
# Proximity Effects and spintronics in low dimensional systems

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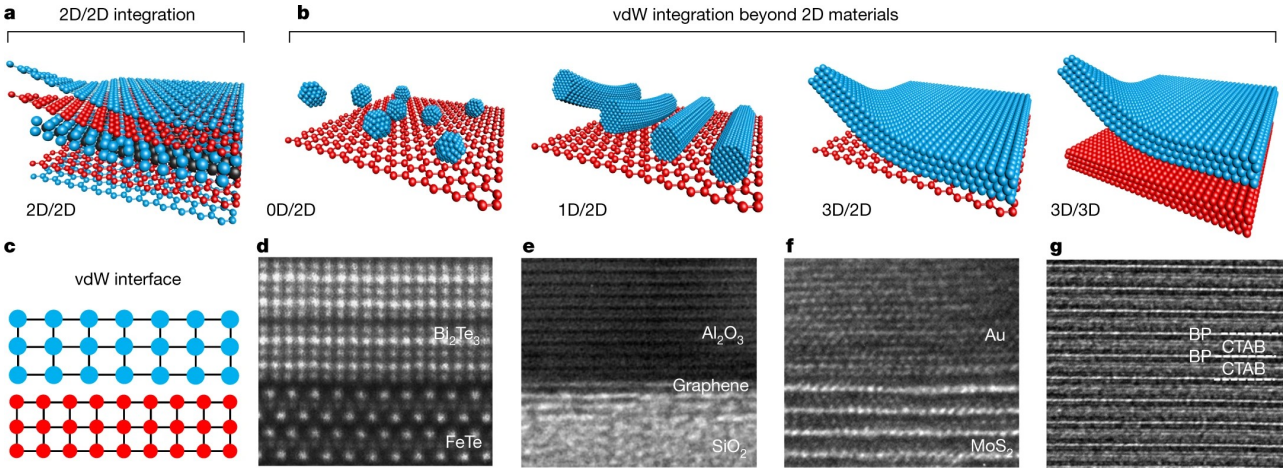
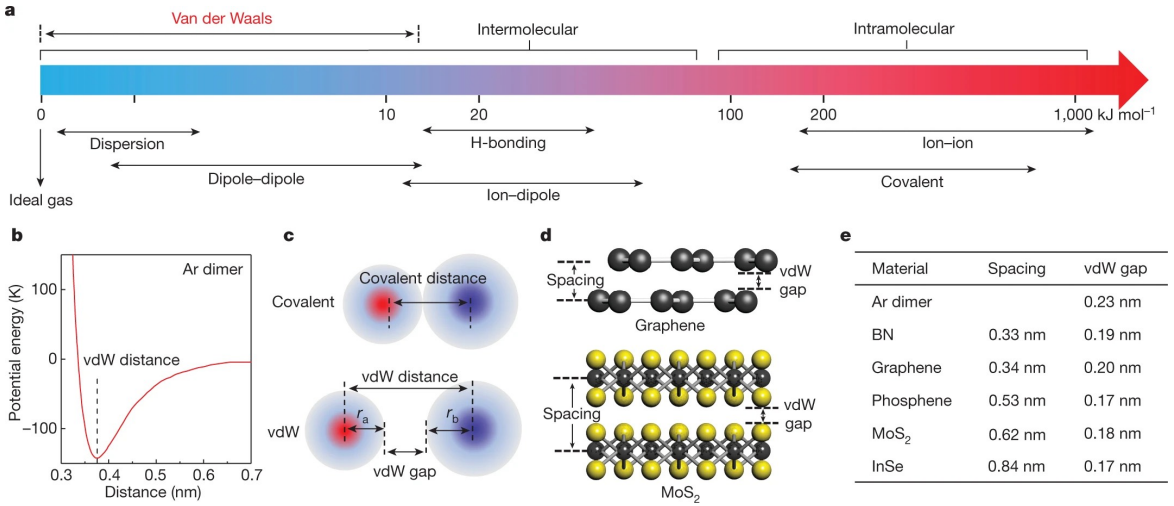
# Summary

- Clarity of simplest models versus ab initio calculations, the case of Ni/Co and Au on graphene: Band folding/Matrix perturbation theory
  - Ferro and AntiFerro on graphene without degrading its properties
  - Strong spin-orbit coupling induced by Au
- Spin activity in the absence of exchange interactions and magnetic centers. The case of CISS
  - Chiral molecules as a spin polarizers
  - Hydrogen bonding generate Rashba interactions
  - Stretching molecules and Molecular spectroscopy/SO enhancement

# Van der Waals Materials/Proximity coupling



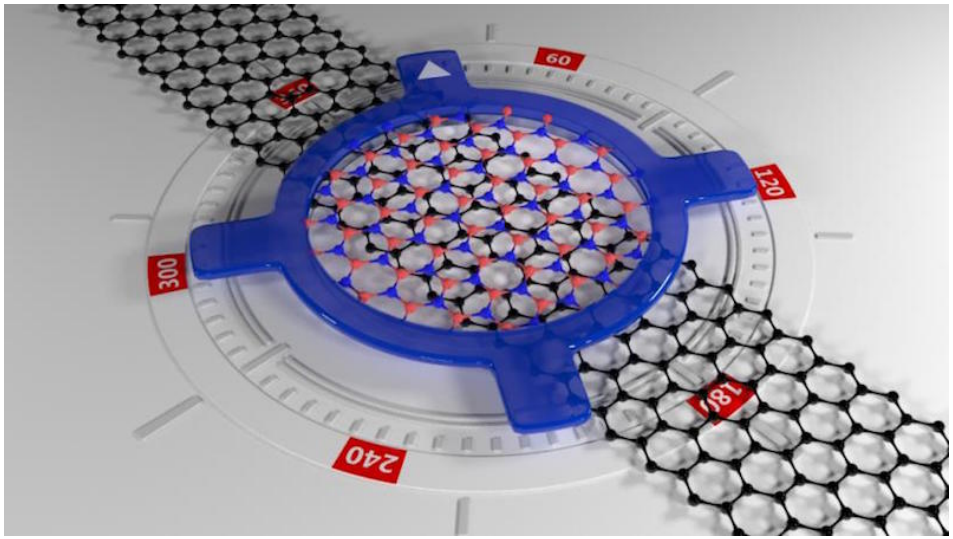

Liu, Huang, Duan, Nature volume, 567, 323–333 (2019)

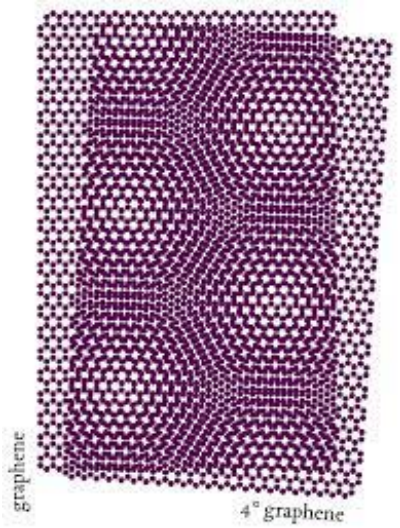



e

| Material | Spacing | vdW gap |
|---|---|---|
| Ar dimer | | 0.23 nm |
| BN | 0.33 nm | 0.19 nm |
| Graphene | 0.34 nm | 0.20 nm |
| Phosphene | 0.53 nm | 0.17 nm |
| $MoS_2$ | 0.62 nm | 0.18 nm |
| InSe | 0.84 nm | 0.17 nm |

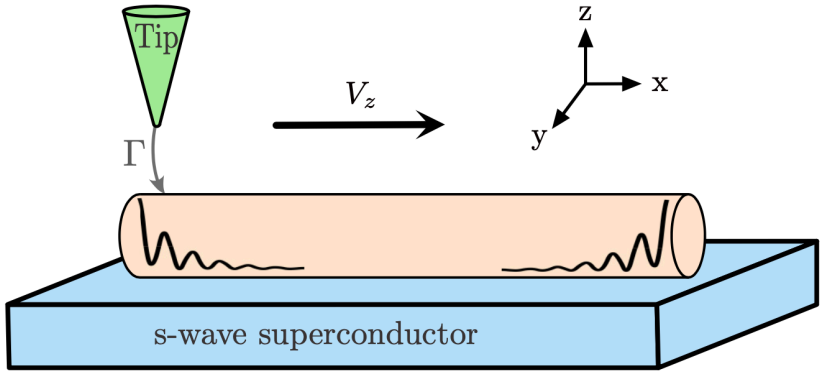
# Twistronics/Majorana



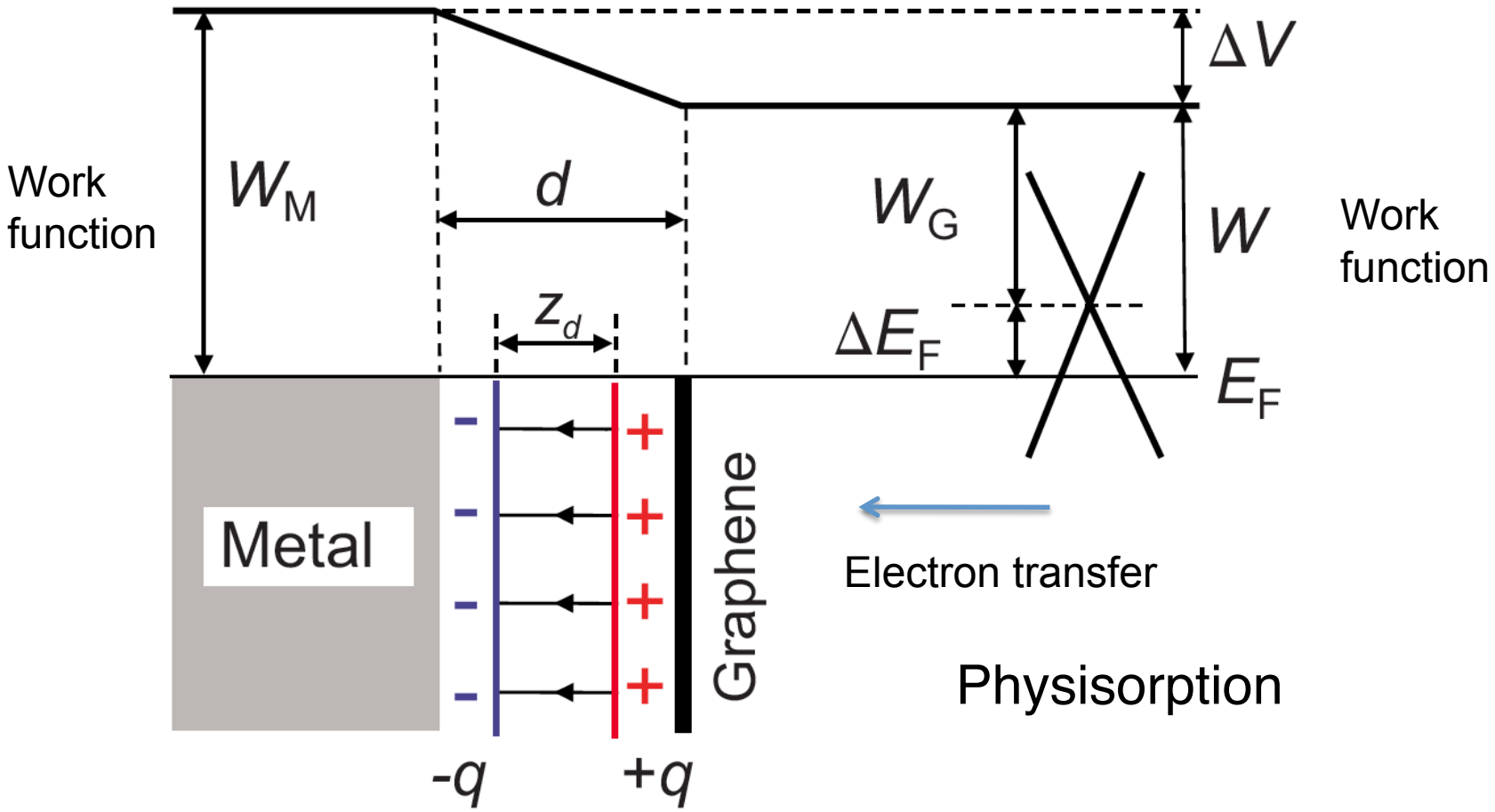




Magic angles at which the fermi velocity —> 0 then magnetism and superconductivity arise

Rashba (SO coupling) nanowire on superconductor

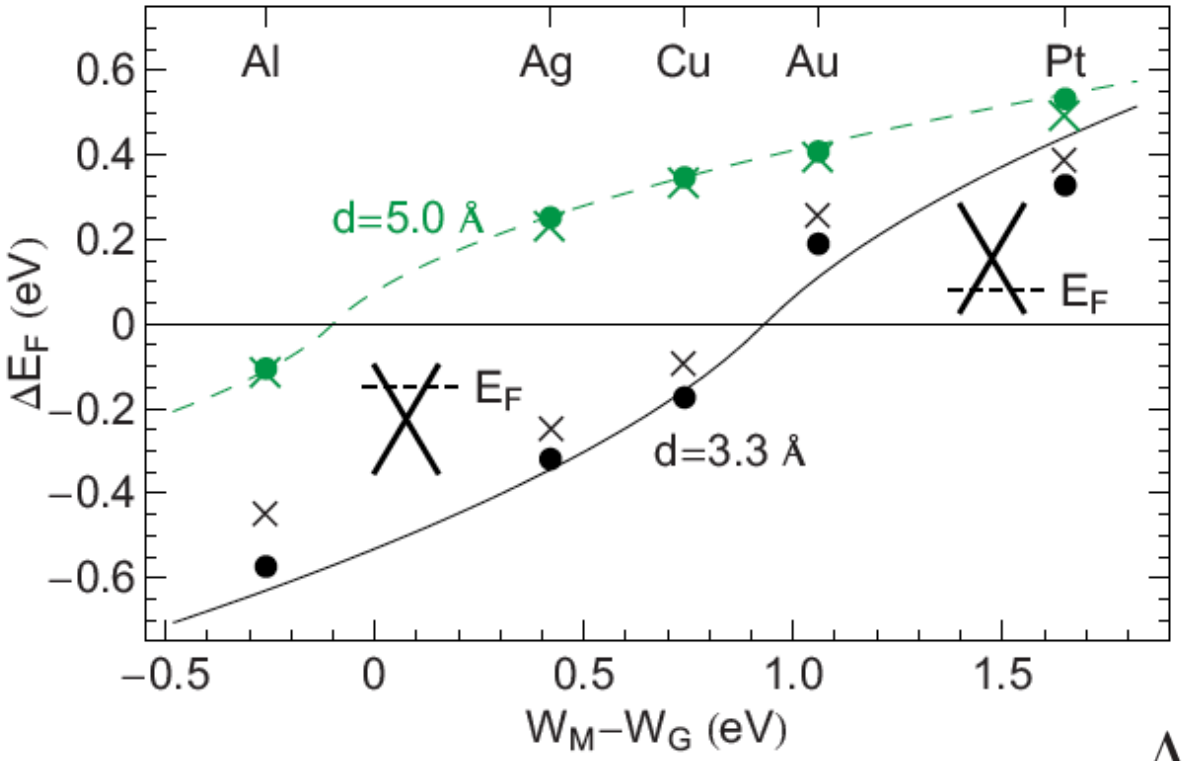


# Proximity regimes: Substrate effects




Khomyakov et al (2009)

# Changes in chemical potential




Δ work function

Wave-f overlap

$$\Delta V(d) = \Delta_{\mathrm{tr}}(d) + \Delta_{\mathrm{c}}(d)$$

Wave-function overlap

$$\Delta_{\mathrm{c}}(d) = e^{-\gamma d}(a_0 + a_1 d + a_2 d^2)$$

$$\Delta E_{\mathrm{F}}(d) = \pm \frac{\sqrt{1 + 2\alpha D_0 (d - d_0)\left|W_{\mathrm{M}} - W_{\mathrm{G}} - \Delta_{\mathrm{c}}(d)\right|} - 1}{\alpha D_0 (d - d_0)}$$

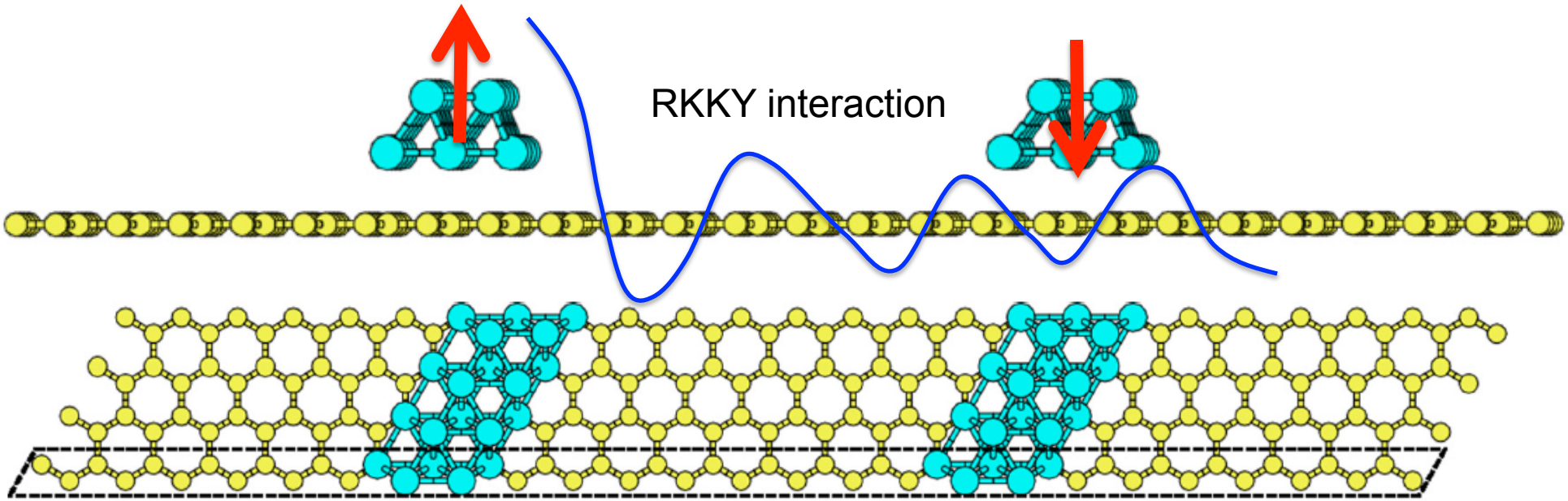
DOS

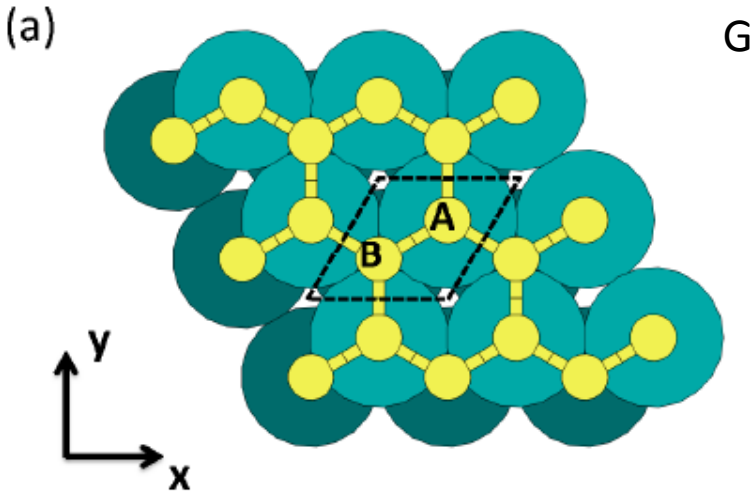
$$D(E) = D_0 |E|$$

# Why proximity effects?

- Defects and impurities reduce desirable mobility properties
- Can dope n or p with metals gauging the distance without gating (graphene has no carriers without doping)
- Can induce spin-orbit interaction without substitutional heavy atoms
- Induce A-B asymmetries for semiconducting properties

# Proximity effects: Co over graphene




ATOP

The sign of the interaction can be manipulated by a gate voltage

BUT! Coupling produces AF interactions!

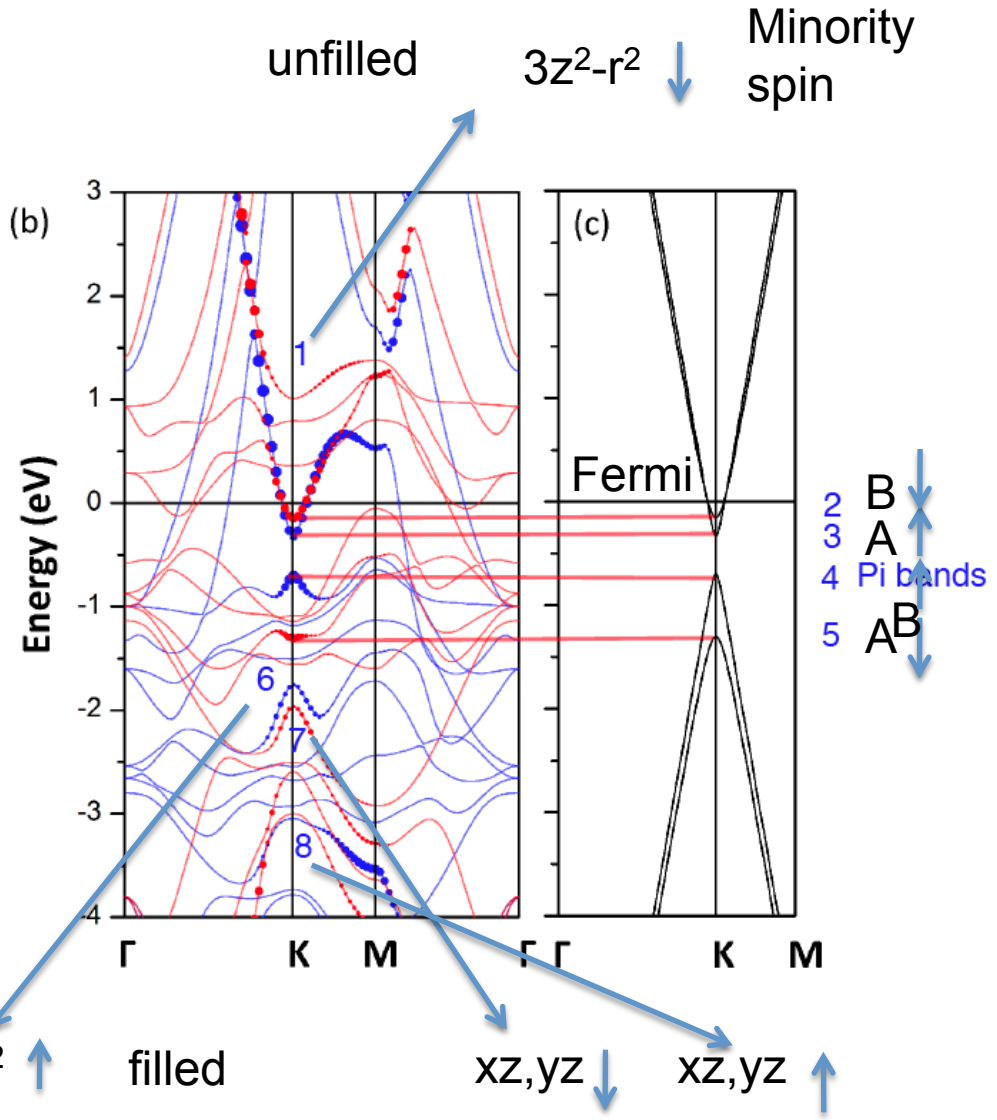
McDonald et al PRB 2013

# Co-Graphene bands

## ATOP configuration

TABLE I. Orbital character of the bands in Fig. 1(b) at the $K$ point of the 2D Brillouin zone. Only those having strong carbon $p_z$ characters are listed. A and B correspond to the two sublattices of graphene, as shown in Fig. 1(a).

| Band No. | Energy (eV) | C $p_z$ character | Co $d$ character |
|---|---|---|---|
| 1 | 1.006 | A↓: 0.069 | $3z^2 - r^2$↓: 0.671 |
| 2 | −0.151 | B↓: 0.319 | $xz, yz$↓: 0.098<br>$x^2 - y^2, xy$↓: 0.099 |
| 3 | −0.328 | A↑: 0.297 | $3z^2 - r^2$↑: 0.368 |
| 4 | −0.703 | B↑: 0.439 | $xz, yz$↑: 0.059<br>$x^2 - y^2, xy$↑: 0.016 |
| 5 | −1.307 | A↓: 0.341 | $3z^2 - r^2$↓: 0.019 |
| 6 | −1.754 | A↑: 0.191 | $3z^2 - r^2$↑: 0.303 |
| 7 | −1.965 | B↓: 0.185 | $xz, yz$↓: 0.19<br>$x^2 - y^2, xy$↓: 0.054 |
| 8 | −3.048 | B↑: 0.055 | $xz, yz$↑: 0.206<br>$x^2 - y^2, xy$↑: 0.166 |




Mixed with A π orbital/ Majority spin  3z²-r²  filled  xz,yz  xz,yz

# Proximity effects: Co over graphene

Empirical model McDonald et al 2012

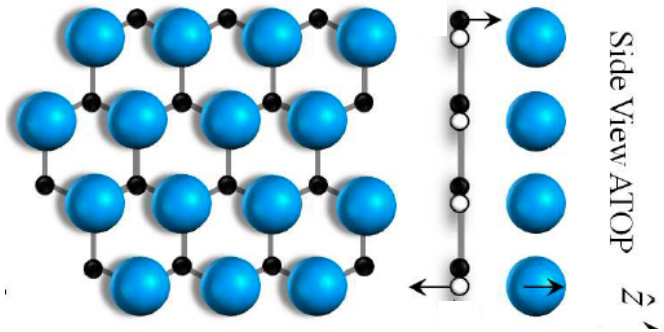
$$H = \mu + \hbar v_F k \cdot \sigma - h_{0z}\sigma_z - h_{z0}s_z - h_{zz}s_z\sigma_z$$

| Electron transfer | Graphene | Asymmetric Lattice/ pseudo spin | Asymmetric spin | Asymmetric Spin/pseudospin |
|---|---|---|---|---|

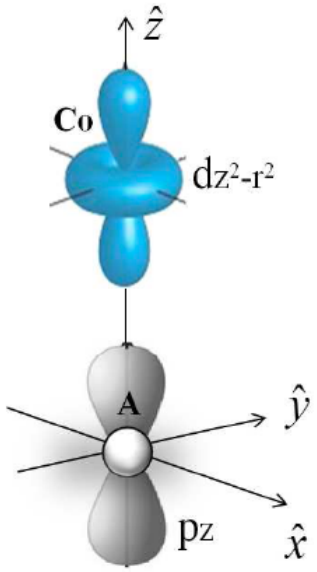
We can derive it from tight binding and determine the coefficients
Design appropriately each term

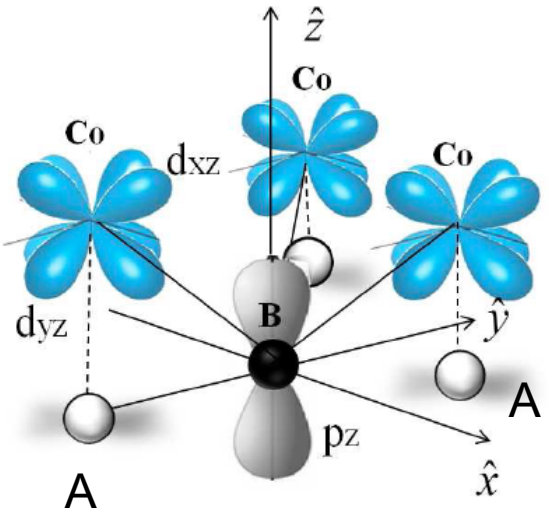
# Lattice registries

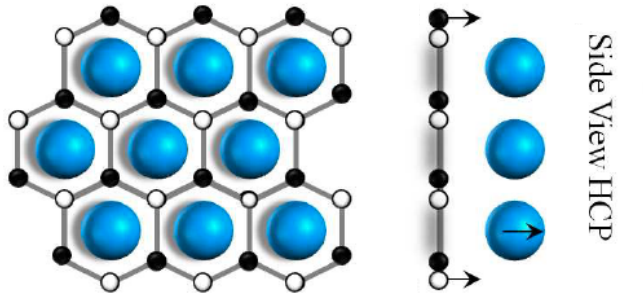
Most stable according to Ab initio



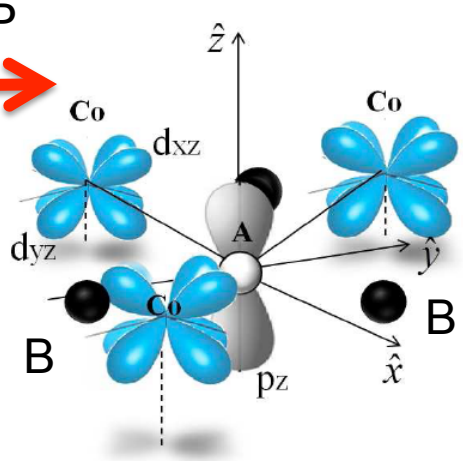

ATOP

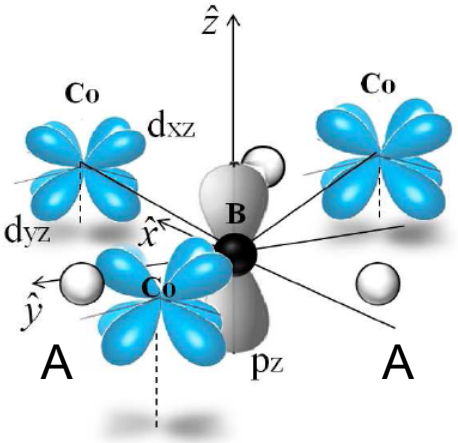


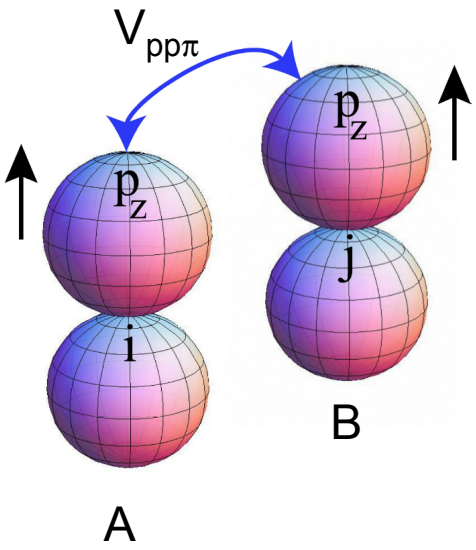

HCP



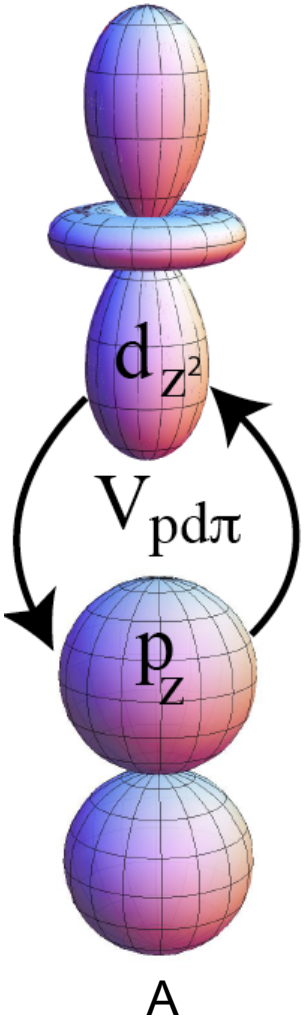



# Atop configuration

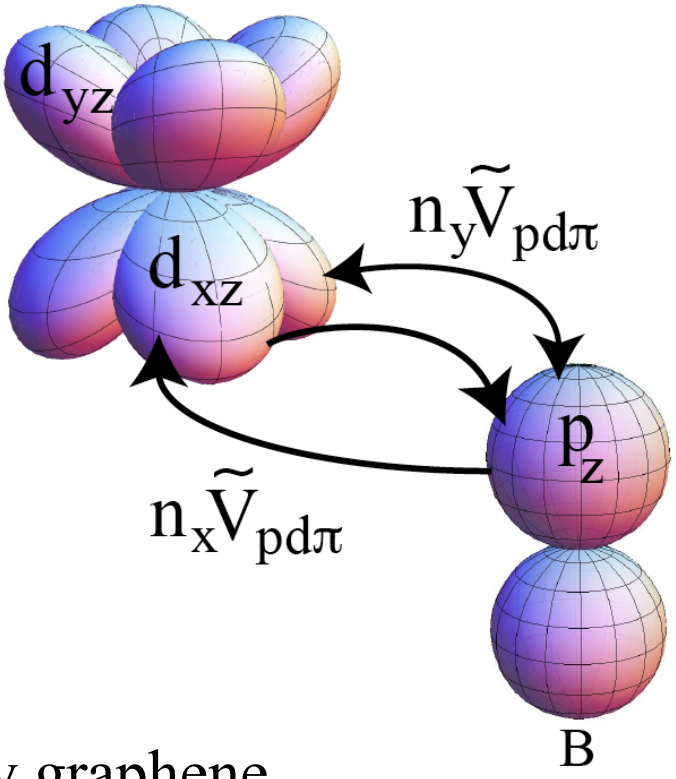
Process on graphene




Also magnetization
Dependent correction




Hopping to Co/Ni




Only graphene
site energies corrected

# Co over graphene couplings

$H_\gamma$ → $T$

| | A,Pz | B,Pz | $d_z^2$ | $d_{xz}$ | $d_{yz}$ |
|---|---|---|---|---|---|
| A,Pz | $\varepsilon_p$ | $V_{pp\pi}$ | $V_{pdz^2}$ | 0 | 0 |
| B,Pz | $V_{pp\pi}$ | $\varepsilon_p$ | 0 | $\hat{n}_x \tilde{V}_{pd\pi}$ | $\hat{n}_y \tilde{V}_{pd\pi}$ |
| $d_z^2$ | $-V_{pdz^2}$ | 0 | $\varepsilon_{dz^2} + \delta_1 s_z$ | 0 | 0 |
| $d_{xz}$ | 0 | $-\hat{n}_x \tilde{V}_{pd\pi}$ | 0 | $\varepsilon_{dxz} + \delta_2 s_z$ | 0 |
| $d_{yz}$ | 0 | $-\hat{n}_y \tilde{V}_{pd\pi}$ | 0 | 0 | $\varepsilon_{dyz} + \delta_2 s_z$ |

Want an effective $\mathcal{H}_{2x2}$

Can also apply real space Feynman method → $H_\chi$

# Matrix perturbation theory

Instead of Feynman paths we use Foldy-Wouthuysen band folding approach

$$\begin{pmatrix} H_\gamma & T \\ T^\dagger & H_\chi \end{pmatrix}\begin{pmatrix} \gamma \\ \chi \end{pmatrix} = E\begin{pmatrix} \gamma \\ \chi \end{pmatrix}$$

$$T^\dagger\gamma + H_\chi\chi = E\chi \qquad H_\gamma\gamma + T\chi = E\gamma$$

$$T^\dagger\gamma = \left(E - H_\chi\right)\chi \qquad \left(H_\gamma + T\left(E - H_\chi\right)^{-1}T^\dagger\right)\gamma = E\gamma$$

$$\left(E - H_\chi\right)^{-1}T^\dagger\gamma = \chi$$

$$\frac{1}{E - H_\chi} = -\frac{1}{H_\chi\left(1 - \left(H_\chi\right)^{-1}E\right)} = -\frac{1}{H_\chi}\left(1 + \frac{E}{H_\chi} + \ldots\right)$$

Eigenvalues of $H_\chi > E$

# Matrix perturbation theory

$$\left( H_\gamma - T\frac{1}{H_\chi}\left(1+\frac{E}{H_\chi}+\ldots\right)T^\dagger \right)\gamma = E\gamma$$

$$\left( H_\gamma - T\frac{1}{H_\chi}T^\dagger \right)\gamma = E\gamma + \left( T\frac{1}{H_\chi}\frac{E}{H_\chi}T^\dagger \right)\gamma = E\left(1+T\left(H_\chi\right)^{-2}T^\dagger\right)\gamma = ES\gamma$$

S

Define

$$\Phi = S^{1/2}\gamma \qquad S^{-1/2}\Phi = \gamma$$

$$S^{-1/2}\left( H_\gamma - T\frac{1}{H_\chi}T^\dagger \right)S^{-1/2}\Phi = E\Phi$$

# Matrix perturbation theory

$$\Phi^{\dagger}\Phi = \gamma^{\dagger} S^{1/2} S^{1/2} \gamma = \gamma^{\dagger}\left(1 + T\left(H_{\chi}\right)^{-2} T^{\dagger}\right)\gamma \approx \gamma^{\dagger}\gamma + \chi^{\dagger}\chi$$

Norm must be Consistent in perturbation

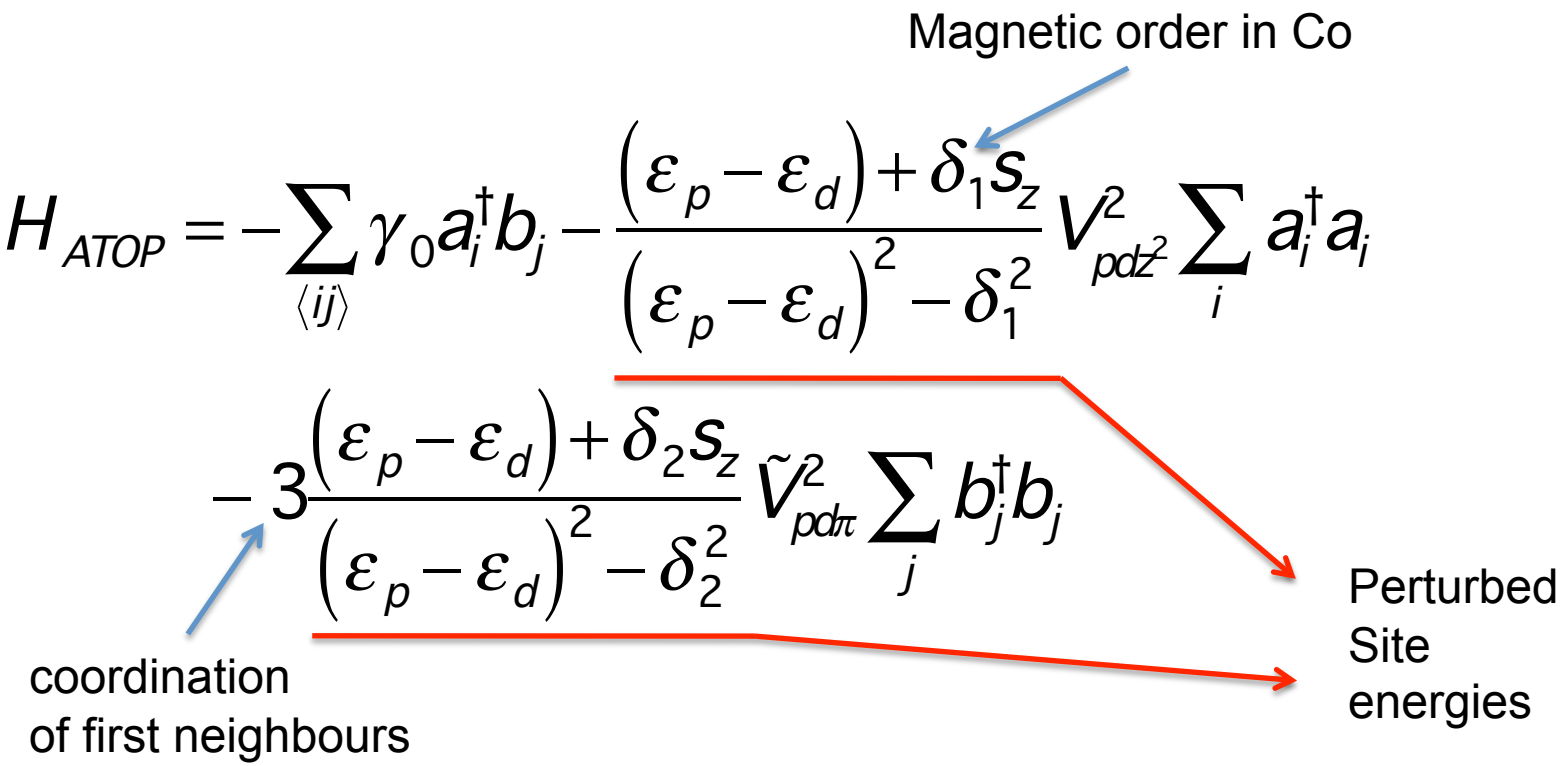
$$S^{-1/2}\left(H_{\gamma} - T\frac{1}{H_{\chi}}T^{\dagger}\right)S^{-1/2}\Phi = E\Phi$$

$$\mathcal{H}_{\text{eff}}$$

With dimension of $H_{\gamma}$

As γ is the subspace of $p_z$ these orbitals are dressed by the couplings.

# ATOP configuration



# ATOP in vicinity of K points

$$H_{\mathrm{ATOP}}(\mathbf{k}) = \begin{pmatrix} \mu - h_{0z} - \frac{h_{z0}}{2} - \frac{h_{zz}}{2} & v(\xi p_x - i p_y) & 0 & 0 \\ v(\xi p_x + i p_y) & \mu - h_{0z} + \frac{h_{z0}}{2} + \frac{h_{zz}}{2} & 0 & 0 \\ 0 & 0 & \mu + h_{0z} - \frac{h_{z0}}{2} + \frac{h_{zz}}{2} & v(\xi p_x - i p_y) \\ 0 & 0 & v(\xi p_x + i p_y) & \mu + h_{0z} + \frac{h_{z0}}{2} - \frac{h_{zz}}{2} \end{pmatrix}$$

$$H_{ATOP}(k=0) = \mu \Uparrow_{\sigma} \Uparrow_{s} - h_{0z} \sigma_z \Uparrow_{s} - \frac{h_{z0}}{2} \Uparrow_{\sigma} s_z - \frac{h_{zz}}{2} \sigma_z s_z$$

The McDonald Hamiltonian

$$-\frac{V_{pdz}^2(\varepsilon_p - \varepsilon_d)}{(\varepsilon_p - \varepsilon_d)^2 - \delta_1^2} = \mu - h_{0z}, \qquad \frac{\delta_1 V_{pdz}^2}{(\varepsilon_p - \varepsilon_d)^2 - \delta_1^2} = \frac{(h_{z0} + h_{zz})}{2}$$

$$-3\frac{\widetilde{V}_{pd\pi}^2(\varepsilon_p - \varepsilon_d)}{(\varepsilon_p - \varepsilon_d)^2 - \delta_2^2} = \mu + h_{0z}, \qquad 3\frac{\delta_2 \widetilde{V}_{pd\pi}^2}{(\varepsilon_p - \varepsilon_d)^2 - \delta_2^2} = \frac{(h_{z0} - h_{zz})}{2}$$

# ATOP in vicinity of K points

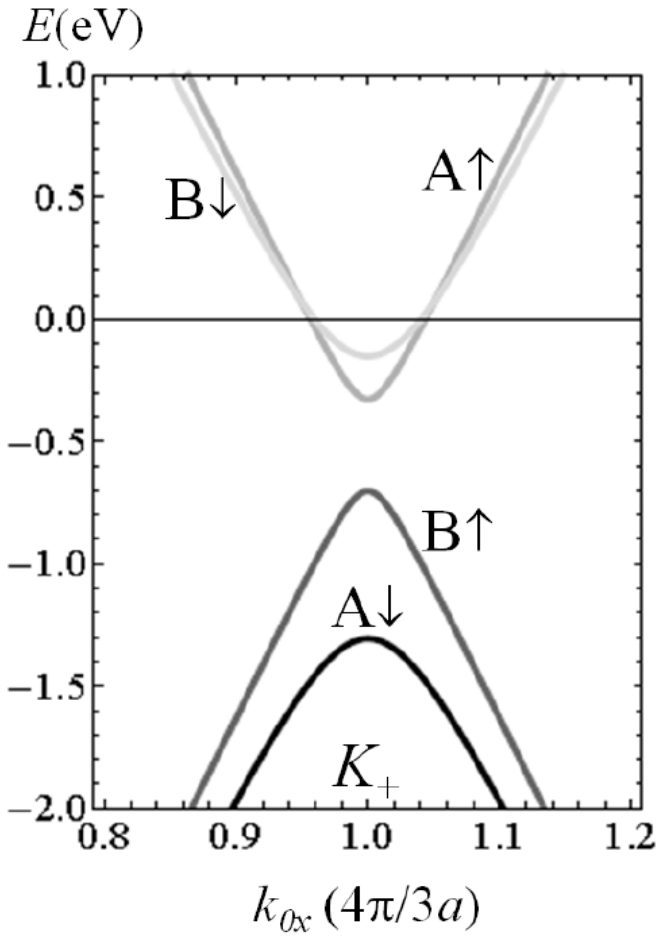
$$\epsilon_v(\mathbf{k}) = \frac{1}{2}\left(2\mu - s_z h_{z0} - \sqrt{(2h_{0z} + s_z h_{zz})^2 + 4v^2\hbar^2|\mathbf{k}|^2}\right)$$

$$\epsilon_c(\mathbf{k}) = \frac{1}{2}\left(2\mu - s_z h_{z0} + \sqrt{(2h_{0z} + s_z h_{zz})^2 + 4v^2\hbar^2|\mathbf{k}|^2}\right)$$

A sublattice AF wrt Co
B sublattice F wrt Co

Result: AF with a slightly higher
Spin component opposite to Co

Depending on overlaps and coordination




**M. Peralta et al PRB (2019)**

# HCP real space Hamiltonian

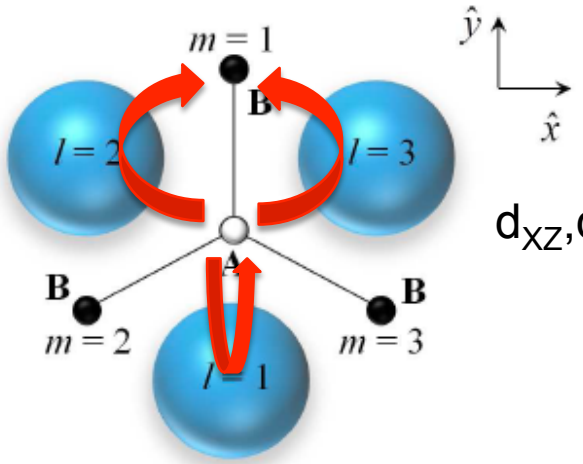
$H_\gamma$ → $T$

| | A,Pz | B,Pz | $d_z^2$ | $d_{xz}$ | $d_{yz}$ |
|---|---|---|---|---|---|
| A,Pz | $\varepsilon_p$ | $V_{pp\pi}$ | 0 | $\hat{n}_x \tilde{V}_{pd\pi}$ | $\hat{n}_y \tilde{V}_{pd\pi}$ |
| B,Pz | $V_{pp\pi}$ | $\varepsilon_p$ | 0 | $\hat{n}_x \tilde{V}_{pd\pi}$ | $\hat{n}_y \tilde{V}_{pd\pi}$ |
| $d_z^2$ | 0 | 0 | $\varepsilon_{dz^2} + \delta_1 s_z$ | 0 | 0 |
| $d_{xz}$ | $-\hat{n}_x \tilde{V}_{pd\pi}$ | $-\hat{n}_x \tilde{V}_{pd\pi}$ | 0 | $\varepsilon_{dxz} + \delta_2 s_z$ | 0 |
| $d_{yz}$ | $-\hat{n}_y \tilde{V}_{pd\pi}$ | $-\hat{n}_y \tilde{V}_{pd\pi}$ | 0 | 0 | $\varepsilon_{dyz} + \delta_2 s_z$ |

Want an effective $\mathcal{H}_{2x2}$

→ $H_\chi$

# HCP bands




$d_{XZ}$,$d_{YZ}$

$$H_{\mathrm{HCP}}(\mathbf{k}) = \begin{pmatrix} -3\frac{\varepsilon+\delta_2}{\varepsilon^2-\delta_2^2}\widetilde{V}_{pd\pi}^2 & 0 & -\frac{v}{\gamma_0}(-\gamma_0+\frac{\varepsilon+\delta_2}{\varepsilon^2-\delta_2^2}\widetilde{V}_{pd\pi}^2)p^* & 0 \\ 0 & -3\frac{\varepsilon-\delta_2}{\varepsilon^2-\delta_2^2}\widetilde{V}_{pd\pi}^2 & 0 & -\frac{v}{\gamma_0}(-\gamma_0+\frac{\varepsilon-\delta_2}{\varepsilon^2-\delta_2^2}\widetilde{V}_{pd\pi}^2)p^* \\ -\frac{v}{\gamma_0}(-\gamma_0+\frac{\varepsilon+\delta_2}{\varepsilon^2-\delta_2^2}\widetilde{V}_{pd\pi}^2)p & 0 & -3\frac{\varepsilon+\delta_2}{\varepsilon^2-\delta_2^2}\widetilde{V}_{pd\pi}^2 & 0 \\ 0 & -\frac{v}{\gamma_0}(-\gamma_0+\frac{\varepsilon-\delta_2}{\varepsilon^2-\delta_2^2}\widetilde{V}_{pd\pi}^2)p & 0 & -3\frac{\varepsilon-\delta_2}{\varepsilon^2-\delta_2^2}\widetilde{V}_{pd\pi}^2 \end{pmatrix}$$

$$\epsilon_v(\mathbf{k}) = -\mu' + s_z h'_{z0} + \frac{v\hbar}{\gamma_0}(-\gamma_0 - h'_{0x} + s_z h'_{zx})|\mathbf{k}|$$

$$\epsilon_c(\mathbf{k}) = -\mu' + s_z h'_{z0} - \frac{v\hbar}{\gamma_0}(-\gamma_0 - h'_{0x} + s_z h'_{zx})|\mathbf{k}|$$

# HCP Bands

$$H_{\mathrm{HCP}}(\mathbf{k}) = -\mu' \begin{pmatrix} A\uparrow+B\uparrow & A\downarrow+B\downarrow & A\uparrow-B\uparrow & A\downarrow-B\downarrow \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} + \frac{v\hbar}{\gamma_0}|\mathbf{k}|(h'_{0x}+\gamma_0) \begin{pmatrix} A\uparrow+B\uparrow & A\downarrow+B\downarrow & A\uparrow-B\uparrow & A\downarrow-B\downarrow \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

$$- h'_{z0} \begin{pmatrix} A\uparrow+B\uparrow & A\downarrow+B\downarrow & A\uparrow-B\uparrow & A\downarrow-B\downarrow \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} + \frac{v\hbar}{\gamma_0}|\mathbf{k}|h'_{zx} \begin{pmatrix} A\uparrow+B\uparrow & A\downarrow+B\downarrow & A\uparrow-B\uparrow & A\downarrow-B\downarrow \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$H_{ATOP}(k=0) = -\mu' \Uparrow_\sigma \Uparrow_s - \frac{v\hbar}{\gamma_0}|k|(h'_{0x}+\gamma_0)\sigma_z \Uparrow_s - h'_{z0} \Uparrow_\sigma s_z$$

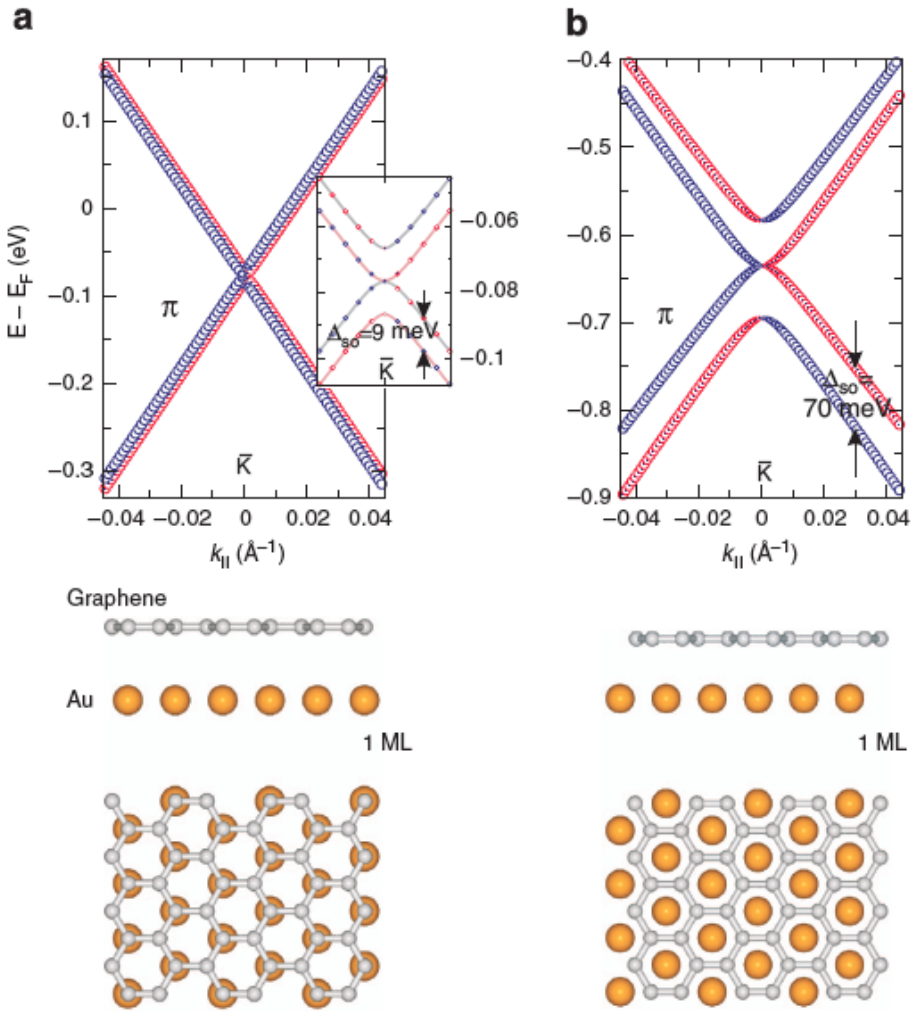
$$-\frac{v\hbar}{\gamma_0}|k| h'_{zx}\sigma_z s_z$$

$$\langle S_z \rangle = \langle A\uparrow -B\uparrow | \mathbb{1}_\sigma S_z | A\uparrow -B\uparrow \rangle$$

$$= \frac{1}{2}\begin{pmatrix} 1 & 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ -1 \\ 0 \end{pmatrix} = 1$$

Magnetization of states

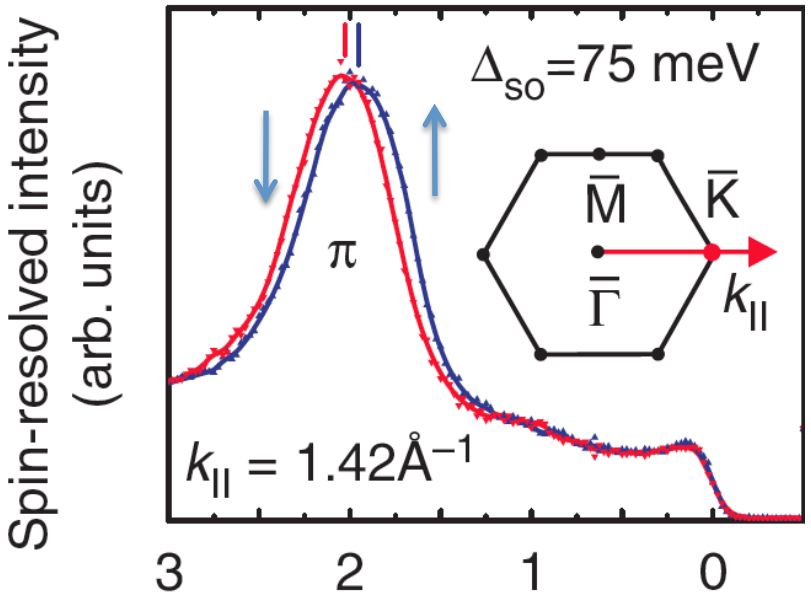
# Enhancing SO on graphene




Heavy atom proximity effect

Marchenko et al 2012
Exp+DFT **Nature Comm.**

Spin resolved ARPES




spin-resolved photoemission

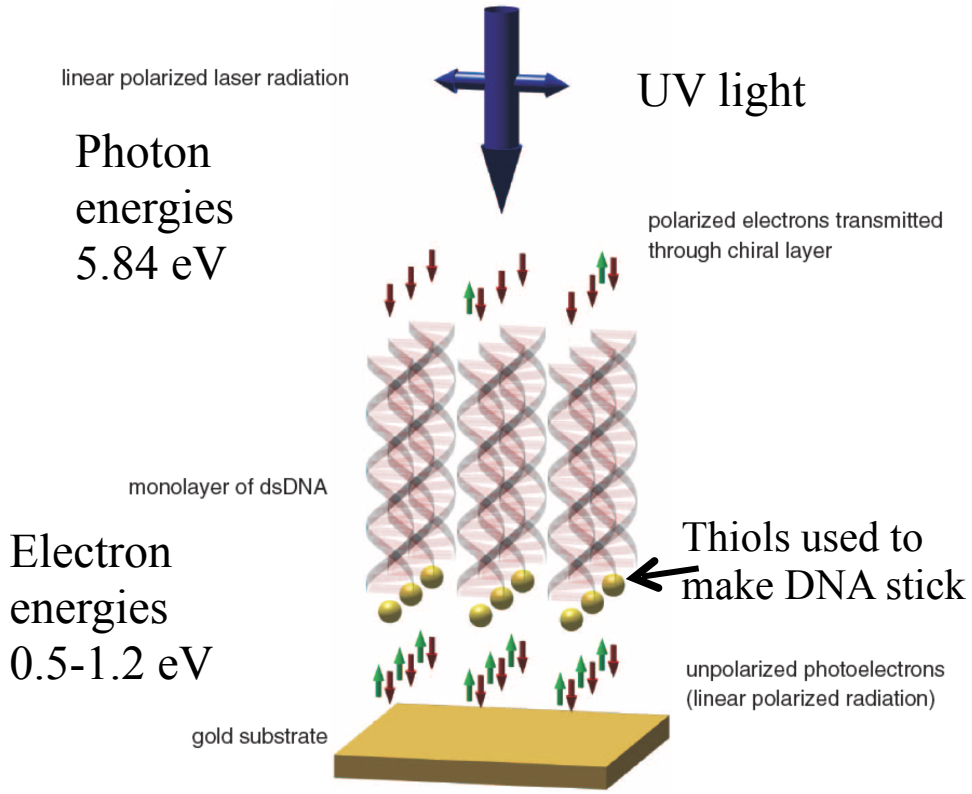
**A. Lopez et al PRB (2019)**

# Experiments: Polarizing photoelectrons

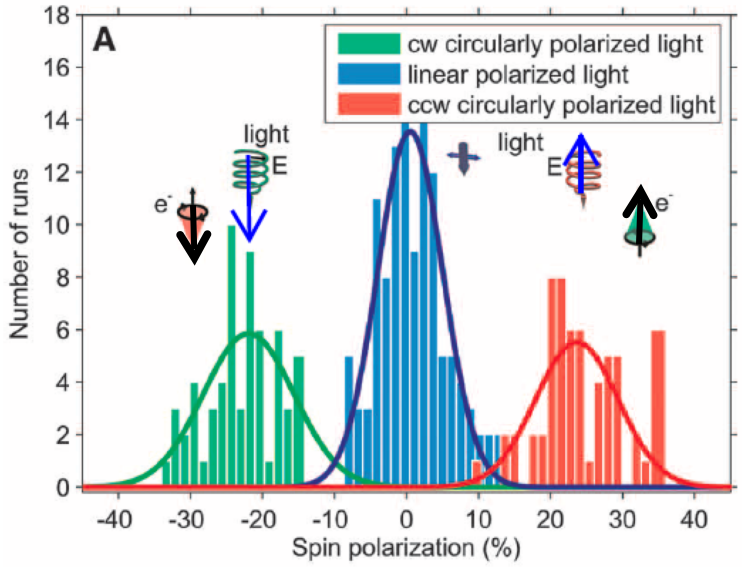
## Spin Selectivity in Electron Transmission Through Self-Assembled Monolayers of Double-Stranded DNA

18 FEBRUARY 2011 VOL 331 SCIENCE

B. Göhler,[1] V. Hamelbeck,[1] T. Z. Markus,[2] M. Kettner,[1] G. F. Hanne,[1] Z. Vager,[3]
R. Naaman,[2]* H. Zacharias[1]

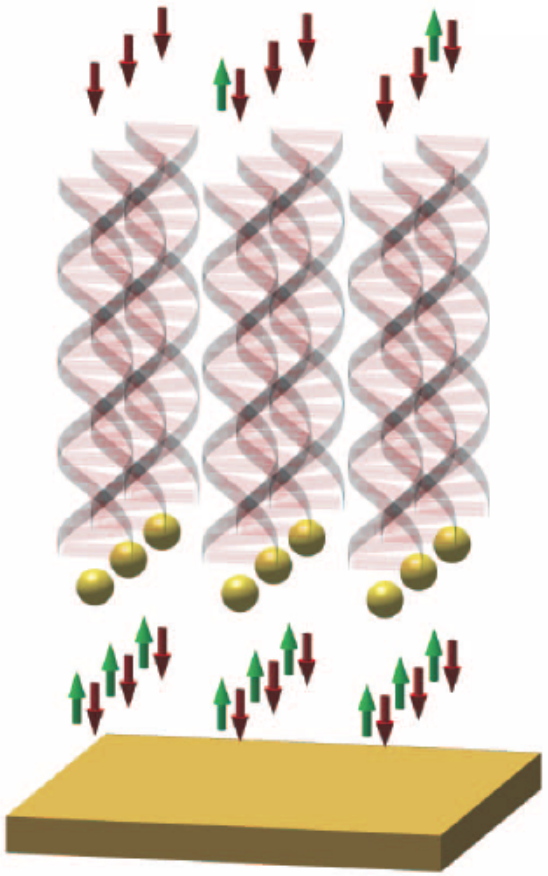


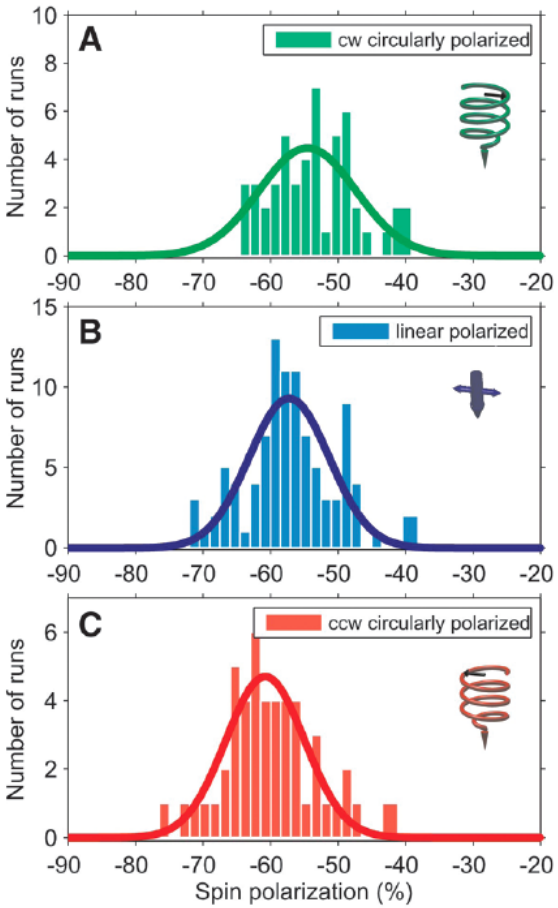

Bare surface



# Electron polarization with organic molecules

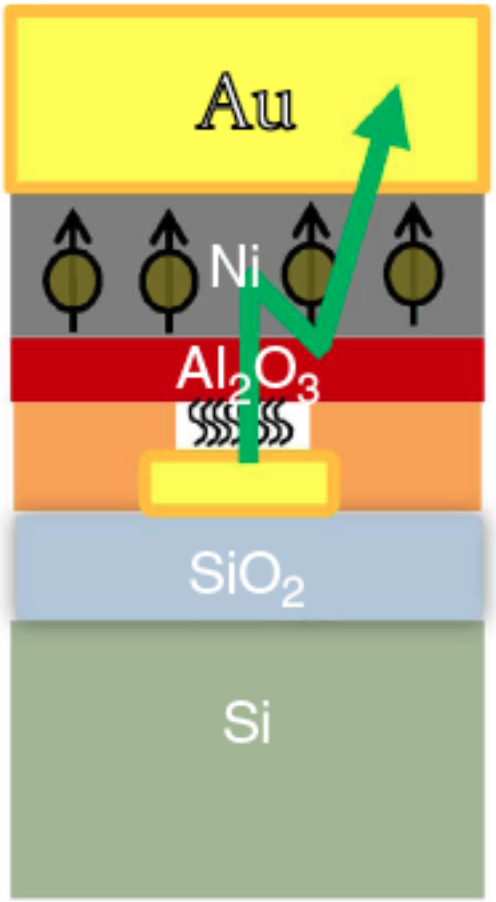
Naaman Nanolett. 2011






Chirality → electron polarization

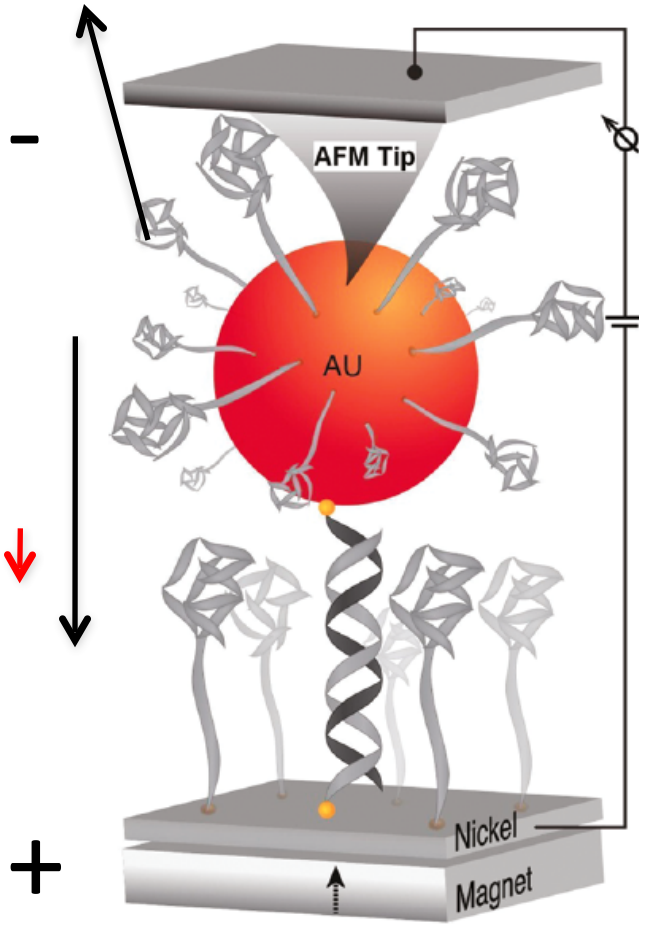
Nature 2013




Devices

# Tunneling electron polarization

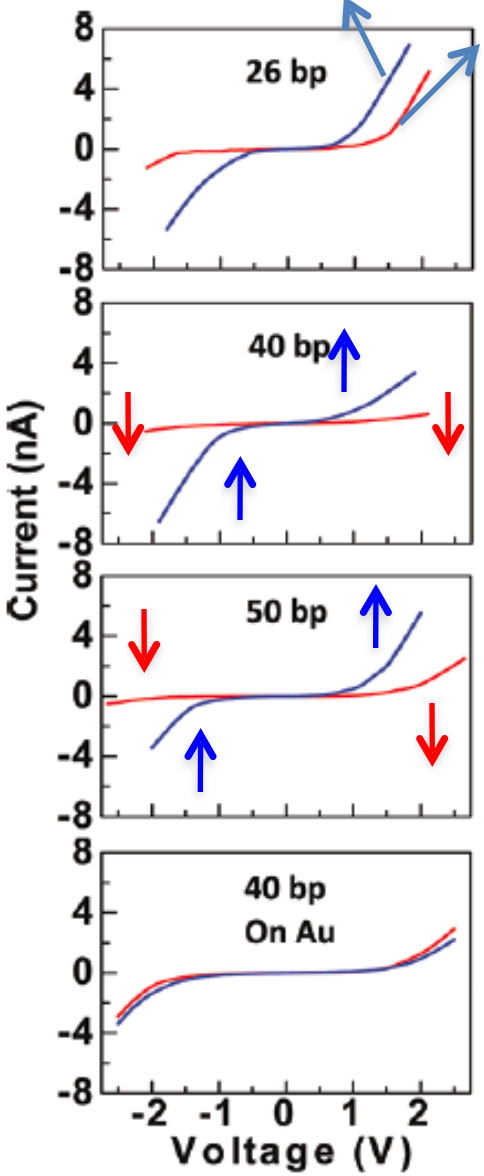
DNA separators




Single ds molecules

UP spin Ni

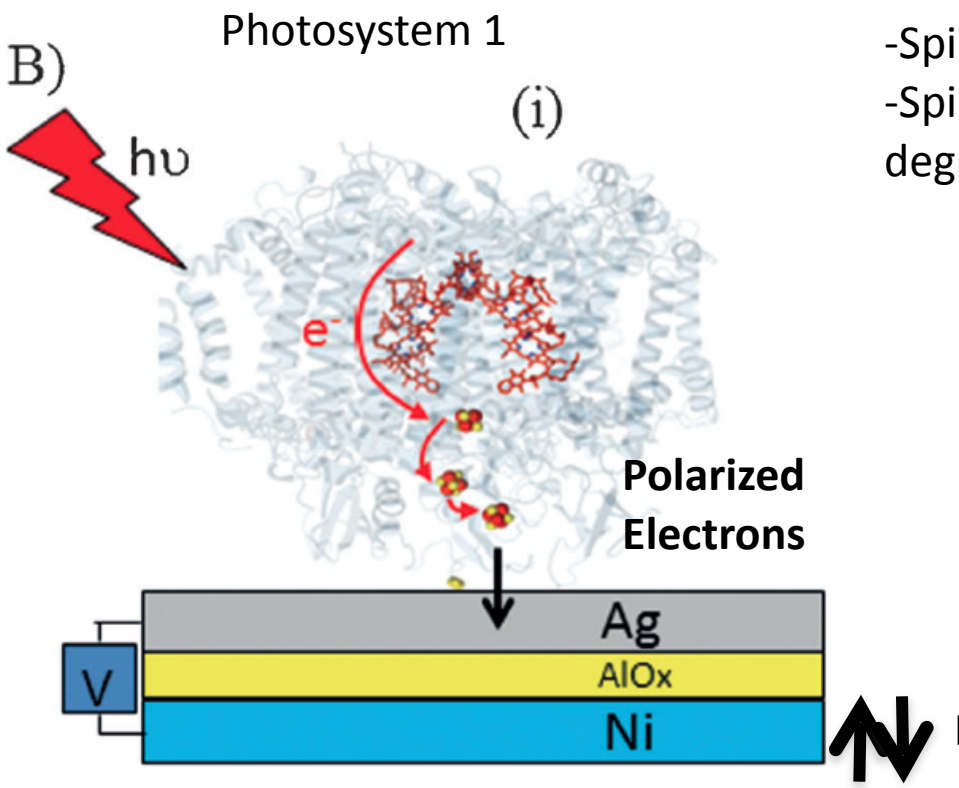
DOWN spin Ni



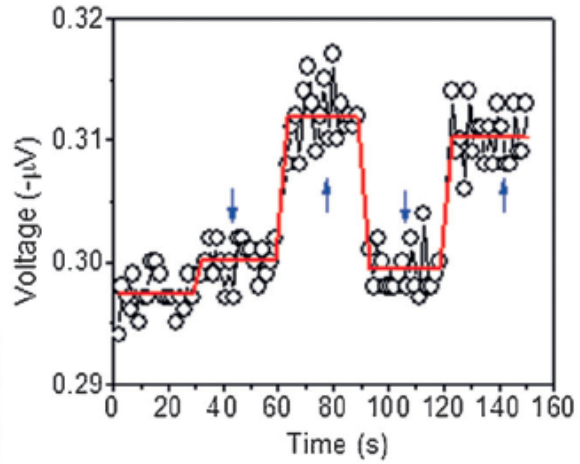

Xie et al Nanoletters 2011.

Barrier for transmission asymmetry between one spin orientation and the other

# Photosystem 1




-Spin aligned paralell to momentum!
-Spin effect optimal at room temp, degrades when you lower temp.

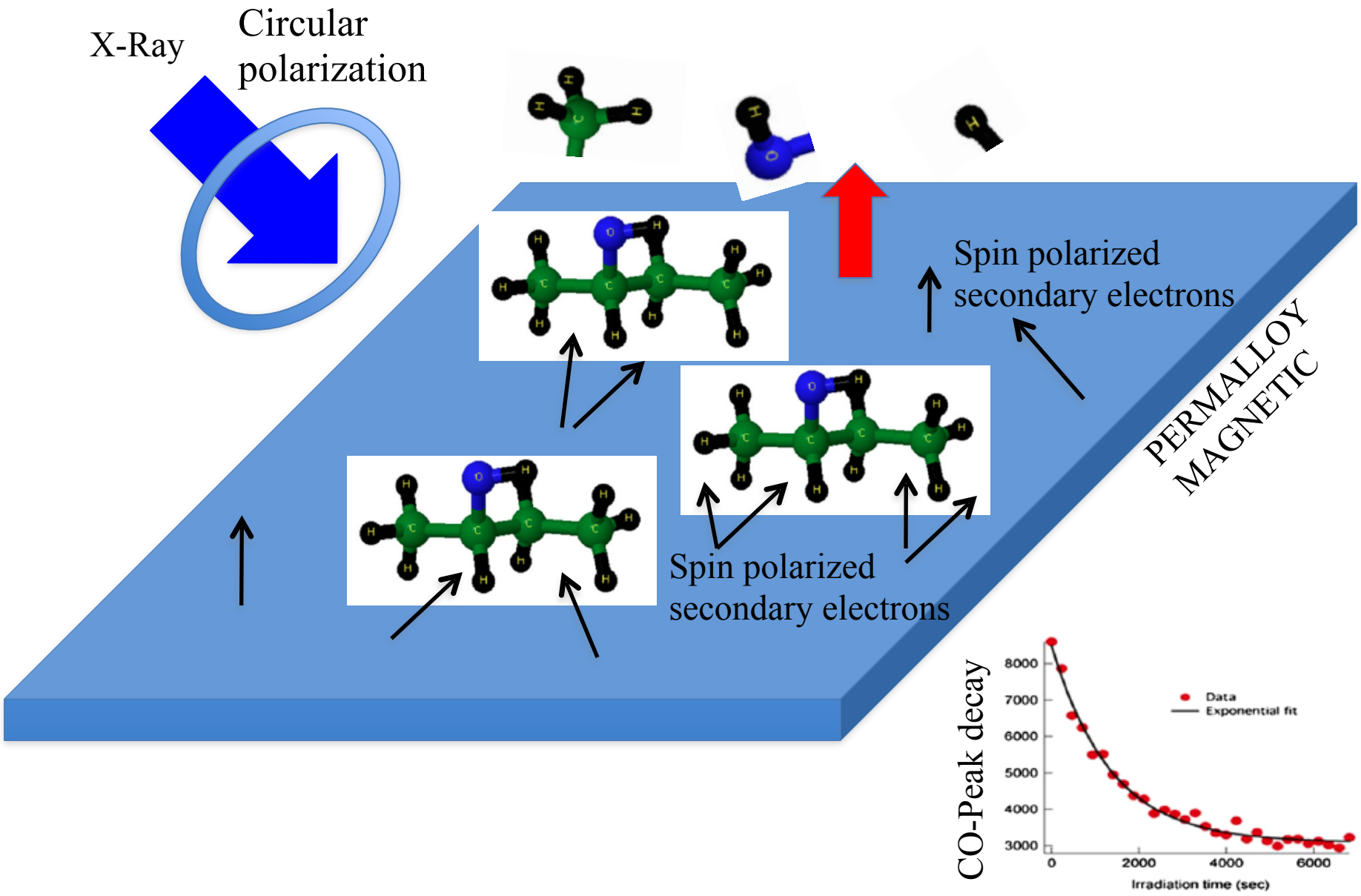



Ni orientation used to probe

Voltage between Ag and Ni tells spin accumulation orientation

Naaman et al Angewandte Chemie 2014

# Chiral reactions



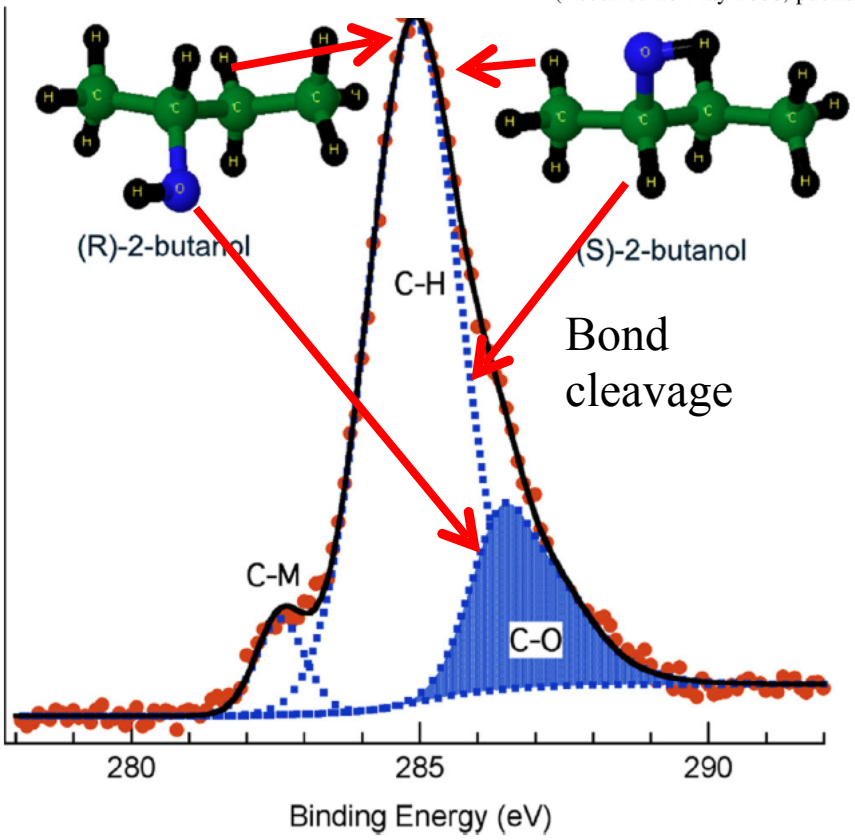
# Experiments: Chiral reactions spin sensitive

PRL 101, 178301 (2008) PHYSICAL REVIEW LETTERS week ending 24 OCTOBER 2008

Adsorbed Butanol on Permalloy

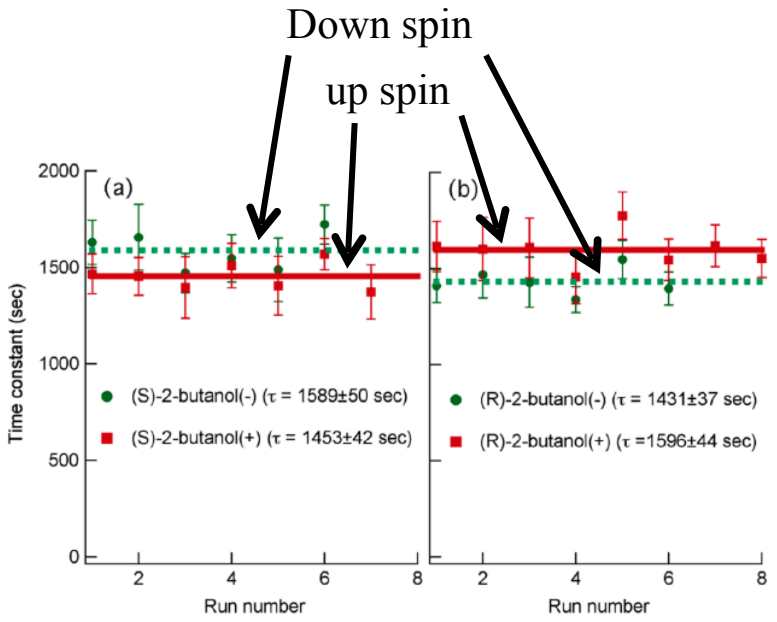
**Chiral-Selective Chemistry Induced by Spin-Polarized Secondary Electrons from a Magnetic Substrate**

R. A. Rosenberg,[1] M. Abu Haija,[1] and P. J. Ryan[2]
[1]*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[2]*MUCAT, Ames Laboratory, Ames, Iowa 50011, USA*
(Received 20 May 2008; published 21 October 2008)




Secondary pol. electron energies

Ease of cleavage depends on electron spin

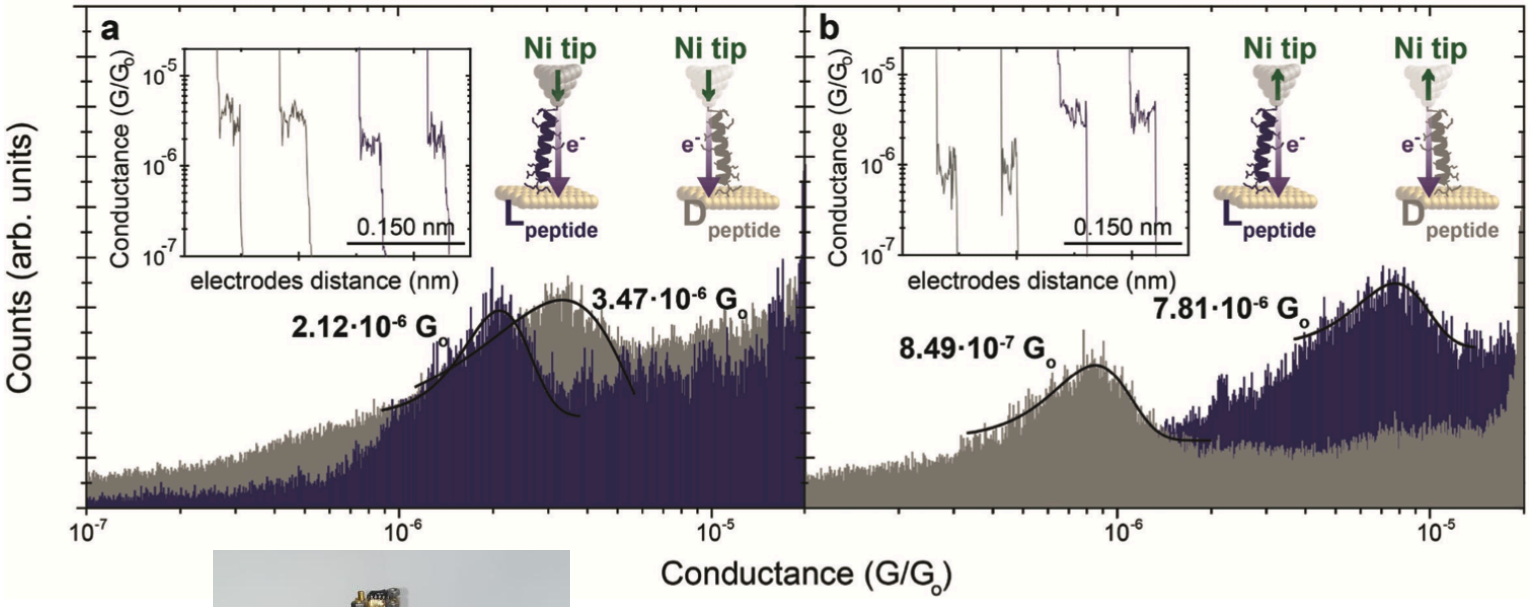


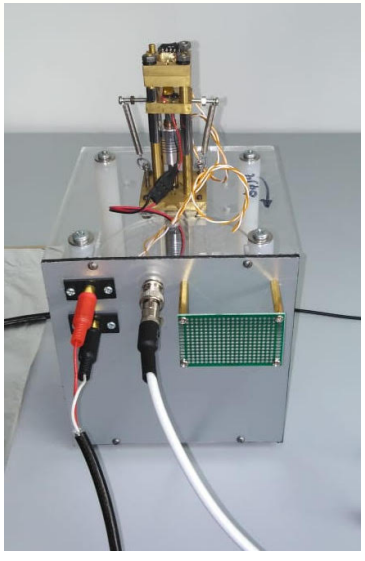

Spin torques involved?

→ SO interaction (No theory here)

# Conductance Histograms

Aragones et al Small 2016



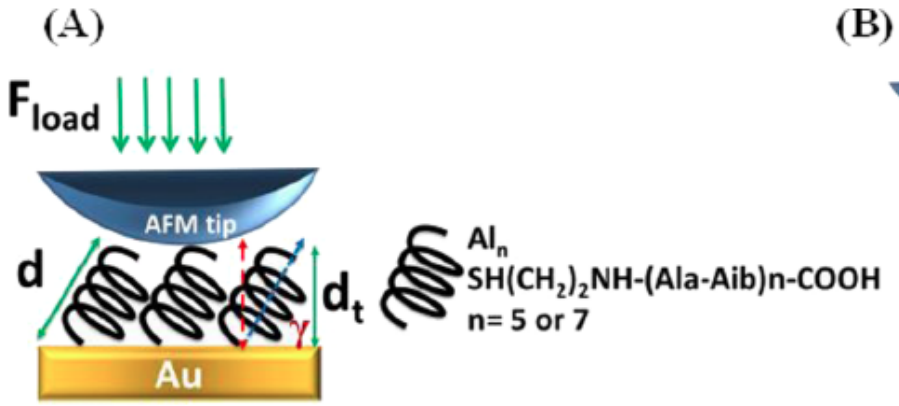
2019

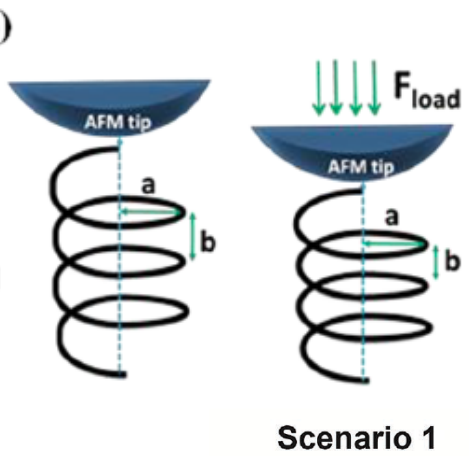
Break junction device built at Yachay Tech

first device of the Quantum Conductance Lab.

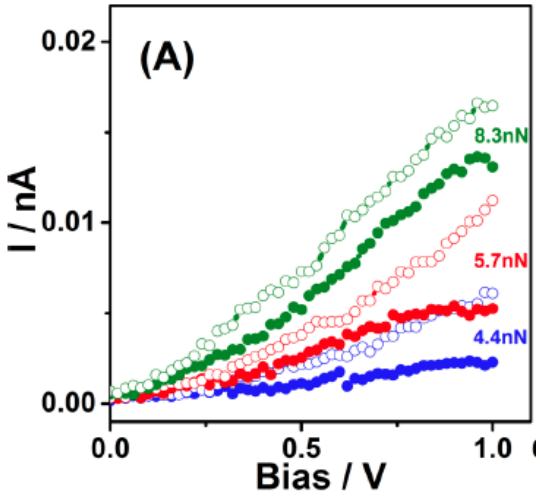
Werner Bramer CEPRA Project 2018

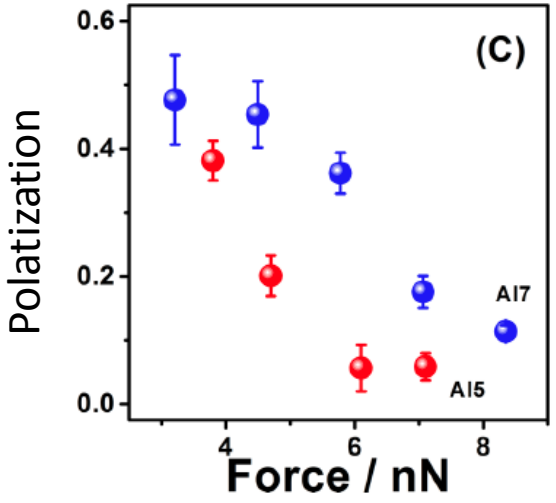
# Experiments stretching oligopeptides

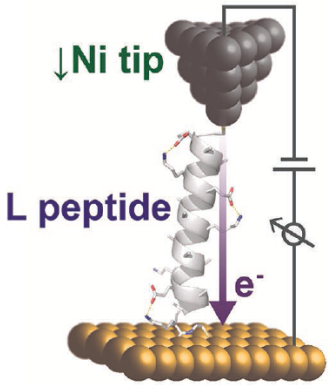



monolayers well oriented




**Spin polarization Is controlled by strain**

Kiran JCP 2017

# Summary of experiments

## Usual suspects

- No magnetic fields present
- No magnetic centers (relatively light atoms C, N, O)
- No sources of exchange interactions

## Spin polarization intensities

- Polarizations measured larger than those induced by a ferromagnet!
- Chirality a critical ingredient (popular in biol. systems)
- Surfaces appear not to play a role

# Where does spin activity come from?

- On the theoretical side we surmised that the spin-orbit interaction was to blame

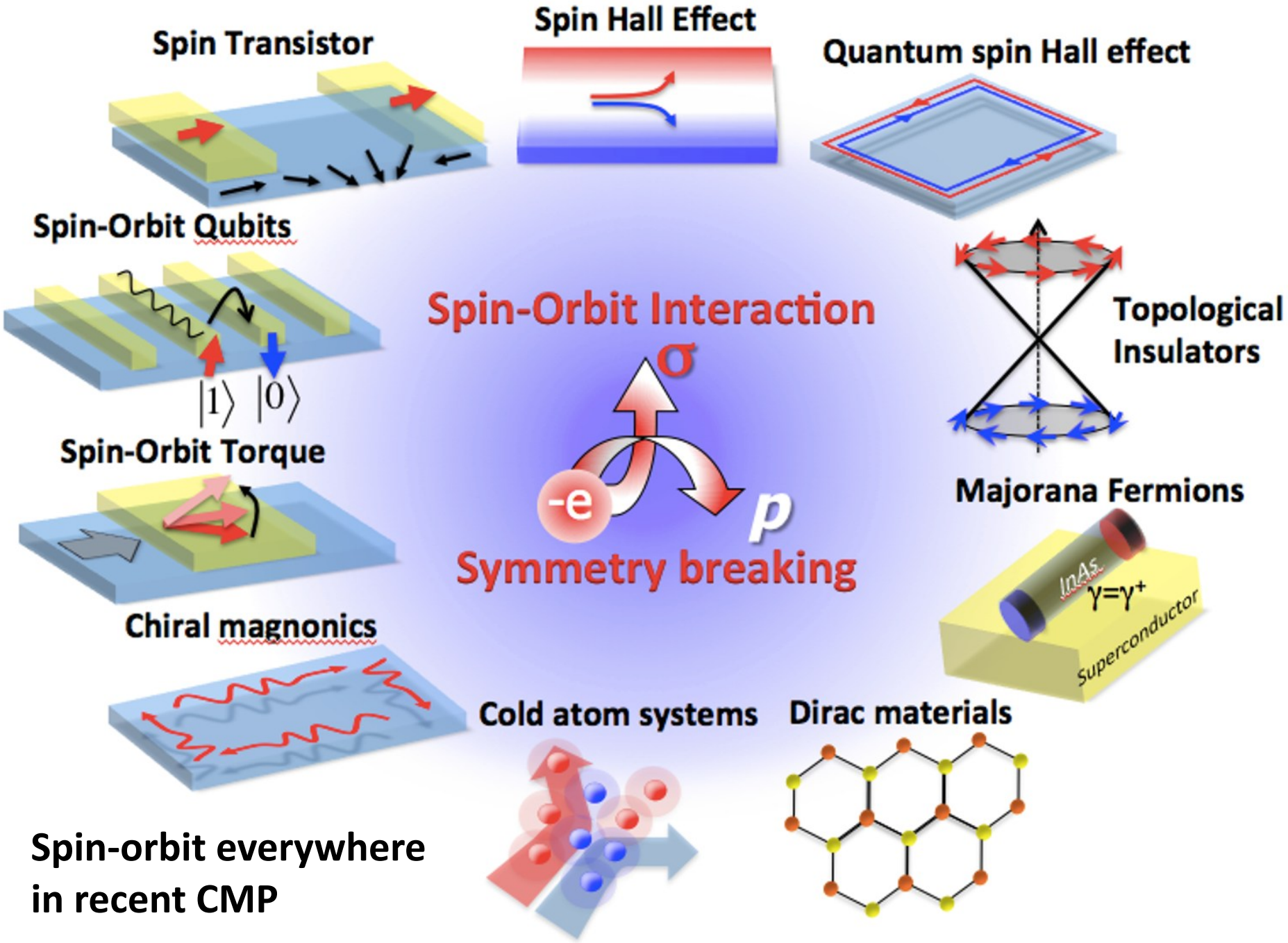

Change frames you get a magnetic field and spin is oriented

THE JOURNAL OF CHEMICAL PHYSICS **131**, 014707 (2009)

**Chiral electron transport: Scattering through helical potentials**

Sina Yeganeh,[1] Mark A. Ratner,[1,a)] Ernesto Medina,[2] and Vladimiro Mujica[1,3,b)]
[1]*Department of Chemistry and Center for Nanofabrication and Molecular Self-Assembly, Northwestern University, Evanston, Illinois 60208-3113, USA*
[2]*Laboratorio de Física Estadística de Sistemas Desordenados, Centro de Física, IVIC, Apartado 21827, Caracas 1020A, Venezuela*
[3]*Argonne National Laboratory, Center for Nanoscale Materials, Argonne, Illinois 60439-4831, USA*

(Received 20 March 2009; accepted 10 June 2009; published online 7 July 2009)




**Spin-orbit everywhere in recent CMP**

# The spin-orbit interaction in the vacuum

- The Spin-orbit interaction in the vacuum (free fields/charges) comes from the Pauli Eq.

$$\mathscr{H} = \frac{p^2}{2m_o} + V + V_0 + \frac{e\hbar}{2m_0}\sigma \cdot B - \frac{e\hbar\sigma \cdot p \times \mathscr{E}}{4m_o^2c^2} - \frac{e\hbar^2}{8m_0^2c^2}\nabla \cdot \mathscr{E}$$

$$-\frac{p^4}{8m_0^3c^2} - \frac{e\hbar p^2}{4m_0^3c^2}\sigma \cdot B - \frac{(e\hbar B)^2}{8m_0^3c^2}$$

$$v = 10^6 \text{ m/s}$$

**Bare SO interaction**

$$-\frac{e\hbar\sigma \cdot p \times \mathscr{E}}{4m_o^2c^2} =$$

$\mathscr{E} = 10^6$ V/m: $2 \times 10^{-9}$ eV

$\mathscr{E} = 10^9$ V/m: $2 \times 10^{-6}$ eV

very small bare interaction because of denominator effects

# Summary of external sources

- Reasonable external sources of electric field cannot explain the experimental results (eV range) $10^6 - 10^9\ V/m$
- Electric fields from electronegativity polarization are also too small
- What about internal fields?

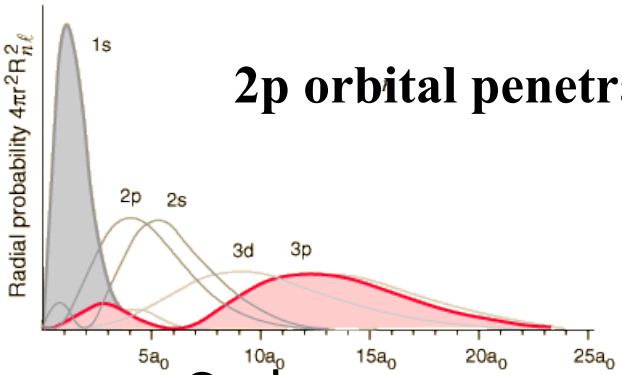
# Spin-orbit interaction from atomic source

**From the strongest electric fields present: Close to the atomic nucleus**

$$\left\langle p_z \left| H_{SO} \right| p_{x,y} \right\rangle = \left\langle p_z \left| \frac{e\hbar}{4m_0^2 c^2} s \cdot (p \times \mathcal{E}) \right| p_{x,y} \right\rangle \approx meV$$ Carbon

$$= \frac{\left( me^4 Z^2 / 2\hbar^2 n^2 \right)^2}{3m_0 c^2}$$

**Evaluated at angular momentum of hydrogenic electron exposure to inner cores**




**2p orbital penetration**

Carbon

**Involved fields top** $10^{12}$ V/m

# SO from atomic source

- Source of SO is from atomic SO coupling, C, N, O involved (Electric field of atomic cores)

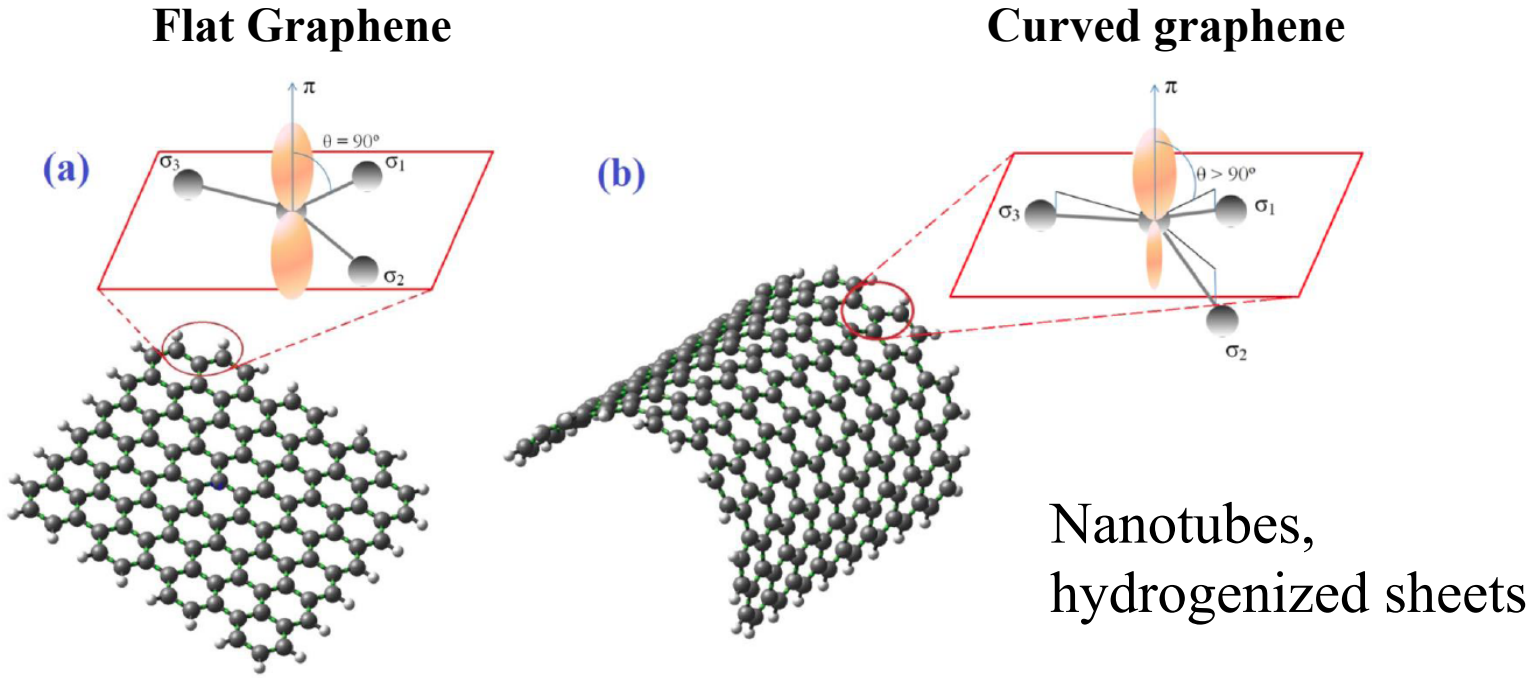
J. Chem. Phys. (2009)
Europhys Lett. (2012)
J. Chem. Phys (2015)
Phys. Rev. B (2016)

**Table 3.2.** Contribution $\Delta_j$ of atom $j$ to the SO splitting $\Delta_0$ from [15]

| | | | | | |
|---|---|---|---|---|---|
| Be | B | C | N | O | F |
| 0.002 | 0.004 | 0.006 | 0.009 | 0.010 | 0.010 |
| Mg | Al | Si | P | S | Cl |
| 0.01 | 0.024 | 0.044 | 0.08 | 0.09 | 0.09 |
| Zn | Ga | Ge | As | Se | Br |
| 0.10 | 0.18 | 0.29 | 0.43 | 0.48 | 0.49 |
| Cd | In | Sn | Sb | Te | I |
| 0.10 | 0.36 | 0.80 | 1.05 | 1.10 | 1.11 |
| Hg | Tl | Pb | | | |
| 0.5 | 0.9 | 2.0 | | | |

# How SO is enhanced by geometry

Example Graphene




Nanotubes,
hydrogenized sheets

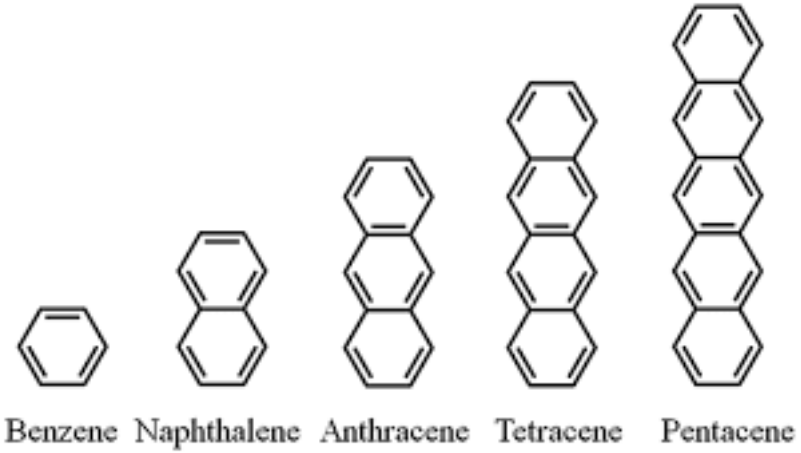
$\text{SO Coupling} = 1\mu eV$

Second order in interaction

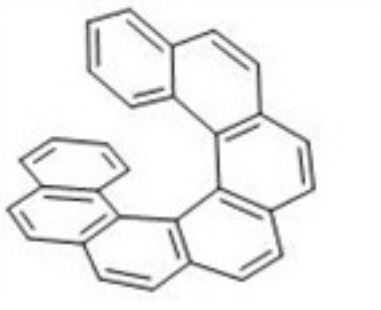
$\text{SO Coupling} = 1meV$

first order in interaction

# Bencene,Napthalene…versus helicene




Helicene



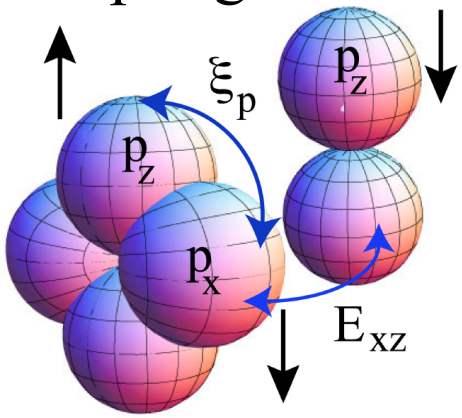
Very small SO second order in atomic SO

Three orders of magnitude larger SO, First order in atomic SO

Evidence SO is coming from the atomic SO and the WF overlaps

# SO from the atomic cores an intuitive approach

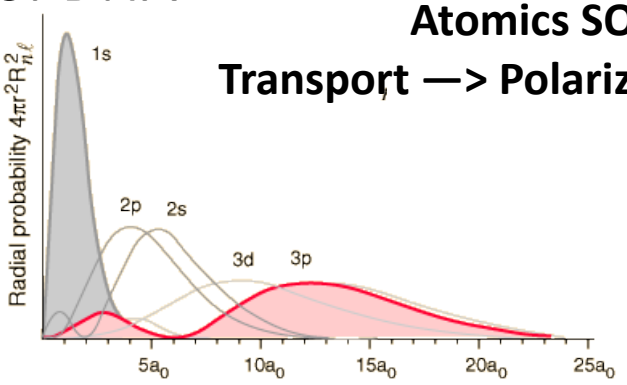
SO comes from Atomic coupling




SO Intrinsic

With geometry of DNA

**Atomics SO to Transport —> Polarized electrons**




**Evaluated at angular momentum of hydrogenic electron exposure to inner cores**

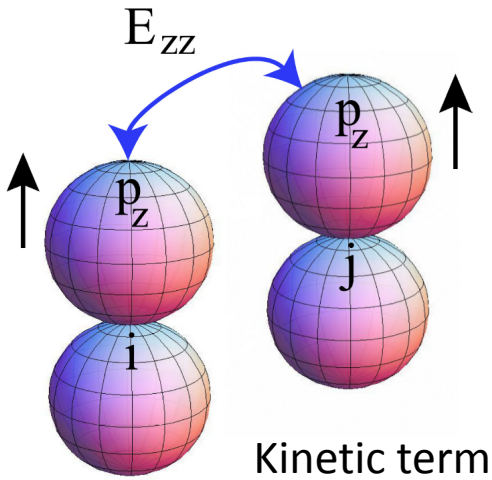
$$\left\langle p_z \left| H_{SO} \right| p_{x,y} \right\rangle = \left\langle p_z \left| \frac{e\hbar}{4m_0^2 c^2} s \cdot (p \times \mathcal{E}) \right| p_{x,y} \right\rangle \approx meV$$

**Carbon**

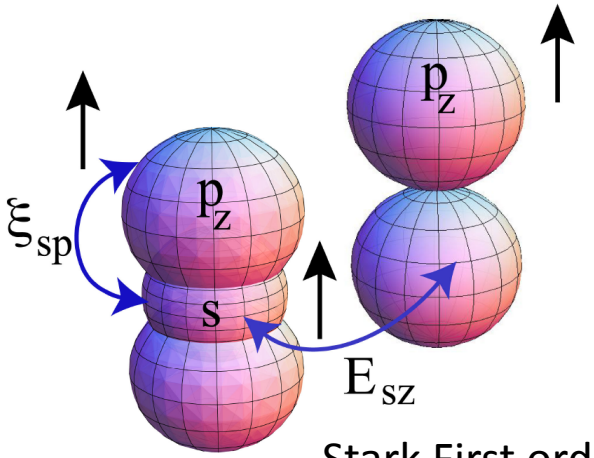
$$= \frac{\left(me^4 Z^2 / 2\hbar^2 n^2\right)^2}{3m_0 c^2} = \xi_p$$

Involved fields top $10^{12}$ V/m

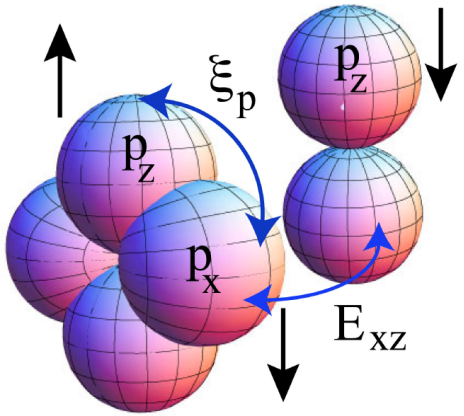
# Orbital hoppings



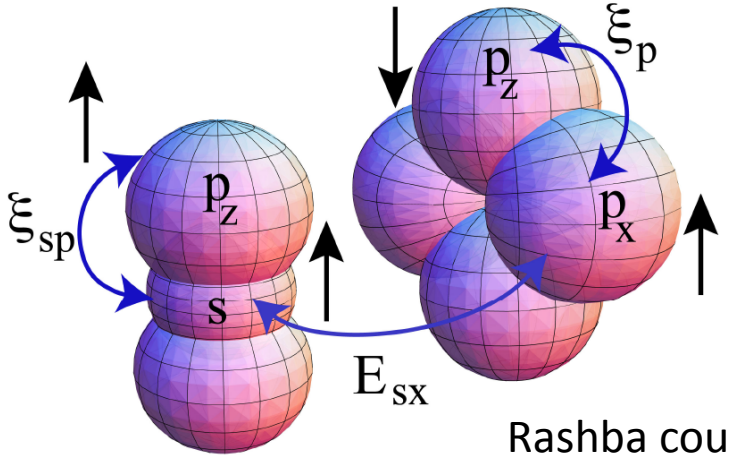

Kinetic term




Stark First order coupling

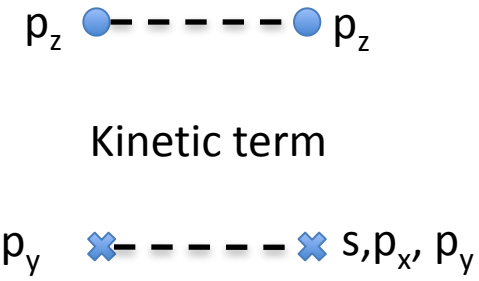


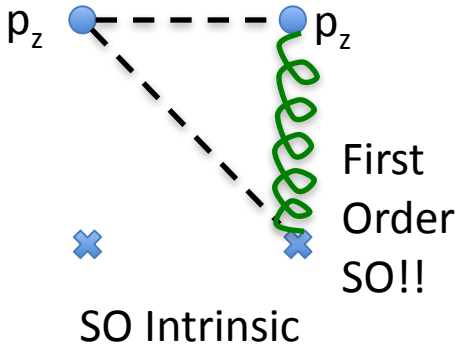

SO Intrinsic

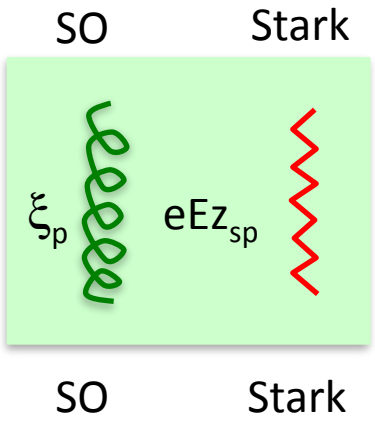


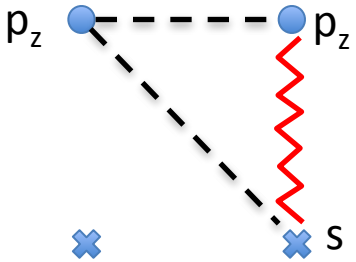

Rashba coupling

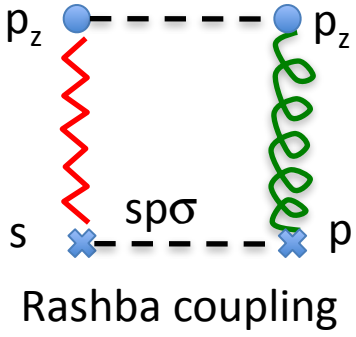
# Lowest order terms

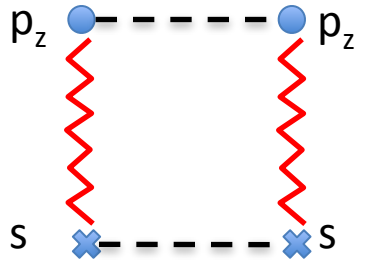


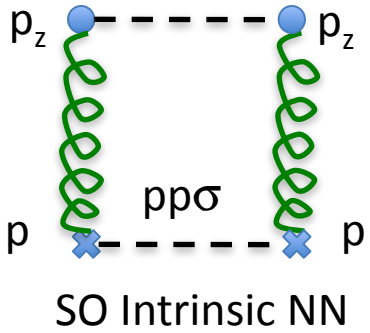



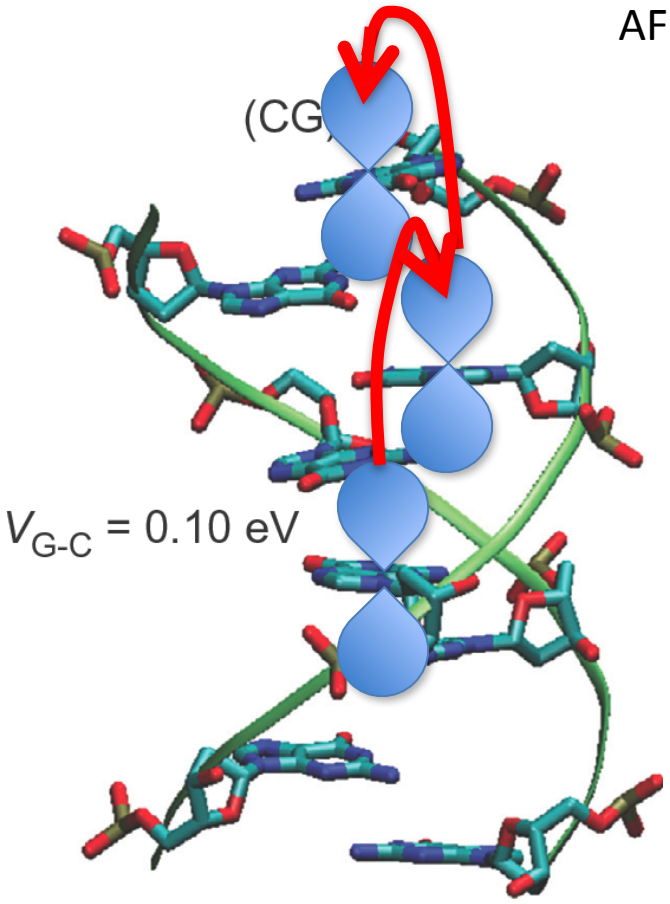



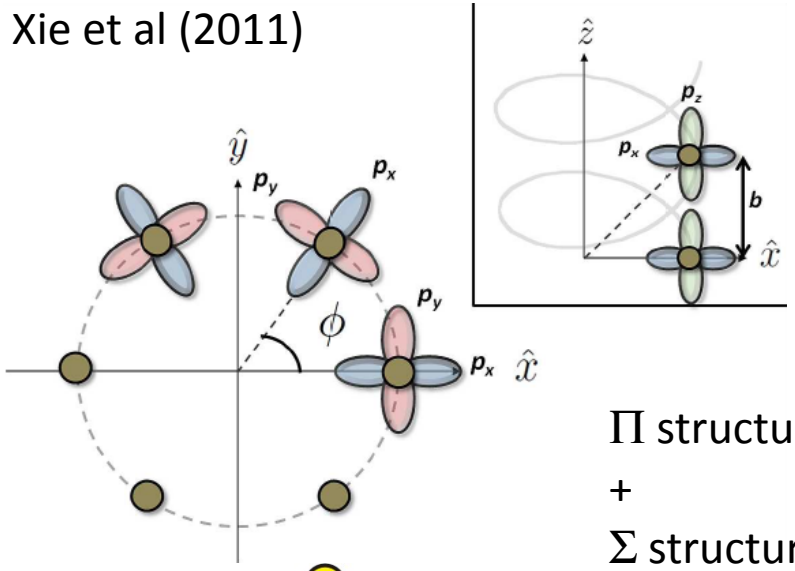




+ NNN terms

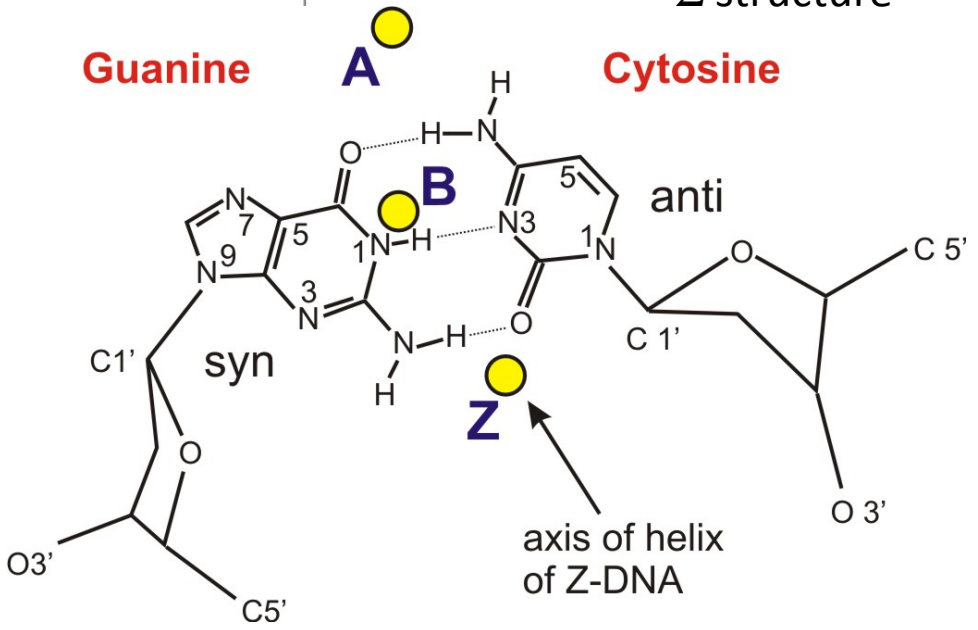
# Electrons bound to states in molecule




AFM setup Xie et al (2011)

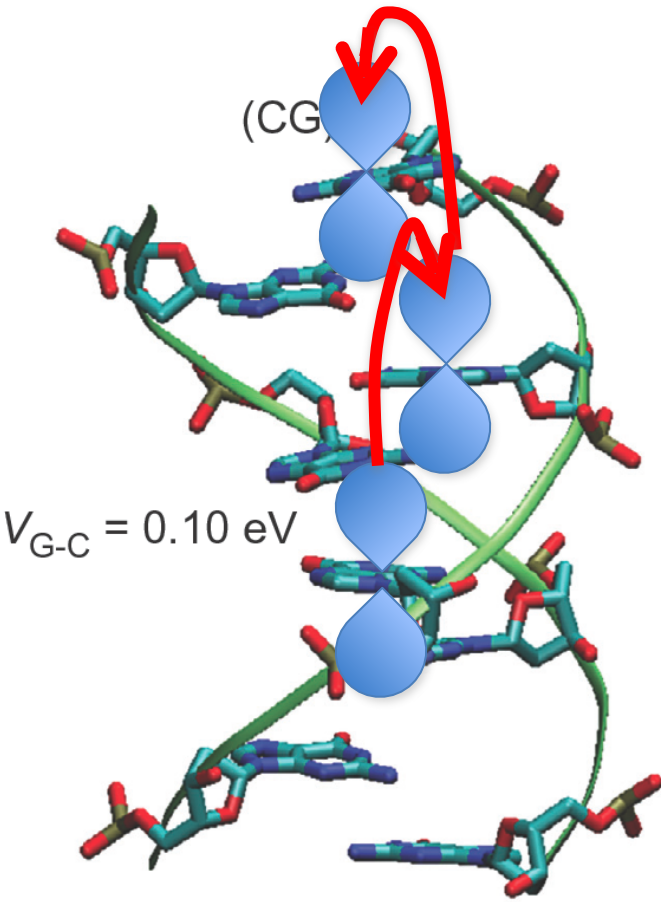


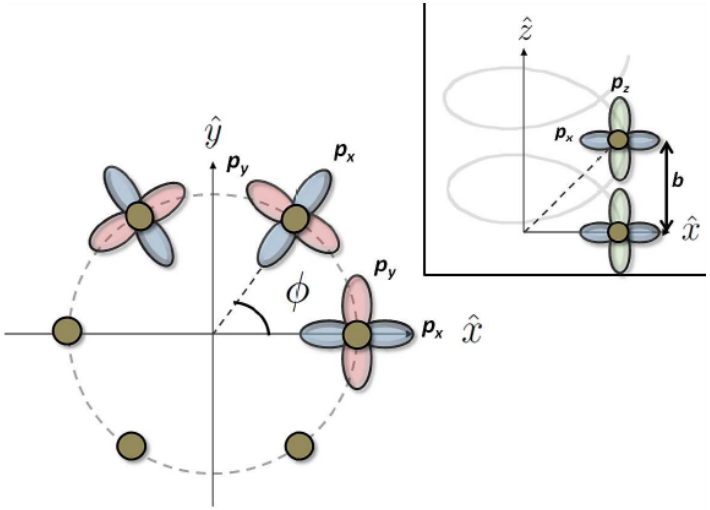

Π structure
+
Σ structure



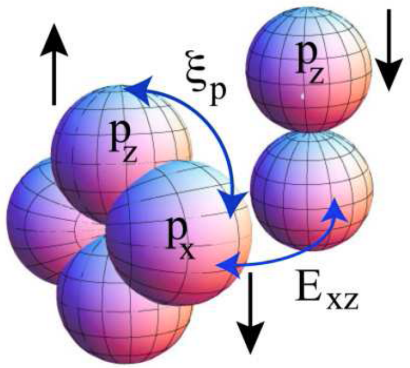

Arrange of orbital results in first order SO coupling

# Transport model DNA

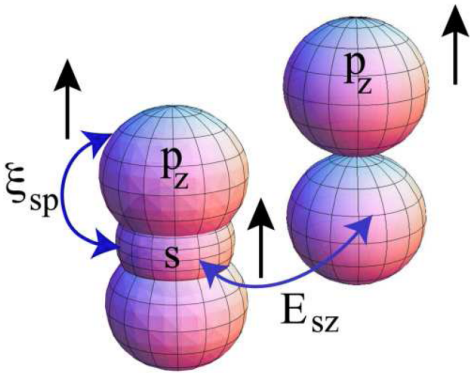



SO 1st order

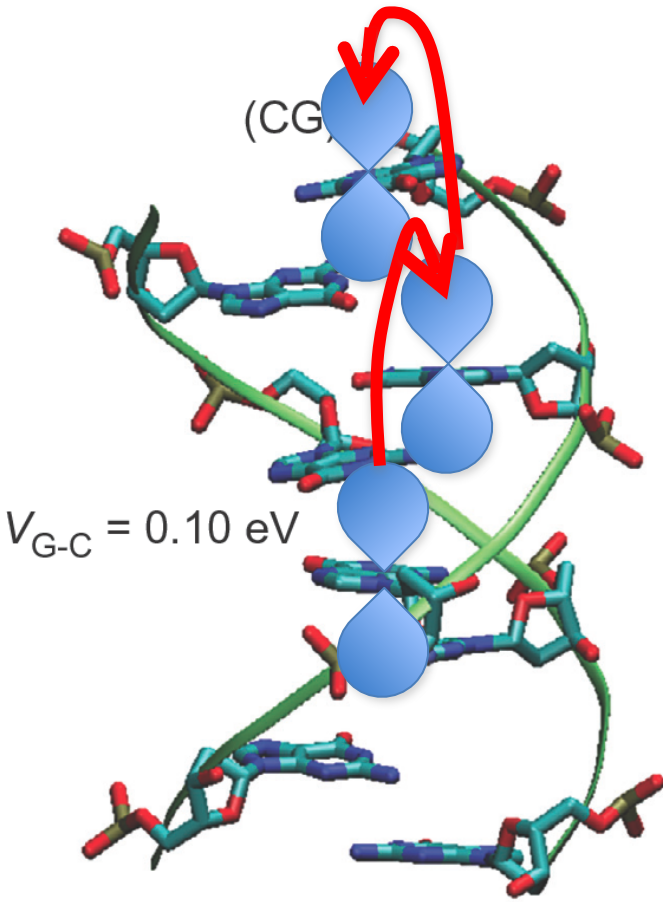


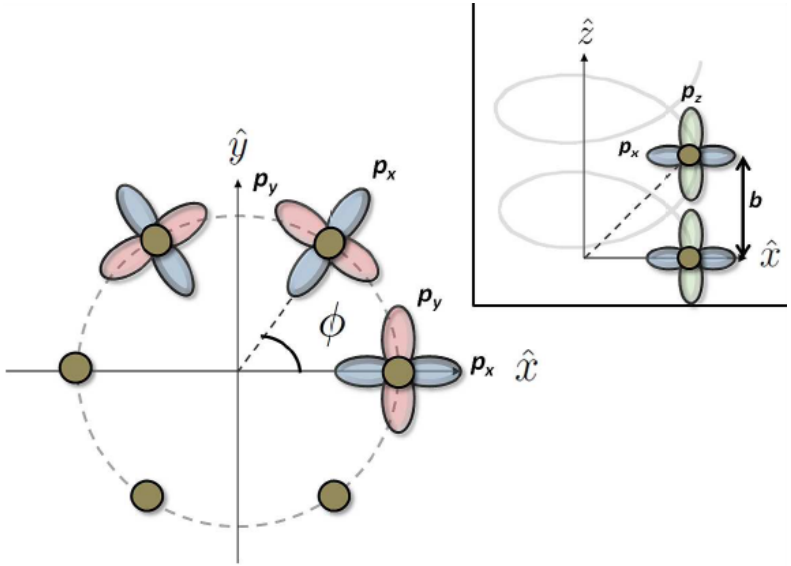

Stark term 1st order

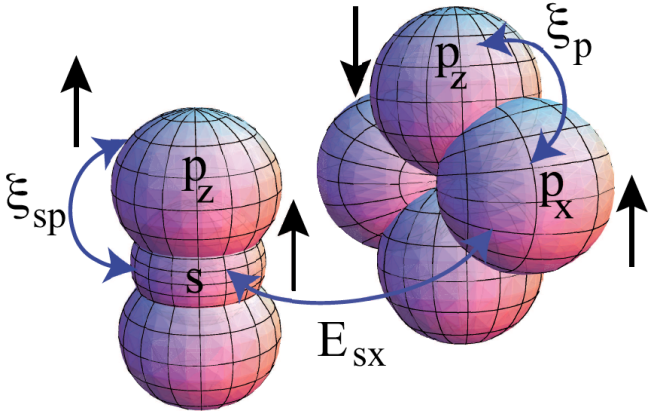



Varela, Mujica, Medina 2016

# Transport model DNA



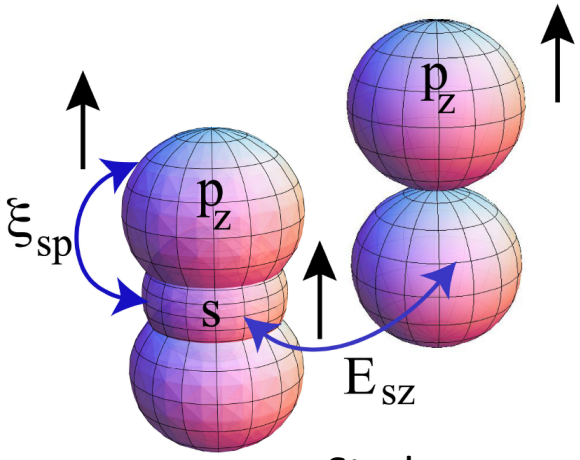

Rashba Term

Varela, Mujica, Medina 2016

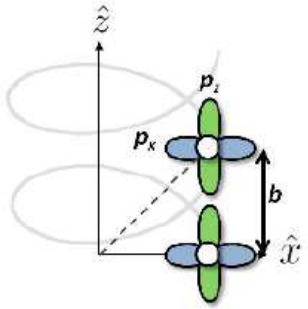
# Overlaps with DNA twist

$$E^{J}_{sx} = \frac{a(1-\cos\Delta\phi)}{|\mathbf{R}_{Ji}|}V^{\sigma}_{sp} = -E^{J}_{xs},$$

$$E^{J}_{sy} = -\frac{a\sin(\phi_J-\phi_i)}{|\mathbf{R}_{Ji}|}V^{\sigma}_{sp} = -E^{J}_{ys}$$

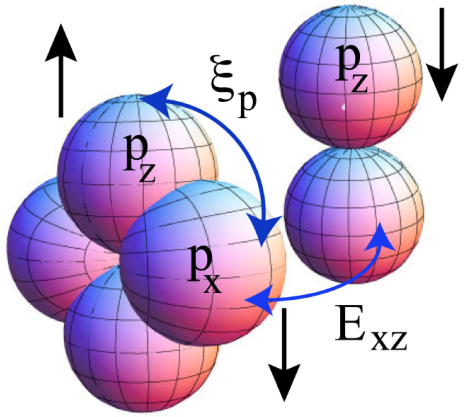



Stark




$$E^{J}_{xz} = \frac{2ab\sin^2\left(\frac{\Delta\phi}{2}\right)(\phi_i-\phi_J)(V^{\sigma}_{pp}-V^{\pi}_{pp})}{2\pi|\mathbf{R}_{Ji}|^2} = E^{J}_{zx}$$

$$E^{J}_{yz} = \frac{ab\sin(\phi_J-\phi_i)(\phi_J-\phi_i)(V^{\sigma}_{pp}-V^{\pi}_{pp})}{2\pi|\mathbf{R}_{Ji}|^2} = E^{J}_{zy}$$




Intrinsic SO

# Tight binding Hamiltonian

$$H_K^{in} = \left[ V_{pp}^{\pi(in)} + \frac{b^2\Delta\phi^2\left(V_{pp}^{\sigma(in)} - V_{pp}^{\pi(in)}\right)}{8\pi^2a^2(1-\cos\Delta\phi) + b^2\Delta\phi^2} \right] \sum_{ij} c_i^\dagger c_j,$$

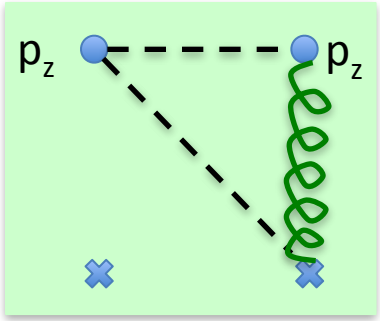
$$= t^{in} \sum_{ij} c_i^\dagger c_j,$$

inside strand (in)

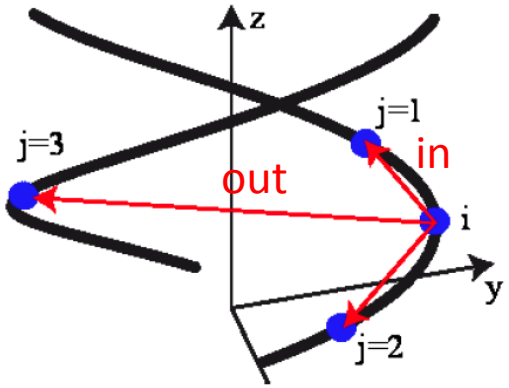
$$H_K^{out} = V_{pp}^{\pi(out)} \sum_{ij} c_i^\dagger c_j,$$

$$= t^{out} \sum_{ij} c_i^\dagger c_j,$$

Between strands (out)




$$H_{SO}^{in} = i\lambda_{SO}^{in} \sum_{ij} c_i^\dagger \nu_{ij} s_y c_j.$$




pitch

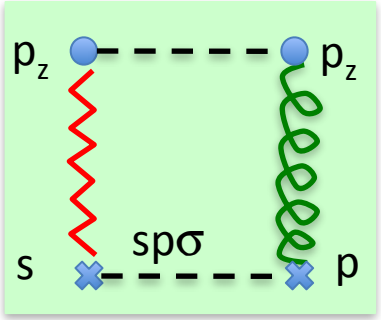
Bare SO

SO Intrinsic

$$\lambda_{SO}^{in} = \frac{4\pi\xi_p ab\Delta\phi(1-\cos\Delta\phi)\left(V_{pp}^{\sigma(in)} - V_{pp}^{\pi(in)}\right)}{\left(\epsilon_{2p}^{\pi} - \epsilon_{2p}^{\sigma}\right)\left(8\pi^2a^2(1-\cos\Delta\phi) + b^2\Delta\phi^2\right)},$$

very small
first order SO
between strands

# Tight binding terms




Rashba coupling

$$H_R^{in} = i \sum_{ij} c_i^\dagger \left( \lambda_R^{in(1)} s_y + \nu_j \lambda_R^{in(2)} s_x \right) c_j,$$

Rashba Interaction (inside strand)

$$\lambda_R^{in(1)} = \frac{2\pi \xi_p \xi_{sp} a (\cos\Delta\phi - 1) V_{sp}^{in}}{\sqrt{8\pi^2 a^2 (1-\cos\Delta\phi) + b^2 \Delta\phi^2}} \left[ \frac{1}{\left(\epsilon_{2p}^{\pi} - \epsilon_{2p}^{\sigma}\right)\left(\epsilon_{2p}^{\pi} - \epsilon_s\right) - \frac{2\left(2\pi a (1-\cos\Delta\phi) V_{sp}^{in}\right)^2}{8\pi^2 a^2 (1-\cos\Delta\phi) + b^2 \Delta\phi^2}} - \alpha \right]$$

$$\lambda_R^{in(2)} = -\frac{2\pi \xi_p \xi_{sp} a \sin\Delta\phi V_{sp}^{in}}{\sqrt{8\pi^2 a^2 (1-\cos\Delta\phi) + b^2 \Delta\phi^2}} \left[ \frac{1}{\left(\epsilon_{2p}^{\pi} - \epsilon_{2p}^{\sigma}\right)\left(\epsilon_{2p}^{\pi} - \epsilon_s\right) - \frac{2\left(2\pi a \sin\Delta\phi V_{sp}^{in}\right)^2}{8\pi^2 a^2 (1-\cos\Delta\phi) + b^2 \Delta\phi^2}} + \alpha \right]$$

# Tight binding terms

Rashba interaction between strands

$$H_R^{out} = i\lambda_R^{out} \sum_{ij} c_i^\dagger s_y c_j$$

$$\lambda_R^{out} = \frac{\xi_p \xi_{sp} V_{sp}^{out}}{(\epsilon_{2p}^\pi - \epsilon_s)(\epsilon_{2p}^\pi - \epsilon_{2p}^\sigma) + (V_{sp}^{out})^2}$$

Full lowest order Hamiltonian

$$\mathcal{H} = t^{in} \sum_{\langle ij \rangle}^{helix} c_i^\dagger c_j + t^{out} \sum_{\langle ij \rangle}^{base} c_i^\dagger c_j + i\lambda_{SO}^{in} \sum_{\langle ij \rangle}^{helix} c_i^\dagger \nu_{ij} s_y c_j + i\lambda_R^{in(1)} \sum_{\langle ij \rangle}^{helix} c_i^\dagger s_y c_j$$
$$+ i\lambda_R^{in(2)} \sum_{\langle ij \rangle}^{helix} c_i^\dagger \nu_{ij} s_x c_j + i\lambda_R^{out} \sum_{\langle ij \rangle}^{base} c_i^\dagger s_y c_j.$$

# Analytical Tight-binding

Effective SO coupling

Bare SO

pitch

$$\lambda_{SO}^{in} = \frac{4\pi\xi_p ab\Delta\phi(1-\cos\Delta\phi)\left(V_{pp}^{\sigma(in)} - V_{pp}^{\pi(in)}\right)}{(\epsilon_{2p}^{\pi} - \epsilon_{2p}^{\sigma})\left(8\pi^2a^2(1-\cos\Delta\phi) + b^2\Delta\phi^2\right)}$$

Within each helix

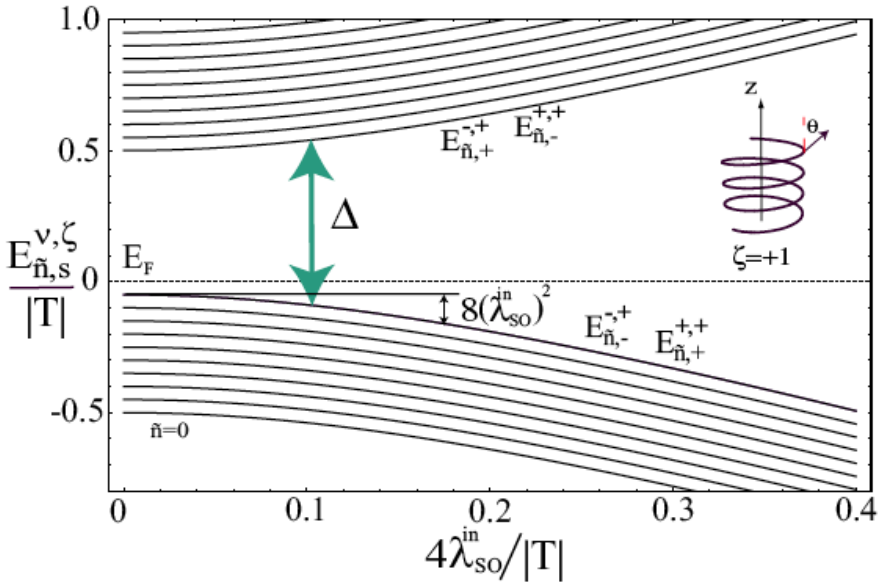
$$\lambda_R^{out} = \frac{\xi_p\xi_{sp}V_{sp}^{out}}{(\epsilon_{2p}^{\pi} - \epsilon_s)(\epsilon_{2p}^{\pi} - \epsilon_{2p}^{\sigma}) + (V_{sp}^{out})^2}$$

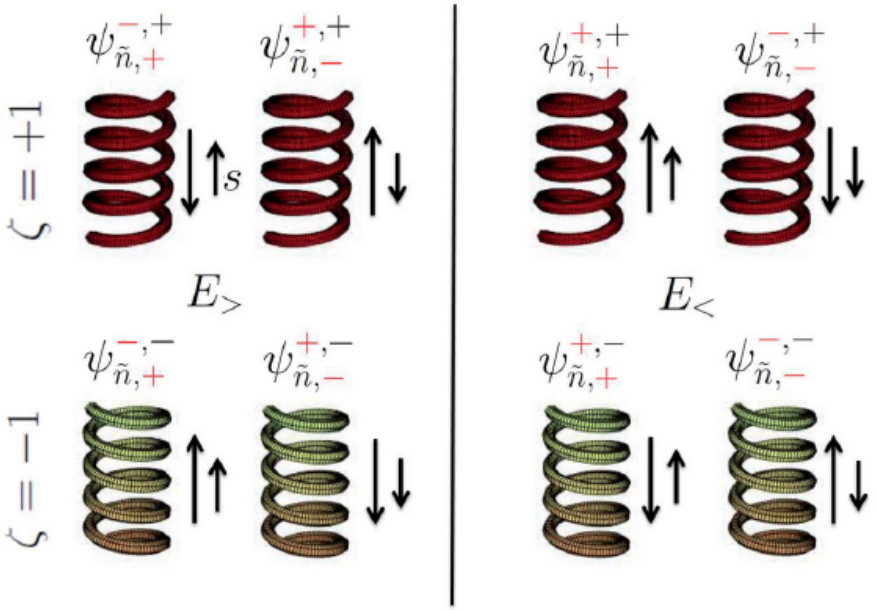
Between helices

Varela, Medina 2016

# Results

- For DNA specifically (two independent strands)




gap 10 meV < room temp!

Polarization one order lower than seen in experiments

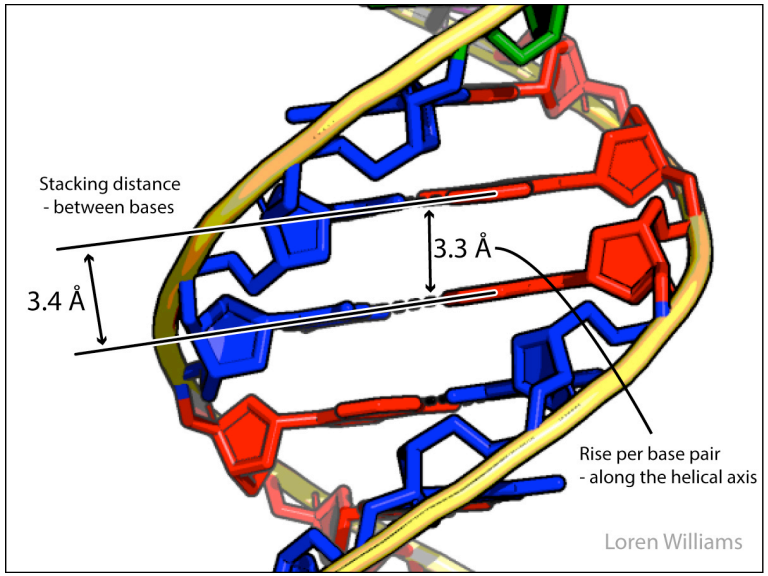
Kramers doublets time reversal symmetry preserved

As in edge states of Topological insulators

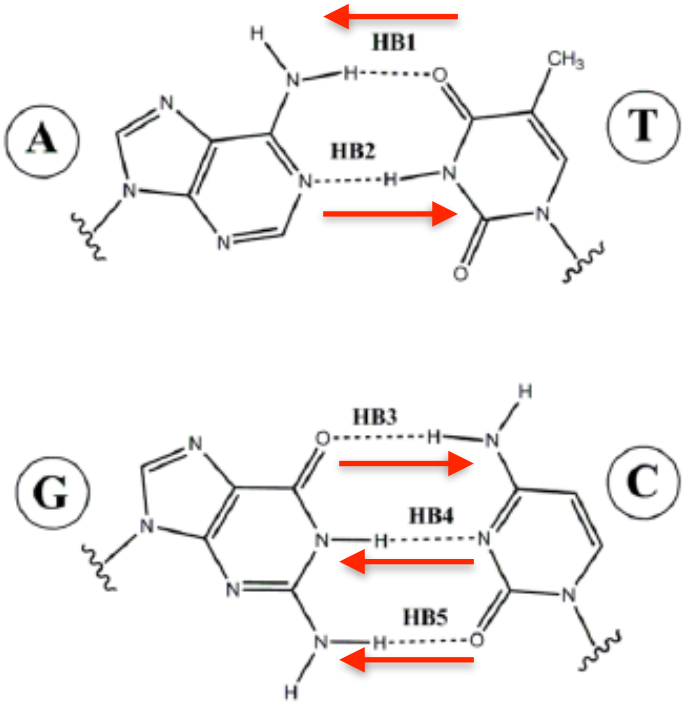
# Summary of theory

- Internal source of electric fields
- tight-binding approach gives a broad scenario of the spin effects to be complemented by more detailed calculations
- All qualitative features of the experiment reproduced…. except
  - **MAGNITUDE OF THE EFFECT**

# Dipoles in DNA on Hydrogen bonds

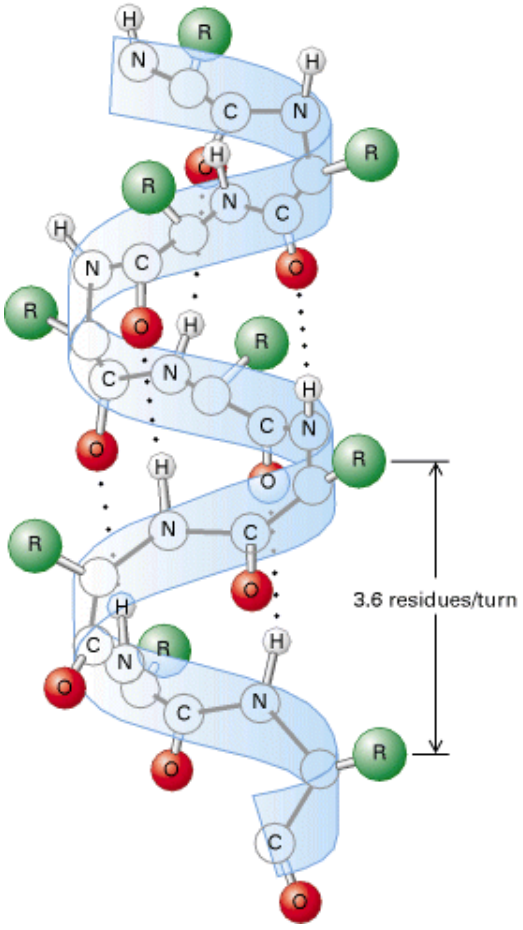



**Radial Dipoles**




**Dipoles almost in plane and tend to cancel out to lower energy**

# Hydrogen bonds in oligopeptides



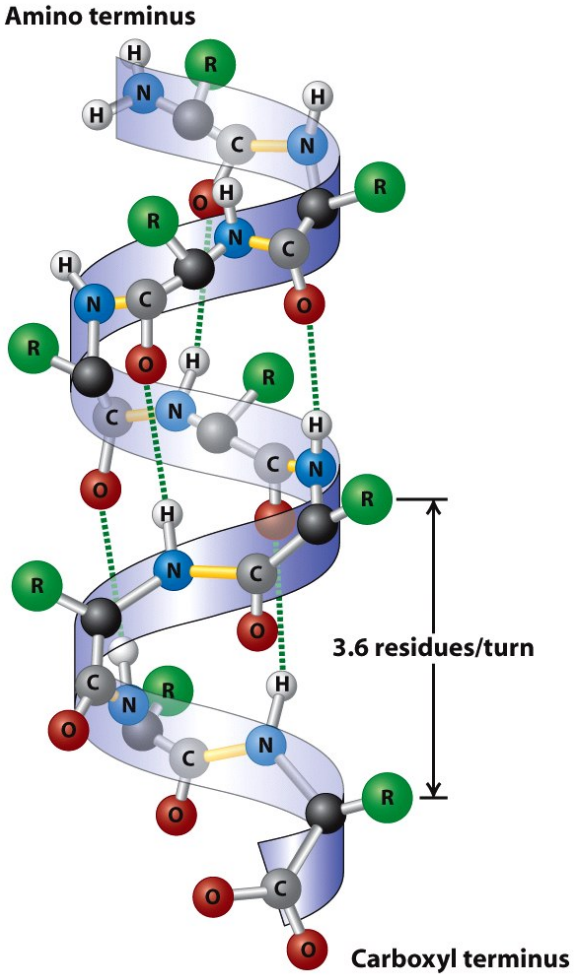




Figure 3-4
*Molecular Cell Biology, Sixth Edition*

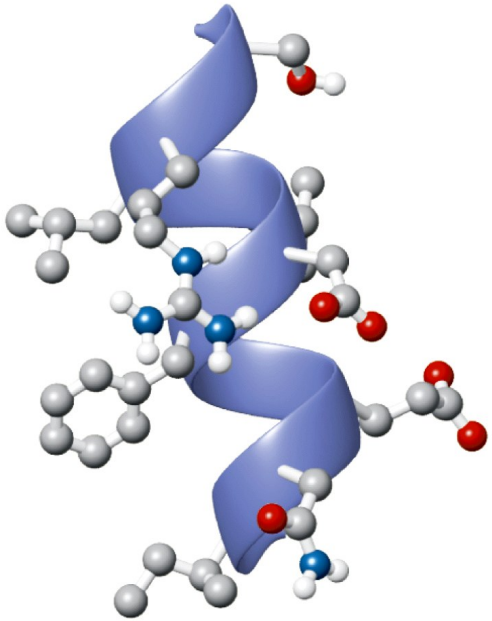
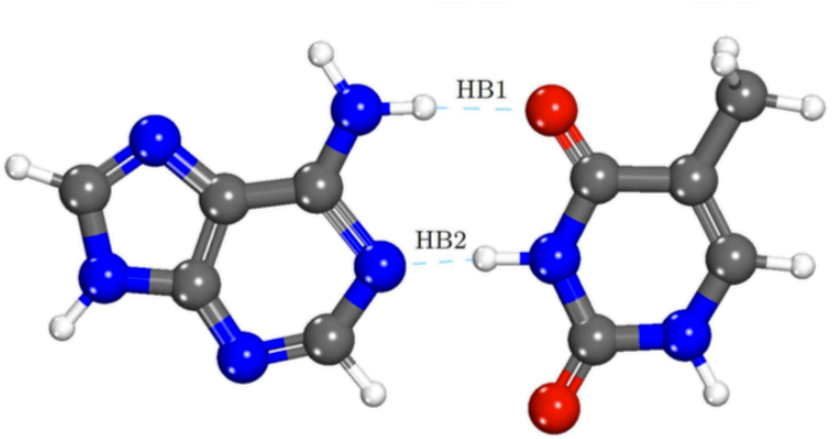



Figure 4-11 Principles of Biochemistry, 4/e

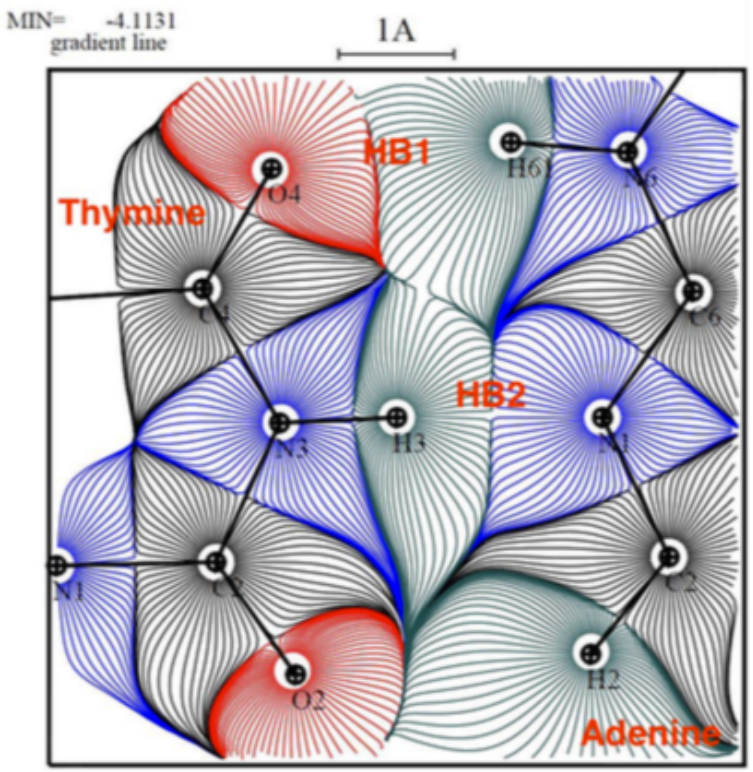

Hidalgo, Torres, Varela
Poster session

# Electric fields due to vicinity of hydrogen bonding

Adenine Thymine

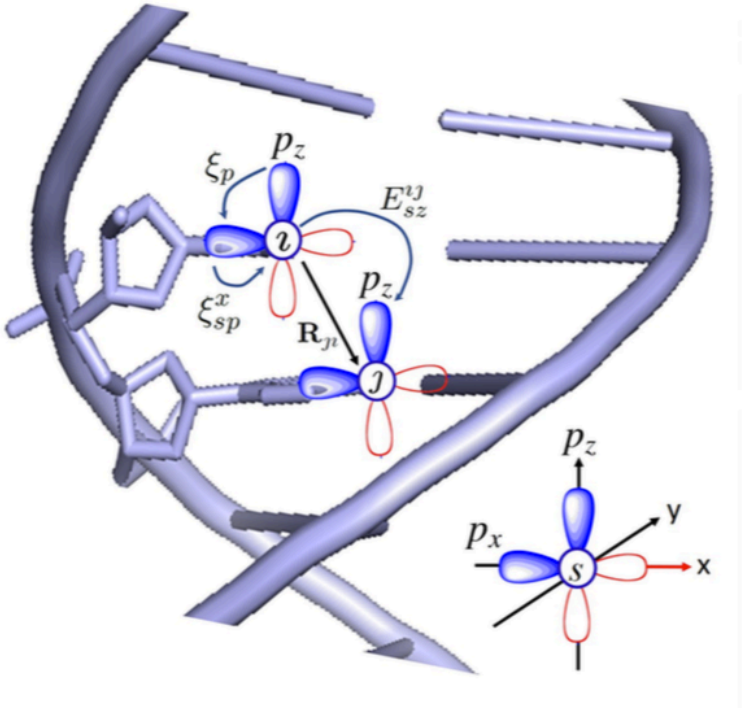



Base pairs




Electric field lines and Bader surfaces

# Hydrogen bond mediated Rashba

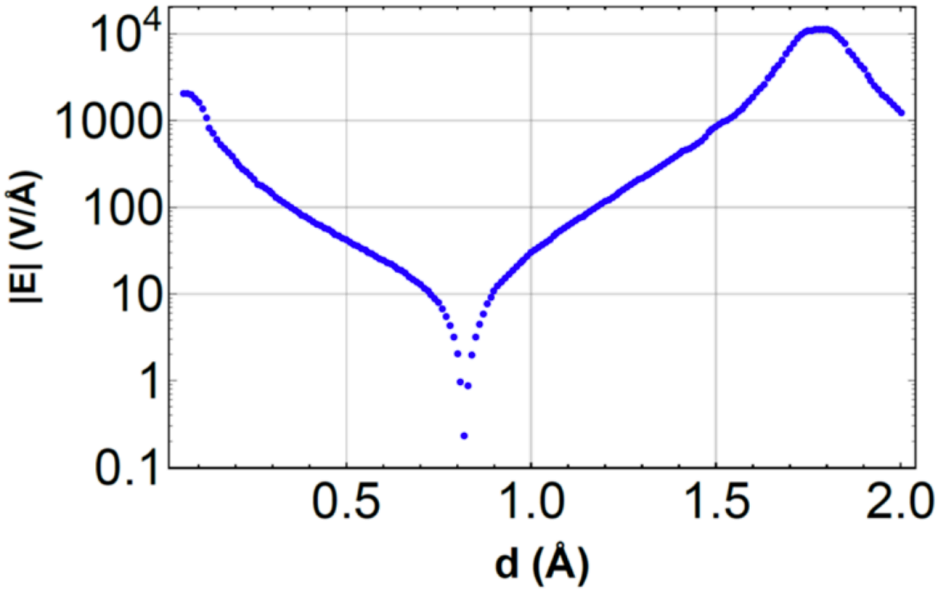



$$H_R = i \sum_{ij} c_i^\dagger \left( \lambda_R^x s_y + \lambda_R^y s_x + \lambda_R^z s_x \right) c_j,$$

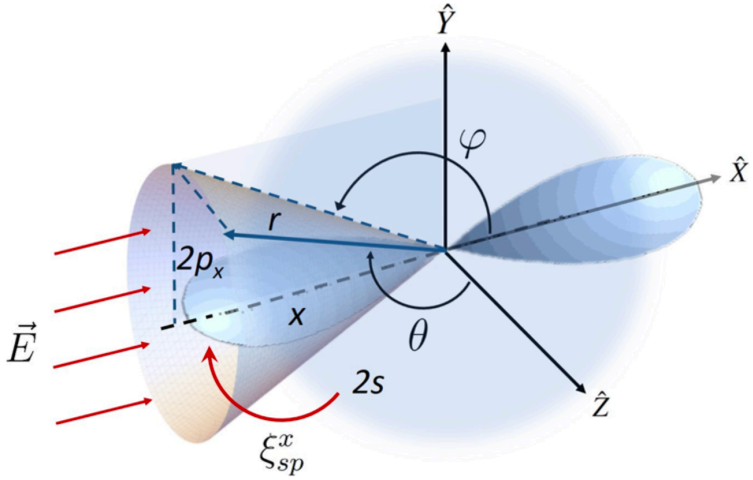
$$\lambda_R^x = -\frac{\xi_p E_{sz}^{ij} \left[ \xi_{sp}^x(i) + \xi_{sp}^x(j) \right]}{\left( \epsilon_{2p}^\pi - \epsilon_s \right) \left( \epsilon_{2p}^\pi - \epsilon_{2p}^\sigma \right)},$$

$$\lambda_R^y = \frac{\xi_p E_{sz}^{ij} \left[ \xi_{sp}^y(i) + \xi_{sp}^y(j) \right]}{\left( \epsilon_{2p}^\pi - \epsilon_s \right) \left( \epsilon_{2p}^\pi - \epsilon_{2p}^\sigma \right)},$$

# Stark interaction with H-Bond electric field




So SO is atomic but Stark is due to the Hydrogen bond another way to increase the effect



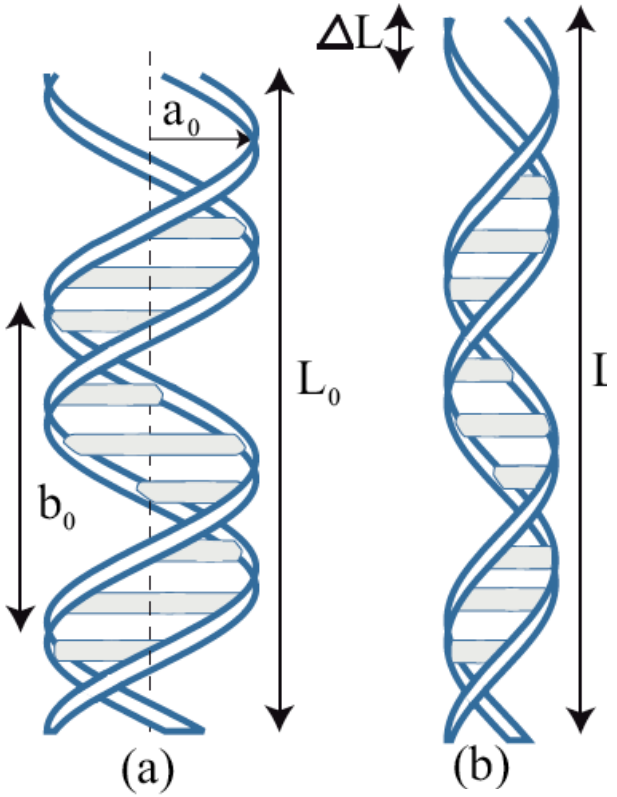

$$\xi_{sp}^{i} = \langle s|H_s|p_i\rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} s^* H_s p_i r^2 \sin\theta dr d\theta d\varphi$$

# Experimental verification

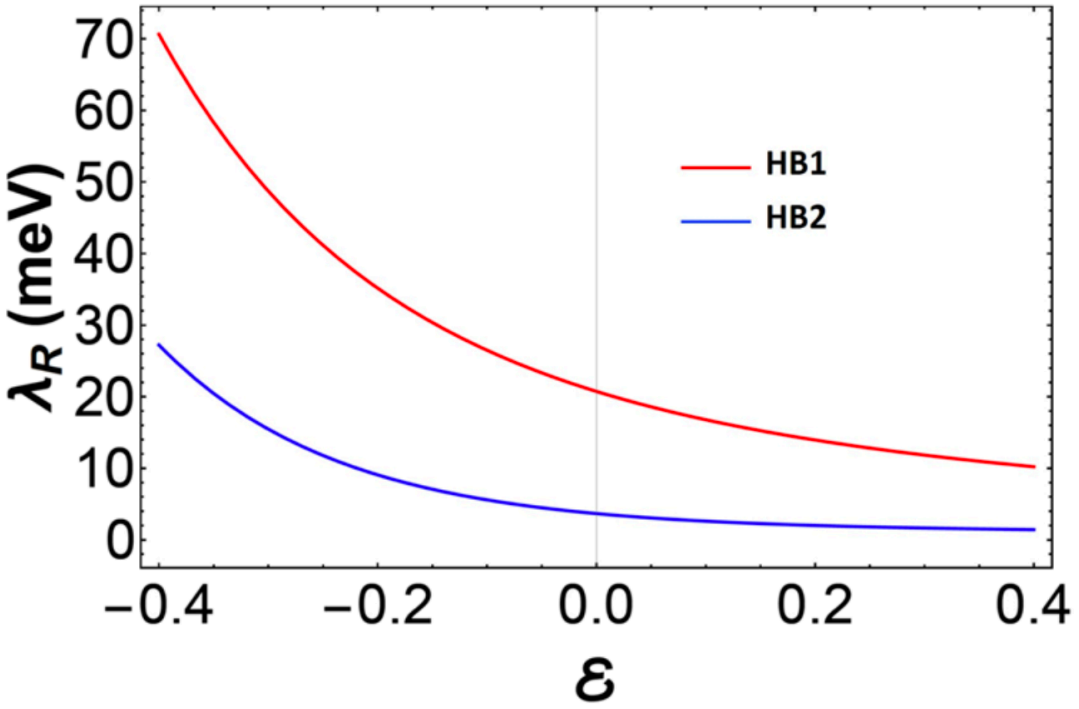
- How can we prove the previous scenario?
- Perhaps with a new spectroscopy christened:
  - MECHANICAL SPECTROSCOPY

# Stretching both ends fixed

Fixed ends




Break junction or STM setups

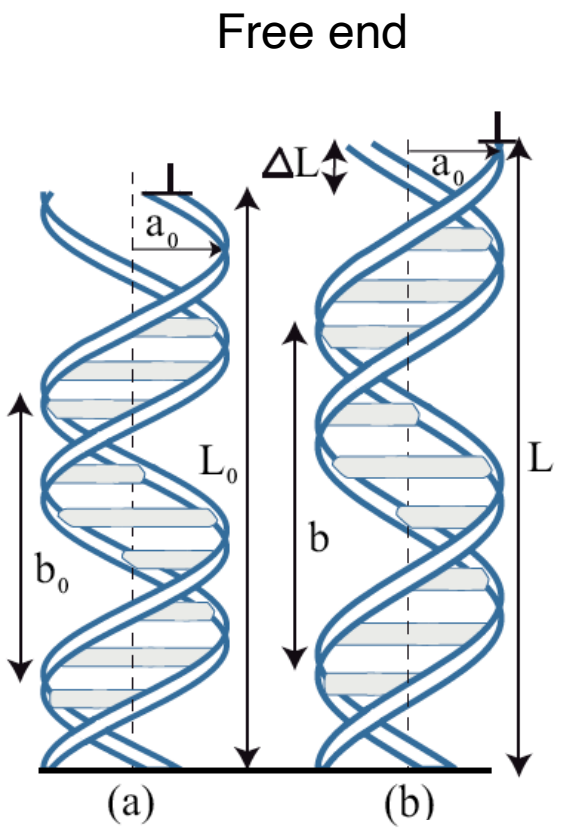


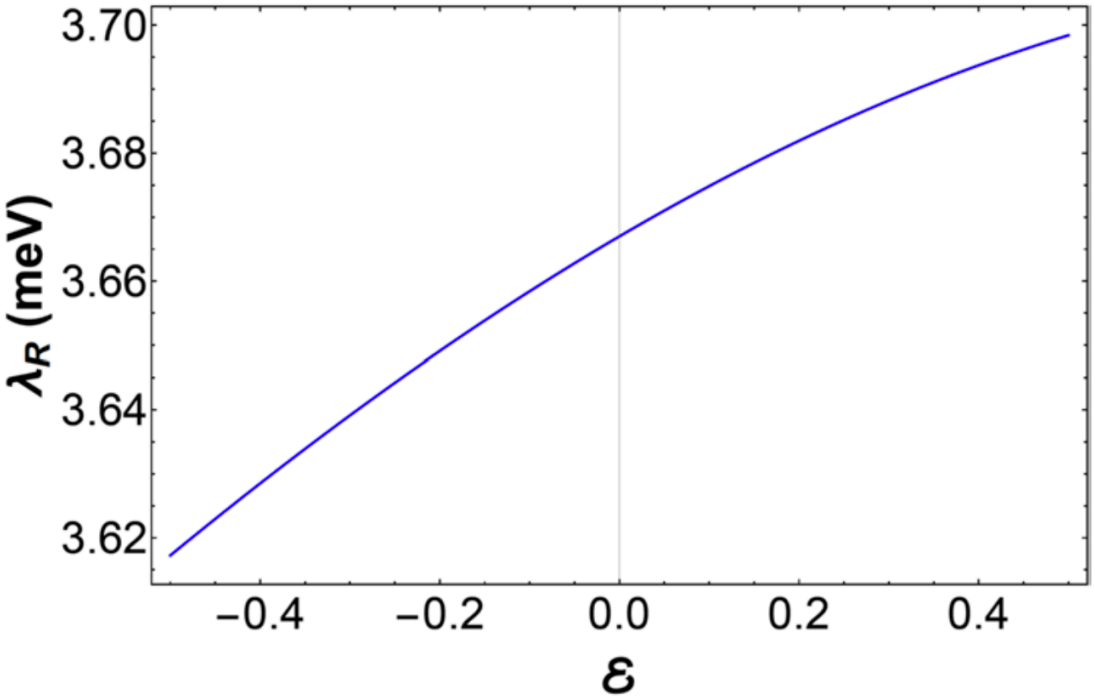

Hydrogen bonds depolarized

Poisson ratio
Reported by
experiments

$$\lambda_R(\varepsilon) = \frac{8\pi^2\hbar^2\kappa_{ps}\xi_p[\xi_{sp}^{(\imath)}(\varepsilon)+\xi_{sp}^{(\jmath)}(\varepsilon)]\left(b_0+\frac{L_0}{\mathcal{N}}\varepsilon\right)\Delta\phi}{(\epsilon_{2p}^{\pi}-\epsilon_s)(\epsilon_{2p}^{\pi}-\epsilon_{2p}^{\sigma})m\left[\left(b_0+\frac{L_0}{\mathcal{N}}\varepsilon\right)^2\Delta\phi^2-8\pi^2a_0^2(1-\nu\varepsilon)^2(\cos\phi-1)\right]^{3/2}}$$

# One free end stretching




Hydrogen bonds untouched

At constant radius a

$$V_{\mu\mu'}^{\sigma,\pi} = \kappa_{\mu\mu'(\sigma,\pi)} \frac{\hbar^2}{m_e R_{jn}^2} \qquad \lambda_{SO}(\varepsilon) = \frac{32\pi\hbar^2 \xi_p (\kappa_{pp}^{\sigma} - \kappa_{pp}^{\pi}) a_0 L_0 (1+\varepsilon) \Delta\phi(\varepsilon) \sin^2\left(\frac{\Delta\phi(\varepsilon)}{2}\right)}{m(\epsilon_{2p}^{\pi} - \epsilon_{2p}^{\sigma}) \left(16\pi^2 a_0^2 \sin^2\left(\frac{\Delta\phi(\varepsilon)}{2}\right) + b_0^2 (1+\varepsilon)^2 \Delta\phi(\varepsilon)^2\right)}.$$

# Conclusions

- Analytical TB approaches coupled to Band folding/ Matrix perturbation/ Renormalization tools can capture major qualitative features of new physical phenomena in low dimensional systems
- Proximity effects (non-bonded interactions/Van der Waals materials) are a novel mechanism to inherit and generate new behavior in low dimensional material.
- TB model can capture interferences between interaction paths that render couplings weak or strong.
- Effects of external fields via the Floquet approach and twisting/warping material next in the pipeline!

# Collaboration

- Solmar Varela, Yachay Tech
- Floralba López, Yachay tech
- Raul Hidalgo
- Juan Torres
- Vladimiro Mujica, ASU
- Bertrand Berche, Lorraine
- Barbara Montañes, IVIC
- Benoit Guillot, Lorraine

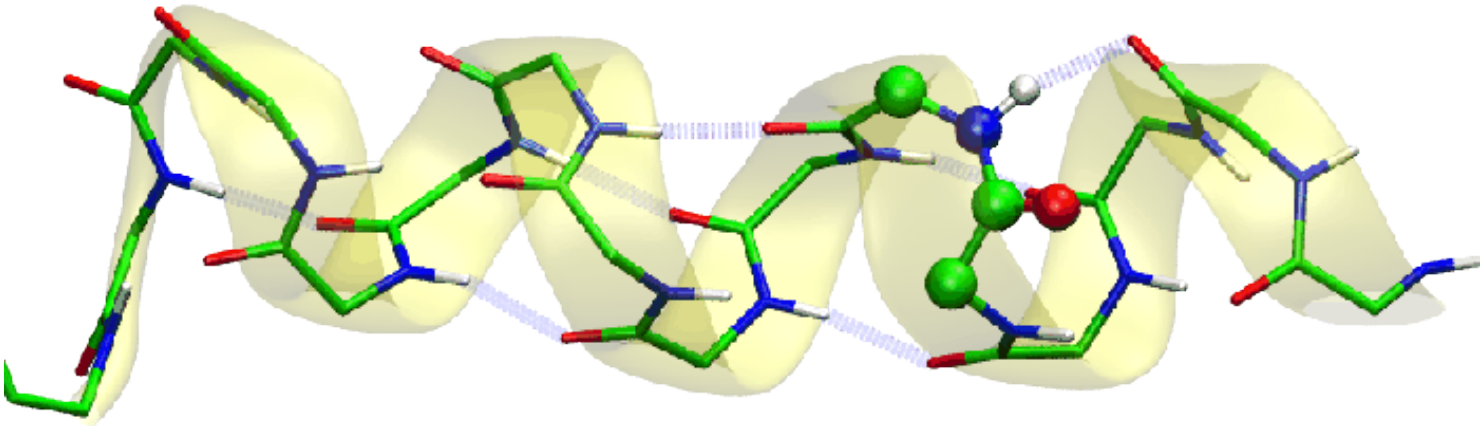






# Chiral peptide

Made in Nature®



Hidalgo and Torres current patient

Chiral inside chiral