Chirality-induced spin selectivity: Open questions and challenges

Bart van Wees, Xu Yang and Caspar van der Wal

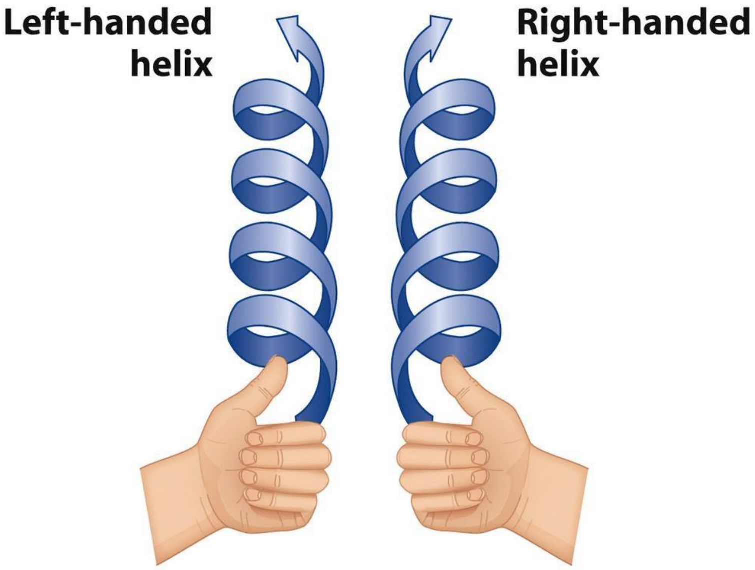
13-1-2021

X. Yang et al., Spin dependent electron transmission model for chiral molecules in mesoscopic devices, Phys. Rev. B99, 024418 (2019)
X. Yang et al., Detecting chirality in two-terminal electronic nanodevices, Nano lett. 20, 8, 6148-6154 (2020)

Overview

- Introduction chirality and “false” chirality
- Electronic/spintronic transport experiments of CISS
- Theoretical description of MR in two-terminal ferromagnet-chiral devices (linear regime and reciprocity)
- Non-linear regime
- Chiral spin valves
- Multiterminal devices
- Open questions (chirality and magnetism, chirality control of chemical synthesis and self assembly)

Chirality in nature



Box 4-1
Lehninger Principles of Biochemistry, Fifth Edition
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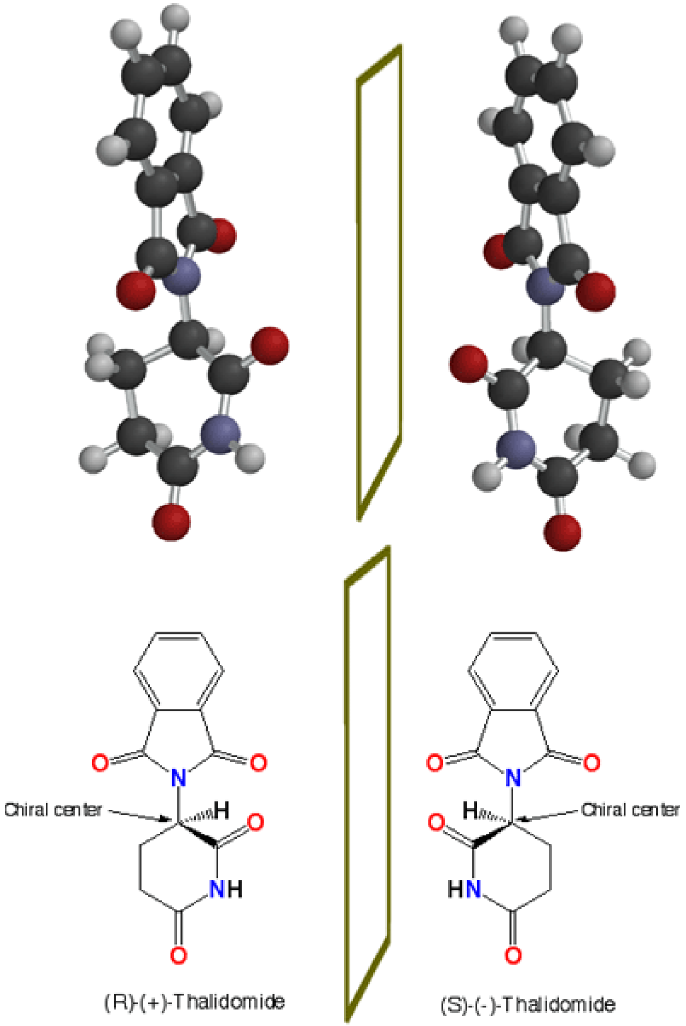
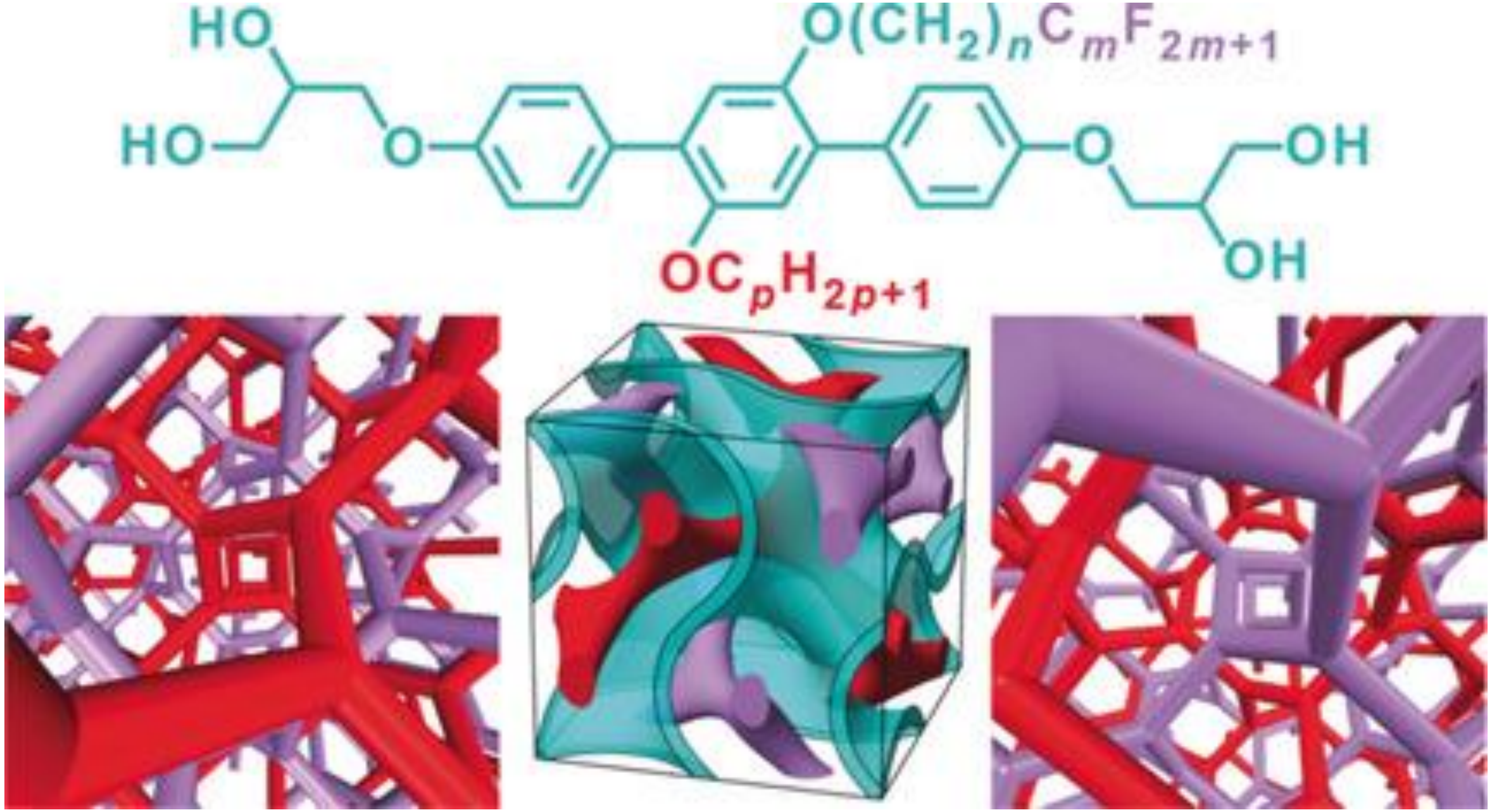
Thalidomide

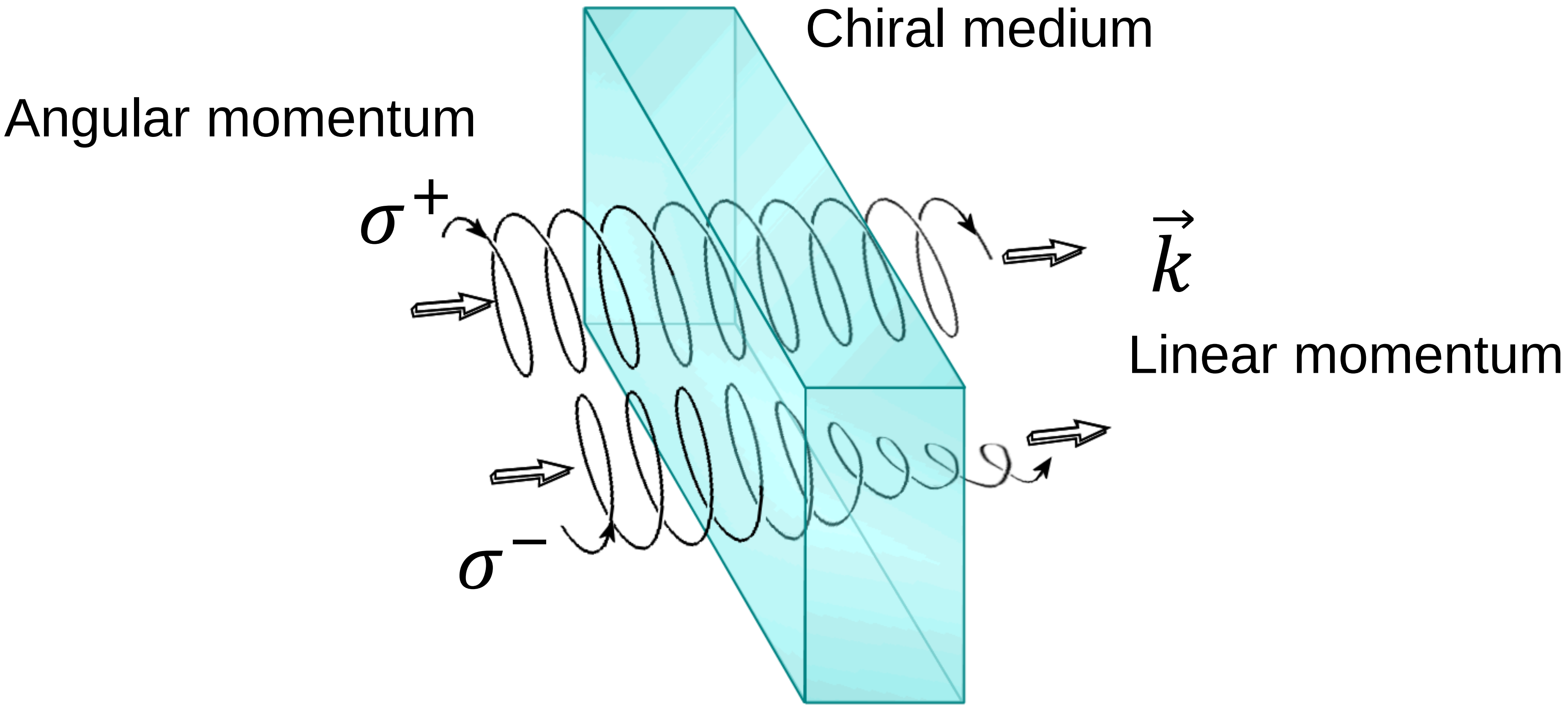


Chirality in gyroids: chirality is a scalar

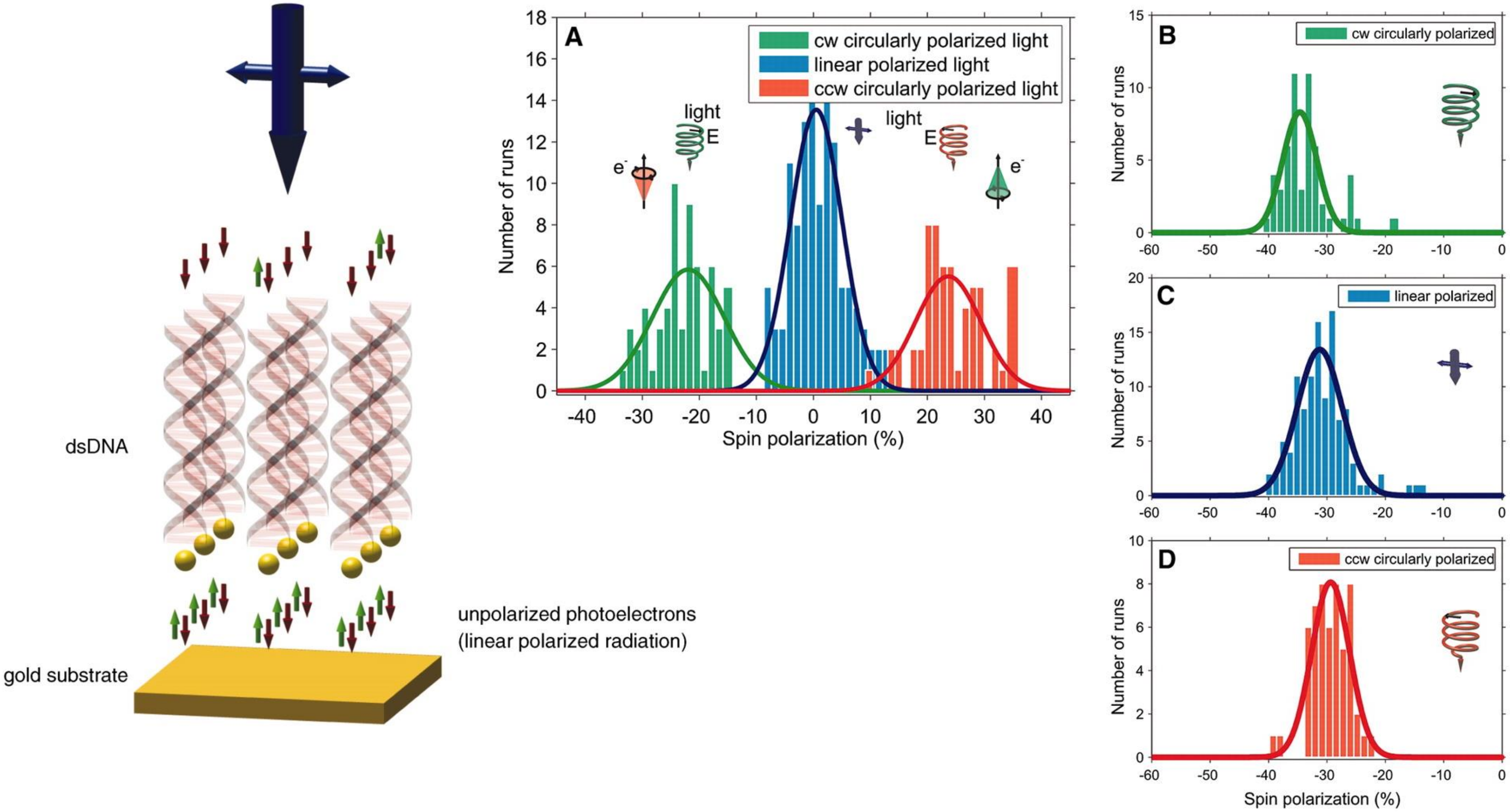


Chiral optical effects

- Optics: optical rotation and circular dichroism



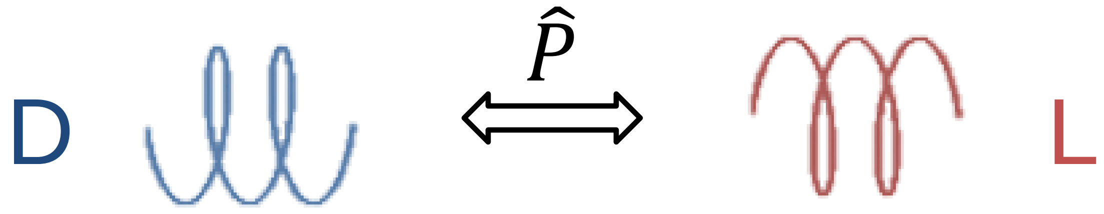
Chirality-induced spin selectivity (CISS)



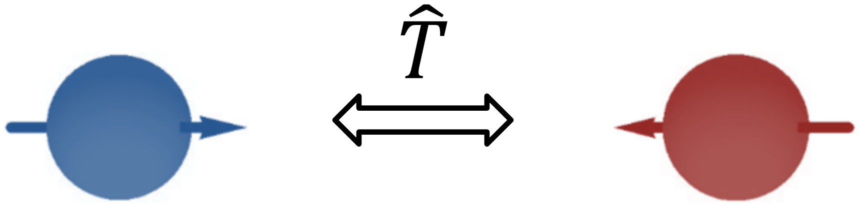
Göhler et al. *Science,* 331, 895 (2011)

Fundamental symmetry operations

- Space inversion

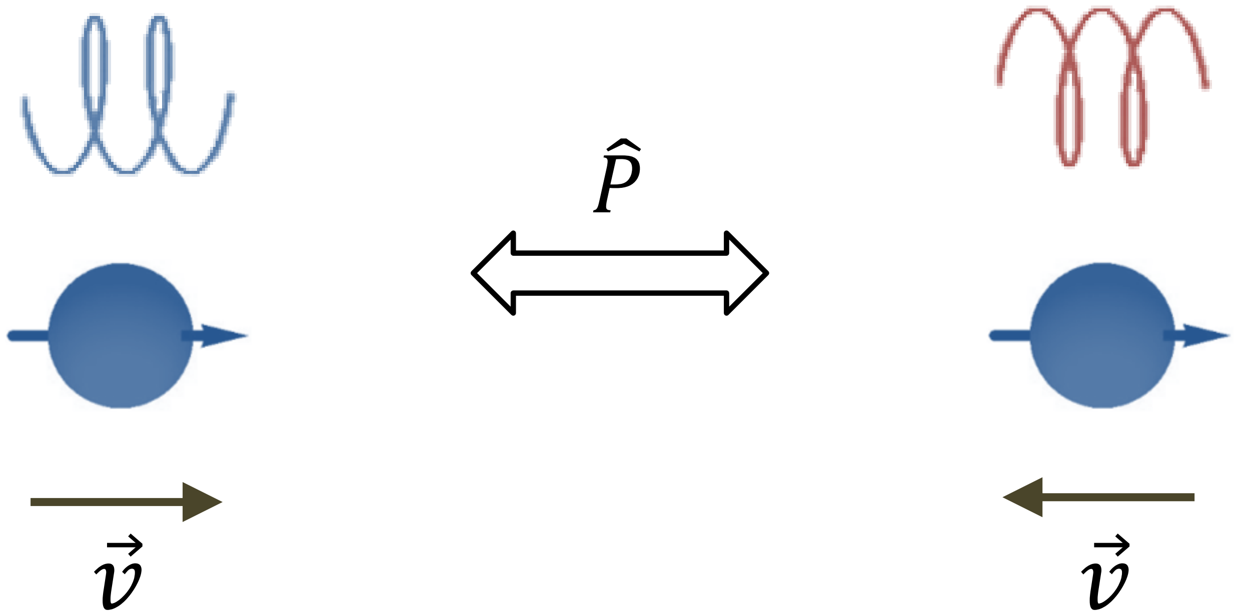


- Time reversal



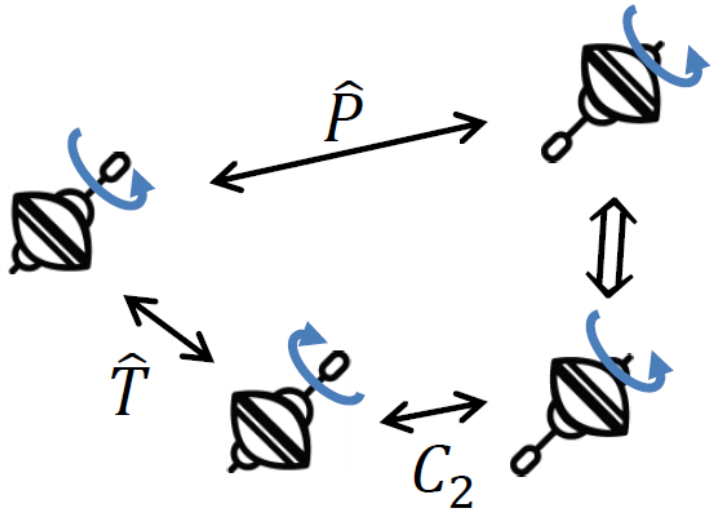
For electromagnetism: physical processes are invariant under these fundamental symmetries.

What is CISS?

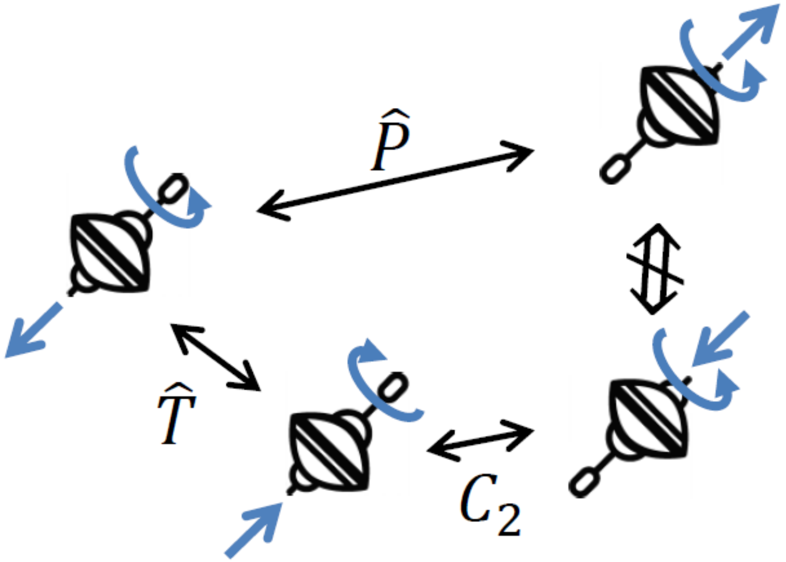


Chirality distinguishes parallel vs. antiparallel configurations of angular and linear momenta!

True and false chirality



False chirality



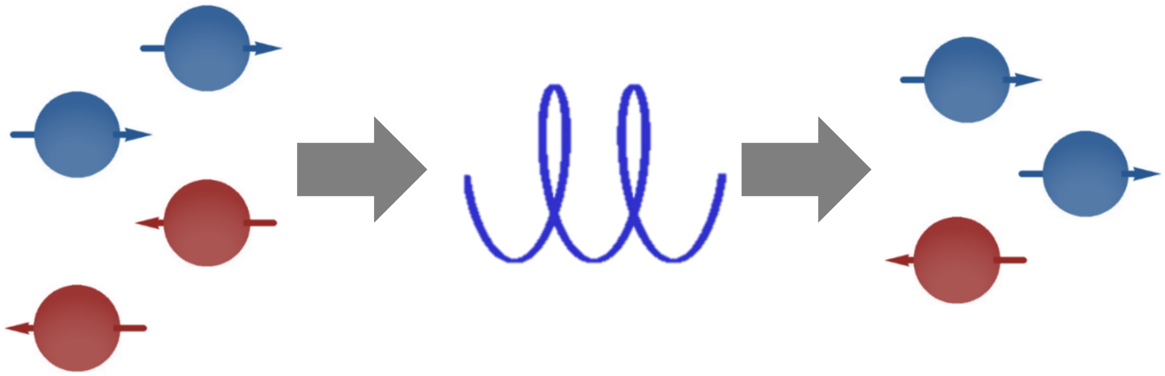
True chirality

(Moving) electron spin helicity is truly chiral, it can distinguish chiral enantiomers.
Magnetic field is falsely chiral, it cannot distinguish chiral enantiomers.
Combination of magnetic and electric field is falsely chiral

Barron, *J. Am. Chem. Soc.* **108,** 5539 (1986)
Barron, *Science* **266**, 1491 (1994)

Chirality-induced spin selectivity (CISS)

1. A symmetry discussion

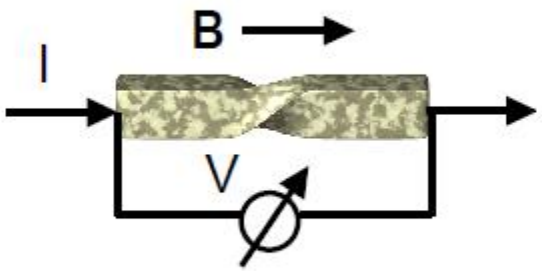


2. Electrical detection

Charge current ⟺ Spin currents

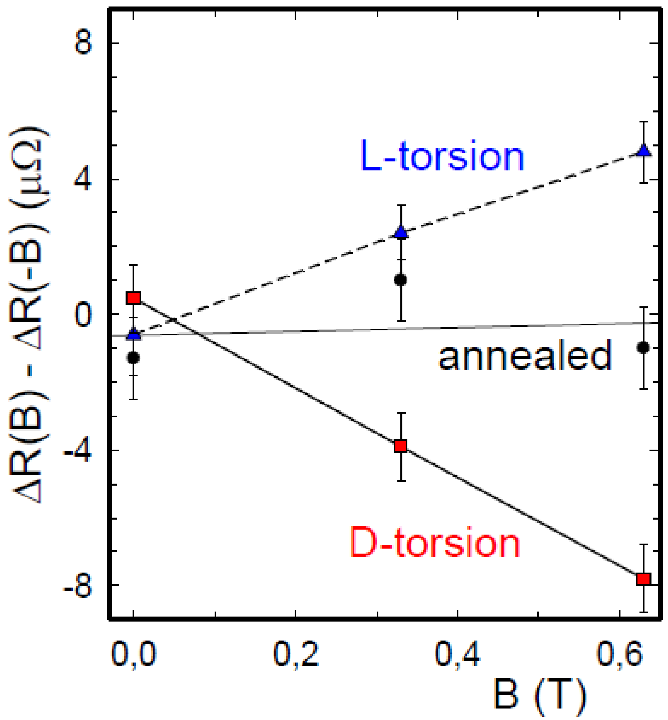
CISS vs magneto chiral effects

- Electron transport: electrical magneto-chiral effect



$$R(\boldsymbol{B}) = R_0 + R_1^{D,L}\, \boldsymbol{I}\cdot\boldsymbol{B}$$

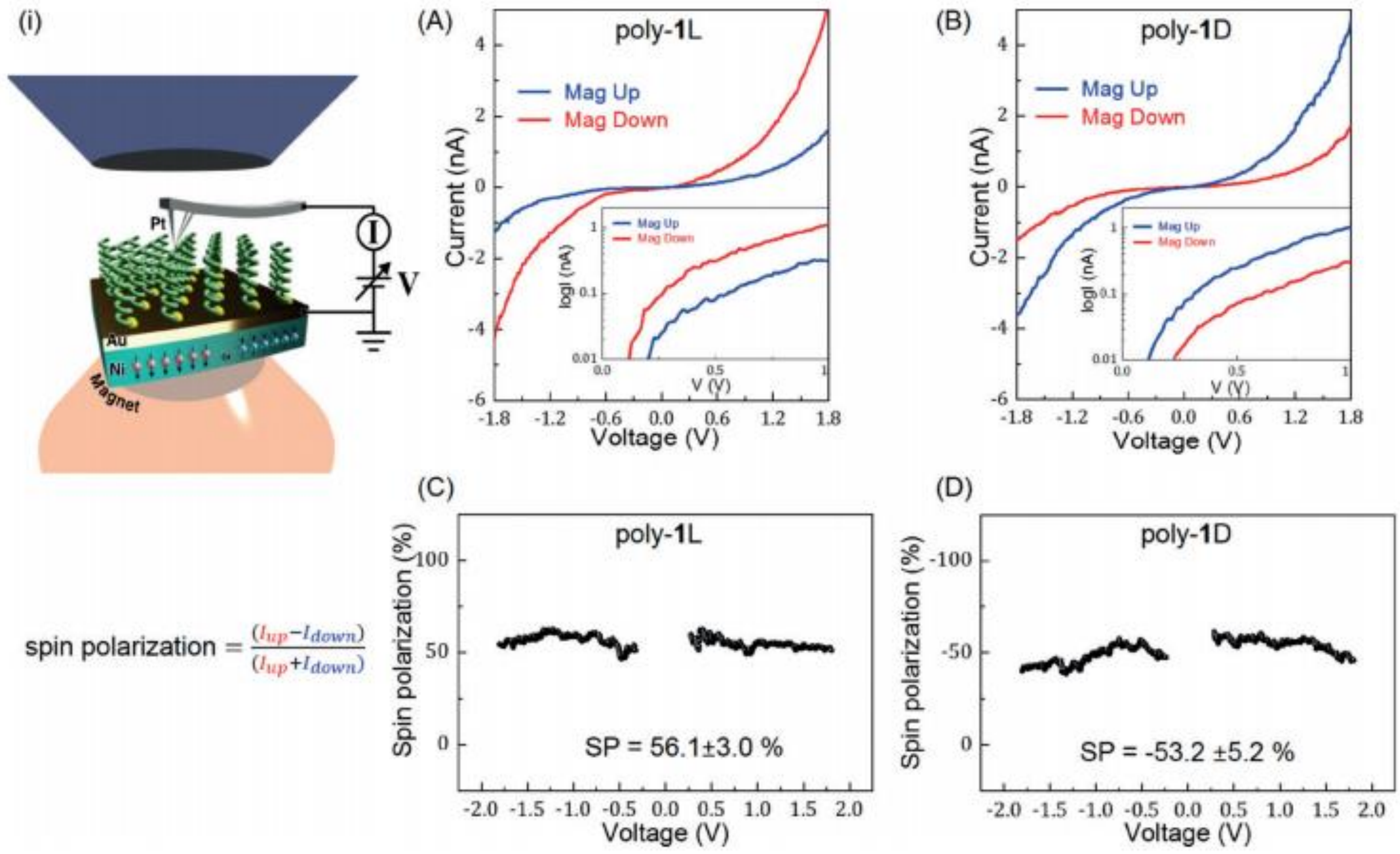
$$\mathrm{MR} = \frac{R(\boldsymbol{B}) - R(-\boldsymbol{B})}{R(\boldsymbol{B}) + R(-\boldsymbol{B})} \propto R_1^{D,L}\, \boldsymbol{I}\cdot\boldsymbol{B}$$



MR linear in $\boldsymbol{I}$ and $\boldsymbol{B}$, changes sign with chirality.

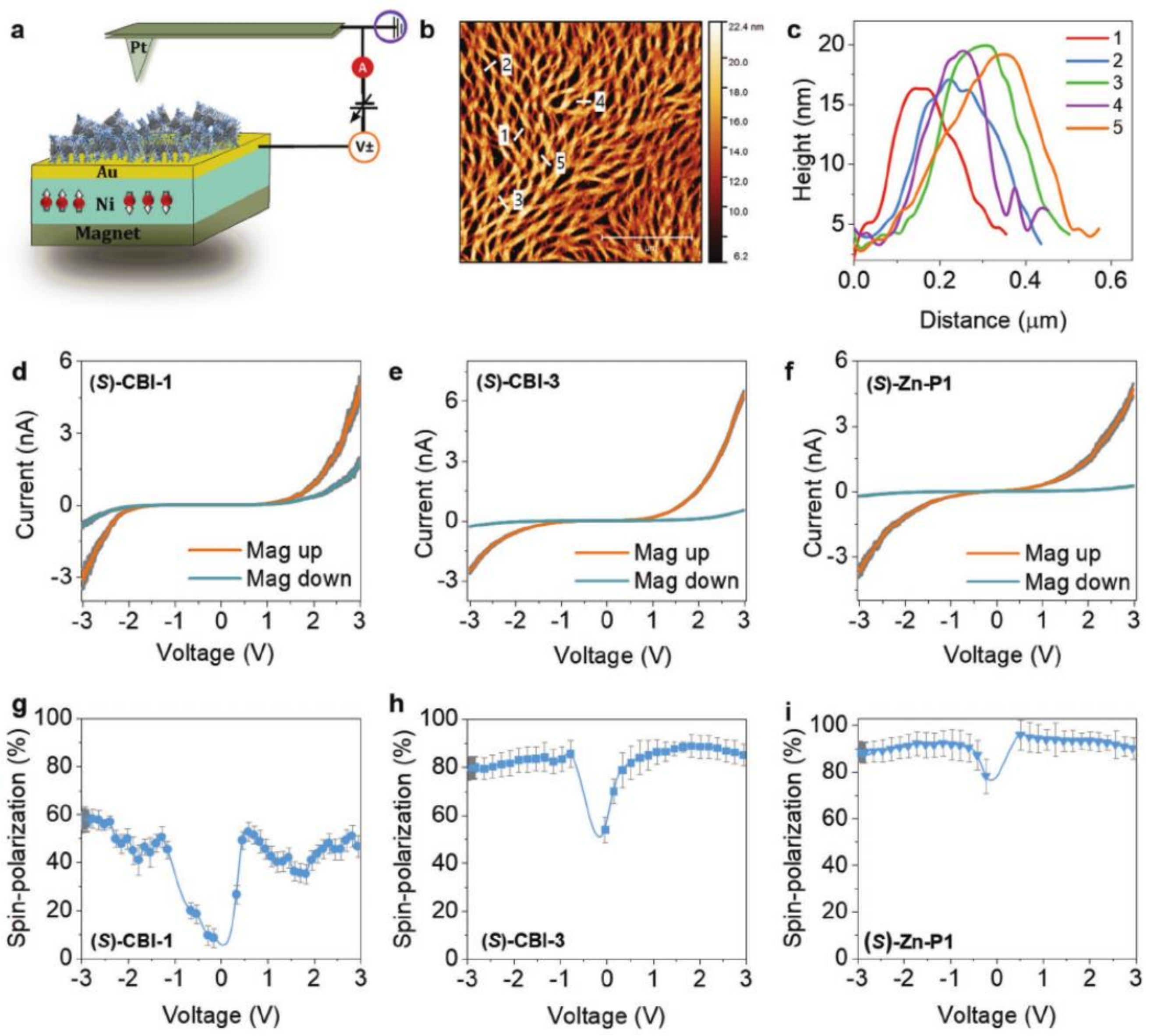
Rikken et al. *Phys. Rev. Lett.* **87**, 236602 (2001)

Large MR ratios in unconventional geometries



Angew. Chem. Int. Ed.
2020, 59, 14671– 14676

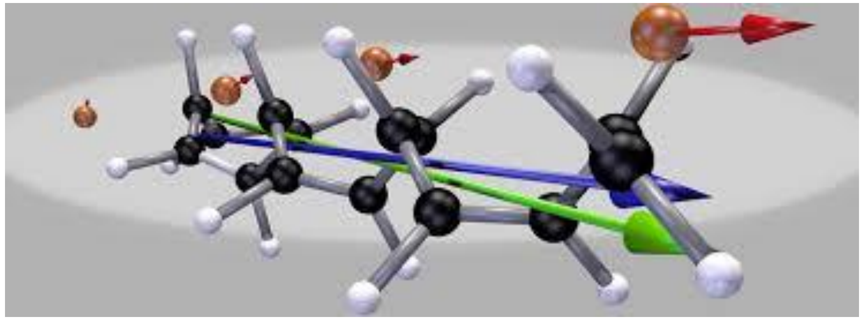
Very large MR ratios



Adv. Mater. 2020, 32, 1904965

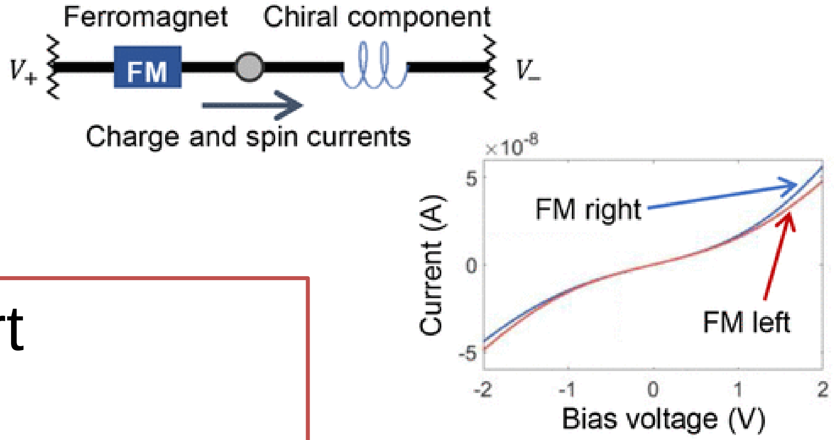
Two questions

1. How is CISS **generated** within a chiral (molecular) structure?



2. How can CISS be **detected** in experiments?

2T electronic charge transport experiments.



Dalum et al. *Nano Lett.* **19**, 5253−5259 (2019)
Liu et al. *arXiv:2008.08881* (2020)

Yang et al. *Phys. Rev. B* **99,** 024418 (2019)
Yang et al. *Nano Lett.* **20**, 8, 6148–6154 (2020)

Reciprocity theorem for electronic measurements

4 Terminal (e.g. Hall effect):

$$R_{12,34}(H) = R_{34,12}(-H)$$

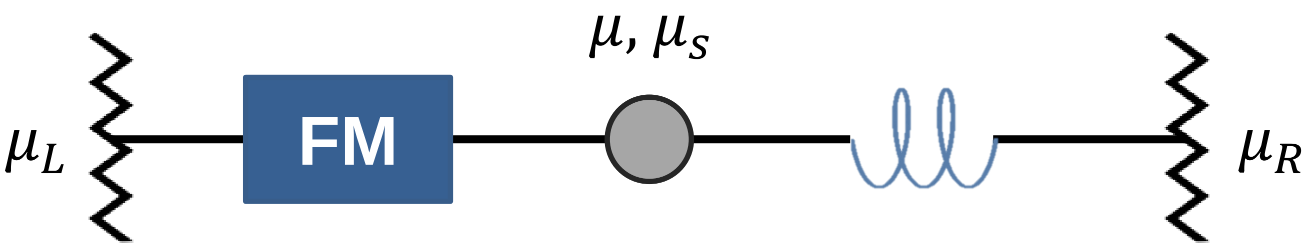
2 Terminal:

$$R_{2T}(H) = R_{2T}(-H)$$

Magnetic field/magnetization reversal cannot change 2T conductance.

Buttiker, *IBM J. Res. Dev.* **32,** 317 (1988)

CISS as 2T MR?



Two processes:

Spin injection by CISS, spin detection by FM.

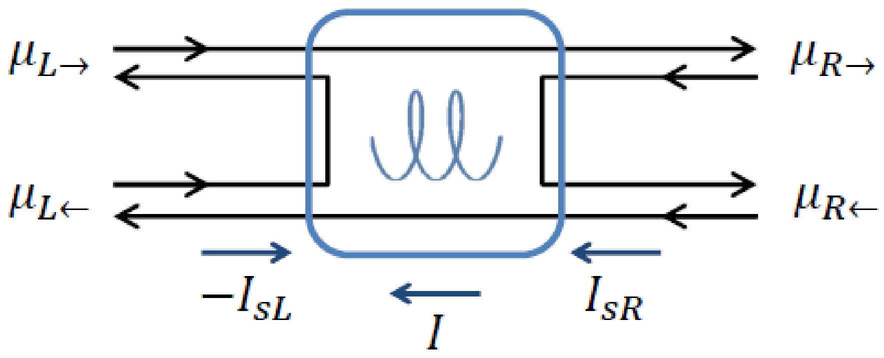
Spin injection by FM, spin detection by CISS.

Onsager reciprocity:

The two processes exactly compensate in the linear response regime.

<u>No MR in linear response</u>.

Spin transmission/reflection matrices

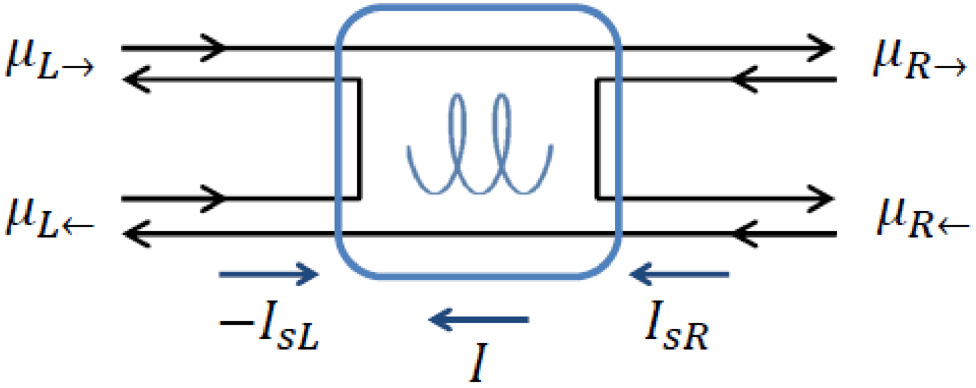


Spin-flip reflection always accompanies spin-selective transmission.
Landauer formula must be extended (because of non conserved spins)

$$\mathbb{T}_{\triangleright} = \begin{pmatrix} t_{\rightarrow\rightarrow} & t_{\leftarrow\rightarrow} \\ t_{\rightarrow\leftarrow} & t_{\leftarrow\leftarrow} \end{pmatrix}, \quad \mathbb{R}_{\triangleright} = \begin{pmatrix} r_{\rightarrow\rightarrow} & r_{\leftarrow\rightarrow} \\ r_{\rightarrow\leftarrow} & r_{\leftarrow\leftarrow} \end{pmatrix}$$

$$\begin{pmatrix} I \\ -I_{sL} \\ I_{sR} \end{pmatrix} = -\frac{Ne}{h} \begin{pmatrix} t & s & s \\ P_r r & \gamma_r & \gamma_t \\ P_t t & \gamma_t & \gamma_r \end{pmatrix} \begin{pmatrix} \mu_L - \mu_R \\ \mu_{sL} \\ \mu_{sR} \end{pmatrix}$$

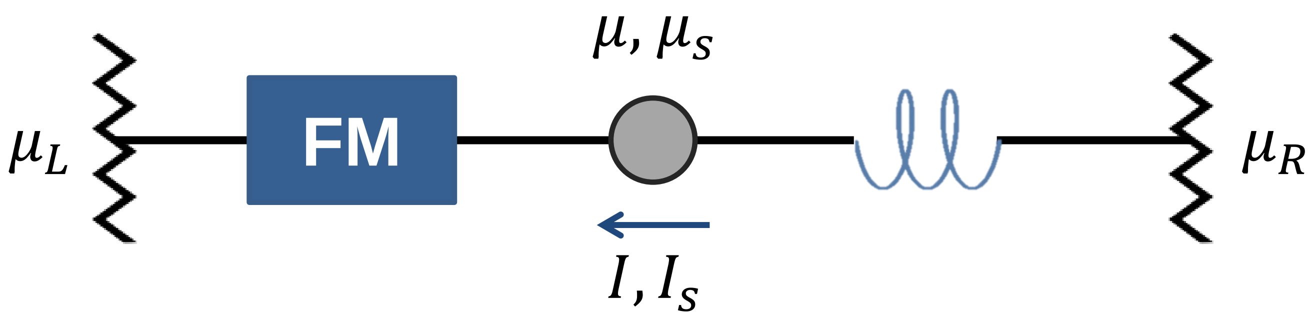
Coupled spin and charge transport



$$\begin{pmatrix} I \\ -I_{sL} \\ I_{sR} \end{pmatrix} = -\frac{Ne}{h} \begin{pmatrix} t & s & s \\ P_r r & \gamma_r & \gamma_t \\ P_t t & \gamma_t & \gamma_r \end{pmatrix} \begin{pmatrix} \mu_L - \mu_R \\ \mu_{sL} \\ \mu_{sR} \end{pmatrix}$$

Coupled charge and spin transport

$$\begin{pmatrix} I \\ I_s \end{pmatrix} = -\frac{G_{N'}}{e} \begin{pmatrix} T & -P_{FM}T \\ P_{FM}T & -T \end{pmatrix} \begin{pmatrix} \mu_L - \mu \\ \mu_s \end{pmatrix}$$



$$\begin{pmatrix} I \\ -I_s \end{pmatrix} = -\frac{G_N}{2e} \begin{pmatrix} t & P_t\ t \\ P_t\ t & -(1 + 2P_t/\eta_r)\ t \end{pmatrix} \begin{pmatrix} \mu - \mu_R \\ \mu_s \end{pmatrix}$$

Symmetric matrix for CISS, antisymmetric for FM.

Coupled charge and spin transport

- Fundamental difference:

FM

Breaks time reversibility

Time-reversal invariant

- Transport matrix formalism

$$\begin{matrix}\text{Charge current} \\ \text{Spin current}\end{matrix}\begin{pmatrix} I \\ I_s \end{pmatrix} = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix}\begin{pmatrix} \Delta\mu \\ \mu_s \end{pmatrix}\begin{matrix}\text{Bias} \\ \text{Spin accumulation}\end{matrix}$$

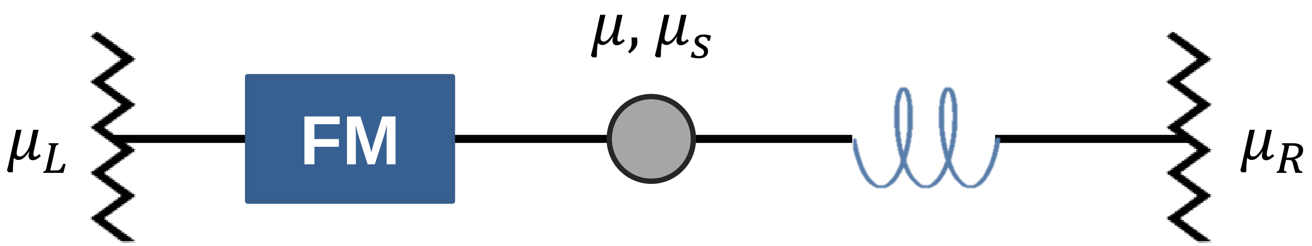
FM $G_{12} = -G_{21}$

 $G_{12} = G_{21}$

Antisymmetric for FM, symmetric matrix for CISS.

Yang et al. *Nano Lett.* **20**, 8, 6148–6154 (2020)

2T conductance



$$\begin{pmatrix} G_{11} & -G_{21} \\ G_{21} & G_{22} \end{pmatrix} \qquad \begin{pmatrix} g_{11} & g_{21} \\ g_{21} & g_{22} \end{pmatrix}$$

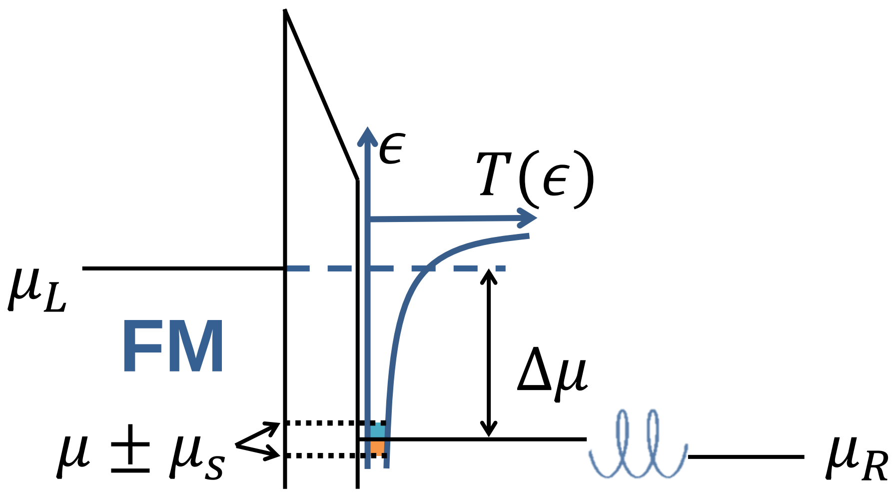
$$G_{2T} = G(G_{21}^2, g_{21}^2)$$

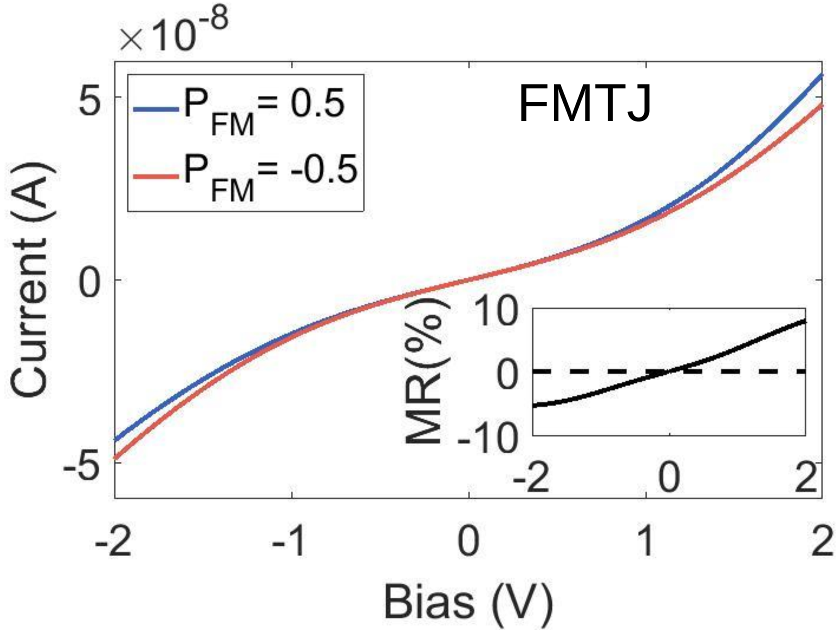
2T conductance does **not** depend on magnetization direction or chirality in the linear regime.
No MR in the linear regime.

Yang et al. *Phys. Rev. B* **99,** 024418 (2019)
Yang et al. *Nano Lett.* **20**, 8, 6148–6154 (2020)

Beyond linear regime

Tunneling at FM tunnel junction



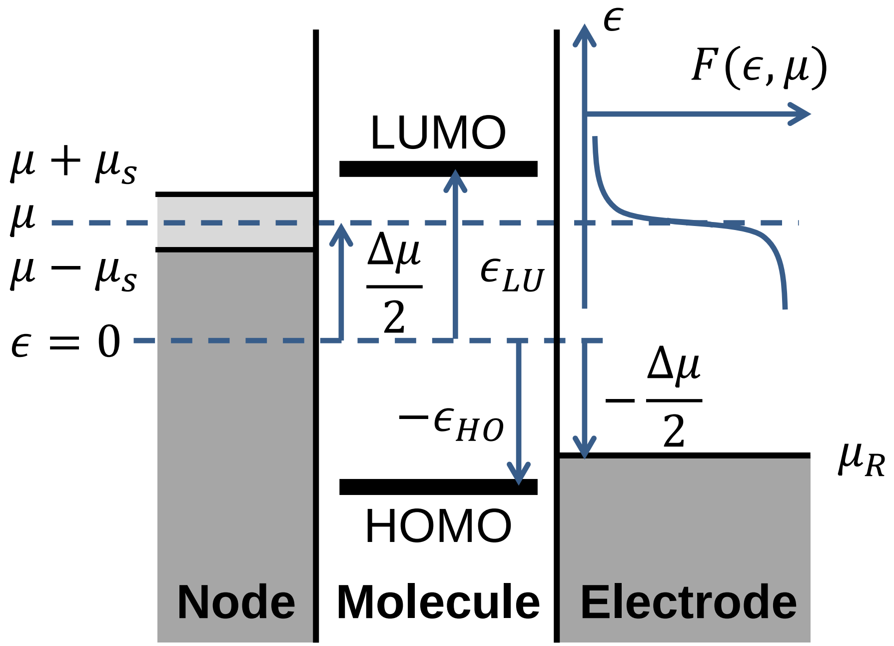


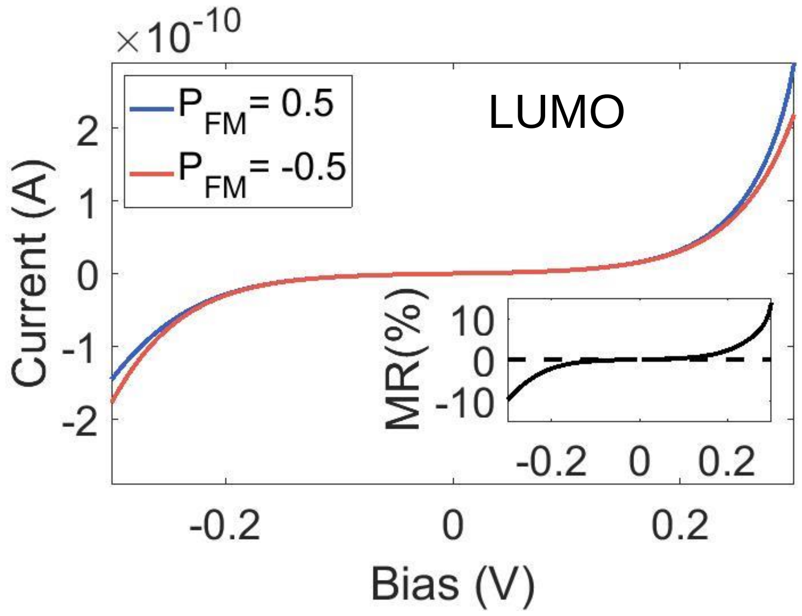
MR can arise from energy dependent transport and energy relaxation.
MR is odd in bias, same as EMC.

Jansen et al., *Phys. Rev. Applied* **10**, 064050 (2018)
Yang et al. *Nano Lett.* **20**, 8, 6148–6154 (2020)

Beyond linear regime

Molecular orbital transmission

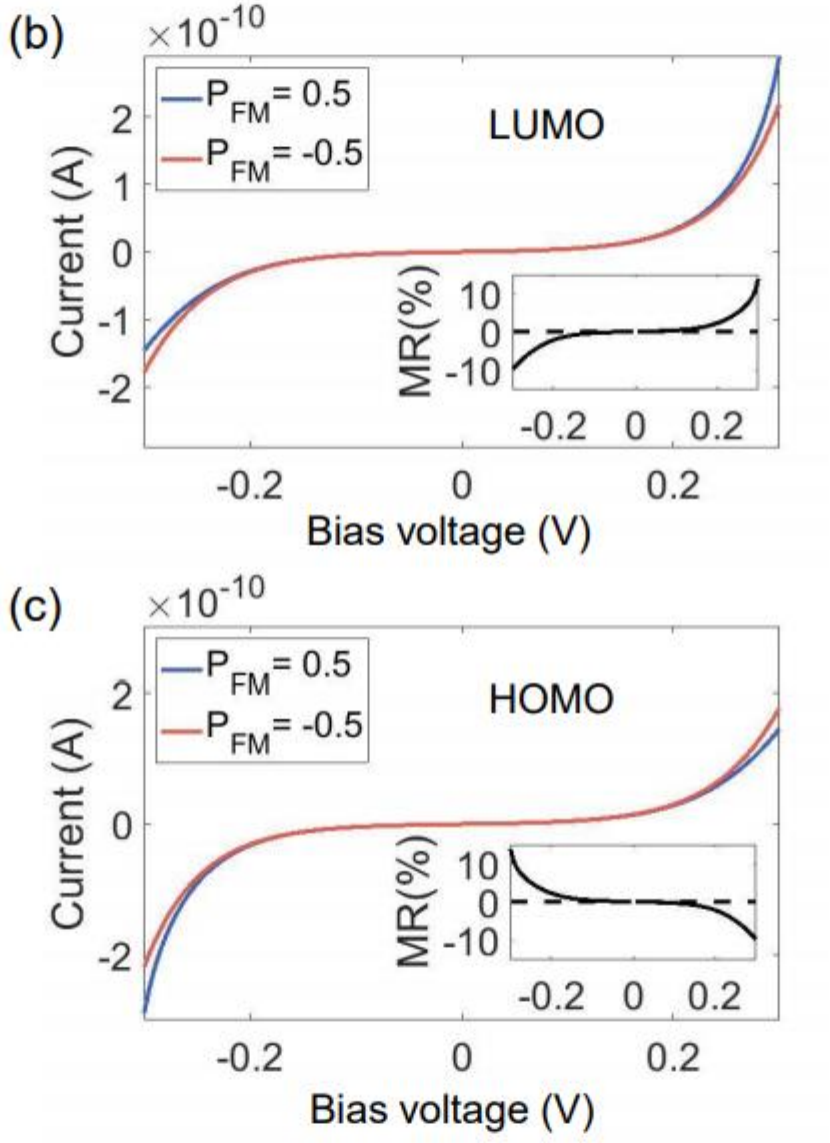


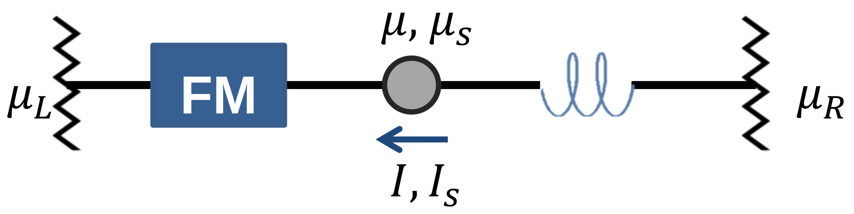


MR can arise in nonlinear regime, but **must vanish in linear regime**.
Sign of MR depends on chirality, charge carrier type, and bias direction.

Yang et al. *Nano Lett.* **20**, 8, 6148–6154 (2020)

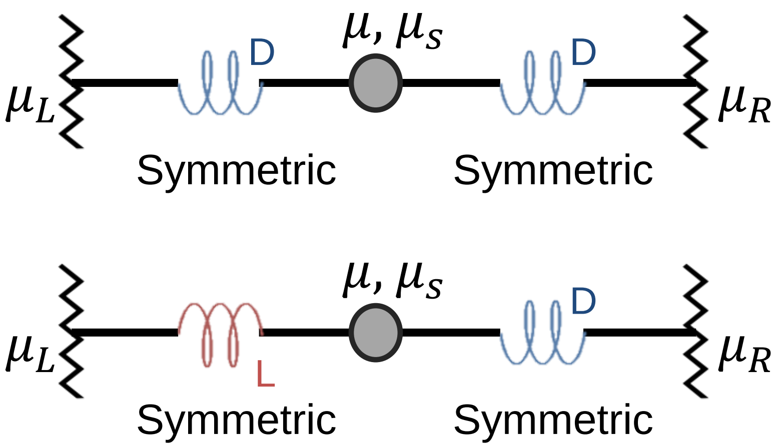
Transmission through HOMO/LUMO

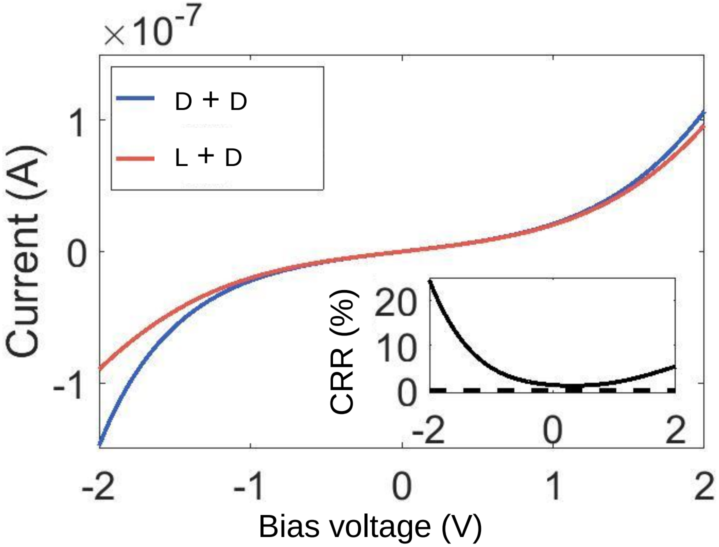




Can we detect 2T CISS in linear regime?

Chiral spin valve

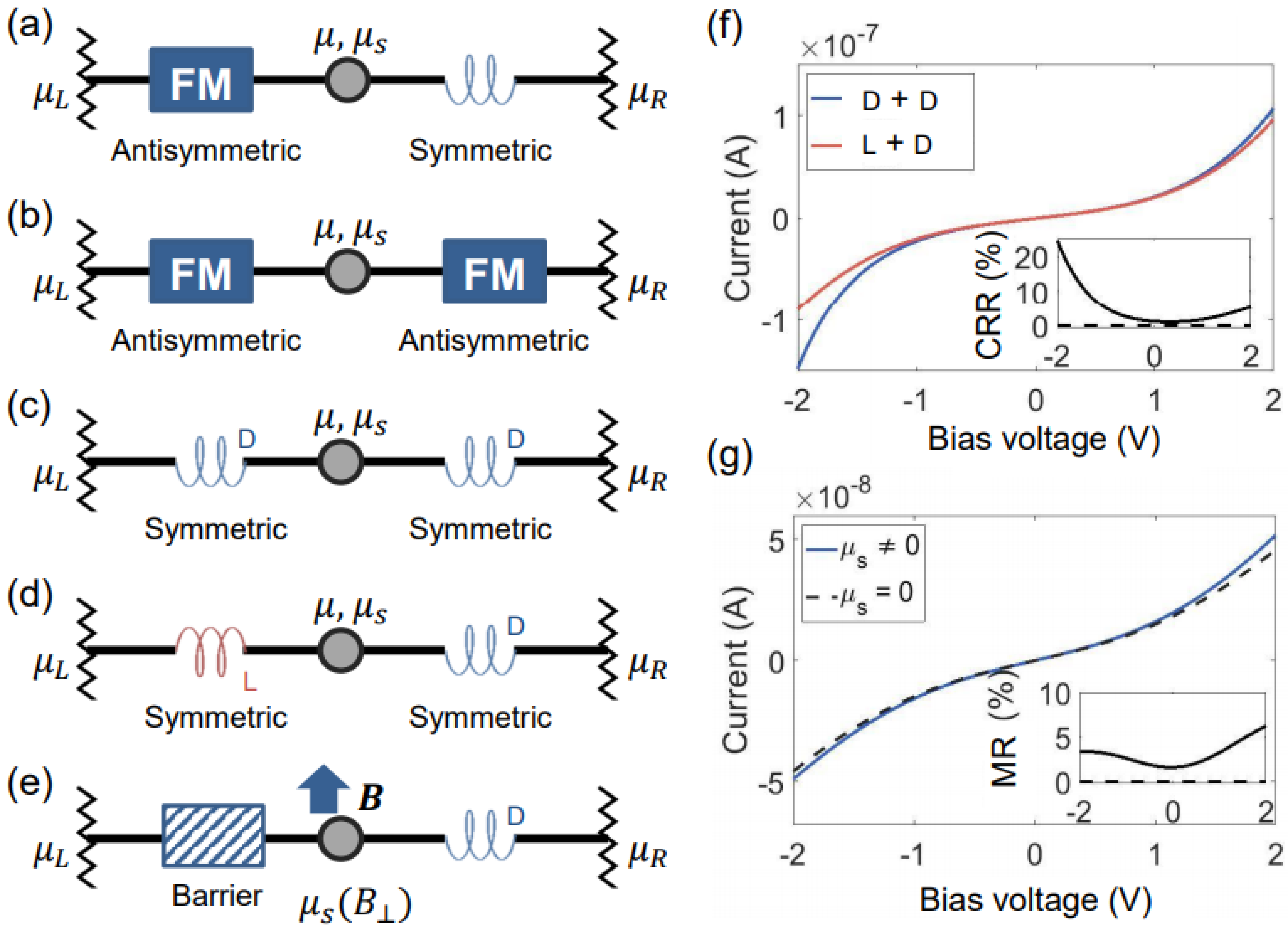




Chiral spin valve without magnet: works in linear regime.

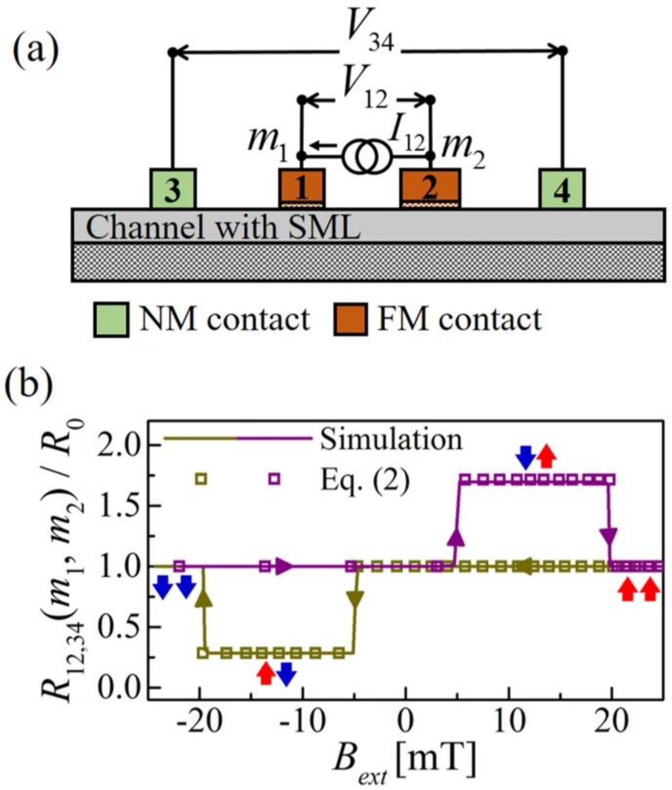
Yang et al. *Nano Lett.* **20**, 8, 6148–6154 (2020)

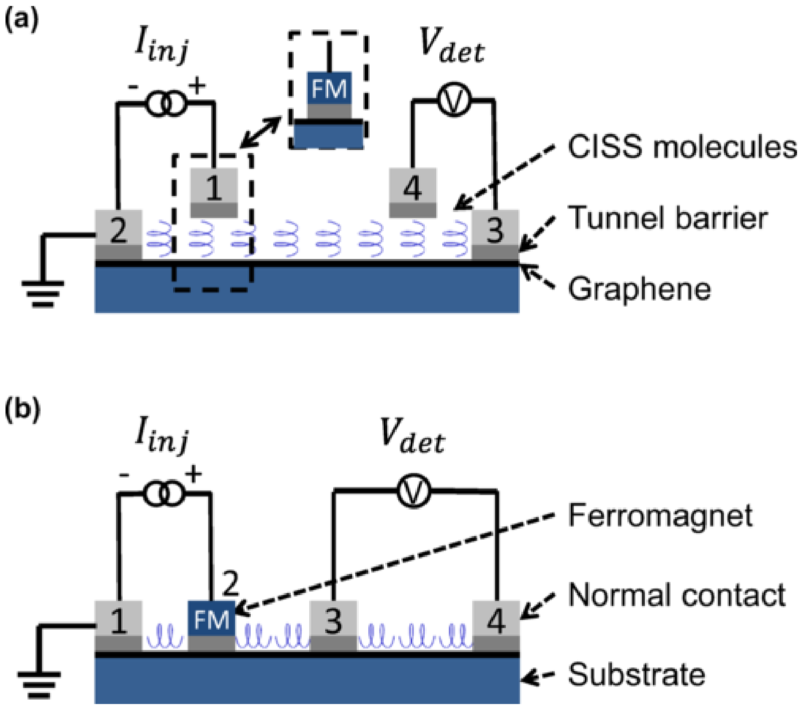
Chiral spin valve



Can we detect CISS in linear regime?

Multi-terminal devices

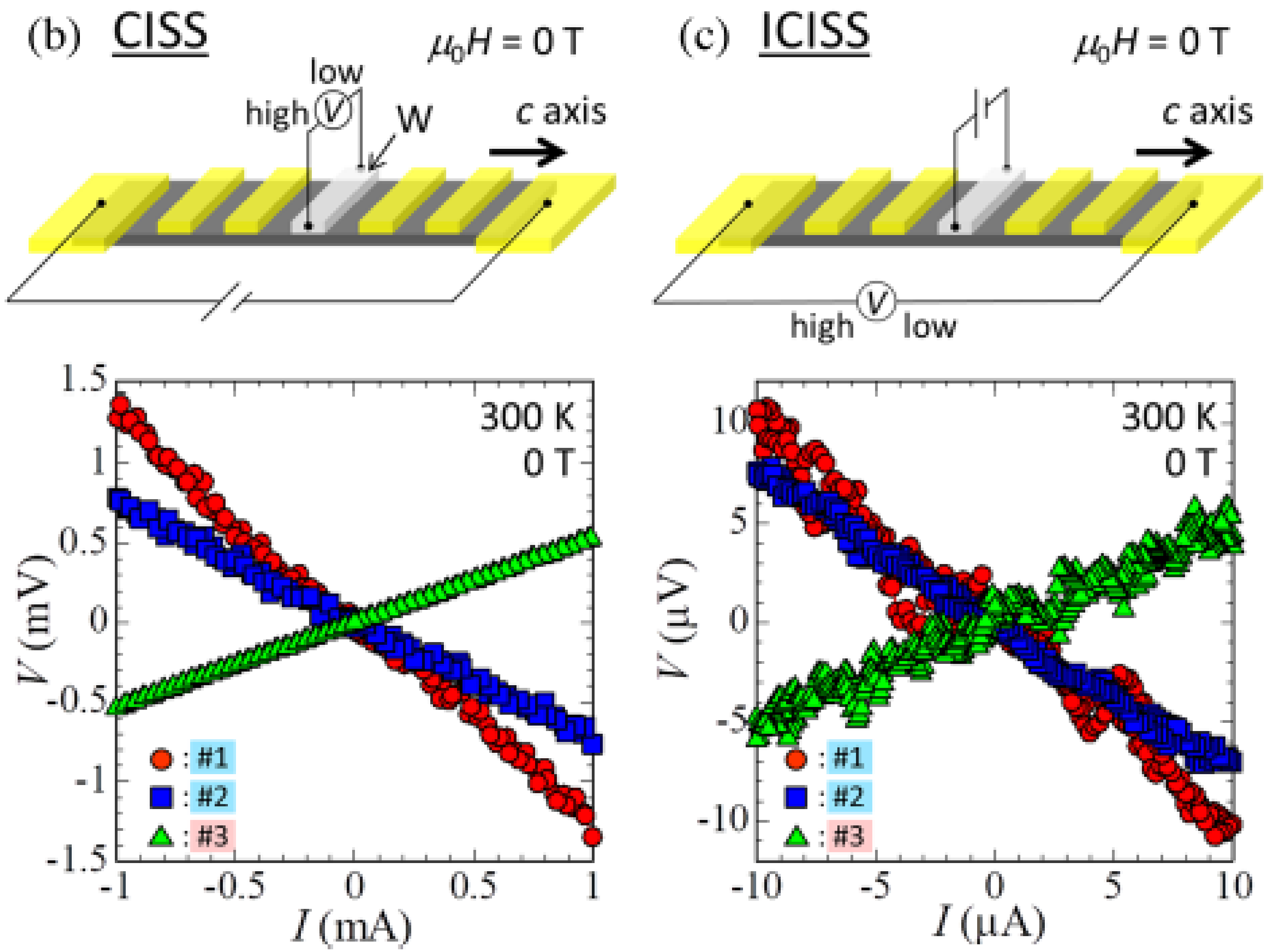




Multi-terminal measurements also work in linear regime.

Sayed et al. *Sci. Rep.* **6,** 35658 (2016)
Yang et al. *Phys. Rev. B* **99,** 024418 (2019)

Multi-terminal: spin Hall geometry

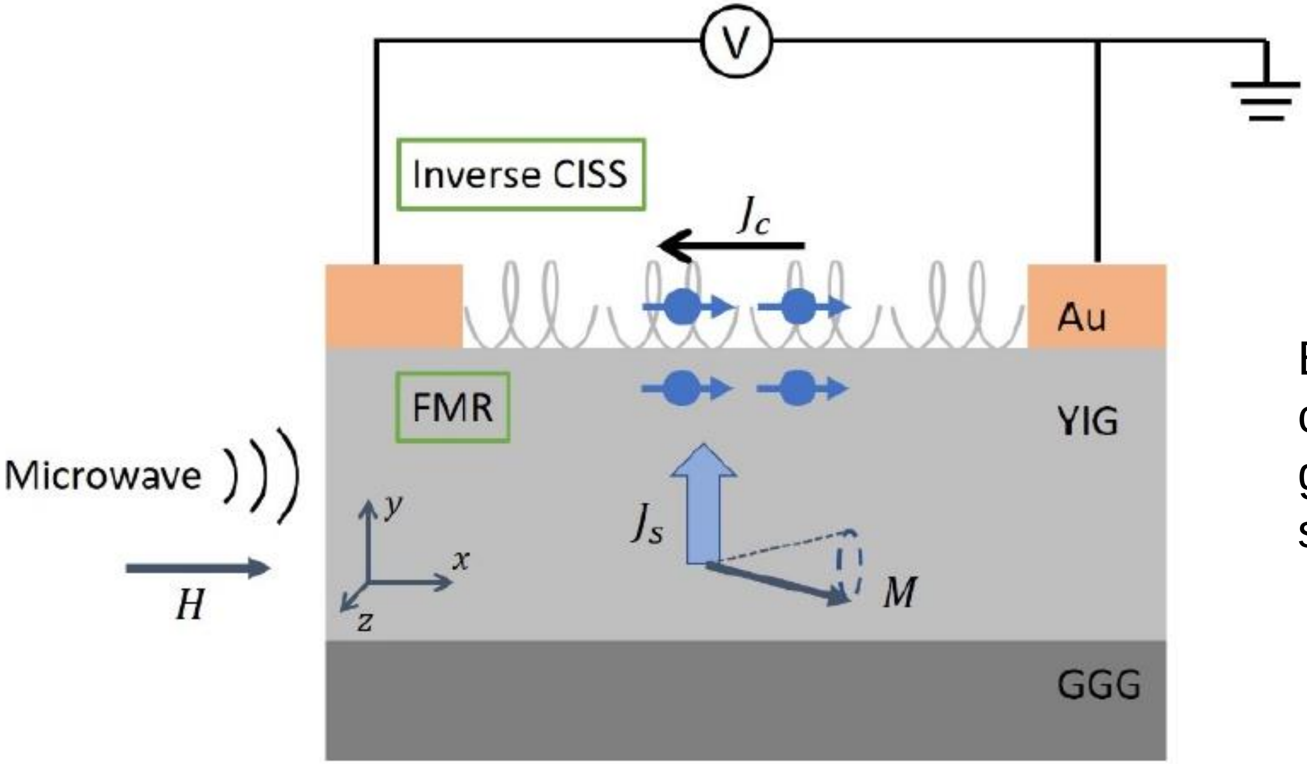


Inui et al. *Phys. Rev. Lett.* **124**, 166602 (2020)

CISS as 2T MR?

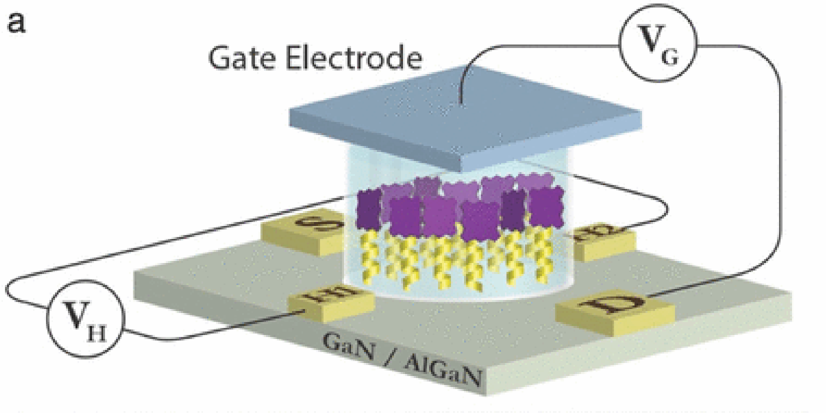
- Linear response: The 2T MR signal due to CISS **must be zero at (close to) zero bias**.
- First-order correction: As bias gradually increases, the MR **must first appear as bias-odd**.
- Observations differ from the above? Double check experimental technique and data analysis!
- Multi-terminal geometries allow linear regime detection.

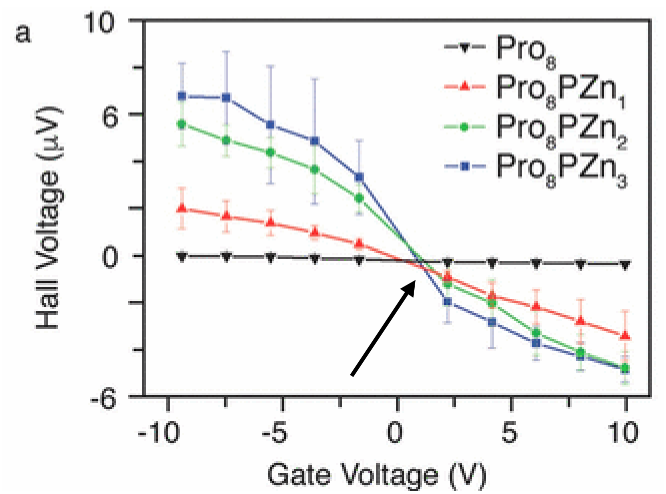
Multi-terminal detection of bulk CISS: FMR spin pumping



Bulk CISS:
charge current generated parallel to spin direction

Our doubts about Hall devices





Static electric field generates static magnetic field/magnetization?
Large “Hall” signal, corresponds to 10 mT perpendicular field. Geim reports only 0.2 mT in vdW 2D magnets (*Nat. Electron.* **2**, 457 (2019)).

No background at zero gate?

No sufficient info in the paper/SI to understand the actual experiments.

J. Am. Chem. Soc. **141**, 14707 (2019)

Summary

- Symmetry analysis is a powerful tool for understanding effects and predicting signals without knowing microscopic details.
- CISS connects the fundamental symmetries of space and time.
- CISS 2T MR must vanish in linear regime, and must first appear bias-odd with increasing bias.
- CISS can be detected in linear regime using various multi-terminal geometries.

Our experimental plan

- Address low-bias regime of 2T MR measurements.
- Detect CISS in linear response using multi-terminal measurements.
- Material choice: ordered chiral molecular assemblies, chiral conductive polymer, chiral solid-state material (e.g. Te, $CrNb_3S_6$, PdTa), twisted van der Waals layers, etc.