Molecular spintronics with spin crossover compounds

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Spin in organic materials

\[ \tau_S = \frac{l_S}{v_F} \]

- Hyperfine weak
- Spin-orbit weak

How to manipulate spins?

Our strategy

**Use molecules that do something!!**

1) Look at spins close to the interface: \( \text{Spinterface} \)


2) Use magnetism: magnetic molecules

3) Use the exchange interaction **not** the anisotropy

4) Find a “convenient handle” to address spin (currents or fields)
Manipulating Spins by electric means

*Exchange*: electrostatic spin crossover effect

*Spin state*: spin crossover, a tricky theory problem

*Valence*: Driving Valence Tautomerism

Reading Spins

Quantitative Transport Theory: *Smeagol*

Transport in spin crossover compounds
**Exchange**: Electrostatic Spin Crossover

Manuel Piacenza, Fabio Della Sala, Tugba Tugsuz, Giuseppe Maruccio (NNL, Lecce)
Use Stark effect!

\[ E = c_0 \vec{p} \cdot \vec{E} + c_1 \sum_{ij} \alpha_{ij} E_i E_j \]
\[ \Delta E_{\text{GS}}^\alpha = - \sum_i \frac{|0\langle \psi^\text{GS}_\alpha | H | \psi_i \rangle|^2}{E_i - E_{\text{GS}}^0} \]

\[ \Delta E_{GS}^{S/T}(V) \sim \Delta E_{GS}^{S/T}(0) + \frac{1}{2a_0} p_{GS}^{S/T} V + \frac{1}{4a_0} \alpha_{GS}^{S/T} V^2 \]

\[ \Delta E_{GS}^{S/T}(V) \sim \Delta E_{GS}^{S/T} + \frac{1}{2a_0} p_{GS}^{S/T} V + \frac{1}{4a_0} \alpha_{GS}^{S/T} V^2 \]
CoCp₂ \hspace{1cm} S=1/2

a) diCo

b) MeO–diCo

Then accurate DFT (B3LYP)
<table>
<thead>
<tr>
<th>$X$</th>
<th>$E_{\text{cross}}$ [V/nm]</th>
<th>$J_{\text{ST}}^0$ [meV]</th>
<th>$p^S$ [D]</th>
<th>$p^T$ [D]</th>
<th>$p^S_{|}$ [D]</th>
<th>$p^T_{|}$ [D]</th>
<th>$\alpha^S_{|}$ [au]</th>
<th>$\alpha^T_{|}$ [au]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.57</td>
<td>1.22</td>
<td>0.64</td>
<td>0.64</td>
<td>460</td>
<td>450</td>
<td></td>
<td></td>
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<tr>
<td>MeO</td>
<td>1.47</td>
<td>2.17</td>
<td>0.10</td>
<td>0.10</td>
<td>482</td>
<td>484</td>
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<tr>
<td>NH$_2$</td>
<td>1.35</td>
<td>4.05</td>
<td>2.85</td>
<td>2.85</td>
<td>467</td>
<td>474</td>
<td></td>
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<tr>
<td>CF$_3$</td>
<td>0.75</td>
<td>6.01</td>
<td>4.19</td>
<td>4.19</td>
<td>474</td>
<td>489</td>
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<td>CN</td>
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</tr>
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</table>

Effect can be tuned.
Mechanisms for manipulating electrically the spin of a molecule

*Electrostatic spin crossover effect*

- Need to generate fields in the V/nm range
- **Problem**: the critical field scale with the exchange
  - either large field or weak magnetic coupling
Spin state: Spin crossover, a tricky problem for theory
\[ \Delta G = G_{\text{HS}} - G_{\text{LS}} = \Delta H - T\Delta S \]

The environment is important!

M. Kepenekian et al., PRB 79, 094428 (2009)
M. Kepenekian et al., JACS 131, 11498 (2009)
$\Delta E = \Delta E^{\text{adia}} + \Delta E^{ZPE}$

Which Theory?
Spin Crossover

Which Theory?

1) Which atomic coordinates? Do I need to relax? How?
2) Is DFT good enough? Do I have alternative? Which functional?
3) How to benchmark with experiments? Should I benchmark against experiments?
4) Is the environment important?
Which functional?

- $[\text{Fe(H}_2\text{O)}_6]^{2+}$
- $[\text{Fe(NH}_3)_6]^{2+}$
- $[\text{Fe(NCH)}_6]^{2+}$
- $[\text{Fe(CO)}_6]^{2+}$

Spin Crossover

### Spin Crossover

<table>
<thead>
<tr>
<th>[Fe(H₂O)₆]²⁺</th>
<th>[Fe(NH₃)₆]²⁺</th>
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<th>[Fe(CO)₆]²⁺</th>
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<tbody>
<tr>
<td>( \Delta E_{\text{adia}} ) (eV)</td>
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<tr>
<td>LDA</td>
<td>-0.49</td>
<td>0.96</td>
<td>2.37</td>
</tr>
<tr>
<td>GGA</td>
<td>-1.04</td>
<td>0.08</td>
<td>1.04</td>
</tr>
<tr>
<td>B3LYP</td>
<td>-1.36</td>
<td>-0.59</td>
<td>-0.20</td>
</tr>
<tr>
<td>PB0</td>
<td>-1.74</td>
<td>-0.88</td>
<td>-0.44</td>
</tr>
<tr>
<td>HH</td>
<td>-2.26</td>
<td>-1.68</td>
<td>-1.49</td>
</tr>
<tr>
<td>DMC</td>
<td>-2.54(1)</td>
<td>-1.59(1)</td>
<td>-1.37(3)</td>
</tr>
</tbody>
</table>

\( \Delta E_{\text{adia}} \) (LDA) > \( \Delta E_{\text{adia}} \) (GGA) > \( \Delta E_{\text{adia}} \) (B3LYP) > \( \Delta E_{\text{adia}} \) (PB0) > \( \Delta E_{\text{adia}} \) (HH)
Spin Crossover

$[\text{FeL}_2](\text{BF}_4)_2$ (L=2,6-dypirazol-1-yl-4-hydroxymethylpyridine)

$\Delta E_{\text{adia}}$ (eV)

DMC $-1.21(4)$

Experimental Structure

Madelung Corrections

DMC $-0.36(4)$

Experimental estimate

0.1-0.3 eV

LS $\Rightarrow$ HS @ 271K

DMC $0.14(0)$
Spin Crossover


Use DFT sensibly !!!

<table>
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<th>DFT</th>
<th>$\Delta E_{\text{adia}}$ (eV)</th>
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Experimental

- 20%: 0.1-0.3 eV
- 25%
- 50%
Valence: driving valence tautomerism
Driving valence tautomerism

$\text{Co(Me}_2\text{tpa})(\text{DBCat})(\text{PF}_6)$

Co-dioxolene

$\pi^*$

semiquinonate
catecholate
Driving valence tautomerism

\[ T_C = 597 \text{ K in solid state, } T_C \approx 300 \text{ K in solution} \]

Driving valence tautomerism

DFT-B3LYP or similar needed!

Driving valence tautomerism

Now apply $E$

- $\pi^*$
- $\pi$
- $t_{2g}$

$\varepsilon$

0.2 V/Å 0.6 V/Å 0.8 V/Å
Driving valence tautomerism

Is that all?

\[ \epsilon = 0.01 \text{ V/Å} \]

for \( \Delta T_C = 20 \text{ K} \)

\[
[T_C(0) - T_C(\epsilon)] \Delta S(0) = \Delta E(0) - \Delta E(\epsilon)
\]
Mechanisms for manipulating electrically the spin of a molecule

Valence Tautomerism

- Need to generate fields in the V/nm range
- Will the molecules survive on a surface?
- Can one address the single molecule? Transport properties?
Transport in spin crossover molecules
NEGF + DFT (Siesta)

\[
G = \Sigma_L + H_{EM}^{\rho} + \Sigma_R
\]

\[
T(E; V)
\]
Also include: Spin-orbit, Spin-Torque, Forces, SIC, LDA+U, HF, Hybrids, order-N ...

Transport in spin crossover molecules

$L_2\ 2,2';6',2''$-terpyridine

B3LYP

- $E$ (eV)
- $\Delta E_{\pi}$ (eV)

(c)
Transport in spin crossover molecules

$T(E, V=0)$

![Graph showing transport properties for different energy levels](image)
Transport in spin crossover molecules

\[ R = \frac{I_{HS} - I_{LS}}{I_{LS}} \]
Transport in spin crossover molecules
Transport in spin crossover molecules

F. Prins et al., Adv. Mat. 23, 1545 (2011)
Transport in spin crossover molecules

Spin crossover molecules

- Massive changes in \( I-V \) originating from spin crossover
- In general one expects larger currents for HS

- Will the molecules survive on a surface?
  - What kind of electronic coupling with the electrodes are possible?
  - Is charging good or bad?

Need care in using electronic structure methods