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here \( N \) is the number of elementary cells, and the functions \( \phi(\vec{r}) \) are the wave-functions of the \( p_z \) orbitals of the carbon atoms. \( P_z \) orbitals stay separated from the rest of the orbitals in this structure and are responsible for the \( \pi \) and \( \pi^* \) bands which will be shown in the band structure plots. The remaining orbitals will form a hybridization \( sp^2 \) responsible for the \( \sigma \)-bonds. These are the bonds that keep nearest neighbors together in the lattice. Now to calculate band structure, we of course wish to find all the possible energies. For this we must derive a dispersion relation. To do so we must solve for a Hamiltonian using the Bloch wave functions shown previously. The Hamiltonian for this will already be in k-space due to the properties of the Bloch wave. It has already accounted for the Fourier transformation of the wave function. This means the construction of the Hamiltonian (all hopping parameters \( t \) will be set to 1) will be all that is needed, this and of course to diagonalize the matrix and find the dispersion relations based on the energy eigenvalues of the Hamiltonian. This is found to be:

\[
E(k) = \pm \gamma \left\{ 1 + 4 \cos \left( \frac{\sqrt{3}k_x a}{2} \right) \cos \left( \frac{k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_y a}{2} \right) \right\}^{1/2}
\]  

Where \( \gamma \) represents a parameter of the system, in my calculations I used a \( \gamma \) value of -2.7 eV. Using this dispersion relation, we can now plot the band structure using mathematica and analyze the physical relevance. This was done and the plots found are shown in FIG. 1. The lattice constant \( a \) was 2.461 \( \text{Å} \) however, for simplicity, I generated values of \( ak_y \) and \( ak_x \) individually over the range [-4,4].

Analyzing this band structure, we see the honeycomb lattice as expected and we see the two bands. The upper band being the conduction band while the lower band is the valence band. The valence band consists of the energies for electrons that are bound to their cell while the conduction electrons can roam throughout the lattice structure. Notice the six points in which the bands are closest. These points are called Dirac points, these points are when the electrons behave like relativistic particles described by the Dirac equation. Density of States was now calculated and graphed as well. This is an important parameter to graph as physical data is derived from the density of states for a structure. This can be seen on figure 2.

The density of states here is very abstract, we notice two singularities, formally known as Van Hove singularities. The wavevectors at which Van Hove singularities occur are often referred to as critical points of the Brillouin zone.
FIG. 1: Energy Bands for Graphene dispersion with $\gamma$ set to be 1 eV for simplicity. The upper band represents the $\pi^*$ and the lower $\pi$. These determine the conduction and valence bands of the electrons in the lattice. Notice the six dirac points forming a hexagonal like shape just as the carbon structure for graphene is anticipated to.

FIG. 2: Density of States plotted over energy. Multiple singularities are found, this is a large area of study in Solid-State Physics known as Van Hove singularities.

**Anderson Model**

We now evaluate a more simplistic case of Tight Binding. The case of a 2 dimensional square lattice where only nearest neighbor effects are needed. This is modeled by what is known as the Anderson Model

$$H = t \sum_{i,j} c_i^\dagger c_j + \sum_i \epsilon_i n_i$$
Where $\epsilon_i$ the randomly generate site energy. Previously, we never considered a possible disorder energy at the site of the electron. Now we generate a random energy on the scale $[-W/2,W/2]$ where $W$ is equal to the disorder width. We will set this in the Fortran90 program I have written and alter it as needed for data analysis. The $c_i^\dagger c_j$ represent the creation and annihilation operators, just as in the quantum harmonic oscillator, these are ladder operators. $C_i$ represents annihilation, for example say we have a state $|1\rangle$, when the annihilation operator acts on such a state, it becomes a vacuum state. The same concept applies on a vacuum states in reverse when applying the creation operator. The number operator is represented by $n_i$ and it is the product of the creation and annihilation operators. Its value is one for our case. For this 2-D example, we will need to consider periodic boundary conditions. In its simplest form we can state the hamiltonian to be as follows:

$$H_{ij} = \langle \psi_i | H | \psi_j \rangle$$ (5)

The 3x3 lattice example is shown below:

$$\begin{pmatrix}
\epsilon_i & 1 & 0 & 1 & 0 & 0 & 1 & 0 & 1 \\
1 & \epsilon_i & 1 & 0 & 1 & 0 & 0 & 1 & 0 \\
0 & 1 & \epsilon_i & 1 & 0 & 1 & 0 & 0 & 1 \\
1 & 0 & 1 & \epsilon_i & 1 & 0 & 1 & 0 & 0 \\
0 & 1 & 0 & 1 & \epsilon_i & 1 & 0 & 1 & 0 \\
0 & 0 & 1 & 0 & 1 & \epsilon_i & 1 & 0 & 1 \\
1 & 0 & 0 & 1 & 0 & 1 & \epsilon_i & 1 & 0 \\
0 & 1 & 0 & 0 & 1 & 0 & 1 & \epsilon_i & 1 \\
1 & 0 & 1 & 0 & 0 & 1 & 0 & 1 & \epsilon_i
\end{pmatrix}$$

With this we can generate an entire matrix and then simply add the random energies along the diagonal. After diagonalization of this matrix, the energy eigenvalues will be output. The hamiltonian will have a 1 at every ij index that represents a nearest neighbor with the given periodic
FIG. 3: Density of states for Anderson model of a 40x40 lattice for different W compared with a histogram plotted in mathematica.

conditions. This was all done in fortran90, refer to the subroutine “neighbors” on the attached code for the algorithm used. For efficiency, it was done without the use of any logical operators. The Hamiltonian was formulated and for a 3x3 lattice for example would be as shown above. We can see this matrix is symmetric, and in the case of our calculation, it will be sparse as well. Using a freely distributed algorithm from LAPACK (linear algebra library for fortran 77/90). This library contained subroutines that were able to output the eigenvalues and the eigenvectors of the input matrix. This was specifically designed for sparse, symmetric matrices which was the case for our hamiltonian. After finding the energy eigenvalues, we now find the density of states for multiple disorder widths W. This is shown below.

We see a high level of consistency between the fortran code and the mathematica. The histogram produced was only for the original disorder width of W = .5. The mathematica and fortran codes are both included for reference. The last quantity calculated was the inverse participation ratio. This is a ratio given by the sum of the squares of all the wave functions squared over the sum of the wave functions to the fourth. Thus the inverse participation ratio is related to the localization length. It is shown in the figure on the top of the next page.

Conclusion

Throughout all the calculations there was a high level of consistency between fortran and mathematica. The band structures physical properties all corresponded to the output accurately.
FIG. 4: Inverse Participation Ratio averaged over all of the eigenvectors as a function of the disorder width $W$. The higher the disorder width, the lower the IPR, meaning the higher the disorder, the smaller the length of the localization is. Less will be localized as $W$ increases.

To further investigate this subject one could read more into the quantum hall effect and how it effects tight binding, Landau levels and the IPR and how exactly it effects the localization.