ICFP M1 - QUANTUM MATTER - TD n°2 - Solutions
Graphene in the Tight-Binding Approximation

Baptiste Coquinot, Lucile Savary

12 & 19 September 2022

Graphene is a honeycomb lattice of carbon atoms with one valence electron. The remaining three electrons per carbon atom are involved in the formation of strong covalent σ bonds, and can be considered as frozen as far as the low energy electronic properties of graphene are concerned. Here we study the low energy properties of graphene.

The graphene lattice is made of two triangular Bravais sublattices spanned by

$$\mathbf{a}_1 = \left(\frac{\sqrt{3}}{2}, \frac{3}{2}\right), \qquad \mathbf{a}_2 = \left(-\frac{\sqrt{3}}{2}, \frac{3}{2}\right). \tag{1}$$

They are denoted A and B according to Fig. 1.

Every atom of A (respectively B) has three nearest neighbors in B (respectively A), whose relative positions are given by the three unit vectors

$$\mathbf{d}_1 = \left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right), \qquad \mathbf{d}_2 = \left(-\frac{\sqrt{3}}{2}, \frac{1}{2}\right), \qquad \mathbf{d}_3 = (0, -1). \tag{2}$$

The distance a between two carbon atoms ($a = 1.42$ **r**A) is set to unity. The reciprocal lattice is spanned by the vectors b_1 and b_2 defined by

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}. \tag{3}$$

The low energy properties of graphene are captured by a tight-binding approximation, in which we consider a spinless nearest-neighbor model on an infinite honeycomb lattice:

$$\mathcal{H} = t \sum_{<i,j>} \left(|\phi_i\rangle\langle\phi_j| + \text{h.c.}\right) \quad \text{where} \quad \langle\phi_i|\phi_j\rangle = \delta_{i,j}. \tag{4}$$

The state $|\phi_i\rangle$ describes the bound state in which the electron is localized around the carbon atom i, whose position is $\mathbf{r}_i$. The corresponding wavefunctions are of the form $\langle\mathbf{r}|\phi_i\rangle = \phi(\mathbf{r} - \mathbf{r}_i)$.

1. Rewrite the tight-binding Hamiltonian in second quantization.

We denote $c_i^\dagger$ the creation operator of an electron localised on the atom i. Then,

$$\mathcal{H} = t \sum_{<i,j>} \left(c_i^\dagger c_j + \text{h.c.}\right) \quad \text{where} \quad \{c_i, c_j^\dagger\} = \delta_{i,j}. \tag{5}$$

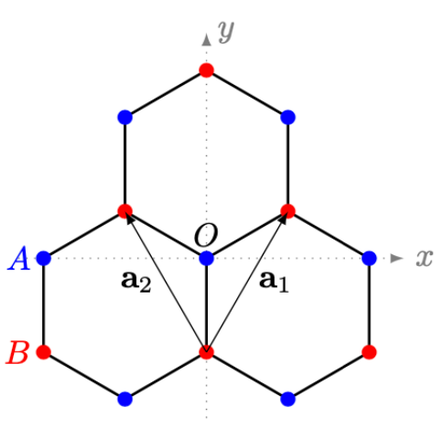

Figure 1: Crystallographic structure of Graphene.

2. The honeycomb lattice is invariant under discrete translations of $\mathbf{a}_1$ and $\mathbf{a}_2$. We denote by T_α the unitary operator that translates a single electron by $\mathbf{a}_\alpha$. What is T_α in first and second quantization? Check that $[\mathcal{H}, T_\alpha] = 0$. What is the standard method to exploit this symmetry ?

In first quantization the translation operator has the form $T^0_\alpha = e^{\mathbf{a}_\alpha \cdot \nabla}$. However, here we assumed the tight-binding approximation. Therefore, we have to project this operator on the associated subspace of the Hilbert space through the projector $P = \sum_i |\phi_i\rangle\langle\phi_i|$. Then, one recovers the expected

$$T_\alpha = P T^0_\alpha P = \sum_i |\phi_{i+\mathbf{a}_\alpha}\rangle\langle\phi_i|. \tag{6}$$

In second quantization, we then have

$$T_\alpha = \sum_i c^\dagger_{i+\mathbf{a}_\alpha} c_i. \tag{7}$$

We now check the commutation with the Hamiltonian:

$$T_\alpha \mathcal{H} = t \sum_k |\phi_{k+\mathbf{a}_\alpha}\rangle\langle\phi_k| \sum_{<i,j>} \left(|\phi_i\rangle\langle\phi_j| + \text{h.c.}\right) = t \sum_{<i,j>} \left(|\phi_{i+\mathbf{a}_\alpha}\rangle\langle\phi_j| + \text{h.c.}\right) \tag{8}$$

$$\mathcal{H} T_\alpha = t \sum_{<i,j>} \left(|\phi_i\rangle\langle\phi_j| + \text{h.c.}\right) \sum_k |\phi_{k+\mathbf{a}_\alpha}\rangle\langle\phi_k| = t \sum_{<i,j>} \left(|\phi_i\rangle\langle\phi_{j-\mathbf{a}_\alpha}| + \text{h.c.}\right) = T_\alpha \mathcal{H} \tag{9}$$

One can therefore diagonalize simultaneously $\mathcal{H}$ and T_α. As usual eigenstates of T_α are obtained by a Fourier transform.

3. Since the honeycomb lattice is made of two Bravais sublattices A and B, one has to define two Fourier modes (one for each sublattice). In this tutorial we work with the following convention for the Fourier transform

$$|\psi^A_{\mathbf{q}}\rangle = \sum_{\mathbf{r}\in A} e^{i\mathbf{q}\cdot\mathbf{r}} |\phi_{\mathbf{r}}\rangle \qquad |\psi^B_{\mathbf{q}}\rangle = \sum_{\mathbf{r}\in B} e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{d}_3)} |\phi_{\mathbf{r}}\rangle = \sum_{\mathbf{r}\in A} e^{i\mathbf{q}\cdot\mathbf{r}} |\phi_{\mathbf{r}+\mathbf{d}_3}\rangle. \tag{10}$$

Check that these states are indeed eigenstates of T_α. Check that $|\psi^A_{\mathbf{q}}\rangle = |\psi^A_{\mathbf{q}+\mathbf{b}_i}\rangle$ and $|\psi^B_{\mathbf{q}}\rangle = |\psi^B_{\mathbf{q}+\mathbf{b}_i}\rangle$. What is the Brillouin zone ? What is its area $\mathcal{A}_{\text{BZ}}$?

Starting with the translation operator, we check that we have eigenvectors:

$$T_\alpha |\psi^A_{\mathbf{q}}\rangle = \sum_{\mathbf{r}\in A} e^{i\mathbf{q}\cdot\mathbf{r}} |\phi_{\mathbf{r}+\mathcal{A}_\alpha}\rangle = e^{-i\mathbf{q}\cdot\mathbf{a}_\alpha} |\psi^A_{\mathbf{q}}\rangle \tag{11}$$

and likewise for $|\psi^B_{\mathbf{q}}\rangle$. Since we are dealing with discrete translations, the momentum $\mathbf{q}$ is defined modulo $\mathbf{b}_1$ and $\mathbf{b}_2$, namely

$$\mathbf{q} \equiv \mathbf{q} + \mathbf{b}_\alpha. \tag{12}$$

The Brillouin Zone could be chosen (for instance) to be a parallelogram $[0,1[\times\mathbf{b}_1 + [0,1[\times\mathbf{b}_2$, but the conventional choice is to choose the haxagone centered on zero. The Brillouin area is

$$\mathcal{A}_{\text{BZ}} = |\mathbf{b}_1 \wedge \mathbf{b}_2| = \frac{4\pi^2}{|\mathbf{a}_1 \wedge \mathbf{a}_2|} = \frac{8\pi^2}{3\sqrt{3}}. \tag{13}$$

4. What are the creation operators $c^\dagger_A(\mathbf{q})$ and $c^\dagger_B(\mathbf{q})$ corresponding to $|\psi^A_{\mathbf{q}}\rangle$ and $|\psi^B_{\mathbf{q}}\rangle$? What is their inverse Fourier transform ? Compute their anti-commutation relations $\{c_\alpha(\mathbf{q}), c^\dagger_{\alpha'}(\mathbf{q}')\}$.

The Fourier transform is

$$c^\dagger_A(\mathbf{q}) = \sum_{\mathbf{r}\in A} e^{i\mathbf{q}\cdot\mathbf{r}} c^\dagger(\mathbf{r}) \qquad c^\dagger_B(\mathbf{q}) = \sum_{\mathbf{r}\in B} e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{d}_3)} c^\dagger(\mathbf{r}) = \sum_{\mathbf{r}\in A} e^{i\mathbf{q}\cdot\mathbf{r}} c^\dagger(\mathbf{r}+\mathbf{d}_3). \tag{14}$$

The inverse Fourier transform is

$$c^\dagger(\mathbf{r}) = \int_{\text{BZ}} \frac{d\mathbf{q}}{\mathcal{A}_{\text{BZ}}} e^{-i\mathbf{q}\cdot\mathbf{r}} c^\dagger_A(\mathbf{q}) \qquad \text{for } \mathbf{r} \in, A \tag{15}$$

$$c^\dagger(\mathbf{r}) = \int_{\text{BZ}} \frac{d\mathbf{q}}{\mathcal{A}_{\text{BZ}}} e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{d}_3)} c^\dagger_A(\mathbf{q}) \qquad \text{for } \mathbf{r} \in B. \tag{16}$$

For the anti-commutator one gets

$$\{c_A(\mathbf{q}), c^\dagger_A(\mathbf{q}')\} = \sum_{\mathbf{r},\mathbf{r}'\in A} e^{i\mathbf{q}'\cdot\mathbf{r}' - i\mathbf{q}\cdot\mathbf{r}} \{c(\mathbf{r}), c^\dagger(\mathbf{r}')\} = \sum_{\mathbf{r}\in A} e^{i(\mathbf{q}'-\mathbf{q})\cdot\mathbf{r}'} = \mathcal{A}_{\text{BZ}} \delta(\mathbf{q}-\mathbf{q}'). \tag{17}$$

Likewise,

$$\{c_B(\mathbf{q}), c_B^\dagger(\mathbf{q}')\} = \mathcal{A}_{\mathrm{BZ}}\delta(\mathbf{q}-\mathbf{q}'), \tag{18}$$

and

$$\{c_A(\mathbf{q}), c_B^\dagger(\mathbf{q}')\} = 0. \tag{19}$$

5. For a system that can contain many electrons, we can also consider the operators $\mathcal{T}_\alpha$ that translates all electrons. They are defined by

$$\mathcal{T}_\alpha c_{\mathbf{r}} \mathcal{T}_\alpha^\dagger = c_{\mathbf{r}+\mathbf{a}_\alpha} \qquad \mathcal{T}_\alpha|0\rangle = |0\rangle \tag{20}$$

Show that states of the form $c_A^\dagger(\mathbf{q}_1)\dots c_A^\dagger(\mathbf{q}_m)c_B^\dagger(\mathbf{q}_{m+1})\dots c_B^\dagger(\mathbf{q}_n)|0\rangle$ are eigenstates of both T_α and $\mathcal{T}_\alpha$.

From $\mathcal{T}_\alpha c_{\mathbf{r}} \mathcal{T}_\alpha^\dagger = c_{\mathbf{r}+\mathbf{a}_\alpha}$ we deduce

$$\mathcal{T}_\alpha c_A^\dagger(\mathbf{q}) \mathcal{T}_\alpha^\dagger = e^{-i\mathbf{q}\cdot\mathbf{a}_\alpha} c_A^\dagger(\mathbf{q}) \tag{21}$$

and the same for B. Meanwhile for T_α we have

$$[T_\alpha, c_A^\dagger(\mathbf{q})] = e^{-i\mathbf{q}\cdot\mathbf{a}_\alpha} c_A^\dagger(\mathbf{q}) \tag{22}$$

and the same for B. Therefore

$$\mathcal{T}_\alpha c_A^\dagger(\mathbf{q}_1)\dots c_A^\dagger(\mathbf{q}_m)c_B^\dagger(\mathbf{q}_{m+1})\dots c_B^\dagger(\mathbf{q}_n)|0\rangle = \left(\prod_{j=1}^n e^{-i\mathbf{q}_j\cdot\mathbf{a}_\alpha}\right) c_A^\dagger(\mathbf{q}_1)\dots c_A^\dagger(\mathbf{q}_m)c_B^\dagger(\mathbf{q}_{m+1})\dots c_B^\dagger(\mathbf{q}_n)|0\rangle \tag{23}$$

while

$$T_\alpha c_A^\dagger(\mathbf{q}_1)\dots c_A^\dagger(\mathbf{q}_m)c_B^\dagger(\mathbf{q}_{m+1})\dots c_B^\dagger(\mathbf{q}_n)|0\rangle = \left(\sum_{j=1}^n e^{-i\mathbf{q}_j\cdot\mathbf{a}_\alpha}\right) c_A^\dagger(\mathbf{q}_1)\dots c_A^\dagger(\mathbf{q}_m)c_B^\dagger(\mathbf{q}_{m+1})\dots c_B^\dagger(\mathbf{q}_n)|0\rangle \tag{24}$$

6. Show that the tight-binding Hamiltonian in momentum space is

$$\mathcal{H} = \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{\mathcal{A}_{\mathrm{BZ}}} \mathbf{c}^\dagger(\mathbf{q}) h(\mathbf{q}) \mathbf{c}(\mathbf{q}) \quad \text{where } \mathbf{c}(\mathbf{q}) = \begin{pmatrix} c_A(\mathbf{q}) \\ c_B(\mathbf{q}) \end{pmatrix}, \quad h(\mathbf{q}) = \begin{pmatrix} 0 & f(\mathbf{q}) \\ f(\mathbf{q})^* & 0 \end{pmatrix} \tag{25}$$

with $f(q) = t(1 + e^{i\mathbf{q}\cdot\mathbf{a}_1} + e^{i\mathbf{q}\cdot\mathbf{a}_2})$.

$$\begin{aligned}
\mathcal{H} &= t\sum_{\mathbf{r}\in A} c_{\mathbf{r}}^\dagger \left(\sum_{i=1}^3 c_{\mathbf{r}+\mathbf{d}_i}\right) + \text{h.c.} && (26)\\
&= t\sum_{\mathbf{r}\in A} c_{\mathbf{r}}^\dagger (c_{\mathbf{r}+\mathbf{a}_1+\mathbf{d}_3} + c_{\mathbf{r}+\mathbf{a}_2+\mathbf{d}_3} + c_{\mathbf{r}+\mathbf{d}_3}) + \text{h.c.} && (27)\\
&= t\sum_{\mathbf{r}\in A} \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{\mathcal{A}_{\mathrm{BZ}}} \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}'}{\mathcal{A}_{\mathrm{BZ}}} e^{-i\mathbf{q}\cdot\mathbf{r}} c_A^\dagger(\mathbf{q}) (e^{i\mathbf{q}'\cdot(\mathbf{r}+\mathbf{a}_1)} + e^{i\mathbf{q}'\cdot(\mathbf{r}+\mathbf{a}_2)} + e^{i\mathbf{q}'\cdot\mathbf{r}}) c_B(\mathbf{q}') + \text{h.c.} && (28)\\
&= \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{\mathcal{A}_{\mathrm{BZ}}} \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}'}{\mathcal{A}_{\mathrm{BZ}}} c_A^\dagger(\mathbf{q}) f(\mathbf{q}') c_B(\mathbf{q}') \sum_{\mathbf{r}\in A} e^{i(\mathbf{q}'-\mathbf{q})\cdot\mathbf{r}} + \text{h.c.} && (29)\\
&= \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{\mathcal{A}_{\mathrm{BZ}}} c_A^\dagger(\mathbf{q}) f(\mathbf{q}) c_B(\mathbf{q}') + \text{h.c.} && (30)
\end{aligned}$$

Adding the hermitian conjugate we recover the expected form.

7. What is the one-body spectrum of $\mathcal{H}$? What are the eigenstates ? Write the Hamiltonian in diagonal form

$$\mathcal{H} = \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{\mathcal{A}_{\mathrm{BZ}}} (\mathbf{d}_+^\dagger(\mathbf{q})\epsilon_+(\mathbf{q})\mathbf{d}_+(\mathbf{q}) + \mathbf{d}_-^\dagger(\mathbf{q})\epsilon_-(\mathbf{q})\mathbf{d}_-(\mathbf{q})). \tag{31}$$

where $d_\pm$ and $\epsilon_\pm$ are to specify.

To have the spectrum, we need to diagonalise these 2 by 2 matrix $h(\mathbf{q})$, which is straightforward. We have

$$h(\mathbf{q}) = |f(\mathbf{q})| \begin{pmatrix} 0 & e^{i\varphi(\mathbf{q})} \\ e^{-i\varphi(\mathbf{q})} & 0 \end{pmatrix} \text{ where } f(\mathbf{q}) = |f(\mathbf{q})|e^{i\varphi(\mathbf{q})}. \tag{32}$$

Therefore the energies are

$$\epsilon_\pm(\mathbf{q}) = \pm|f(\mathbf{q})| \tag{33}$$

and the corresponding eigenstates are

$$|u_\pm(\mathbf{q})\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm e^{-i\varphi(\mathbf{q})} \end{pmatrix} = \frac{|\psi^A_\mathbf{q}\rangle \pm e^{-i\varphi(\mathbf{q})}|\psi^B_\mathbf{q}\rangle}{\sqrt{2}} \tag{34}$$

The state $|u_\pm(\mathbf{q})\rangle$ is a plane wave with quasi-momentum $\mathbf{q}$, and has support on both sublattices (it is a linear superposition of the states $|\psi^A_\mathbf{q}\rangle$ and $|\psi^B_\mathbf{q}\rangle$). The associated creation operators are

$$d^\dagger_\pm(\mathbf{q}) = \frac{c^\dagger_A(\mathbf{q}) \pm e^{-i\varphi(\mathbf{q})}c^\dagger_B(\mathbf{q})}{\sqrt{2}} \tag{35}$$

and they are normalized as

$$\{d_\alpha(\mathbf{q}), d^\dagger_\beta(\mathbf{q}')\} = \langle u_\alpha(\mathbf{q})|u_\beta(\mathbf{q}')\rangle = \mathcal{A}_{\mathrm{BZ}}\delta_{\alpha,\beta}\delta(\mathbf{q}-\mathbf{q}'). \tag{36}$$

8. We want to describe undopped graphene. What is the corresponding filling of the spinless tight-binding model ?

In graphene each carbon atom contributes one electron. In the tight-binding approxima- tion, each carbon atom has only one orbital available. Since electrons may occupy either a spin-up or a spin-down state, there are 2 quantum states per atom. We therefore get that in the absence of doping graphene is at half filling.

9. What is the Fermi surface?

For our spinless model, half-filling means that the lowest band, with energy $-|f(\mathbf{q})|$, is filled, and the upper band is unoccupied. The Fermi surface is where these two bands meet, namely for $f(\mathbf{q}) = 0$, i.e.

$$1 + e^{i\mathbf{q}\cdot\mathbf{a}_1} + e^{i\mathbf{q}\cdot\mathbf{a}_2} = 0 \tag{37}$$

Since $e^{i\mathbf{q}\cdot\mathbf{a}_i}$ both have modulus 1, there is only one way for this sum to vanish : $1 + j + j2 = 0$. So there are two possibilities

$$e^{i\mathbf{q}\cdot\mathbf{a}_1} = j^\zeta \quad e^{i\mathbf{q}\cdot\mathbf{a}_2} = j^{-\zeta} \quad \zeta = \pm 1 \tag{38}$$

Decomposing $\mathbf{q} = q_1\mathbf{b}_1 + q_2\mathbf{b}_2$, this means

$$e^{2i\pi q_1} = e^{\zeta 2i\pi/3} \quad e^{2i\pi q_2} = e^{-\zeta 2i\pi/3} \tag{39}$$

i.e.

$$q_1 \equiv \zeta/3[1] \quad q_2 \equiv -\zeta/3[1]. \tag{40}$$

So there are two points in the Brilloin Zone for which $f(\mathbf{q}) = 0$:

$$\mathcal{K}_\zeta = \zeta\frac{\mathbf{b}_1 - \mathbf{b}_2}{3}. \tag{41}$$

This gives two corners of the hexagonal BZ but all corners by symmetries. The FS is not really a surface, but only points (called Dirac points).

10. We define the corners of the Brillouin zone by

$$\mathcal{K}_\zeta = \zeta\frac{\mathbf{b}_1 - \mathbf{b}_2}{3}. \tag{42}$$

where $\zeta = \pm 1$ is called the chirality. Check that to first order in $\mathbf{q}$ we have: $f(\mathcal{K}_\zeta + \mathbf{q}) \approx -\zeta v_\mathrm{F}|\mathbf{q}|e^{i\zeta\theta_\mathbf{q}}$ with $v_\mathrm{F} = 3t/2$ and $\theta_\mathbf{q}$ is the polar angle of the wave vector $\mathbf{q}$ with respect to the direction $\mathbf{a}_1 - \mathbf{a}_2$. The quantity $\zeta\theta_\mathbf{q}$ is called in the literature the pseudospin.

From $e^{i\mathcal{K}_\zeta\cdot\mathbf{a}_1} = j^\zeta$ and $e^{i\mathcal{K}_\zeta\cdot\mathbf{a}_2} = j^{-\zeta}$ it follows that

$$f(\mathcal{K}_\zeta + \mathbf{q}) = t\left(j^\zeta e^{i\mathbf{q}\cdot\mathbf{a}_1} + j^{-\zeta}e^{i\mathbf{q}\cdot\mathbf{a}_2} + 1\right) \tag{43}$$

whose linear approximation is

$$f(\mathcal{K}_\zeta + \mathbf{q}) = it\mathbf{q}\cdot\left(j^\zeta\mathbf{a}_1 + j^{-\zeta}\mathbf{a}_2\right) = -\zeta\frac{3t}{2}(q_x + i\zeta q_y) = -\zeta v_\mathrm{F}|\mathbf{q}|e^{i\zeta\theta_\mathbf{q}}. \tag{44}$$

11. What are the excitation energies in the neighborhood of $\mathcal{K}_\zeta$ (to first order in $\mathbf{q}$) ?

To first order in $\mathbf{q}$, the eigenenergies are:

$$\epsilon_\pm(\mathcal{K}_\zeta + \mathbf{q}) = \pm v_\mathrm{F}|\mathbf{q}| + O(\mathbf{q}^2). \tag{45}$$

We have cones of excitations near the Dirac points (the cone appears if you plot $\epsilon_\pm(\mathcal{K}_\zeta + \mathbf{q})$ as a function of $\mathbf{q}$).

12. Show that the mode $\mathbf{q}$ eigenvectors near $\mathcal{K}_\pm$ are $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \mp\zeta e^{-i\zeta\theta_\theta} \end{pmatrix}$.

We have already found the eigenstates of $h(\mathbf{q})$: $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \mp \pm e^{-i\varphi(\mathbf{q})} \end{pmatrix}$ where $e^{i\varphi} = f/|f|$. The result is straightforward using the linearisation of f.

13. Argue that the low-energy effective Hamiltonian of graphene at half-filling is given by:

$$\mathcal{H} = \sum_\zeta v_\mathrm{F}\int_\mathrm{BZ}\frac{\mathrm{d}\mathbf{q}}{\mathcal{A}_\mathrm{BZ}}c_\zeta^\dagger(\mathbf{q})(-\zeta q_x\sigma_x + q_y\sigma_y)c_\zeta(\mathbf{q}) \tag{46}$$

which is the sum of two Dirac Hamiltonians. At low energy graphene has effectively two independent Dirac fermions.

We can split the Hamiltonian into two integrals over a half of the BZ, each containing one Dirac point. Then, linearizing the Hamiltonian near $\mathcal{K}_\zeta$ in each integral does not change the low energy physics. It remains to extend the integral over the full reciprocal space.

Besides translation invariance, the tight-binding model of graphene has many symmetries.

14. Chirality symmetry is a unitary operator Γ such that

$$\Gamma c_i\Gamma^\dagger = \begin{cases} c_i \text{ if } i \in A \\ -c_i \text{ if } i \in B \end{cases} \tag{47}$$

Check that Γ anti-commute with $\mathcal{H}$. It implies that the energy spectrum of H is symmetric about zero (show it). What is $\Gamma c_A^\dagger(\mathbf{q})\Gamma^\dagger$? $\Gamma c_B^\dagger(\mathbf{q})\Gamma^\dagger$? Check that $\Gamma d_\pm^\dagger(\mathbf{q})\Gamma^\dagger = d_\mp^\dagger(\mathbf{q})$.

It is straightforward to check that $\Gamma\mathcal{H}\Gamma^\dagger = -\mathcal{H}$. This implies that if $\mathcal{H}|\psi\rangle = E|\psi\rangle$, then $\mathcal{H}\Gamma|\psi\rangle = -E\Gamma|\psi\rangle$: if $|\psi\rangle$ is an eigenstate with energy E, then $\Gamma|\psi\rangle$ is an eigenstate with energy $-E$ (note that $\Gamma^2 = 1$, so $\Gamma|\psi\rangle$ cannot vanish). From

$$c_A^\dagger(\mathbf{q}) = \sum_{\mathbf{r}\in A}e^{i\mathbf{q}\cdot\mathbf{r}}c^\dagger(\mathbf{r}) \qquad c_B^\dagger(\mathbf{q}) = \sum_{\mathbf{r}\in B}e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{d}_3)}c^\dagger(\mathbf{r}) = \sum_{\mathbf{r}\in A}e^{i\mathbf{q}\cdot\mathbf{r}}c^\dagger(\mathbf{r}+\mathbf{d}_3) \tag{48}$$

we have

$$\Gamma c_A^\dagger(\mathbf{q})\Gamma^\dagger = c_A^\dagger(\mathbf{q}), \quad \Gamma c_B^\dagger(\mathbf{q})\Gamma^\dagger = -c_B^\dagger(\mathbf{q}) \tag{49}$$

and it follows that $\Gamma d_\pm^\dagger(\mathbf{q})\Gamma^\dagger = d_\mp^\dagger(\mathbf{q})$.

15. Time-reversal symmetry is an anti-linear, anti-unitary operator θ defined by

$$\theta c_i\theta^\dagger = c_i, \quad \theta c_i^\dagger\theta^\dagger = c_i^\dagger. \tag{50}$$

Show that graphene is invariant under time-reversal symmetry (i.e. $[\theta, \mathcal{H}] = 0$). What is $\theta c_A^\dagger(\mathbf{q})\theta\dagger$? $\theta c_B^\dagger(\mathbf{q})\theta^\dagger$?

Since the hopping amplitudes are real, the Hamiltonian is invariant under θ. From

$$c_A^\dagger(\mathbf{q}) = \sum_{\mathbf{r}\in A} e^{i\mathbf{q}\cdot\mathbf{r}} c^\dagger(\mathbf{r}) \qquad c_B^\dagger(\mathbf{q}) = \sum_{\mathbf{r}\in B} e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{d}_3)} c^\dagger(\mathbf{r}) = \sum_{\mathbf{r}\in A} e^{i\mathbf{q}\cdot\mathbf{r}} c^\dagger(\mathbf{r}+\mathbf{d}_3) \tag{51}$$

we have

$$\theta c_A^\dagger(\mathbf{q})\theta^\dagger = \sum_{\mathbf{r}\in A} e^{-i\mathbf{q}\cdot\mathbf{r}} \theta c^\dagger(\mathbf{r})\theta^\dagger = c_A^\dagger(-\mathbf{q}) \tag{52}$$

and likewise $\theta c_B^\dagger(\mathbf{q})\theta\dagger = c_B^\dagger(-\mathbf{q})$. As expected time-reversal changes the sign of the momentum.

16. Inversion symmetry is a a unitary operator I such that $Ic_{\mathbf{r}}I^\dagger = c_{\mathbf{d}_3-\mathbf{r}}$. Check that graphene is invariant under inversion. What is $Ic_A^\dagger(\mathbf{q})I^\dagger$? $Ic_B^\dagger(\mathbf{q})I^\dagger$?

Since inversion leaves the lattice invariant, the Hamiltonian is invariant under I. We have

$$Ic_A^\dagger(\mathbf{q})I^\dagger = \sum_{\mathbf{r}\in A} e^{i\mathbf{q}\cdot\mathbf{r}} Ic^\dagger(\mathbf{r})I^\dagger = \sum_{\mathbf{r}\in A} e^{i\mathbf{q}\cdot\mathbf{r}} c^\dagger(\mathbf{d}_3-\mathbf{r}) = c_B^\dagger(-\mathbf{q}). \tag{53}$$

Likewise $Ic_B^\dagger(\mathbf{q})I^\dagger = c_A^\dagger(-\mathbf{q})$. Inversion swaps the two sublattices A and B, and changes the sign of the momentum.

17. Show that under time-reversal we have $h(\mathbf{q}) \to h(-\mathbf{q})^*$ while under inversion we have $h(\mathbf{q}) \to \sigma_x h(-\mathbf{q})\sigma_x$. Check this way that graphene is indeed time-reversal and inversion symmetric.

Under time-reversal we have $\mathbf{c}(\mathbf{q}) \to \mathbf{c}(-\mathbf{q})$, so

$$\theta\mathcal{H}\theta^\dagger = \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{\mathcal{A}_{\mathrm{BZ}}} \mathbf{c}^\dagger(-\mathbf{q}) h(\mathbf{q})^* \mathbf{c}(-\mathbf{q}) = \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{\mathcal{A}_{\mathrm{BZ}}} \mathbf{c}^\dagger(\mathbf{q}) h(-\mathbf{q})^* \mathbf{c}(\mathbf{q}) \tag{54}$$

while under inversion $\mathbf{c}(|q) \to \sigma_x \mathbf{c}(-\mathbf{q})$, so

$$I\mathcal{H}I^\dagger = \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{\mathcal{A}_{\mathrm{BZ}}} \mathbf{c}^\dagger(-\mathbf{q}) \sigma_x h(\mathbf{q}) \sigma_x \mathbf{c}(-\mathbf{q}) = \int_{\mathrm{BZ}} \frac{\mathrm{d}\mathbf{q}}{\mathcal{A}_{\mathrm{BZ}}} \mathbf{c}^\dagger(\mathbf{q}) \sigma_x h(-\mathbf{q}) \sigma_x \mathbf{c}(\mathbf{q}). \tag{55}$$

Reminder of Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$