I. HAMILTONIAN OF UNIFORM GRAPHENE IN CARTESIAN COORDINATES

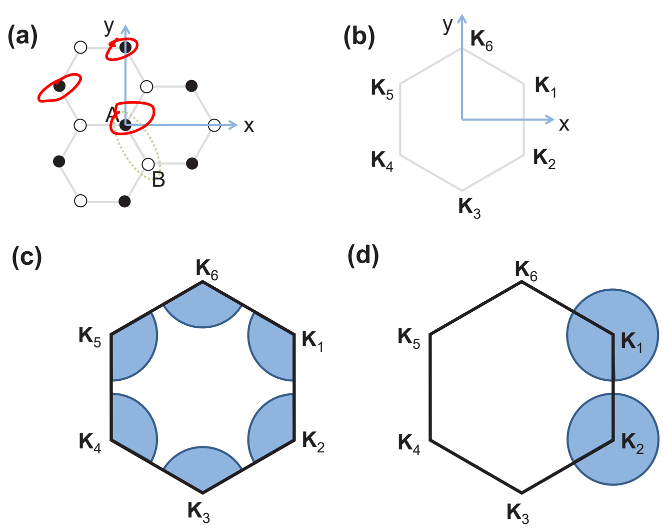

FIG. 1: (a) Lattice structure of graphene: filled (empty) circles for sublattice A (B). (b) Six Dirac points at the edge of the first Brillouin zone (FBZ) of graphene.

As shown in Fig. 1(a), the honeycomb lattice of graphene consists of two sublattices (denoted by A and B) and each unit cell contains two carbon atoms (or π_z-orbitals), one on each sublattice. The tight-binding Hamiltonian of graphene is

$$\hat{H}_0 = -\sum_{\langle i,j\rangle} |i,A\rangle\langle j,B| - h.c.,$$

where $\langle i,j\rangle$ sums over all the nearest-neighbor carbon pairs, $|i,\lambda\rangle$ ($\lambda = A, B$) is the π_z-orbital on the sublattice λ of unit cell i. We take the A site as the origin of each unit cell, so the relative displacements of the two carbon atoms inside the unit cell are $\boldsymbol{\tau}_A = 0$ and $\boldsymbol{\tau}_B = (a/2, -\sqrt{3}a/2)$, where a is the carbon-carbon bond length. In terms of the unit cell location $\mathbf{R}_i$, the location of the site λ in unit cell i is $\mathbf{R}_{i,\lambda} = \mathbf{R}_i + \boldsymbol{\tau}_\lambda$. We Fourier transform the real-space basis $|i,\lambda\rangle$ into the momentum space basis

$$|\mathbf{k},\lambda\rangle \equiv \frac{1}{\sqrt{N}}\sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i}|i,\lambda\rangle, \tag{1}$$

where $\mathbf{k}$ lies inside the first Brillouin zone (FBZ). The graphene Hamiltonian can be transformed into the momentum space:

$$\hat{H} = \sum_{\mathbf{k}\in\mathrm{FBZ}} f(\mathbf{k})|\mathbf{k},A\rangle\langle\mathbf{k},B| + h.c.,$$

where $f(\mathbf{k}) = -t\sum_{i=1,2,3} e^{i\mathbf{k}\cdot\mathbf{d}_i}$ and $\mathbf{d}_1, \mathbf{d}_2, \mathbf{d}_3$ denote the relative displacements of the three nearest-neighbor *unit cells* [black filled circles in Fig. 1(a)] with respect to the central *unit cell* [blue filled circle in Fig. 1(a)]:

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

The function $f(\mathbf{k})$ satisfies $f^*(\mathbf{k}) = f(-\mathbf{k})$. Under time reversal operation θ, we have

$$\theta|i,\lambda\rangle = |i,\lambda\rangle \Rightarrow \theta|\mathbf{k},\lambda\rangle = \theta|-\mathbf{k},\lambda\rangle.$$

Using $\theta|a\rangle\langle b| = |\theta a\rangle\langle\theta b|$, we have

$$\begin{aligned}\theta H\theta^{-1} &= \sum_{\mathbf{k}\in\mathrm{FBZ}} f^*(\mathbf{k})|-\mathbf{k},A\rangle\langle-\mathbf{k},B| + h.c.\\ &= \sum_{\mathbf{k}\in\mathrm{FBZ}} f^*(-\mathbf{k})|\mathbf{k},A\rangle\langle\mathbf{k},B| + h.c.\end{aligned}$$

Therefore, the property $f^*(-\mathbf{k}) = f(\mathbf{k})$ ensures the time-reversal invariance of the graphene Hamiltonian. Diagonalizing the Hamiltonian in the momentum space gives one conduction band and one valence band $E_\pm(\mathbf{k}) = \pm|f(\mathbf{k})|$ or explicitly

$$E_\pm(\mathbf{k}) = \pm t\sqrt{3 + 2\cos(\sqrt{3}k_y a) + 4\cos\frac{3k_x a}{2}\cos\frac{\sqrt{3}k_y a}{2}}, \tag{2}$$

which touch each other (i.e., $f(\mathbf{k}) = 0$) at six Dirac points $\mathbf{K}_1, \mathbf{K}_2, \mathbf{K}_3$ and $\mathbf{K}_4 \equiv -\mathbf{K}_1, \mathbf{K}_5 \equiv -\mathbf{K}_2, \mathbf{K}_6 \equiv -\mathbf{K}_3$ at the corner of the first Brillouin zone [Fig. 1(b)]. Here $\mathbf{K}_1$, $\mathbf{K}_3, \mathbf{K}_5$ only differ by a reciprocal vector, so they are equivalent and

$$|\mathbf{K}_1,\lambda\rangle = |\mathbf{K}_3,\lambda\rangle = |\mathbf{K}_5,\lambda\rangle.$$

Similarly, $\mathbf{K}_2, \mathbf{K}_4, \mathbf{K}_6$ only differ by a reciprocal vector, so they are equivalent and

$$|\mathbf{K}_2,\lambda\rangle = |\mathbf{K}_4,\lambda\rangle = |\mathbf{K}_6,\lambda\rangle.$$

In the continuum model, we restrict the summation $\sum_{\mathbf{k}\in\mathrm{FBZ}}$ near the Dirac points [shaded regions in Fig. 1(c)]. By definition Eq. (1), we have $|\mathbf{k},\lambda\rangle = |\mathbf{k}+\mathbf{G},\lambda\rangle$ when $\mathbf{G}$ is a reciprocal vector. Therefore, the sum of $\mathbf{k}$ over the shaded regions in Fig. 1(c) is equal to the sum of $\mathbf{k}$ over the shaded regions in Fig. 1(d): $H = H_1 + H_2$, where

$$\begin{aligned}H_m &\equiv \sum_{\mathbf{k}\approx\mathbf{K}_m} f(\mathbf{k})|\mathbf{k},A\rangle\langle\mathbf{k},B| + h.c.\\ &= \sum_{\mathbf{q}\approx\mathbf{0}} f_m(\mathbf{q})|\mathbf{K}_m+\mathbf{q},A\rangle\langle\mathbf{K}_m+\mathbf{q},B| + h.c.\end{aligned}$$

is the Hamiltonian for the mth valley ($m = 1, 2$), $\mathbf{q} \equiv \mathbf{k} - \mathbf{K}_m$, and $f_m(\mathbf{q}) \equiv f(\mathbf{K}_m + \mathbf{q})$. The property $f^*(-\mathbf{k}) = f(\mathbf{k})$ leads to $f_1^*(-\mathbf{q}) = f_2(\mathbf{q})$. Since $-\mathbf{K}_1$ and $\mathbf{K}_2$ differ by a reciprocal vector, time reversal brings the $\mathbf{q}$ state of the $\mathbf{K}_1$ valley to the $-\mathbf{q}$ state of the $\mathbf{K}_2$ valley:

$$\theta|\mathbf{K}_1+\mathbf{q},\lambda\rangle = |-\mathbf{K}_1-\mathbf{q},\lambda\rangle = |\mathbf{K}_2-\mathbf{q},\lambda\rangle.$$

Therefore, time reversal brings H_1 to H_2 and vice versa:

$$\begin{aligned}\theta H_1\theta^{-1} &= \sum_{\mathbf{q}\approx 0} f_1^*(\mathbf{q})|-\mathbf{K}_1-\mathbf{q},A\rangle\langle-\mathbf{K}_1-\mathbf{q},B| + h.c.\\ &= \sum_{\mathbf{q}\approx 0} f_1^*(\mathbf{q})|\mathbf{K}_2-\mathbf{q},A\rangle\langle\mathbf{K}_2-\mathbf{q},B| + h.c.\\ &= H_2.\end{aligned}$$

The total Hamiltonian $H = H_1 + H_2$ is time-reversal invariant: $\theta H \theta^{-1} = H$.

In the effective-mass approximation, we factor $|\mathbf{K}_m + \mathbf{q}, \lambda\rangle = |\mathbf{q}\rangle|\mathbf{K}_m, \lambda\rangle$ as the product of the slowly-varying plane wave $|\mathbf{q}\rangle$ and the rapidly oscillating band-edge Bloch state $|\mathbf{K}_m, \lambda\rangle$, then

$$\begin{aligned} H_m &\equiv |\mathbf{K}_m, A\rangle \left(\sum_{\mathbf{q}\approx 0} f_m(\mathbf{q}) |\mathbf{q}\rangle\langle\mathbf{q}| \right) \langle \mathbf{K}_m, B| + h.c \\ &= |\mathbf{K}_m, A\rangle f_m(\hat{\mathbf{p}}) \langle \mathbf{K}_m, B| + h.c, \end{aligned}$$

where $\hat{\mathbf{p}} \equiv \sum_{\mathbf{q}\approx 0} \mathbf{q}|\mathbf{q}\rangle\langle\mathbf{q}|$ is the momentum operator (restricted to small momentum). Since $\theta|\mathbf{K}_m + \mathbf{q}, \lambda\rangle = |-\mathbf{K}_m - \mathbf{q}, \lambda\rangle$, we have

$$\begin{aligned} \theta|\mathbf{K}_1, \lambda\rangle &= |-\mathbf{K}_1, \lambda\rangle = |\mathbf{K}_2, \lambda\rangle, \\ \theta|\mathbf{q}\rangle &= |-\mathbf{q}\rangle, \end{aligned}$$

and hence

$$\theta \hat{\mathbf{p}} \theta^{-1} = \sum_{\mathbf{q}} \mathbf{q} |-\mathbf{q}\rangle\langle -\mathbf{q}| = -\sum_{\mathbf{q}} \mathbf{q}|\mathbf{q}\rangle\langle\mathbf{q}| = -\hat{\mathbf{p}}.$$

Using $\theta f_1(\hat{\mathbf{p}})\theta^{-1} = f_1^*(-\hat{\mathbf{p}}) = f_2(\hat{\mathbf{p}})$, we confirm $\theta H_1 \theta^{-1} = H_2$. Up to the first order of $\mathbf{q}$, we have

$$\begin{aligned} f_1(\mathbf{q}) &= v_F e^{-i\pi/6}(q_x + iq_y), \\ f_2(\mathbf{q}) &= v_F e^{i\pi/6}(-q_x + iq_y), \end{aligned}$$

where $v_F \equiv (3/2)at$. Therefore, the Hamiltonian for the valleys $\mathbf{K}_1$ and $\mathbf{K}_2$ are

$$\begin{aligned} H_1 &= e^{-i\pi/6}|\mathbf{K}_1, A\rangle v_F(\hat{p}_x + i\hat{p}_y)\langle\mathbf{K}_1, B| + h.c., \\ H_2 &= e^{i\pi/6}|\mathbf{K}_2, A\rangle v_F(-\hat{p}_x + i\hat{p}_y)\langle\mathbf{K}_2, B| + h.c. = \theta H_1 \theta^{-1}. \end{aligned}$$

For the $\mathbf{K}_1$ valley, we identify $e^{-i\pi/6}|\mathbf{K}_1, A\rangle \equiv |\uparrow_1\rangle$ as the spin-up state and $|\downarrow_1\rangle \equiv |\mathbf{K}_1, B\rangle$ as the spin-down state, then the Hamiltonian for the $\mathbf{K}_1$ valley is

$$H_1 = |\uparrow_1\rangle v_F(\hat{p}_x + i\hat{p}_y)\langle\downarrow_1| + h.c.$$

For the $\mathbf{K}_2$ valley, we identify $|\uparrow_2\rangle \equiv e^{i\pi/6}|\mathbf{K}_2, A\rangle = \theta|\uparrow_1\rangle$ as the spin-up state and $|\downarrow_2\rangle \equiv |\mathbf{K}_2, B\rangle = \theta|\downarrow_1\rangle$ as the spin-down state, then the Hamiltonian for the $\mathbf{K}_2$ valley is

$$H_2 = |\uparrow_2\rangle v_F(-\hat{p}_x + i\hat{p}_y)\langle\downarrow_2| + h.c. = \theta H_1 \theta^{-1}.$$

To recover the conventional form, we define

$$\begin{aligned} \sigma_x &\equiv [|\uparrow\rangle, |\downarrow\rangle] \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} \langle\uparrow| \\ \langle\downarrow| \end{bmatrix} = |\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\uparrow|, \\ \sigma_y &\equiv [|\uparrow\rangle, |\downarrow\rangle] \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} \langle\uparrow| \\ \langle\downarrow| \end{bmatrix} = -i|\uparrow\rangle\langle\downarrow| + i|\downarrow\rangle\langle\uparrow|, \\ \sigma_z &\equiv [|\uparrow\rangle, |\downarrow\rangle] \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \langle\uparrow| \\ \langle\downarrow| \end{bmatrix} = |\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow|, \end{aligned}$$

then

$$\begin{aligned} H_1 &= v_F(p_x\sigma_x^{(1)} - p_y\sigma_y^{(1)}), \\ H_2 &= v_F(-p_x\sigma_x^{(2)} - p_y\sigma_y^{(2)}). \end{aligned}$$

Using $\theta|\uparrow_1\rangle = |\uparrow_2\rangle$ and $\theta|\downarrow_1\rangle = |\downarrow_2\rangle$, we have

$$\begin{aligned} \theta\sigma_x^{(1)}\theta^{-1} &= \sigma_x^{(2)}, \\ \theta\sigma_y^{(1)}\theta^{-1} &= -\sigma_y^{(2)}, \\ \theta\sigma_z^{(1)}\theta^{-1} &= \sigma_z^{(2)}. \end{aligned}$$

Therefore, time reversal brings H_1 to H_2.