II Symmetries of graphene

In chapter I, we did not fully explore the spatial symmetries of graphene. Exploiting them is useful for understanding how the band structure evolves when breaking some in graphene-related materials such as BN, bilayer graphene, etc.

Outline

A| Boron nitride B| Bilayer graphene

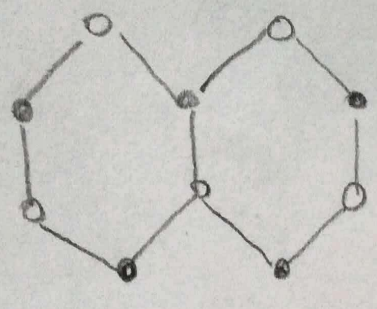
C| Hints from group theory D| Symmetry representation close to K

A| Boron nitride

in graphene, the structure $H_k = \begin{pmatrix} \varepsilon_2(k) & f^*(k) \\ f(k) & \varepsilon_2(k) \end{pmatrix}$ is due to the equivalence between the atoms A and B.

BN is very similar to graphene:

hexagonal 2D plane structure - Lattice constant within 1.5% to the one of graphene



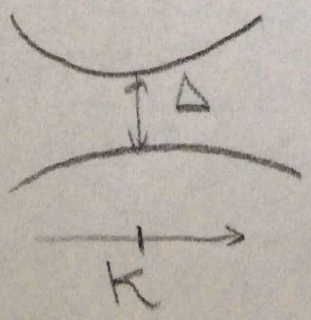
but A and B sites are different

close $K(K')$, the Bloch Hamiltonian is

$$H_k = \hbar v_F (q_x \sigma_x + q_y \sigma_y) + \frac{\Delta}{2}\sigma_z$$

where Δ is the energy difference between the B and N atomic orbitals. [~5eV]

Diagonalizat° $\quad \varepsilon_\pm(k) = \pm\sqrt{\left(\frac{\Delta}{2}\right)^2 + (\hbar v_F q)^2}$



(same for K')

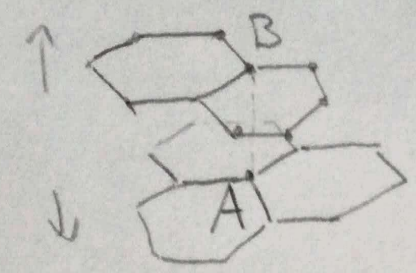
- still time-reversal symmetry $H_k^* = H_{-k}$
- but inversion symmetry is broken

$$\sigma_x H_k \sigma_x \neq H_{-k} \quad \text{since } \Delta \neq 0$$

B) Bilayer graphene

two planes of graphene on top of each other

the most stable configuration: Bernal stacking with B on top of A atoms.



tunneling between B↑ and A↓

close to K(K') pt

$$H_k = \begin{pmatrix} U/2 & \pi^+ & 0 & 0 \\ \pi & U/2 & t_\perp & 0 \\ 0 & t_\perp & -U/2 & \pi^+ \\ 0 & 0 & \pi & -U/2 \end{pmatrix} \begin{matrix} A\uparrow \\ B\uparrow \\ A\downarrow \\ B\downarrow \end{matrix}$$

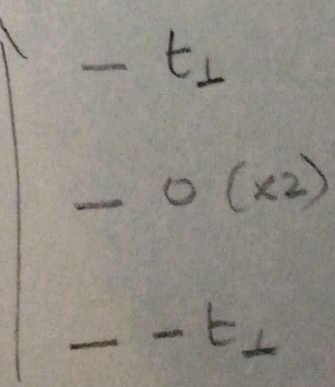
with $\pi = \hbar v_F(\xi q_x + i q_y)$ $\xi = \pm 1$ valley index for K/K'

- U is the energy difference between ↑ layer and ↓ layer - can be tuned with perpendicular electric field

① first $U = 0$ - no electric field

K point $q_x = q_y = 0$ $\pi = 0$

$$H_K = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & t_\perp & 0 \\ 0 & t_\perp & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \xrightarrow{\text{diagonalize}}$$



② $U=0$ $|\pi| \ll t_\perp$

$$H_k = t_\perp \begin{pmatrix} \sigma_x & 0 \\ 0 & 0 \end{pmatrix} + \underbrace{\begin{pmatrix} 0 & V^+ \\ V & 0 \end{pmatrix}}_{\text{perturbat°}} \qquad V = \begin{pmatrix} \pi^+ & 0 \\ 0 & \pi \end{pmatrix}$$

second order for the low-energy subspace

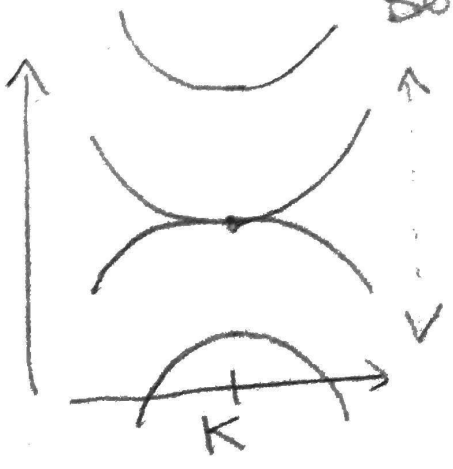
$$h = -V (t_\perp \sigma_x)^{-1} V^+ = \begin{pmatrix} 0 & -\pi^{+2}/t_\perp \\ -\pi^2/t_\perp & 0 \end{pmatrix}$$

diagonalizat°

$$\boxed{\varepsilon_\pm = \pm \frac{(\hbar v_F)^2}{t_\perp} q^2}$$

→ quadratic band touching $\qquad \psi_\pm = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm e^{2i\theta_k} \end{pmatrix}$

Berry phase of $2\pi = \pi + \pi$



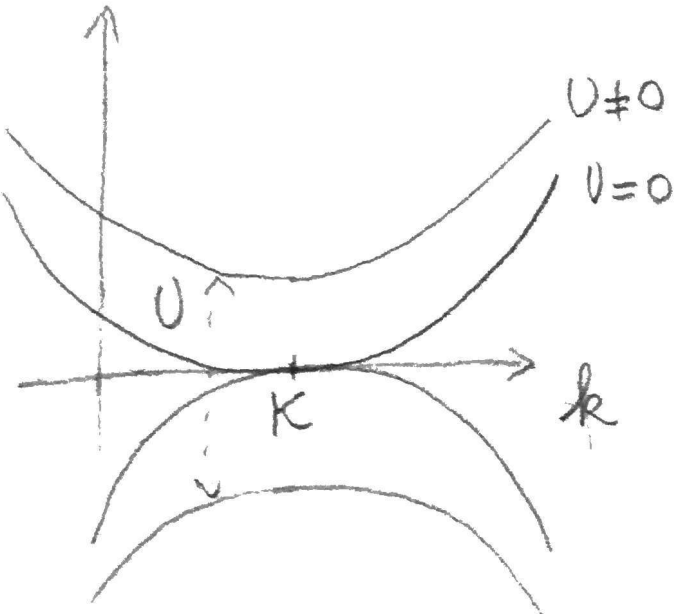
semi-metal

③ $U \neq 0$, low-energy subspace

$$h = \begin{pmatrix} U/2 & -\pi^{+2}/t_\perp \\ -\pi^2/t_\perp & -U/2 \end{pmatrix} \begin{matrix} A\uparrow \\ B\downarrow \end{matrix}$$

diagonalizat°

$$\varepsilon_{\pm} = \pm \sqrt{\frac{U^2}{4} + \frac{(\hbar v_F)^4}{t_\perp^2} q^4} \qquad k = K + q$$



gap opening - and controlled - by the perpendicular electric field

C/ Hints from group theory

Principle: the microscopic model is governed by symmetries constraining the band spectrum and the shape of wavefunctions.

Definitions

Space Group: symmetries of a crystalline lattice.
Combination of lattice translation (Bravais lattice)

with point group operation such as reflexion, rotation, improper rotation + screw axis and glide plane symmetries

In total 230 different space group (in 3D) out of 32 point group symmetries - crystallographic - which leave a point invariant.

Each crystalline structure has a space group and crystallographic point group applying to each high-symmetry point in the Brillouin zone - and high-symmetry lines.

Exemple: (see also slides...)

single-layer graphene	Γ	K(K')	M
$P6/mmm\ (D_{6h}^1)$	D_{6h}	D_{3h}	D_{2h}

the Hamiltonian is symmetric under a group operation g, ie

$$D_k(g)\, H_k\, D_k(g^{-1}) = H(gk)$$

$D_k(g)$ is the representat° matrix of g.

At high-symmetry points such $gk^* = k^* + G$ (reciproqual vector)

Then $D_{k^*}(g) H_{k^*} D_{k^*}(g)^{-1} = H_{k^*}$

$D_{k^*}(g)$ commutes with the Hamiltonian (for graphene at the K pt, g can be a C_3 rotat°, a σ_v reflection, rotc. forming the D_{3h} point group):

consequence, each energy level at k^*, possibly degenerate, provides a representation of the point group.

We continue with the example of graphene

Character table for D_{3h} (K pt)

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	−1	1	1	−1
A_1''	1	1	1	−1	−1	−1
A_2''	1	1	−1	−1	−1	1
E'	2	−1	0	2	−1	0
E''	2	−1	0	−2	1	0

(symmetry operation)

(size of the (non-) degenerate subspace)

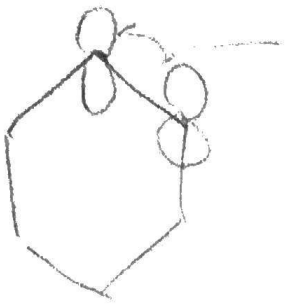
6 different representation

In graphene $\underbrace{1s^2}_{\text{low energy}}$ $\underbrace{2s^2\,2p^2}_{\text{4 orbitals}}$ $\underbrace{s, p_x, p_y, p_z}_{\text{hybridize}}$

σ_h : reflexion around the graphene layer

p_z : $\sigma_h = -1$ vs p_x / p_y : $\sigma_h = +1$

relevant close to Fermi-energy : form the π-bands



only A_1'', A_2'' and E'' appear for p_z orbitals

This symmetry brings an additional layer of protection to the K Dirac point - same for K'.

The DP is two-fold degenerate and represented by E''. Any perturbation respecting the graphene space group D_{6h}^1 cannot open a gap at K otherwise the character of C_3 would change abruptly from -1 (E'') to $+1$ (A_1'' or A_2'').

Note: the character is the trace of the matrix representing the symmetry operation.

D] Symmetry representation close to K

$D_{3h} = D_3 \times \sigma_h$ ← -1 for p_z orbitals

$$T_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad T_2 = \begin{pmatrix} 0 & \omega \\ \omega^* & 0 \end{pmatrix} \quad T_3 = \begin{pmatrix} 0 & \omega^* \\ \omega & 0 \end{pmatrix}$$

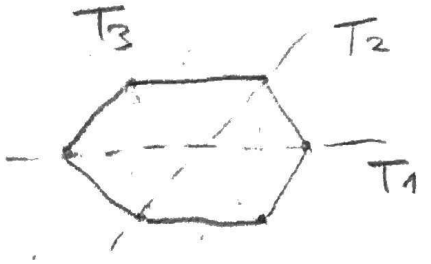
$$R = \begin{pmatrix} \omega & 0 \\ 0 & \omega^* \end{pmatrix} \qquad \omega = e^{2i\pi/3}$$

$\mathbb{1}, T_1, T_2, T_3, R, R^2$ form a representation of D_3
(→ see Cayley table on slides)

$T_1 T_j = 0 \qquad T_1 R = 2\cos(2\pi/3) = -1$

→ representat° E''

T_j corresponds to a vertical plane reflection



$R \vec{\sigma} R^{-1}$ = Rotation of angle $-\frac{2\pi}{3}$ of $\begin{pmatrix} \sigma_x \\ \sigma_y \end{pmatrix}$

$H_k = \hbar v_F \vec{q} \cdot \vec{\sigma}$

low-energy form respects the symmetry

$D(g) H_k D(g)^{-1} = H_{gk}$

with $D(g) = T_j, R, R^2$

Remark: a gap term such as $\Delta\sigma_z$

$T_1 \sigma_z T_1 = -\sigma_z$ → not invariant under T_j

but remains invariant under C_3 $\quad R\sigma_z R^{-1} = \sigma_z$

→ this is the case of BN (lower symmetry group C_3 at K pt)