Honeycomb Schrödinger Operators in the Tight-Binding Model

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MA 611

May 2, 2021

1 Introduction

This article is motivated by the study of graphene, an experimentally fabricated monolayer of carbon atoms arranged in a two-dimensional honeycomb lattice. Graphene has been a subject of deep interest and exploration by scholars in theoretical and applied science, mathematics, and engineering for over a decade, thanks to its unique properties [2]. In particular, graphene has been described as the ideal two-dimensional electronic material, as graphene is a monolayer and carrier dynamics (the flow of charge in semiconductors) is necessarily confined in this strict two-dimensional layer. Moreover, the electron moving in the honeycomb lattice is special because there are two equivalent lattice sites (A-sites and B-sites) which give rise to the asymmetry in the graphene carrier dynamics [3]. Furthermore, graphene offers prospects of critical advances in device performance at the atomic limit [1].

Here we formally construct the regular honeycomb structure $\mathbf{H}$ in terms of an equilateral triangular lattice Λ_h, and determine the dual lattice Λ_h^* and the Brillouin zone $\mathcal{B}_h$ (which is itself a regular hexagon). In the direct space, we will tile $\mathbb{R}^2$ by parallelograms which each contain two lattice points of the hexagonal lattice, so that each parallelogram contains two atomic sites: one A-type and one B-type. The parallelograms serve as our fundamental cells. These constructions allow us to study Wallace's tight-binding model [4] and its mathematical implications.

We then introduce the square-summable, complex-valued amplitude functions of the ground states centered at the A- and B-sites of any given fundamental cell, and couple the amplitude of the ground state centered at the A-site with that centered at the B-site to form the amplitude on the cell. This allows us to develop and study the tight-binding Hamiltonian H_{TB} for the amplitude of a fundamental cell, noting that each A-type atom has three nearest neighbors which are all B-type atoms and vice-versa.

Upon computing the discrete Fourier transform $\widehat{H}_{TB}$ of the tight-binding Hamiltonian H_{TB}, which varies over the Brillouin zone $\mathcal{B}_h$, we show that $\widehat{H}_{TB}$ has two eigenvalue expressions and explore the two corresponding dispersion surfaces. We then show that these dispersion surfaces touch conically at the six vertices of the Brillouin zone $\mathcal{B}_h$.

Next, we examine the effects of a perturbation on the dispersion relation by adding a symmetric potential to $\widehat{H}_{TB}$. After computing the new eigenvalue expressions, we find that there is now an energy gap and the dispersion surfaces no longer touch.

Finally, the density of states measure is introduced and used to prove a physically relevant result.

2 Construction and Setup

First we construct the (regular) honeycomb structure $\mathbf{H}$. Given the vectors

$$\mathbf{v}_1 = (\frac{\sqrt{3}}{2},\ \frac{1}{2}),\ \mathbf{v}_2 = (\frac{\sqrt{3}}{2},\ -\frac{1}{2}),$$

the equilateral triangular lattice is given by

$$\Lambda_h := \mathbb{Z}\mathbf{v}_1 \oplus \mathbb{Z}\mathbf{v}_2.$$

Then, given

$$\mathbf{v}_A = (0,\ 0),\ \mathbf{v}_B = (\frac{1}{\sqrt{3}},\ 0),$$

define two interpenetrating triangular lattices

$$\Lambda_A := \mathbf{v}_A + \Lambda_h,\ \Lambda_B := \mathbf{v}_B + \Lambda_h.$$

We then define

$$\mathbf{H} := \Lambda_A \cup \Lambda_B.$$

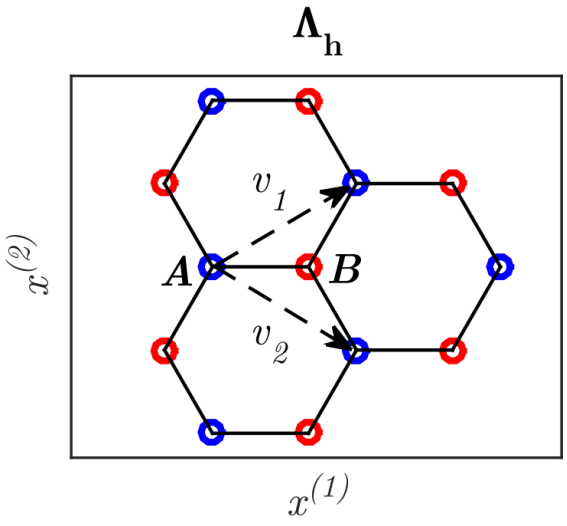

Figure 1 (See [2].)

Given

$$\Lambda_h := \mathbb{Z}\mathbf{v}_1 \oplus \mathbb{Z}\mathbf{v}_2,$$

the *dual lattice* of Λ_h, Λ_h^*, is defined by

$$\Lambda_h^* := \mathbb{Z}\mathbf{k}_1 \oplus \mathbb{Z}\mathbf{k}_2,$$

where the dual basis vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ are uniquely determined by the relation

$$\mathbf{k}_i \cdot \mathbf{v}_j = 2\pi\delta_{ij}.$$

Recalling that

$$\mathbf{v}_1 = (\frac{\sqrt{3}}{2},\ \frac{1}{2}),\ \mathbf{v}_2 = (\frac{\sqrt{3}}{2},\ -\frac{1}{2}),$$

we deduce from the required relation that

$$\mathbf{k}_1 = (\frac{2\pi}{\sqrt{3}},\ 2\pi),\ \mathbf{k}_2 = (\frac{2\pi}{\sqrt{3}},\ -2\pi).$$

Now, we define the Brillouin zone to be the smallest volume completely enclosed by planes which are the perpendicular bisectors of the dual lattice vectors drawn from the origin. (This is exactly the Wigner-Seitz cell in the dual lattice Λ_h^*.) Here, the Brillouin zone $\mathcal{B}_h$ is the hexagon in $\mathbb{R}^2_{\mathbf{k}}$ with vertices

$$(0,\ \frac{4\pi}{3}),\ (0,\ -\frac{4\pi}{3}),\ (\frac{2\pi}{\sqrt{3}},\ -\frac{2\pi}{3}),\ (-\frac{2\pi}{\sqrt{3}},\ \frac{2\pi}{3}),\ (-\frac{2\pi}{\sqrt{3}},\ -\frac{2\pi}{3}),\ (\frac{2\pi}{\sqrt{3}},\ \frac{2\pi}{3}).$$

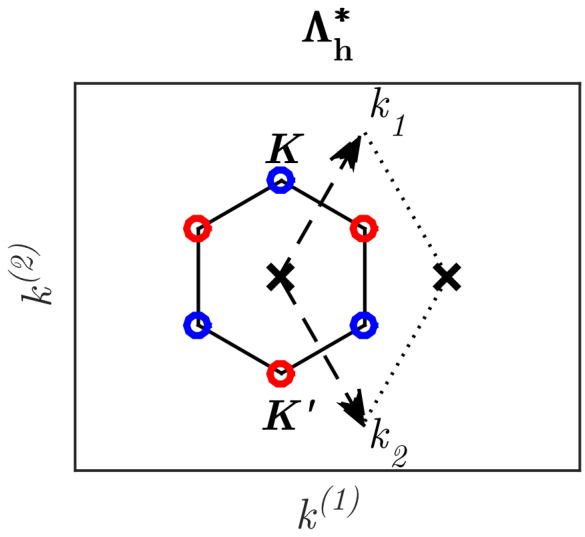

Figure 2 (See [2].)

Finally, in the direct space, we tile $\mathbb{R}^2$ by parallelograms that each contain two lattice points of the hexagonal lattice, so that each parallelogram contains two atomic sites: one A-type and one B-type. We label $(n,\ m)$ the parallelogram containing

$$\mathbf{v}_A^{(n,\ m)} := \mathbf{v}_A + n\mathbf{v}_1 + m\mathbf{v}_2,\ \ \mathbf{v}_B^{(n,\ m)} := \mathbf{v}_B + n\mathbf{v}_1 + m\mathbf{v}_2.$$

These parallelograms are the fundamental period cells, as information does not change from one such parallelogram to another.

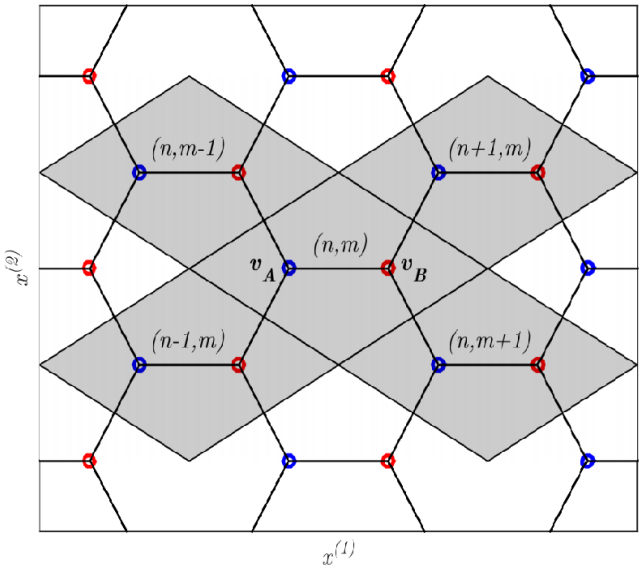

Figure 3 (See [2].)

3 Amplitudes

We have established that in each fundamental period cell, there is one A-type atomic site and one B-type atomic site. Let

$$\psi_A^{(n,\ m)} :\ \mathbb{Z}^2 \to \mathbb{C},\ \psi_B^{(n,\ m)} :\ \mathbb{Z}^2 \to \mathbb{C}$$

denote the amplitudes of the ground states centered at the A- and B-sites, respectively, of the cell with label $(n,\ m)$, where

$$\psi_A^{(n,\ m)},\ \psi_B^{(n,\ m)} \in \ell^2(\mathbb{Z}^2)$$

and $\ell^2(\mathbb{Z}^2)$ is the Hilbert space consisting of square-summable functions varying over $\mathbb{Z}^2$, and equipped with the norm

$$\|\psi\|^2_{\ell^2(\mathbb{Z}^2)} := \sum_{(n,\ m)\in\mathbb{Z}^2} |\psi^{(n,\ m)}|^2.$$

We bring together $\psi_A^{(n,\ m)}$ and $\psi_B^{(n,\ m)}$ to form the amplitude

$$\begin{bmatrix} \psi_A^{(n,\ m)} \\ \psi_B^{(n,\ m)} \end{bmatrix} :\ \mathbb{Z}^2 \to \mathbb{C}^2$$

on the fundamental cell with label $(n,\ m)$, where

$$\begin{bmatrix} \psi_A^{(n,\ m)} \\ \psi_B^{(n,\ m)} \end{bmatrix}_{(n,\ m)\in\mathbb{Z}^2} \in \ell^2(\mathbb{Z}^2) \times \ell^2(\mathbb{Z}^2).$$

4 The Tight-Binding Model

Hereafter, given a lattice point P, we say a lattice point $Q \neq P$ is a *nearest neighbor* of P if P and Q are no farther apart than P and any other lattice point.

Observe that, in Figure 1, each A-type atom has three nearest neighbors which are all B-type atoms, while each B-type atom has three nearest neighbors which are all A-type atoms. (This is true in any fundamental cell.) By definition, we attain the tight-binding Hamiltonian for

$$\psi := \begin{bmatrix} \psi_A^{(n,\ m)} \\ \psi_B^{(n,\ m)} \end{bmatrix} \in \ell^2(\mathbb{Z}^2) \times \ell^2(\mathbb{Z}^2)$$

by adding (componentwise) the values of ψ at each of the nearest neighbors of the respective components. The tight-binding Hamiltonian for ψ (with no added potential) is then given by

$$H_{TB} :\ \ell^2(\mathbb{Z}^2) \times \ell^2(\mathbb{Z}^2) \to \ell^2(\mathbb{Z}^2) \times \ell^2(\mathbb{Z}^2),$$

$$H_{TB}(\psi)^{(n,\ m)} = \begin{bmatrix} \psi_B^{(n,\ m)} + \psi_B^{(n,\ m-1)} + \psi_B^{(n-1,\ m)} \\ \psi_A^{(n,\ m)} + \psi_A^{(n+1,\ m)} + \psi_A^{(n,\ m+1)} \end{bmatrix}.$$

Next, we define the discrete Fourier transform $\hat{\cdot}$. We have, for a scalar-valued function $\psi \in \ell^2(\mathbb{Z}^2)$,

$$\hat{\cdot} : \ell^2(\mathbb{Z}^2) \to L^2(\mathcal{B}_h) : \ \hat{\psi}(\mathbf{k}) := \frac{1}{\sqrt{|\mathcal{B}_h|}} \sum_{n,\ m} e^{-i\mathbf{k}\cdot(n\mathbf{v}_1 + m\mathbf{v}_2)} \psi^{(n,\ m)}.$$

For $\psi := \begin{bmatrix} \psi_A \\ \psi_B \end{bmatrix} \in \ell^2(\mathbb{Z}^2) \times \ell^2(\mathbb{Z}^2)$, this extends to

$$\hat{\cdot} : \ \ell^2(\mathbb{Z}^2) \times \ell^2(\mathbb{Z}^2) \to L^2(\mathcal{B}_h) \times L^2(\mathcal{B}_h), \ \begin{bmatrix} \hat{\psi}_A \\ \hat{\psi}_B \end{bmatrix}(\mathbf{k}) := \frac{1}{\sqrt{|\mathcal{B}_h|}} \sum_{n,\ m} e^{-i\mathbf{k}\cdot(n\mathbf{v}_1 + m\mathbf{v}_2)} \begin{bmatrix} \psi_A^{(n,\ m)} \\ \psi_B^{(n,\ m)} \end{bmatrix}.$$

We wish to compute the discrete Fourier transform of $H_{TB}(\psi)$, which is given by

$$\widehat{H_{TB}\psi}(\mathbf{k}) := \frac{1}{\sqrt{|\mathcal{B}_h|}} \sum_{n,\ m} e^{-i\mathbf{k}\cdot(n\mathbf{v}_1 + m\mathbf{v}_2)} \begin{bmatrix} \psi_B^{(n,\ m)} + \psi_B^{(n,\ m-1)} + \psi_B^{(n-1,\ m)} \\ \psi_A^{(n,\ m)} + \psi_A^{(n+1,\ m)} + \psi_A^{(n,\ m+1)} \end{bmatrix},$$

where $\mathbf{k}$ varies over the Brillouin zone $\mathcal{B}_h$. For the first row, we compute

$$\frac{1}{\sqrt{|\mathcal{B}_h|}} \sum_{n,\ m} e^{-i\mathbf{k}\cdot(n\mathbf{v}_1 + m\mathbf{v}_2)} (\psi_B^{(n,\ m)} + \psi_B^{(n,\ m-1)} + \psi_B^{(n-1,\ m)})$$

$$= \hat{\psi}_B(\mathbf{k}) + e^{-i\mathbf{k}\cdot\mathbf{v}_1}\hat{\psi}_B(\mathbf{k}) + e^{-i\mathbf{k}\cdot\mathbf{v}_2}\hat{\psi}_B(\mathbf{k})$$

$$= (1 + e^{-i\mathbf{k}\cdot\mathbf{v}_1} + e^{-i\mathbf{k}\cdot\mathbf{v}_2})\hat{\psi}_B(\mathbf{k}).$$

Similarly, for the second row,

$$\frac{1}{\sqrt{|\mathcal{B}_h|}} \sum_{n,\ m} e^{-i\mathbf{k}\cdot(n\mathbf{v}_1 + m\mathbf{v}_2)} (\psi_A^{(n,\ m)} + \psi_A^{(n,\ m+1)} + \psi_A^{(n+1,\ m)})$$

$$= (1 + e^{i\mathbf{k}\cdot\mathbf{v}_1} + e^{i\mathbf{k}\cdot\mathbf{v}_2})\hat{\psi}_A(\mathbf{k}).$$

Therefore we may write

$$\widehat{H_{TB}\psi}(\mathbf{k}) = \begin{bmatrix} 0 & 1 + e^{-i\mathbf{k}\cdot\mathbf{v}_1} + e^{-i\mathbf{k}\cdot\mathbf{v}_2} \\ 1 + e^{i\mathbf{k}\cdot\mathbf{v}_1} + e^{i\mathbf{k}\cdot\mathbf{v}_2} & 0 \end{bmatrix} \begin{bmatrix} \hat{\psi}_A(\mathbf{k}) \\ \hat{\psi}_B(\mathbf{k}) \end{bmatrix} =: \hat{H}_{TB}(\mathbf{k})\hat{\psi}(\mathbf{k}).$$

(Note, for completeness, that $|\mathcal{B}_h| = 8\sqrt{3}\pi^2$. To see this, note that $\mathcal{B}_h$ is a regular hexagon which is composed of six equilateral triangles of side length $\frac{4\pi}{\sqrt{3}}$. By the Pythagorean theorem, the height of each triangle is given by $\sqrt{(\frac{4\pi}{\sqrt{3}})^2 - (\frac{2\pi}{\sqrt{3}})^2} = 2\pi$. Hence the area of each triangle is given by $\frac{1}{2}\frac{4\pi}{\sqrt{3}}2\pi = \frac{4\pi^2}{\sqrt{3}} = \frac{4\pi^2\sqrt{3}}{3}$, and multiplying this by six, as there are six triangles, shows that $|\mathcal{B}_h| = 8\sqrt{3}\pi^2$.)

Now, let

$$\sigma(\mathbf{k}) := 1 + e^{i\mathbf{k}\cdot\mathbf{v}_1} + e^{i\mathbf{k}\cdot\mathbf{v}_2},$$

so that we may write

$$\widehat{H}_{TB}(\mathbf{k}) = \begin{bmatrix} 0 & \overline{\sigma(\mathbf{k})} \\ \sigma(\mathbf{k}) & 0 \end{bmatrix}.$$

Notice that

$$\det(\widehat{H}_{TB}(\mathbf{k}) - \lambda(\mathbf{k})I_2) = \det \begin{bmatrix} -\lambda(\mathbf{k}) & \overline{\sigma(\mathbf{k})} \\ \sigma(\mathbf{k}) & -\lambda(\mathbf{k}) \end{bmatrix} = \lambda(\mathbf{k})^2 - |\sigma(\mathbf{k})|^2.$$

Then, setting this equal to zero and solving for $\lambda(\mathbf{k})$, we see that for each $\mathbf{k} \in \mathcal{B}_h$, $\hat{H}_{TB}(\mathbf{k})$ has two eigenvalues, namely

$$\lambda_+(\mathbf{k}) := |\sigma(\mathbf{k})|, \ \lambda_-(\mathbf{k}) := -|\sigma(\mathbf{k})|.$$

Hence the spectrum lies in the interval [-3, 3], and the system has two *dispersion surfaces*, namely

$$(\mathbf{k}, \ \lambda_+(\mathbf{k})), \ (\mathbf{k}, \ \lambda_-(\mathbf{k})),$$

which give rise to two spectral bands: one corresponding to the graph of $\lambda_+(\mathbf{k})$, and the other corresponding to that of $\lambda_-(\mathbf{k})$. The dispersion relation for the two spectral bands of the tight-binding model is given by

$$\mathcal{E}_\pm(\mathbf{k}) = \pm|t|\mathcal{W}_{TB}(\mathbf{k}), \ \mathbf{k} \in \mathcal{B}_h,$$

where

$$\mathcal{W}_{TB}(\mathbf{k}) := |\sigma(\mathbf{k})| = |1 + e^{i\mathbf{k}\cdot\mathbf{v}_1} + e^{i\mathbf{k}\cdot\mathbf{v}_2}|.$$

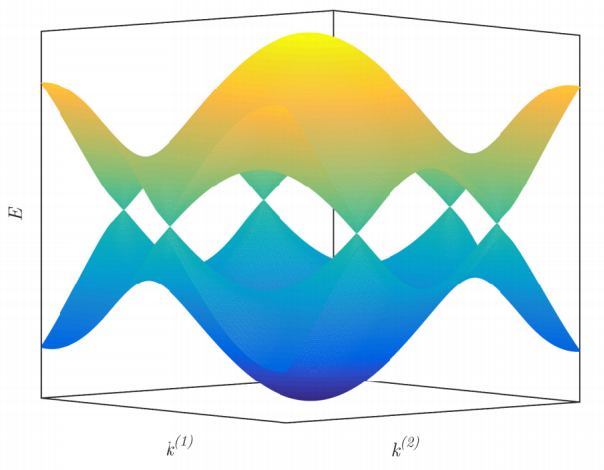

Figure 4 (See [2].)

The two dispersion surfaces touch conically ($\mathcal{W}_{TB}(\mathbf{k}) = 0$) at the six vertices of $\mathcal{B}_h$. In fact, it is straightforward to check that $\mathcal{W}_{TB}(\mathbf{k}) = 0$ at each of the six vertices, which are listed above, by using Euler's formula. To see that the surfaces touch conically, we let $\mathbf{k}^* = (k_1^*,\ k_2^*)$ be any vertex of $\mathcal{B}_h$ and use a Taylor expansion for σ about $\mathbf{k}^*$. Note that σ is a function of two variables, as seen by writing $\sigma(\mathbf{k}) = \sigma(k_1,\ k_2)$, and let $Hess[\sigma](\mathbf{k})$ denote its Hessian matrix at $\mathbf{k}$. Using $\sigma(\mathbf{k}^*) = 1 + e^{i\mathbf{k}^*\cdot\mathbf{v}_1} + e^{i\mathbf{k}^*\cdot\mathbf{v}_2} = 0$, we have

$$\sigma(\mathbf{k}) = \sigma(\mathbf{k}^*) + \nabla\sigma(\mathbf{k}^*)\cdot(\mathbf{k}-\mathbf{k}^*) + \frac{1}{2}(\mathbf{k}-\mathbf{k}^*)Hess[\sigma](\mathbf{k}^*)(\mathbf{k}-\mathbf{k}^*)^\top + R_3(\mathbf{k}-\mathbf{k}^*)$$

$$= (i\frac{\sqrt{3}}{2}(e^{i\mathbf{k}^*\cdot\mathbf{v}_1}+e^{i\mathbf{k}^*\cdot\mathbf{v}_2}),\ i\frac{1}{2}(e^{i\mathbf{k}^*\cdot\mathbf{v}_1}-e^{i\mathbf{k}^*\cdot\mathbf{v}_2}))\cdot(\mathbf{k}-\mathbf{k}^*)+\frac{1}{2}(\mathbf{k}-\mathbf{k}^*)Hess[\sigma](\mathbf{k}^*)(\mathbf{k}-\mathbf{k}^*)^\top+R_3(\mathbf{k}-\mathbf{k}^*)$$

$$= (-i\frac{\sqrt{3}}{2},\ i\frac{1}{2}(e^{i\mathbf{k}^*\cdot\mathbf{v}_1} - e^{i\mathbf{k}^*\cdot\mathbf{v}_2}))\cdot(\mathbf{k}-\mathbf{k}^*) + \frac{1}{2}(\mathbf{k}-\mathbf{k}^*)Hess[\sigma](\mathbf{k}^*)(\mathbf{k}-\mathbf{k}^*)^\top + R_3(\mathbf{k}-\mathbf{k}^*),$$

where

$$Hess[\sigma](\mathbf{k}) = \begin{bmatrix} -\frac{3}{4}(e^{i\mathbf{k}\cdot\mathbf{v}_1} + e^{i\mathbf{k}\cdot\mathbf{v}_2}) & -\frac{\sqrt{3}}{4}(e^{i\mathbf{k}\cdot\mathbf{v}_1} - e^{i\mathbf{k}\cdot\mathbf{v}_2}) \\ -\frac{\sqrt{3}}{4}(e^{i\mathbf{k}\cdot\mathbf{v}_1} - e^{i\mathbf{k}\cdot\mathbf{v}_2}) & -\frac{1}{4}(e^{i\mathbf{k}\cdot\mathbf{v}_1} + e^{i\mathbf{k}\cdot\mathbf{v}_2}) \end{bmatrix}$$

and, writing $\mathbf{k} = (k_1,\ k_2)$ and $\mathbf{k}^* = (k_1^*,\ k_2^*)$, the remainder term $R_3(\mathbf{k}-\mathbf{k}^*)$ is given by

$$R_3(\mathbf{k}-\mathbf{k}^*) = \frac{1}{3!}[\sigma_{k_1k_1k_1}(\xi,\ \eta)(k_1-k_1^*)^3 + 3\sigma_{k_1k_1k_2}(\xi,\ \eta)(k_1-k_1^*)^2(k_2-k_2^*)$$

$$+3\sigma_{k_1k_2k_2}(\xi,\ \eta)(k_1-k_1^*)(k_2-k_2^*)^2 + \sigma_{k_2k_2k_2}(\xi,\ \eta)(k_2-k_2^*)^3]$$

for some $\xi \in [\min\{k_1,\ k_1^*\},\ \max\{k_1,\ k_1^*\}]$ and $\eta \in [\min\{k_2,\ k_2^*\},\ \max\{k_2,\ k_2^*\}]$.
(Here, for example, $\sigma_{k_1k_1k_1}$ denotes the third partial derivative of σ with respect to k_1.)
Note that for any $\mathbf{k} = (k_1,\ k_2) \in \mathcal{B}_h$ and any vertex $\mathbf{k}^* = (k_1^*,\ k_2^*)$ of $\mathcal{B}_h$, by the triangle inequality and the fact that $|e^{i\theta}| = 1$ for any $\theta \in \mathbb{R}$, we have

$$|R_3(\mathbf{k}-\mathbf{k}^*)| \le \frac{\sqrt{3}}{8}|k_1-k_1^*|^3+\frac{3}{8}|k_1-k_1^*|^2|k_2-k_2^*|+\frac{\sqrt{3}}{8}|k_1-k_1^*||k_2-k_2^*|^2+\frac{1}{24}|k_2-k_2^*|^3 \le \frac{3\sqrt{3}+5}{12}\|\mathbf{k}-\mathbf{k}^*\|^3.$$

Thus, letting $\mathbf{k} \to \mathbf{k}^*$, we see that indeed the dispersion surfaces touch conically, as $\nabla\sigma(\mathbf{k}^*)$, the coefficient of $\mathbf{k}-\mathbf{k}^*$ above, does not vanish; hence the Taylor expansion of $\sigma(\mathbf{k})$ at $\mathbf{k}^*$ is of order $\|\mathbf{k}-\mathbf{k}^*\|$. The six vertices of the Brillouin zone $\mathcal{B}_h$ are called the *Dirac points*.

Note that, by direct computation, letting $\mathbf{k}^*$ be any vertex of $\mathcal{B}_h$,

$$|\nabla\sigma(\mathbf{k}^*)\cdot(\mathbf{k}-\mathbf{k}^*)|^2 = \frac{3}{4}\|\mathbf{k}-\mathbf{k}^*\|^2,$$

i.e.,

$$|\nabla\sigma(\mathbf{k}^*)\cdot(\mathbf{k}-\mathbf{k}^*)| = \frac{\sqrt{3}}{2}\|\mathbf{k}-\mathbf{k}^*\|,$$

for any $\mathbf{k} \in \mathcal{B}_h$. In particular, this implies that, whenever $\mathbf{k} \neq \mathbf{k}^*$, $\nabla\sigma(\mathbf{k}^*)$ and $\mathbf{k}-\mathbf{k}^*$ are not orthogonal vectors.

5 Summary of the Tight-Binding Model Without Perturbations

Thus far, we have constructed the (regular) honeycomb structure $\mathbf{H}$ and described the dual lattice and the Brillouin zone $\mathcal{B}_h$, which is itself a regular hexagon. To form the fundamental period cells, we tiled $\mathbb{R}^2$ (in the direct space) by parallelograms that each contain two lattice points of the hexagonal lattice, so that each parallelogram would contain two atomic sites: one A-type and one B-type. We then introduced the amplitudes

$$\psi_A^{(n,\ m)} :\ \mathbb{Z}^2 \to \mathbb{C},\ \psi_B^{(n,\ m)} :\ \mathbb{Z}^2 \to \mathbb{C}$$

of the ground states centered at the A- and B-sites, respectively, of the cell labeled $(n,\ m)$, and brought them together to form the amplitude

$$\begin{bmatrix} \psi_A^{(n,\ m)} \\ \psi_B^{(n,\ m)} \end{bmatrix} :\ \mathbb{Z}^2 \to \mathbb{C}^2$$

on the fundamental cell with label $(n,\ m)$, where

$$\begin{bmatrix} \psi_A^{(n,\ m)} \\ \psi_B^{(n,\ m)} \end{bmatrix}_{(n,\ m)\in\mathbb{Z}^2} \in \ell^2(\mathbb{Z}^2) \times \ell^2(\mathbb{Z}^2).$$

After noting that, in any given fundamental cell, each A-type atom has three nearest neighbors which are all B-type atoms and vice-versa, we defined the tight-binding Hamiltonian for $\psi := \begin{bmatrix} \psi_A^{(n,\ m)} \\ \psi_B^{(n,\ m)} \end{bmatrix}$ by

$$H_{TB} :\ \ell^2(\mathbb{Z}^2) \times \ell^2(\mathbb{Z}^2) \to \ell^2(\mathbb{Z}^2) \times \ell^2(\mathbb{Z}^2),$$

$$H_{TB}(\psi)^{(n,\ m)} = \begin{bmatrix} \psi_B^{(n,\ m)} + \psi_B^{(n,\ m-1)} + \psi_B^{(n-1,\ m)} \\ \psi_A^{(n,\ m)} + \psi_A^{(n+1,\ m)} + \psi_A^{(n,\ m+1)} \end{bmatrix}.$$

Lastly, we computed the discrete Fourier transform of the tight-binding Hamiltonian and attained the matrix

$$\hat{H}_{TB}(\mathbf{k}) = \begin{bmatrix} 0 & 1 + e^{-i\mathbf{k}\cdot\mathbf{v}_1} + e^{-i\mathbf{k}\cdot\mathbf{v}_2} \\ 1 + e^{i\mathbf{k}\cdot\mathbf{v}_1} + e^{i\mathbf{k}\cdot\mathbf{v}_2} & 0 \end{bmatrix} =: \begin{bmatrix} 0 & \overline{\sigma(\mathbf{k})} \\ \sigma(\mathbf{k}) & 0 \end{bmatrix},$$

where

$$\sigma(\mathbf{k}) := 1 + e^{i\mathbf{k}\cdot\mathbf{v}_1} + e^{i\mathbf{k}\cdot\mathbf{v}_2},$$

which, for any $\mathbf{k} \in \mathcal{B}_h$, has eigenvalues

$$\lambda_+(\mathbf{k}) := |\sigma(\mathbf{k})|,\ \lambda_-(\mathbf{k}) := -|\sigma(\mathbf{k})|.$$

We showed that the corresponding dispersion surfaces touch conically at each of the six vertices of the Brillouin zone $\mathcal{B}_h$, which are called the *Dirac points*.

6 Perturbations

Heretofore we have studied the tight-binding model without adding a potential. We now wish to study the effects of a perturbation on the two spectral bands discussed previously. Given $\rho \in \mathbb{R}\backslash\{0\}$, define

$$V_\rho := \begin{bmatrix} \rho & 0 \\ 0 & -\rho \end{bmatrix},$$

which is the (symmetric) matrix we obtain from assigning the value ρ to the A-type atoms, and -ρ to the B-type atoms. Then the matrix

$$\hat{H}_{TB}(\mathbf{k}) + V_\rho$$

has eigenvalues

$$\lambda_{\pm\rho}(\mathbf{k}) := \pm\sqrt{|\sigma(\mathbf{k})|^2 + \rho^2}.$$

Notice that if $\mathbf{k}^*$ is any of the six vertices of $\mathcal{B}_h$, it follows from our work in the previous section that

$$\lambda_{\pm\rho}(\mathbf{k}^*) = \pm\sqrt{\rho^2} = \pm|\rho|.$$

Notably, the dispersion surfaces no longer touch at any of these vertices; rather, there is an energy gap of $2|\rho|$.

More generally, assign values $\rho_A \in \mathbb{R}\backslash\{0\}$ to each A-type atom and $\rho_B \in \mathbb{R}\backslash\{0\}$ to each B-type atom, and consider the corresponding (symmetric) potential

$$V_{AB} := \begin{bmatrix} \rho_A & 0 \\ 0 & \rho_B \end{bmatrix}.$$

Then the matrix

$$\hat{H}_{TB}(\mathbf{k}) + V_{AB}$$

has eigenvalues

$$\lambda_{\pm AB}(\mathbf{k}) := \frac{1}{2}(\rho_A + \rho_B) \pm \frac{1}{2}\sqrt{(\rho_A - \rho_B)^2 + 4|\sigma(\mathbf{k})|^2}.$$

Hence, if $\mathbf{k}^*$ is any of the six vertices of $\mathcal{B}_h$, it follows that

$$\lambda_{\pm AB}(\mathbf{k}^*) = \frac{1}{2}(\rho_A + \rho_B) \pm \frac{1}{2}|\rho_A - \rho_B|.$$

Observe that

$$\begin{aligned} \rho_A > \rho_B &\implies \lambda_{+AB}(\mathbf{k}^*) = \rho_A,\ \lambda_{-AB}(\mathbf{k}^*) = \rho_B, \\ \rho_A < \rho_B &\implies \lambda_{+AB}(\mathbf{k}^*) = \rho_B,\ \lambda_{-AB}(\mathbf{k}^*) = \rho_A, \\ \rho_A = \rho_B &\implies \lambda_{+AB}(\mathbf{k}^*) = \rho_A = \rho_B = \lambda_{-AB}(\mathbf{k}^*). \end{aligned}$$

Thus, if $\rho_A = \rho_B$, then the dispersion surfaces still touch at each vertex $\mathbf{k}^*$ of the Brillouin zone $\mathcal{B}_h$. Otherwise, there is an energy gap of $|\rho_A - \rho_B|$.

7 Density of States

We next define the *density of states* measure. Let $\tilde{Q}$ be a basic period cell in the dual lattice, and let $E_n(\mathbf{k})$ be the energy levels, listed in nondecreasing order, of a Schrödinger operator $H(\mathbf{k})$. The density of states measure N is the measure on $\mathbb{R}$ given by

$$N(E) = \frac{2}{|\tilde{Q}|} \sum_n |\{\mathbf{k} \in \tilde{Q} : \ E_n(\mathbf{k}) \leq E\}|,$$

where $|\cdot|$ denotes the Lebesgue measure.

The corresponding *density of states* function n is defined by

$$n(E) = N'(E).$$

For our case, given $E \in \mathbb{R}$, the integrated density of states function N is given by

$$N(E) = \frac{2}{|\mathcal{B}_h|}[|\{\mathbf{k} \in \mathcal{B}_h : \ \lambda_-(\mathbf{k}) \leq E\}| + |\{\mathbf{k} \in \mathcal{B}_h : \ \lambda_+(\mathbf{k}) \leq E\}|],$$

so that $N(E)$ gives the number of eigenvalues of $\hat{H}_{TB}(\mathbf{k})$, per unit volume, up to energy E. By definition, N is monotone nondecreasing.

Then the corresponding density of states function n is given by

$$n(E) = N'(E),$$

so that $n(E)$ gives, roughly speaking, the number of allowed electron states per volume at a given energy.

We claim that $n(0) = 0$, as in [4]. Physically, this means that there is no transport between the two energy bands.
To see this, we omit the multiple $\frac{2}{|\mathcal{B}_h|}$ in the definition of $N(E)$ for convenience and use difference quotients, noting that $\lambda_+(\mathbf{k}) \geq 0$ and $\lambda_-(\mathbf{k}) \leq 0$ for all $\mathbf{k} \in \mathcal{B}_h$. Fix $\epsilon > 0$.

First, we have

$$\begin{aligned}\frac{N(\epsilon) - N(0)}{\epsilon} &= \frac{1}{\epsilon}[|\{\mathbf{k} \in \mathcal{B}_h : \ \lambda_+(\mathbf{k}) \leq \epsilon\}| + |\{\mathbf{k} \in \mathcal{B}_h : \ \lambda_-(\mathbf{k}) \leq \epsilon\}| \\ &\quad -|\{\mathbf{k} \in \mathcal{B}_h : \ \lambda_+(\mathbf{k}) \leq 0\}| - |\{\mathbf{k} \in \mathcal{B}_h : \ \lambda_-(\mathbf{k}) \leq 0\}|] \\ &= \frac{1}{\epsilon}[|\{\mathbf{k} \in \mathcal{B}_h : \ \lambda_+(\mathbf{k}) \leq \epsilon\}| + |\mathcal{B}_h| - |\{\mathbf{k} \in \mathcal{B}_h : \ \lambda_+(\mathbf{k}) \leq 0\}| - |\mathcal{B}_h|]\end{aligned}$$

$$= \frac{1}{\epsilon}|\{\mathbf{k} \in \mathcal{B}_h : \ 0 \leq \lambda_+(\mathbf{k}) \leq \epsilon\}|.$$

We claim that

$$|\{\mathbf{k} \in \mathcal{B}_h : \ 0 \leq \lambda_+(\mathbf{k}) \leq \epsilon\}| \sim \epsilon^2.$$

Indeed, for $\mathbf{k} \in \mathcal{B}_h$, we use the Taylor expansion (neglecting higher order terms) and prior remark to write

$$\lambda_+(\mathbf{k}) = |\nabla\sigma(\mathbf{k}^*) \cdot (\mathbf{k} - \mathbf{k}^*)| = \frac{\sqrt{3}}{2}\|\mathbf{k} - \mathbf{k}^*\|.$$

Therefore

$$|\{\mathbf{k} \in \mathcal{B}_h : \ 0 \leq \lambda_+(\mathbf{k}) \leq \epsilon\}| = |\{\mathbf{k} \in \mathcal{B}_h : \ \|\mathbf{k} - \mathbf{k}^*\| \leq \frac{2\sqrt{3}}{3}\epsilon\}|.$$

The set of $\mathbf{k} \in \mathcal{B}_h$ satisfying

$$\|\mathbf{k} - \mathbf{k}^*\| \leq \frac{2\sqrt{3}}{3}\epsilon$$

is the intersection of $\mathcal{B}_h$ and the closure of the disk, centered at $\mathbf{k}^*$, of radius $\frac{2\sqrt{3}}{3}\epsilon$. Therefore

$$|\{\mathbf{k} \in \mathcal{B}_h : \ 0 \leq \lambda_+(\mathbf{k}) \leq \epsilon\}| = |\{\mathbf{k} \in \mathcal{B}_h : \ \|\mathbf{k} - \mathbf{k}^*\| \leq \frac{2\sqrt{3}}{3}\epsilon\}|$$

is bounded above by the area of the disk, which is

$$\pi(\frac{2\sqrt{3}}{3}\epsilon)^2 = \frac{4}{3}\pi\epsilon^2;$$

it is bounded below by the area of a triangle of base 2ϵ and height $\frac{\sqrt{3}}{3}\epsilon$, i.e.,

$$\frac{1}{2}(2\epsilon)\frac{\sqrt{3}}{3}\epsilon = \frac{\sqrt{3}}{3}\epsilon^2.$$

We have shown that

$$\frac{\sqrt{3}}{3}\epsilon^2 \leq |\{\mathbf{k} \in \mathcal{B}_h : \ 0 \leq \lambda_+(\mathbf{k}) \leq \epsilon\}| \leq \frac{4}{3}\pi\epsilon^2.$$

It follows that

$$|\{\mathbf{k} \in \mathcal{B}_h : \ 0 \leq \lambda_+(\mathbf{k}) \leq \epsilon\}| \sim \epsilon^2$$

as claimed, and thus

$$\frac{N(\epsilon) - N(0)}{\epsilon} \sim \frac{1}{\epsilon}\epsilon^2 = \epsilon \to 0 \text{ as } \epsilon \to 0.$$

In a similar way, we attain

$$\frac{N(0) - N(-\epsilon)}{\epsilon} = \frac{1}{\epsilon}[|\{\mathbf{k} \in \mathcal{B}_h : \ \lambda_+(\mathbf{k}) \leq 0\}| + |\{\mathbf{k} \in \mathcal{B}_h : \ \lambda_-(\mathbf{k}) \leq 0\}|$$

$$-|\{\mathbf{k} \in \mathcal{B}_h : \ \lambda_+(\mathbf{k}) \leq -\epsilon\}| - |\{\mathbf{k} \in \mathcal{B}_h : \ \lambda_-(\mathbf{k}) \leq -\epsilon\}|]$$
$$= \frac{1}{\epsilon}|\{\mathbf{k} \in \mathcal{B}_h : \ -\epsilon \leq \lambda_-(\mathbf{k}) \leq 0\}| \sim \frac{1}{\epsilon}\epsilon^2 = \epsilon \to 0 \text{ as } \epsilon \to 0.$$

We conclude that $n(0) = 0$ as desired.

8 Summary

We constructed the (regular) honeycomb structure $\mathbf{H}$ and described the dual lattice and the *Brillouin zone* $\mathcal{B}_h$, which is itself a regular hexagon. To form the fundamental cells, we tiled $\mathbb{R}^2$ (in the direct space) by parallelograms that each contain two lattice points of the hexagonal lattice, so that each parallelogram would contain an A-type atomic site and a B-type atomic site.

We then introduced the amplitudes of the ground states centered at the A- and B-sites of any given fundamental cell and noted that in any such cell, each A-type atom has three *nearest neighbors* which are all B-type atoms and vice-versa. This allowed us to define the tight-binding Hamiltonian. Upon doing so, we computed the *discrete Fourier transform* of the tight-binding Hamiltonian, which, for any $\mathbf{k} \in \mathcal{B}_h$, has two eigenvalues; we showed that the corresponding dispersion surfaces touch conically at each of the six vertices of the Brillouin zone $\mathcal{B}_h$, which are called the *Dirac points*. We showed that adding a perturbation to the discrete Fourier transform of the tight-binding matrix leads to an energy gap, as the two dispersion surfaces become separated.

Lastly, we introduced the *integrated density of states* and *density of states* and showed, essentially, that there are zero allowed electron states per volume at energy zero.

References

[1] Deji Akinwande, Cedric Huyghebaert, Ching-Hua Wang, Martha I Serna, Stijn Goossens, Lain-Jong Li, H-S Philip Wong, and Frank HL Koppens. Graphene and two-dimensional materials for silicon technology. *Nature*, 573(7775):507–518, 2019.

[2] Charles L Fefferman, James P Lee-Thorp, and Michael I Weinstein. Honeycomb schrödinger operators in the strong binding regime. *Communications on Pure and Applied Mathematics*, 71(6):1178–1270, 2018.

[3] S Das Sarma, Shaffique Adam, EH Hwang, and Enrico Rossi. Electronic transport in two-dimensional graphene. *Reviews of modern physics*, 83(2):407, 2011.

[4] Philip Richard Wallace. The band theory of graphite. *Physical review*, 71(9):622, 1947.