21/09/19

Lectures on 2D materials

III Transition metal dichalcogenides

Outline

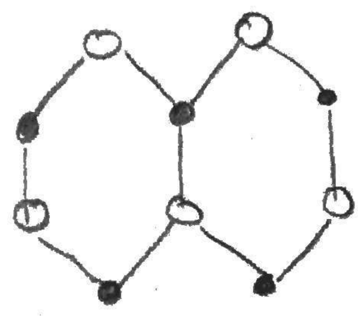
A] Group symmetry analysis B] $k \cdot p$ Hamiltonian

C] Valley and spin Hall effects

We will consider MX_2 TMD with $M = Mo, W$
$X = S, Se$; (see slides), more specifically MoS_2

Lattice structure (see slides) one mono-layer of Mo atoms - in a triangular lattice, sandwiched between two triangular layers of S atoms.

From to top



o S atoms - top and bottom layers
• Mo atoms

Bulk MoS_2 has D^4_{6h} ($P6_3/mmc$) space group symmetry - including inversion symmetry.

Monolayer has D^1_{3h} or $P\bar{6}m2$, this is the same space group symmetry as three-layer graphene in a ABA Bernal stacking arrangement.

Ref. PRB 79, 125426

Space group	Γ	$K(K')$	M
D^1_{3h}	D_{3h}	C_{3h}	C_{2v}

main orbitals close to the Fermi energy:

1) 5d orbitals of Mo, $d_{xy}, d_{x^2-y^2}, d_{xz}, d_{yz}, d_{3z^2-r^2}$

2) 3p orbitals of S, $p_{x/y}, p_z$

p orbital play only a subleading role in the band structure, we shall focus on d orbitals.

Band spectrum: see slides

Character table C_{3h} (see slides)

	E	C_3	C_3^2	σ_h
A'	1	1	1	1
E'	1	ω	ω^2	1
	1	ω^2	ω	1

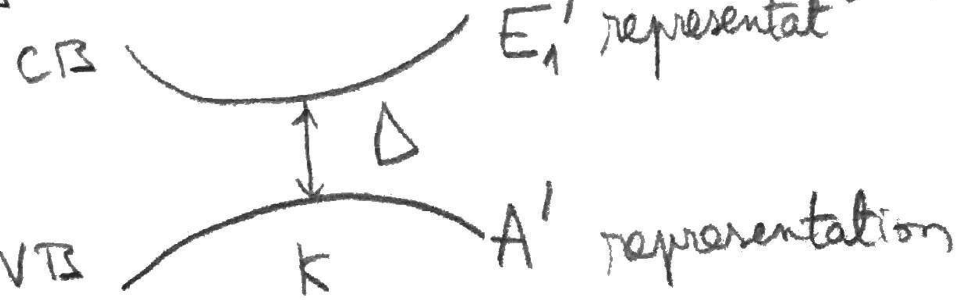
Simplified

$\omega = e^{2i\pi/3}$

only the even sector matters close to the K (K') point

σ_h is the horizontal plane (Mo atoms) reflection symmetry

DFT calculat° show (absence of spin-orbit) the following structure close to K (K')



- CB has 82% of $d_{3z^2-r^2}$, 12% of $p_x - ip_y$ (p_x+ip_y for K')
- VB has 76% of $d_{x^2-y^2} + i d_{xy}$ ($d_{x^2-y^2} - i d_{xy}$ for K'), 20% of $p_x + ip_y$ ($p_x - ip_y$ for K')

Proof that $d_{3z^2-r^2}$ has the correct symmetry

$$\psi^{\eta}_{l,m}(k,r) = \sum_{n} e^{ik(R_n+t_\eta)}\, Y_l^m\left[r-(R_n+t_\eta)\right]$$

$t_\eta = 0$ for S atoms
$= (0,-1)$ for Mo atoms

quantum numbers l, m for the orbital

R_n: positions of the Bravais triangular lattice points

for $d_{3z^2-r^2}$: $l = 2$, $m = 0$ (invariance by rotation around z-axis)

$$\psi^{\eta}_{2,0}(k, \omega r) = \sum_{n} e^{ik(R_n+t_\eta)}\, Y_2^0\left[\omega r-(R_n-t_\eta)\right]$$

$\omega = e^{2i\pi/3}$

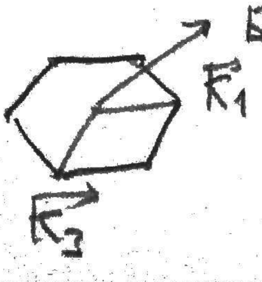
the lattice sites are invariant upon a ω ($2\pi/3$) rotat°

$$\psi^{\eta}_{2,0}(k,\omega r) = \sum_{n} e^{ik\{\omega(R_n+t_\eta)\}}\, \underbrace{Y_2^0\left[\omega\{r-(R_n+t_\eta)\}\right]}$$

$$= Y_2^0\left[r-(R_n+t_\eta)\right]$$

$$= \sum_{n} e^{i(\omega^* k).(R_n+t_\eta)}\, Y_2^0\left[r-(R_n+t_\eta)\right]$$

- we consider $k = K_1$, then $\omega^* K_1 = K_3 = K_1 - b_1$



$$e^{-i\vec{K}_1 \cdot \vec{t}_{Mo}} = e^{2i\pi/3}$$

$$\Psi_{2,0}^{Mo}(K, \omega r) = e^{2i\pi/3}\, \Psi_{2,0}^{Mo}(K, r)$$

$\longrightarrow E_1'$ representat° of C_{3h}.

Same way, we prove

$$\Psi_{2,2}^{Mo}(K, \omega r) = e^{2i\pi/3} \times \left(e^{2i\pi/3}\right)^2 \Psi_{2,2}^{Mo}(K, r)$$

consistent with A' representation of C_{3h}.

B/ k.p Hamiltonian

We want to describe the vicinity of $K(K')$ more precisely by using a k p approach $\rightarrow$ $H_p = \frac{\hbar}{m} \vec{q} \cdot \vec{p}$ $\quad k = K + q$

$$H_p = \frac{\hbar}{2m}\left(q_+ \cdot \hat{p}_- + q_- \cdot \hat{p}_+\right) \qquad q_{+/-} = q_x \pm i q_y$$

$$\hat{p}_{+/-} = \hat{p}_x \pm i \hat{p}_y$$

Effectively, this is a perturbative approach describing the kinetic energy close to $K(K')$.

We keep only the subspace with the two orbitals :

$C_3 |A\rangle = \underbrace{|A\rangle}_{\text{valence band}} \qquad C_3 |E_1\rangle = \underbrace{\omega |E_1\rangle}_{\text{conduction band}}$

$$\langle A | H_p | E_1 \rangle \longrightarrow \langle A | \hat{p}_{+/-} | E_1 \rangle$$

$$= \underbrace{\langle A | C_3^+}_{\langle A|} \underbrace{C_3\, \hat{p}_{+/-}\, C_3^+}_{\hat{p}_{+/-}\, e^{\mp i 2\pi/3}} \underbrace{C_3 | E_1 \rangle}_{\omega |E_1\rangle}$$

$$= \langle A| \hat{p}_{+/-} |E_1\rangle \, \omega \, e^{\mp i 2\pi/3}$$

$\neq 0$ for $\hat{p}_+$

$= 0$ for $\hat{p}_-$

<u>Result:</u>
restricted to $|A\rangle, |E_1\rangle$

$$H_p = \begin{bmatrix} \varepsilon_v & \hbar v_F (q_x - i q_y) \\ \hbar v_F (q_x + i q_y) & \varepsilon_c \end{bmatrix}$$

$$\boxed{H_p = \hbar v_F \, \vec{q}\,\vec{\sigma} + \frac{\Delta}{2}\sigma_z \qquad \Delta = \varepsilon_c - \varepsilon_v}$$

PRL 108, 196802 (2012)

$q_y \sigma_y + \tau\, q_x \sigma_x$ when valley is taken into account

$\tau = \pm 1$ for $K (K')$

We now include spin-orbit - left aside so far -
At the microscopic level $H_{so} = \dfrac{\hbar}{4 m^2 c^2} \dfrac{1}{r} \dfrac{d V(r)}{dr} \vec{L}.\vec{S}$

$\vec{S}$ is the electron spin operator, $\vec{L}$ its angular momentum.

$\sigma_h L_{+/-} \sigma_h = -L_{+/-} \rightarrow$ horizontal plane symmetry reverses sign of $L_{+/-}$

$L_{+/-} = L_x \pm i L_y$

induces no coupling between $A'_1 E'_1$ which are both even under σ_h. $\langle E'_1 | L_z | E'_1 \rangle = 0$ zero angular momentum

$\langle A' | L_z | A' \rangle \neq 0$

$$= \langle A | \hat{p}_{+/-} | E_1 \rangle \, \omega \, e^{\mp i 2\pi/3}$$

$\neq 0$ for $\hat{p}_+$

$= 0$ for $\hat{p}_-$

Result: restricted to $|A\rangle, |E_1\rangle$

$$H_p = \begin{bmatrix} \varepsilon_v & \hbar v_F (q_x - i q_y) \\ \hbar v_F (q_x + i q_y) & \varepsilon_c \end{bmatrix}$$

$$\boxed{H_p = \hbar v_F \, \vec{q} \cdot \vec{\sigma} + \frac{\Delta}{2} \sigma_z \qquad \Delta = \varepsilon_c - \varepsilon_v}$$

PRL 108, 196802 (2012)

$q_y \sigma_y + \tau q_x \sigma_x$ when valley is taken into account

$\tau = \pm 1$ for $K (K')$

We now include spin-orbit – left aside so far –

At the microscopic level $H_{SO} = \dfrac{\hbar}{4 m^2 c^2} \dfrac{1}{r} \dfrac{dV(r)}{dr} \vec{L} \cdot \vec{S}$

$\vec{S}$ is the electron spin operator, $\vec{L}$ its angular momentum.

$\sigma_h L_{+/-} \sigma_h = - L_{+/-} \rightarrow$ horizontal plane symmetry reverses sign of $L_{+/-}$

$L_{+/-} = L_x \pm i L_y$

induces no coupling between $A'_1 E'_1$ which are both even under σ_h.

$\langle E'_1 | L_z | E'_1 \rangle = 0$ zero angular momentum

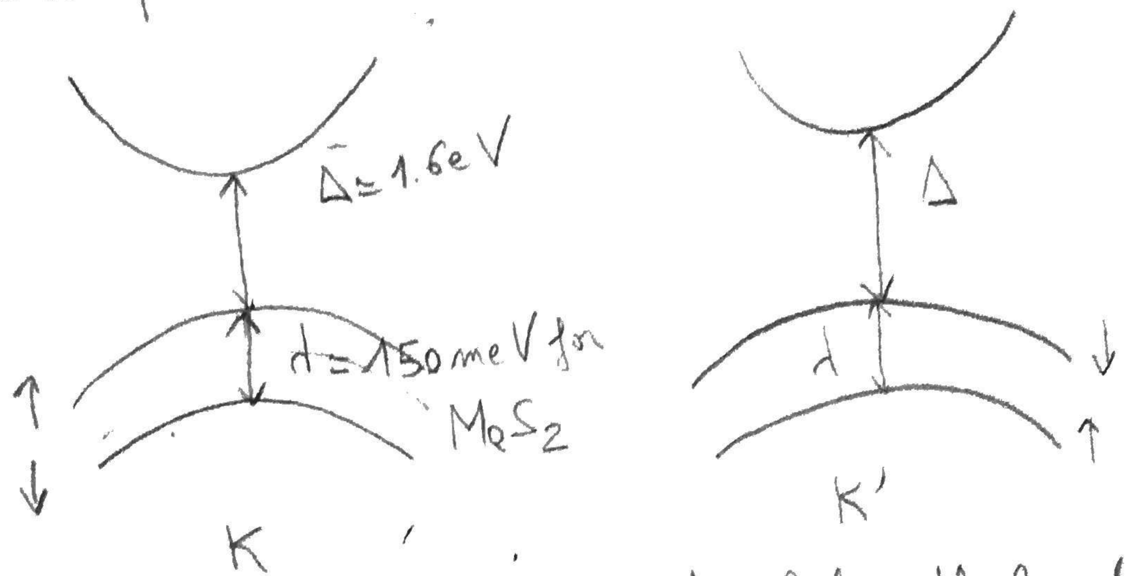
$\langle A'_1 | L_z | A'_1 \rangle \neq 0$

so the total Hamiltonian including spin-orbit is

$$H = \hbar v_F (q_x \sigma_x \tau + q_y \sigma_y) + \frac{\Delta}{2}\sigma_z + \lambda \tau \frac{1-\sigma_z}{2} s_z$$

= 1 for VB A'
= 0 for CB E₁'

Band spectrum



- valley and spin are sort of entangled in the band structure

C| Valley and spin Hall effects

① Circular dichroism: differential spectroscopic response between left and right circularly polarized light

$$P_{x/y} = \langle \psi_c(k) | \underbrace{\frac{m}{\hbar}\frac{\partial H}{\partial k_{x/y}}}_{\hat{P}_{x/y}} | \psi_v(k) \rangle$$

$$|P_\pm(k)|^2 = m v_F \left(1 \pm \tau \frac{\Delta'}{(\Delta'^2 + 4\hbar^2 v_F^2 q)^{1/2}}\right)$$

$$\Delta' = \Delta - \tau s_z \lambda$$

for $\hbar v_F q \ll \Delta'$: σ^+ couples only at K

σ^- ———— K'

Experimental observation: Zeng, Cui et al. Arxiv 1202.1592

[Nature Nanot. 7, 490 (2012)]

(2) Hall conductivity

semiclassical dynamics in a given band n

$$\hbar \dot{k} = -eE$$

$$\dot{r} = \frac{\partial E_n}{\partial k} - \underbrace{\dot{k} \times \Omega_n(k)}$$

velocity orthogonal to the applied electrical field

→ Hall effect: charge accumulation normal to applied bias

quantum description,

$$\sigma_{xy} = \frac{e^2}{h} \int dk\, f(k)\, \Omega(k)$$

Fermi function

Berry curvature

in general
- TRS $\Omega_k = -\Omega_{-k}$
- Inversion symmetry $\Omega_k = \Omega_{-k}$

in presence of both $\Omega_k = 0$: no Hall effect

in TMD, inversion symmetry is broken

$$\Omega_n(k) = \hat{z} \cdot \nabla_k \times \langle u_n(k) | \frac{\nabla_k}{i} | u_n(k) \rangle$$

(also defined through the Wilson loop)

Calculation goes: (in the conduction band)

$$\Omega(k) = \tau \frac{2(\hbar v_F)^2 \Delta'}{\left[\Delta'^2 + 4(\hbar v_F k)^2\right]^{3/2}}$$

$$= \tau \Omega_0(k)$$

differs in sign for the two valleys so vanishes when summed over valley (due to TRS)

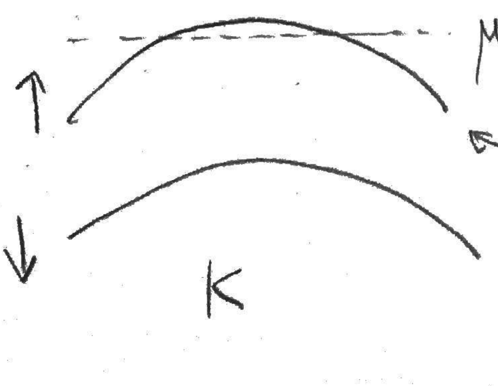
$$\left| \begin{array}{l} CB \longrightarrow VB \quad \text{also} \\ \Omega \longrightarrow -\Omega \end{array} \right.$$

<u>Definitions:</u>

Valley Hall conductivity

$$\sigma_v = \frac{2e^2}{\hbar} \int dk \left\{ f_\uparrow(k) \Omega_\uparrow(k) + f_\downarrow(k) \Omega_\downarrow(k) \right\}$$

sum is restricted to the vicinity of K



μ chemical potential

energy $\varepsilon_k \simeq -\frac{\Delta'}{2} - \frac{(\hbar v_F k)^2}{\Delta'}$

hole doping $\boxed{\frac{(\hbar v_F k)^2}{\Delta'} \leq \mu}$

$$\sigma_v = \frac{2e^2}{\hbar} 2\pi \int_0^{|\varepsilon| < \mu} \frac{dk\, k}{(2\pi)^2} \frac{2(\hbar v_F)^2 \Delta'}{\Delta'^3}$$

$\mu \ll \Delta'$

here $\Delta' = \Delta - \lambda$

$$\boxed{\sigma_v = \frac{e^2}{\hbar} \frac{\mu}{\pi(\Delta - \lambda)}}$$

electrons in each valley are deflected in opposite directions

also spin polarisat°

$$\boxed{\sigma_s = \frac{e}{2} \frac{\mu}{(\Delta - \lambda)\pi}}$$

holes in valley K have spin ↑ move opposite to holes with spin ↓ in valley K'

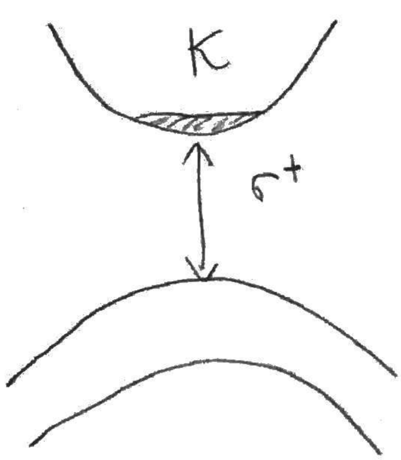
→ spin differential accumulation perpendicular to bias voltage

measurement via indirect transport probe (of Hall valley effect)

see Nat. comm. 10, 611 (2019)
Wu, KT Law, Zhang, Wang

(3) generation of valley Hall effect by selective valley excitation

see experiment by Mak, ..., MacEuen, Science 344 1489 (2014)



light σ^+
generates
out-of-equilibrium valley
polarization distribution
breaks time-reversal symmetry

leads to Hall current

$$|\sigma_H| = \frac{e^2}{h}\,\frac{\hbar^2\pi}{2m}\,\frac{n_K - n_{K'}}{\Delta}$$