③ Graphene

3.1 Low-energy theory

$$h_{eff}(\vec{q}) = v\left(\tau^z \sigma^x q_x + \sigma^y q_y\right)$$

$\sigma^z \uparrow (\downarrow)$: A (B) site

$\tau^z \uparrow (\downarrow)$: K (K') valley

3.2 Symmetries (I) : time-reversal

$t \to -t$

* Time-reversal operator Θ.

$$\Theta \underbrace{\vec{r}}_{\substack{\uparrow \\ \text{position} \\ \text{operator}}} \underbrace{\Theta^{-1}}_{} = \vec{r} \qquad (1)$$

$(\Theta \Theta^{-1} = \mathbb{1})$

$$\Theta \, \underbrace{\vec{p}}_{\text{momentum operator}} \, \Theta^{-1} = -\vec{p} \quad (2)$$

(1) and (2) $\longrightarrow$ $\Theta [x, p_x] \Theta^{-1}$

$$= -[x, p_x]$$

But, $[x, p_x] = i\hbar$

$\Rightarrow \quad \Theta \; i\hbar \; \Theta^{-1} = -i\hbar$

$\Rightarrow \quad \Theta \; i \; \Theta^{-1} = -i$

$\Rightarrow \quad \Theta$ is "antiunitary"

* Two properties of antiunitary operators:

(i) $\Theta\,(c_1|\alpha\rangle + c_2|\beta\rangle)$

$$= c_1^*\,\Theta|\alpha\rangle + c_2^*\,\Theta|\beta\rangle$$

(ii) $|\tilde{\alpha}\rangle \equiv \Theta|\alpha\rangle$

$|\tilde{\beta}\rangle \equiv \Theta|\beta\rangle$

Then, $\langle\tilde{\beta}|\tilde{\alpha}\rangle = \langle\beta|\alpha\rangle^*$

For a unitary operator, we would have

$$\langle\tilde{\beta}|\tilde{\alpha}\rangle = \langle\beta|\alpha\rangle$$

* $\boxed{\Theta = U\,K}$

where U = unitary operator

K = complex conjugation

J. J. Sakurai, Modern Q. Mech.

* For a spinless particle,

$$U = \mathbb{1} \rightarrow \boxed{\Theta = K}$$

$$\Rightarrow \boxed{\Theta^2 = K K = \mathbb{1}}$$

* For spinful particles:

$$\Theta \underbrace{\vec{S}}_{} \Theta^{-1} = - \vec{S}$$

spin operator

$$U = e^{-i \pi S^y} =$$

$= \text{rotation of angle } \pi$ around $\hat{y}$.

assume a representation in which S^y is purely imaginary.

$$\Theta^2 = e^{-i\pi S^y} \, K \, e^{-i\pi S^y} \, K$$

$$= e^{-i\pi S^y} \, e^{+i\pi (S^y)^*} \, \underbrace{K \, K}_{1}$$

$$= e^{-2i\pi S^y}$$

$$= \boxed{\begin{cases} +\mathbb{1}, & \text{for integer spin} \\ -\mathbb{1}, & \text{for half-integer spin.} \end{cases}}$$

* For spin $\frac{1}{2}$ particles,

$$\Theta = e^{-i\pi S^y} \, K$$

$$= \boxed{-i\sigma^y \, K}$$

where $\sigma^y = 2 S^y$

* A crystal has time-reversal symmetry (TRS) iff $[\mathcal{H}, \Theta] = 0$

* $$\mathcal{H} = \sum_{\vec{k}} \sum_{\sigma\sigma'} \sum_{\alpha\alpha'} c^{\dagger}_{\vec{k}\alpha\sigma} \, h^{\alpha\alpha'}_{\sigma\sigma'}(\vec{k}) \, c_{\vec{k}\alpha'\sigma'}$$

σ, σ' : spin indices

α, α' : all other degrees of freedom (orbital, sublattice, valley)

TRS $\Leftrightarrow$ $[\mathcal{H}, \Theta] = 0$

$\Leftrightarrow$ $\mathcal{H}\Theta = \Theta\mathcal{H}$ $\Leftrightarrow$ $\Theta\mathcal{H}\Theta^{-1} = \mathcal{H}$.

$$\Theta \mathcal{H} \Theta^{-1} = \sum_{\vec{k}} \sum_{\alpha\alpha'} \sum_{\sigma\sigma'}$$

$$\underbrace{\Theta c^{+}_{\vec{k}\alpha\sigma} \Theta^{-1}}_{?} \underbrace{\Theta h^{\alpha\alpha'}_{\sigma\sigma'}(\vec{k}) \Theta^{-1}}_{?} \underbrace{\Theta c_{\vec{k}\alpha'\sigma'} \Theta^{-1}}_{?}$$

$$* \quad \Theta c_{j\sigma\alpha} \Theta^{-1} = \sum_{\sigma'} U_{\sigma\sigma'} c_{j\sigma'\alpha}$$

j = lattice site

N.B: we assume (for simplicity) that TR leaves orbitals unchanged. In reality, this assumption must be re-evaluated on a case-by-case basis.

(i) spinless particles:

$$\Theta\, c_{j\alpha}\, \Theta^{-1} = c_{j\alpha}$$

(ii) spin $\frac{1}{2}$ particles:

$$\Theta\, c_{j\alpha\uparrow}\, \Theta^{-1} = c_{j\alpha\downarrow}$$

z-spin $\uparrow$

$$\Theta\, c_{j\alpha\downarrow}\, \Theta^{-1} = -\, c_{j\alpha\uparrow}$$

b/c $\Theta^2 = -\mathbb{1}$

* Then,

$$\boxed{\Theta\, c_{\vec{k}\alpha\sigma}\, \Theta^{-1} =}$$

$$= \Theta \sum_j e^{-i\vec{k}\cdot\vec{r}_j} c_{j\alpha\sigma} \Theta^{-1}$$

$$= \sum_j e^{i\vec{k}\cdot\vec{r}_j} \Theta c_{j\alpha\sigma} \Theta^{-1}$$

$$= \sum_j e^{i\vec{k}\cdot\vec{r}_j} \sum_{\sigma'} U_{\sigma\sigma'} c_{j\alpha\sigma'}$$

$$= \boxed{\sum_{\sigma'} U_{\sigma\sigma'} c_{-\vec{k},\alpha,\sigma'}}$$

* Also,

$$\Theta \underbrace{h^{\alpha\alpha'}_{\sigma\sigma'}(\vec{k})}_{\text{a number}} \Theta^{-1} =$$

$$= h^{\alpha\alpha'}_{\sigma\sigma'}(\vec{k})^* \Theta \Theta^{-1}$$

$$= h^{\alpha\alpha'}_{\sigma\sigma'}(\vec{k})^*$$

* Consequently,

$$\Theta \mathcal{H} \Theta^{-1} = \sum_{\vec{k}} \sum_{\dots}$$

$$c^{+}_{-\vec{k},\alpha\sigma''} \left(U^{+}\right)_{\sigma''\sigma} h^{\alpha\alpha'}_{\sigma\sigma'}(\vec{k})^{*}$$

$$U_{\sigma'\sigma'''} \, c_{-\vec{k},\alpha',\sigma'''}$$

$$= \sum_{\vec{k}} \underbrace{c^{+}_{-\vec{k}}} \underbrace{U^{+}}_{\text{matrix}} \underbrace{h(\vec{k})^{*}}_{\text{matrix}} U \, c_{-\vec{k}}$$

shorter notation

where

$$c_{\vec{k}} \equiv \{ c_{\vec{k}\alpha\sigma} \}$$

For example, if $\sigma = \uparrow, \downarrow$,

and $\alpha = A, B$, then

$$c_{\vec{k}} = \begin{pmatrix} c_{\vec{k}A\uparrow} \\ c_{\vec{k}A\downarrow} \\ c_{\vec{k}B\uparrow} \\ c_{\vec{k}B\downarrow} \end{pmatrix}$$ column vector

$$c^{\dagger}_{\vec{k}} = \left(c^{\dagger}_{\vec{k}A\uparrow},\ c^{\dagger}_{\vec{k}A\downarrow},\ c^{\dagger}_{\vec{k}B\uparrow},\ c^{\dagger}_{\vec{k}B\downarrow} \right)$$ row vector

In general, $c_{\vec{k}}$ has $(2s+1)M$ components, where

s = spin of particle and

M = # of orbitals.

$$U = \underbrace{e^{-i\pi S^y}}_{(2S+1)\times(2S+1)} \otimes \underbrace{\mathbb{1}}_{M\times M \text{ identity}}$$

is a $(2S+1)M \times (2S+1)M$

matrix.

$h(\vec{k})$: $(2S+1)M \times (2S+1)M$

matrix.

Repeat:

$$\Theta \mathcal{H} \Theta^{-1} = \sum_{\vec{k}} c^{\dagger}_{-\vec{k}} \, U^{\dagger} h(\vec{k})^{*} \, U \, c_{-\vec{k}}$$

$$= \sum_{\vec{k}} c^{\dagger}_{\vec{k}} \, U^{\dagger} h(-\vec{k})^{*} \, U \, c_{\vec{k}}$$

If $\Theta \mathcal{H} \Theta^{-1} = \mathcal{H}$ (TRS),

$$\Theta \mathcal{H} \Theta^{-1} = \sum_{\vec{k}} c^{\dagger}_{\vec{k}} \, h(\vec{k}) \, c_{\vec{k}}$$

$$\Rightarrow \quad U^{\dagger} h(-\vec{k})^{*} U = h(\vec{k})$$

$$\Rightarrow \quad \boxed{h(\vec{k}) = \Theta^{-1} h(-\vec{k}) \, \Theta}$$

$$(\Theta = U K)$$

Even though $[\mathcal{H}, \Theta] = 0$,

$[h(\vec{k}), \Theta] \neq 0$ in general

* Impact of TRS in electronic structure:

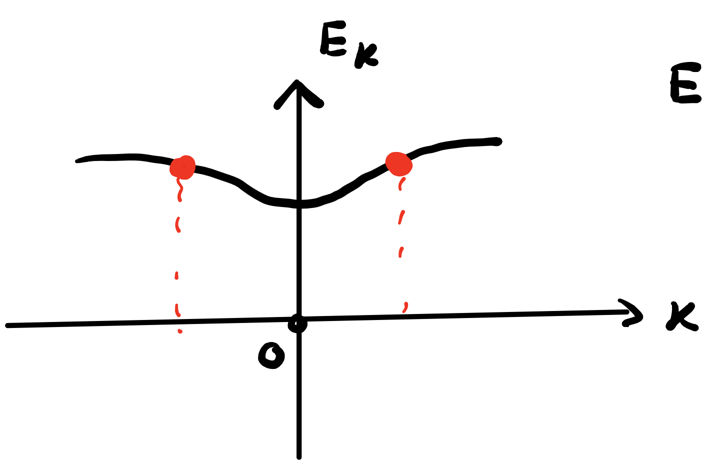
If $h(\vec{k})\,|u_{\vec{k}}\rangle = E_{\vec{k}}\,|u_{\vec{k}}\rangle$,

then

$$\Theta^{-1} h(-\vec{k})\,\Theta\,|u_{\vec{k}}\rangle = E_{\vec{k}}\,|u_{\vec{k}}\rangle$$

$$\Rightarrow\ h(-\vec{k})\left(\Theta\,|u_{\vec{k}}\rangle\right) = E_{\vec{k}}\left(\Theta\,|u_{\vec{k}}\rangle\right)$$

If $|u_{\vec{k}}\rangle$ is an eigenstate of $h(\vec{k})$, then $\Theta\,|u_{\vec{k}}\rangle$ is an eigenstate of $h(-\vec{k})$, with same energy.



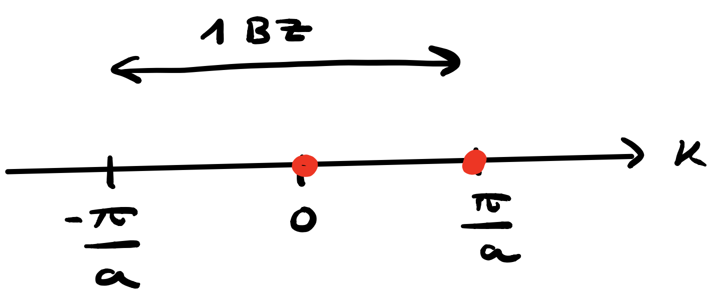
$$E_{-k} = E_k$$

* "Time-reversal-invariant momenta" (TRIM):

$$\vec{k}_{tr} = -\vec{k}_{tr} + \underbrace{\vec{G}}_{\text{reciprocal lattice vector}}$$

examples:

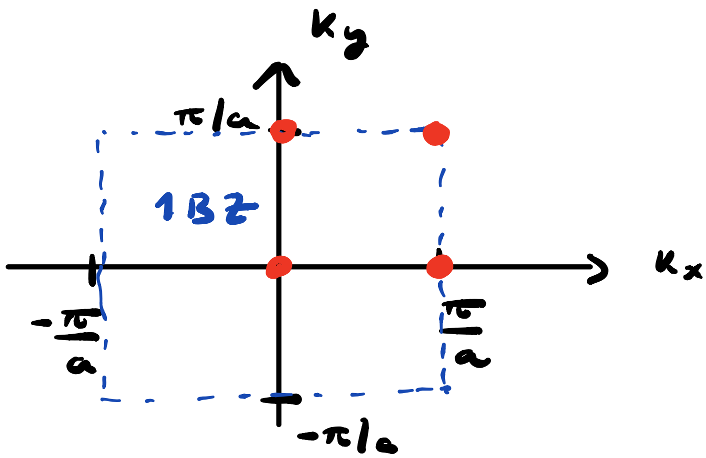
(i) 1D:



$$k_{tr} = \begin{cases} 0 \\ \pi/a \end{cases}$$

2 TRIM

(ii) 2D square lattice



4 TRIM

$$\vec{k}_{tr} = \begin{cases} (0,0) \\ (0,\pi/a) \\ (\pi/a,0) \\ (\pi/a,\pi/a) \end{cases}$$

(iii) 3D cubic lattice

$$\vec{k}_{tr} = \begin{cases} (0,0,0) \\ (\pi/a,0,0) \\ (0,\pi/a,0) \\ (0,0,\pi/a) \\ (\pi/a,\pi/a,0) \\ \vdots \end{cases}$$

$$\left.\begin{array}{l}(0, \pi/a, \pi/a) \\ (\pi/a, 0, \pi/a) \\ (\pi/a, \pi/a, \pi/a)\end{array}\right.$$

8 TRIM.

$$* \quad \boxed{h(-\vec{K}_{tr})} = h(\vec{K}_{tr} + \vec{G}) = \boxed{h(\vec{K}_{tr})}$$

$h(\vec{x})$ is periodic

In presence of TRS,

$$h(\vec{K}_{tr}) = \Theta\, h(\vec{K}_{tr})\, \Theta^{-1}$$

i.e. $[h(\vec{K}_{tr}), \Theta] = 0$

If $|u_{\vec{k}_{tr}}\rangle$ is an eigenstate of $h(\vec{k}_{tr})$, then

$\Theta|u_{\vec{k}_{tr}}\rangle$ is also an eigenstate of $h(\vec{k}_{tr})$ w/ same energy.

Are $|u_{\vec{k}_{tr}}\rangle$ and $\Theta|u_{\vec{k}_{tr}}\rangle$ the same state (mod. a phase), or are they different states?

Begin by assuming they are the same:

$$\Theta|u_{\vec{k}_{tr}}\rangle = \underbrace{e^{i\delta}}_{\text{arbitrary phase}}|u_{\vec{k}_{tr}}\rangle$$

$$\Theta^2 |u_{\vec{k}tr}\rangle = \Theta e^{i\delta} |u_{\vec{k}tr}\rangle$$

$$= e^{-i\delta} \Theta |u_{\vec{k}tr}\rangle$$

$$= e^{-i\delta} e^{i\delta} |u_{\vec{k}tr}\rangle$$

$$= |u_{\vec{k}tr}\rangle$$

$$\Rightarrow \quad \Theta^2 = \mathbb{1}$$

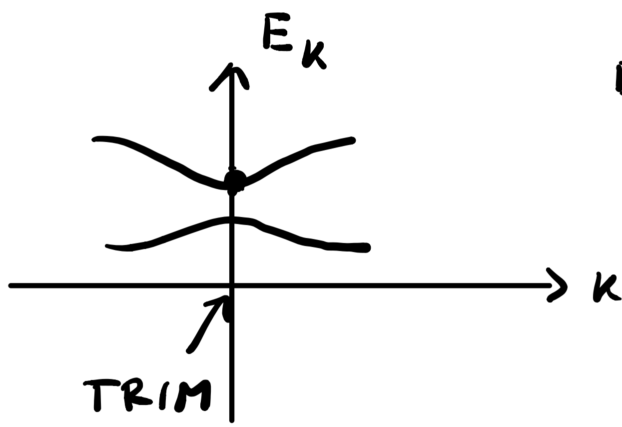
This makes sense only for integer spin particles.

For particles of half-integer spin, $\Theta^2 = -\mathbb{1}$

$\Rightarrow$ $|u_{\vec{k}tr}\rangle$ and $\Theta |u_{\vec{k}tr}\rangle$

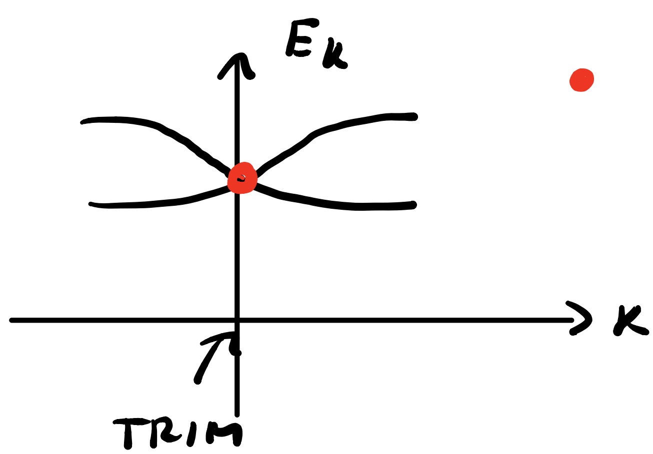
are different states.

(i) Integer spin (or spinless)



E_k symmetric around $\vec{k}_{tr}$

(ii) Half-integer spin



• Kramers degeneracy

At least 2-fold degeneracy at TRIM.

Kramers degeneracy is "enforced" by TRS. It can be lifted only by breaking TRS.

Corollary: any 2-band model of half-integer spin particles with TRS is always a metal. In this case, the minimal model for an insulator contains 4 bands.