COSMOS 2021 Final Project

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1 Background

The general time-independent Schrödinger equation states that

$$\mathbf{H}\psi = E\psi,$$

where $\mathbf{H}$ is the linear operator known as the Hamiltonian operator, and E, the energy, is a scalar. In other words, the equation states that the spacial component of any wave function must be an eigenvector of the Hamiltonian operator, and the corresponding eigenvalue is the energy of the quantum state.

It is well-known in linear algebra that any linear operator over a finite-dimensional vector space can be written as a matrix, facilitating simple computation of eigenvectors and eigenvalues (our desired solutions). However, the space of wave functions in general is an infinite-dimensional vector space. To alleviate this problem, we consider a finite-dimensional subspace of this vector space generated by a few chosen basis wave functions, claiming that sufficiently accurate approximations for the actual solutions of the Schrödinger equation lie in this subspace.

Of course, this approximation will only be accurate if a fortuitous basis is chosen. In our case, we are dealing with graphene, modeled as an infinitely periodic sheet. Because of this periodicity, we need only to consider the solution on a single unit cell. A good choice for the basis is the atomic orbitals of atoms in the unit cell.

2 Part b

For graphene, we use two adjacent carbon atoms as the repeating unit cell. It turns out to be sufficient to use the two $2p_z$ orbitals of the carbon atoms as a basis when calculating the band structure. This is because, much like in aromatic rings such as benzene, the $2p_z$ orbitals of graphene carbon atoms form delocalized electron bands above and below the sheet, while the other orbitals are localized and mainly involved in bonding. The unit cell is shown below, along with the lattice vectors $\vec{d_1}, \vec{d_2}$.

The Schrödinger equation states that

$$\mathbf{H}(\vec{k})\vec{\phi_0} = E\vec{\phi_0},$$

where $\vec{\phi_0}$ is a 2D vector representing an eigenstate with respect to the basis. The central result of bandstructure of periodic solids states that

$$\mathbf{H}(\vec{k}) = \sum_m H_{nm} e^{i\vec{k}\cdot(\vec{d_m}-\vec{d_n})},$$

where H_{nm} is the matrix whose i, j element is equal to the integral

$$\int u_i^*(\vec{r})\mathbf{H}u_j(\vec{r})d\vec{r}$$

where u_i is the ith basis function of unit cell n and u_j is the jth basis function of unit cell m, and $\vec{d_i}$ are position vectors of unit cells. The sum over m runs over all neighboring unit cells as well as unit cell n itself. In the case of graphene, each unit cell has four neighboring unit cells

We assume that the overlap between two orbitals is only nonzero if they are adjacent or equivalent. Let E_0 be the overlap between the orbital and itself, and let $-t$ be the overlap of two adjacent orbitals. (We denote this by $-t$ because the overlap integral evaluates to a negative value.) Plugging into equation, we obtain

$$\begin{aligned}\mathbf{H}(\vec{k}) &= \begin{bmatrix} E_0 & -t \\ -t & E_0 \end{bmatrix} + \begin{bmatrix} 0 & 0 \\ -t & 0 \end{bmatrix} e^{i\vec{k}\cdot\vec{d}_1} + \begin{bmatrix} 0 & 0 \\ -t & 0 \end{bmatrix} e^{i\vec{k}\cdot\vec{d}_2} + \begin{bmatrix} 0 & -t \\ 0 & 0 \end{bmatrix} e^{-i\vec{k}\cdot\vec{d}_1} + \begin{bmatrix} 0 & -t \\ 0 & 0 \end{bmatrix} e^{-i\vec{k}\cdot\vec{d}_2} \\ &= \begin{bmatrix} E_0 & -t(1+e^{-i\vec{k}\cdot\vec{d}_1}+e^{-i\vec{k}\cdot\vec{d}_2}) \\ -t(1+e^{i\vec{k}\cdot\vec{d}_1}+e^{i\vec{k}\cdot\vec{d}_2}) & E_0 \end{bmatrix} \\ &= \begin{bmatrix} E_0 & h_0^* \\ h_0 & E_0 \end{bmatrix}\end{aligned}$$

(We let $h_0 = -t(1 + e^{i\vec{k}\cdot\vec{d}_1} + e^{i\vec{k}\cdot\vec{d}_2})$ to simplify.)

3 Part c

Routinely calculating the eigenvalues yields $E(\vec{k}) = E_0 \pm |h_0|$. To rewrite E we write our vectors in terms of the standard basis:

$$\begin{aligned}\vec{k} &= k_x\hat{x} + k_y\hat{y} \\ \vec{d_1} &= \frac{3}{2}a\hat{x} + \frac{\sqrt{3}}{2}a\hat{y} \\ \vec{d_2} &= \frac{3}{2}a\hat{x} - \frac{\sqrt{3}}{2}a\hat{y}\end{aligned}$$

Then, we have

$$h_0 = -t\left(1 + \exp\left(ia(\frac{3}{2}k_x + \frac{\sqrt{3}}{2}k_y)\right) + \exp\left(ia(\frac{3}{2}k_x - \frac{\sqrt{3}}{2}k_y)\right)\right)$$

$$= -t\left(1 + \exp\left(\frac{3}{2}iak_x\right)\left(\exp(\frac{\sqrt{3}}{2}iak_y) + \exp(-\frac{\sqrt{3}}{2}iak_y)\right)\right)$$

$$= -t\left(1 + 2\exp\left(\frac{3}{2}iak_x\right)\cos\left(\frac{\sqrt{3}}{2}ak_y\right)\right)$$

$$= -t\big(1 + 2\exp(i\theta_1)\cos\theta_2\big)$$

(In the last step we substitute $\theta_1 = \frac{3}{2}ak_x, \theta_2 = \frac{\sqrt{3}}{2}ak_y$.) So,

$$\begin{aligned}
E &= E_0 \pm |h_0| \\
&= E_0 \pm \sqrt{h_0 h_0^*} \\
&= E_0 \pm \sqrt{t^2\big(1 + 2\exp(i\theta_1)\cos\theta_2\big)\big(1 + 2\exp(-i\theta_1)\cos\theta_2\big)} \\
&= E_0 \pm t\sqrt{1 + 2\cos\theta_2(\exp(i\theta_1) + \exp(-i\theta_1)) + 4\cos^2\theta_2} \\
&= \boxed{E_0 \pm t\sqrt{1 + 4\cos\theta_1\cos\theta_2 + 4\cos^2\theta_2}}.
\end{aligned}$$

4 Part d

To find the eigenvectors, we impose the normalization condition $\psi_1^2 + \psi_2^2 = 1$ and solve the equation

$$\begin{bmatrix} E_0 & h_0^* \\ h_0 & E_0 \end{bmatrix}\begin{bmatrix}\phi_1 \\ \phi_2\end{bmatrix} = (E_0 \pm |h_0|)\begin{bmatrix}\phi_1 \\ \phi_2\end{bmatrix}$$

$$\implies \begin{cases} h_0^*\phi_2 = \pm|h_0|\phi_1 \\ h_0\phi_1 = \pm|h_0|\phi_2 \\ \phi_1^2 + \phi_2^2 = 1 \end{cases}$$

Dividing the second equation by the first and rearranging yields $\phi_2^2 = \frac{h_0}{h_0*}\phi_1^2$, telling us that ϕ_1^2, ϕ_2^2 have the same magnitude. The third equation shows that their sum is real, so they must be conjugates. We let $\phi_1^2 = ch_0^*, \phi_2^2 = ch_0$ for some real c. Then, the third equation gives

$$2c\,\mathrm{Re}(h_0) = 1$$

$$\implies -2ct(1 + 2\cos\theta_1\cos\theta_2) = 1$$

$$\implies c = -\frac{1}{2t(1 + 2\cos\theta_1\cos\theta_2)}$$

So, if we let ω be a square root of h_0, we obtain the four solutions

$$\boxed{\psi = \begin{bmatrix}\phi_1 \\ \phi_2\end{bmatrix} = \pm\sqrt{c}\begin{bmatrix}\pm\omega^* \\ \omega\end{bmatrix}}.$$

The $\pm$ inside the vector differentiates the two energy levels $E_0+|h_0|$ and $E_0-|h_0|$. The $\pm$ outside the vector differentiated the two eigenvectors present for a single energy level.

$$\omega^2 = h_0$$

5 Part e

We consider when the energy is low. Since square roots are nonnegative, the minimum value of $E(\vec{k})$ is when the square root term is 0. There are infinitely many roots; we focus on roots with $\theta_1 = 0$ for simplicity. We find the roots:

$$4\cos^2\theta_2 + 4\cos\theta_2 + 1 = 0$$

$$(2\cos\theta_2 + 1)^2 = 0$$

$$\cos\theta_2 = -\frac{1}{2}$$

The two smallest values of θ_2 are $-\frac{2\pi}{3}$ and $\frac{2\pi}{3}$. These correspond to two points K, K':

$$K = (0, \frac{4\pi\sqrt{3}a}{9}), K' = (0, -\frac{4\pi\sqrt{3}a}{9})$$

6 Part f

We approximate $E(\vec{k})$ around K and K' as first order in the magnitude of the change in $\vec{k}$, i.e. approximating E with a circular cone. We first approximate h_0 around K:

$$\begin{aligned} h_0 &= -t\big(1 + 2\exp(i\theta_1)\cos\theta_2\big) \\ &\approx -t\big(1 + 2(1 + id\theta_1)(-\frac{1}{2} - \frac{\sqrt{3}}{2}d\theta_2)\big) \\ &= t(id\theta_1 + \sqrt{3}d\theta_2) \\ &= \frac{3}{2}at(idk_x + dk_y) \end{aligned}$$

Using $E = E_0 \pm |h_0|$, we immediately obtain the low-energy cone approximation

$$\boxed{E(\vec{k}) = E_0 \pm \frac{3}{2}at|\vec{k} - K|.}$$