Vallico di Sotto, 30th July 2012

First- principles studies of spin-crossover molecules

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School of Physics and CRANN, Trinity College Dublin
Dario Alfe'
London Centre for Nanotechnology, Dept. Earth Science, Dept. Physics and Astronomy, University College London

Outline

Introduction and motivation

- Molecular spintronics
- Spin-crossover molecules

Model systems

- Assessment of density functionals

Spin-crossover molecules

- Gas phase vs condensed phase

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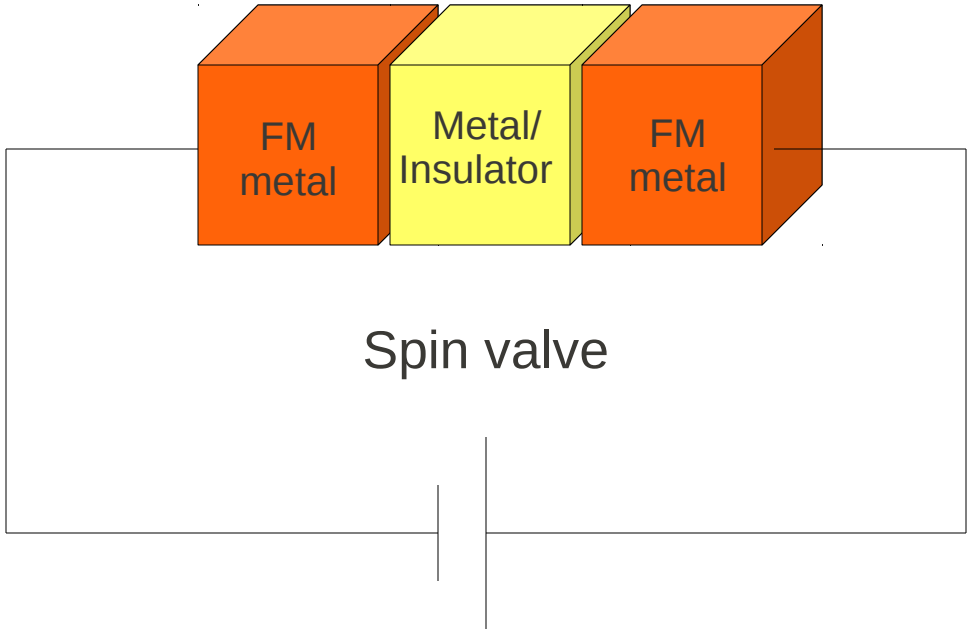
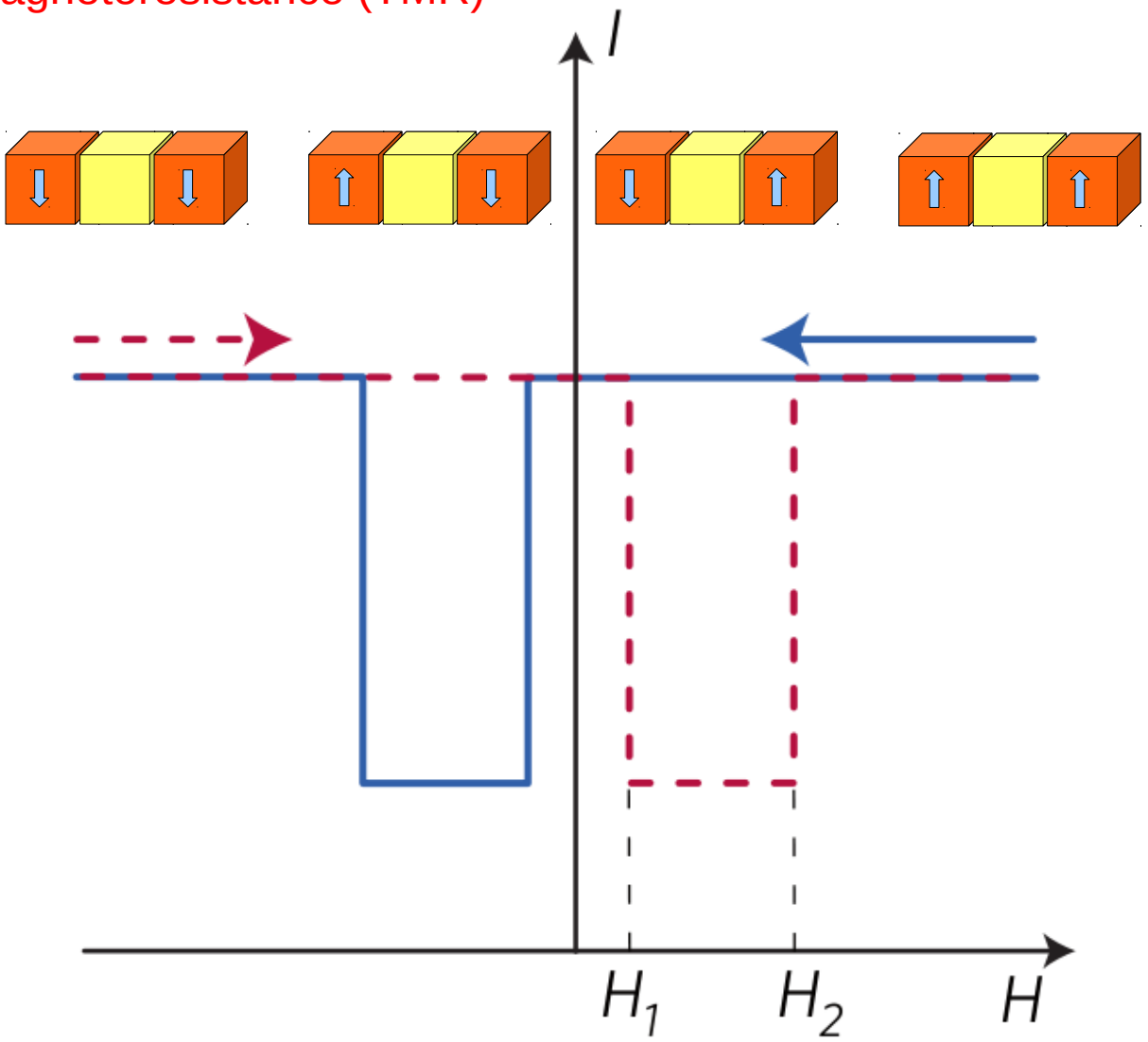
The spin valve



M.N. Baibich et al., Phys. Rev. Lett., **61**, 2472 (1988)
G.Binash et al., Phys. Rev. B, **39**, 4828 (1989)

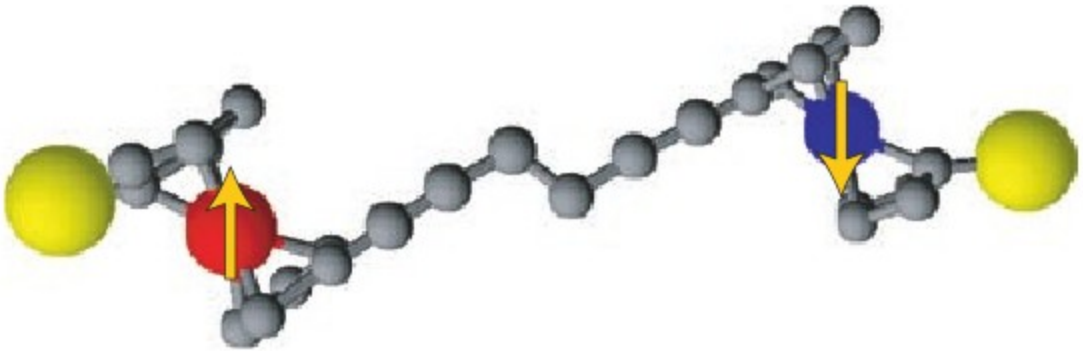
The spin valve

Giant Magnetoresistance (GMR)
Tunneling Magnetoresistance (TMR)



Molecular spintronics

Molecular spintronics has been prophesied for long time...

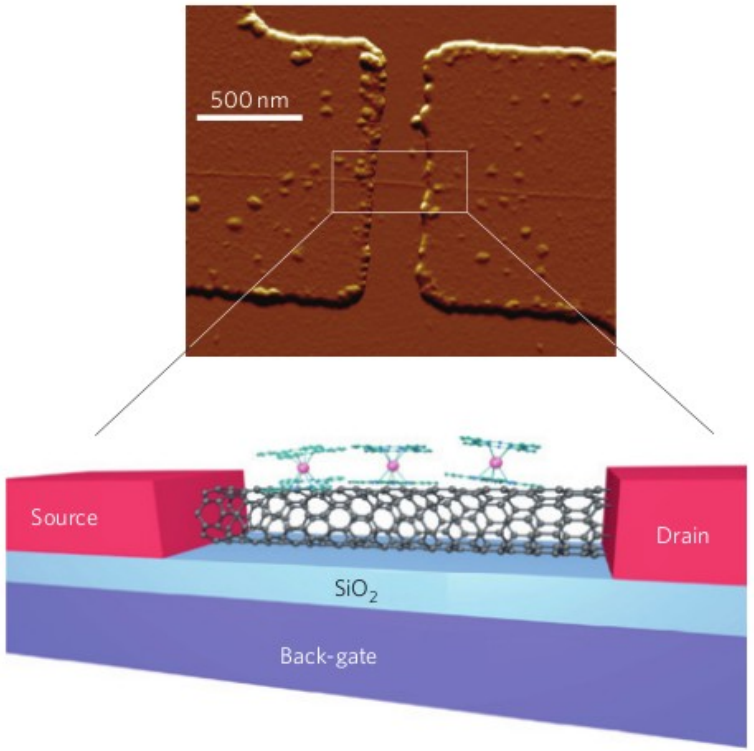


A. Rocha, S. Sanvito et al., Nature Materials **4**, 335 (2005)

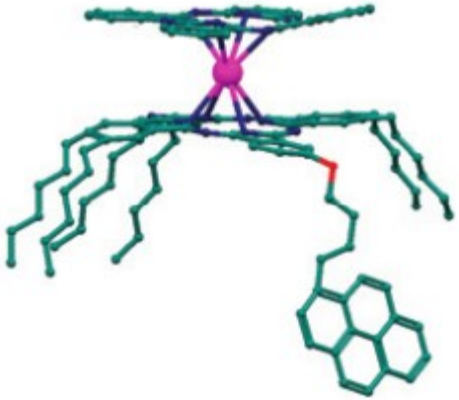
L. Bogani & W. Wernsdorfer, Nature Materials **7**, 179 (2008)

Molecular spintronics

…and finally real devices have been realized



$TbPc_2$



M. Urdampilleta et al., Nature Materials **10**, 502 (2011)

Molecular spintronics

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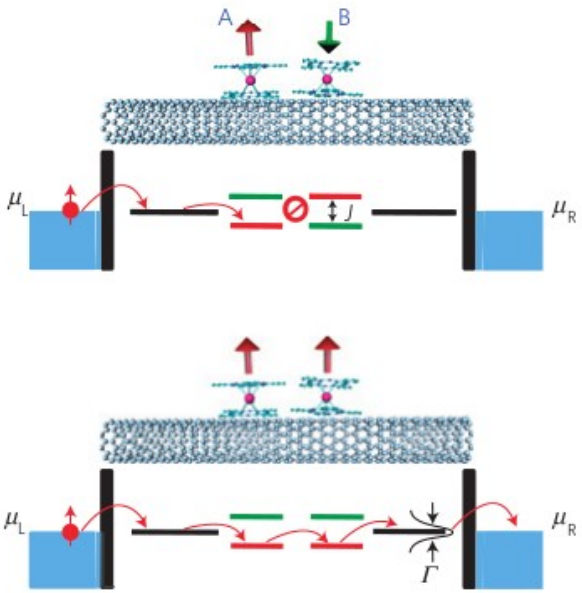

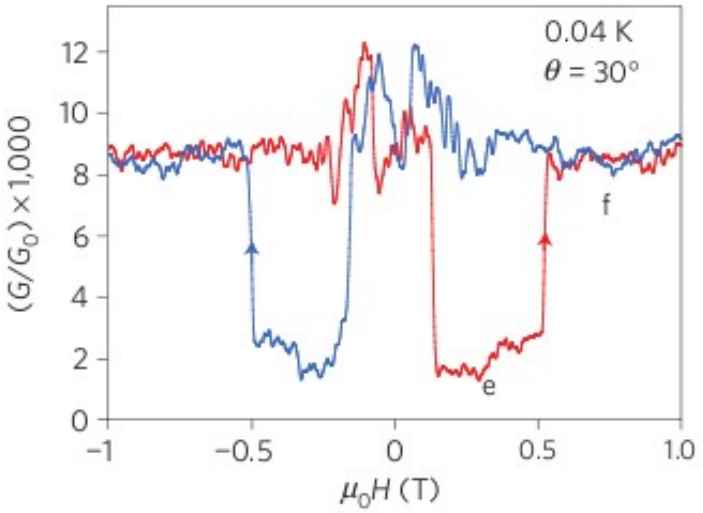

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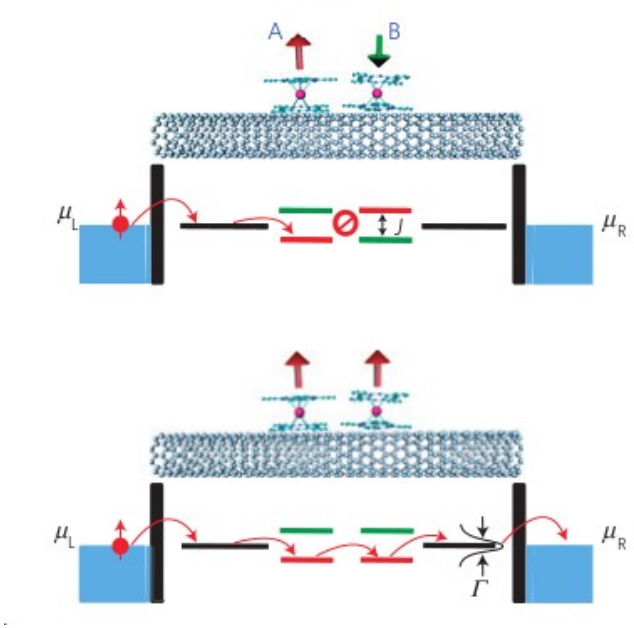

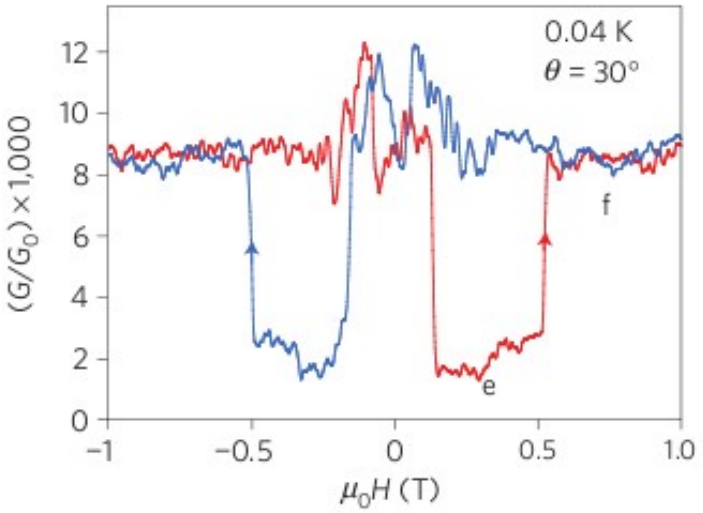

Magnetic anisotropy = 1 K

M. Urdampilleta et al., Nature Materials, **10**,502 (2011)

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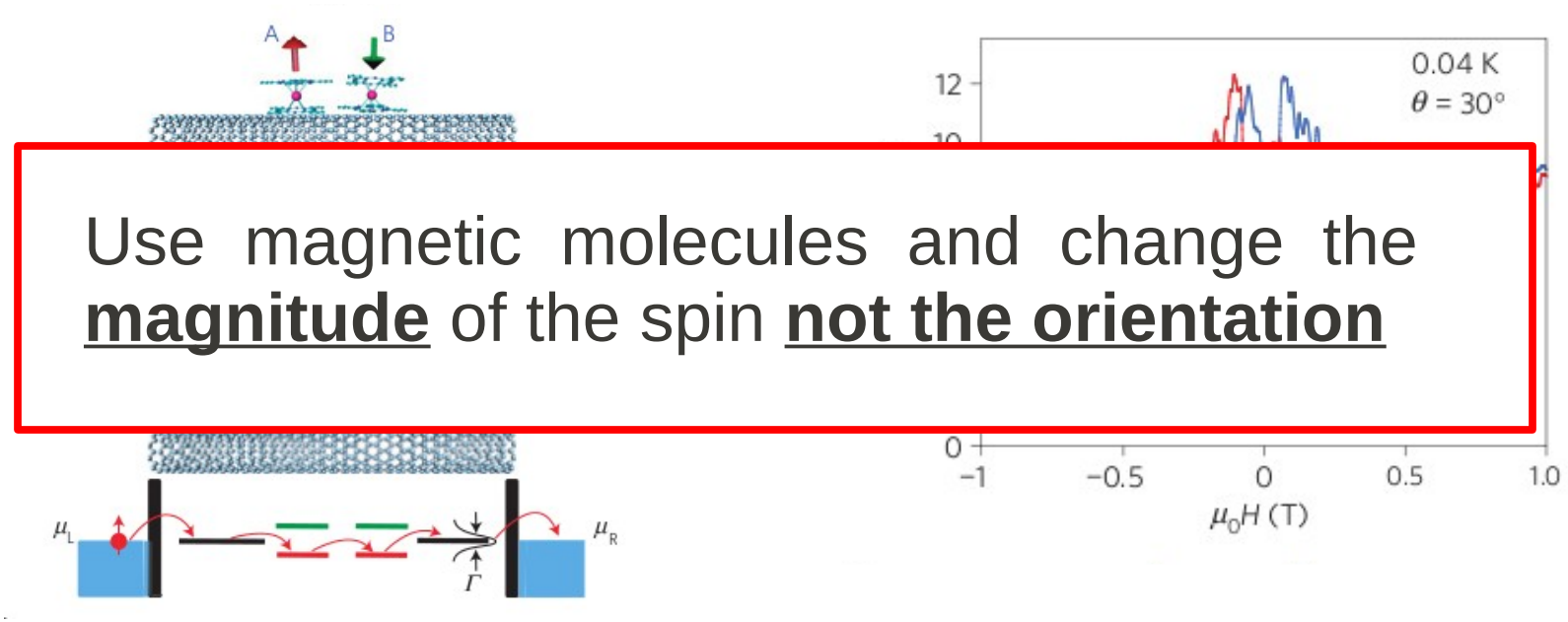

Use magnetic molecules and change the **magnitude** of the spin **not the orientation**

Magnetic anisotropy = 1 K

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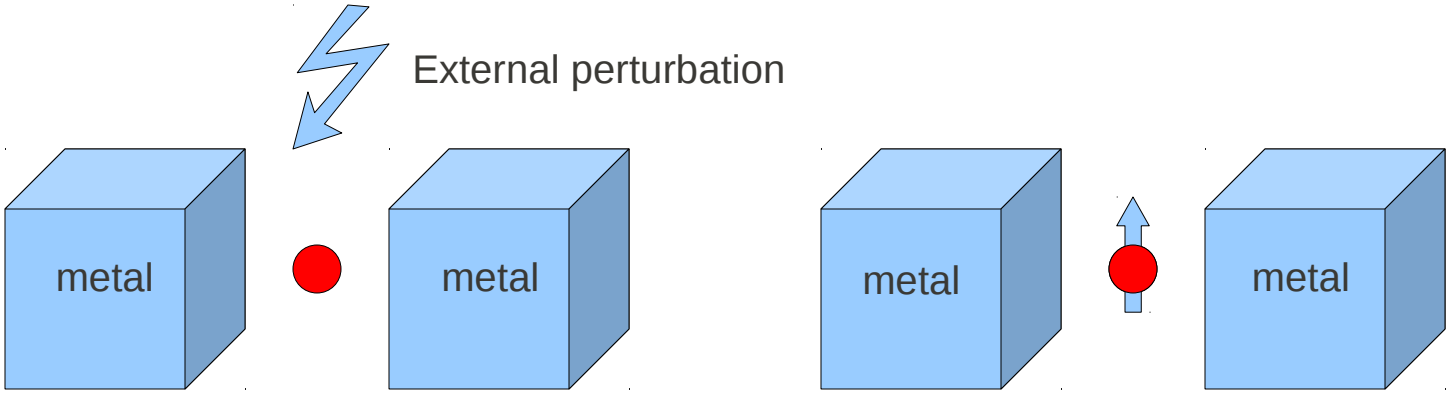
Introduction

Use magnetic molecules and change the **magnitude** of the spin **not the orientation**



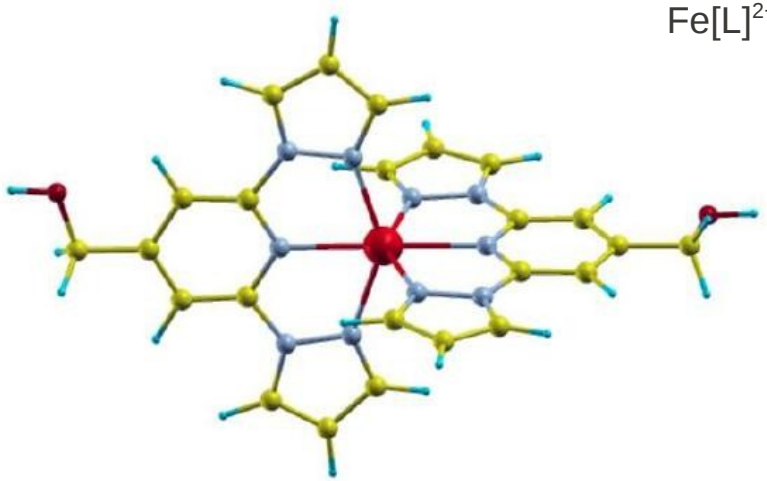
Low spin (LS) molecule
(S=0)

High spin (HS) molecule
(S=2)

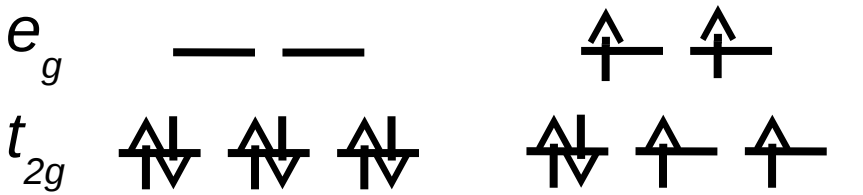
Spin crossover molecules

P. Gutlich & H.A. Goodwin (eds.),
Spin Crossover In Transition Metal Compounds
(Springer-Verlag, Berlin, 2004)

$Fe[L]^{2+}$ (L= 2-6-dypirazol-1-yl-4-hydroxymethylpyridine)



Fe^{2+}



Ground state

$S=0$

$^1A_{1g}$

Metastable state

$S=2$

$^5T_{2g}$

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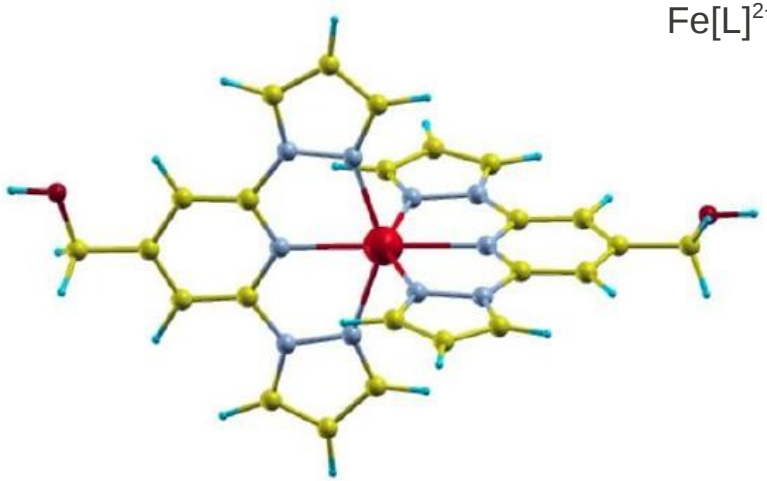
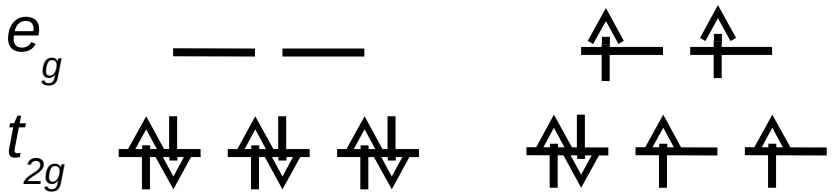


Fe^{2+}



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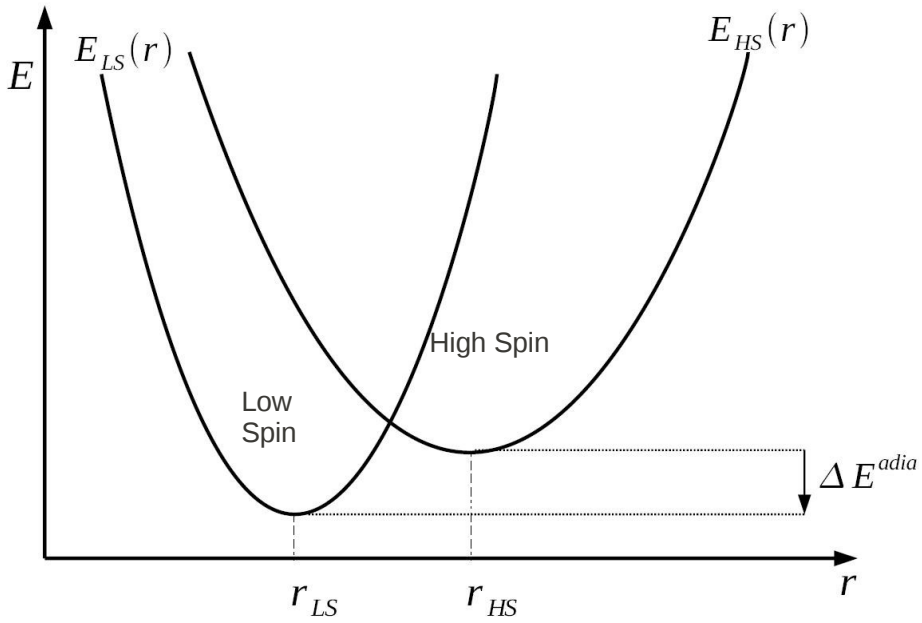


Spin crossover molecules

P. Gutlich & H.A. Goodwin (eds.),
Spin Crossover In Transition Metal Compounds
(Springer-Verlag, Berlin, 2004)

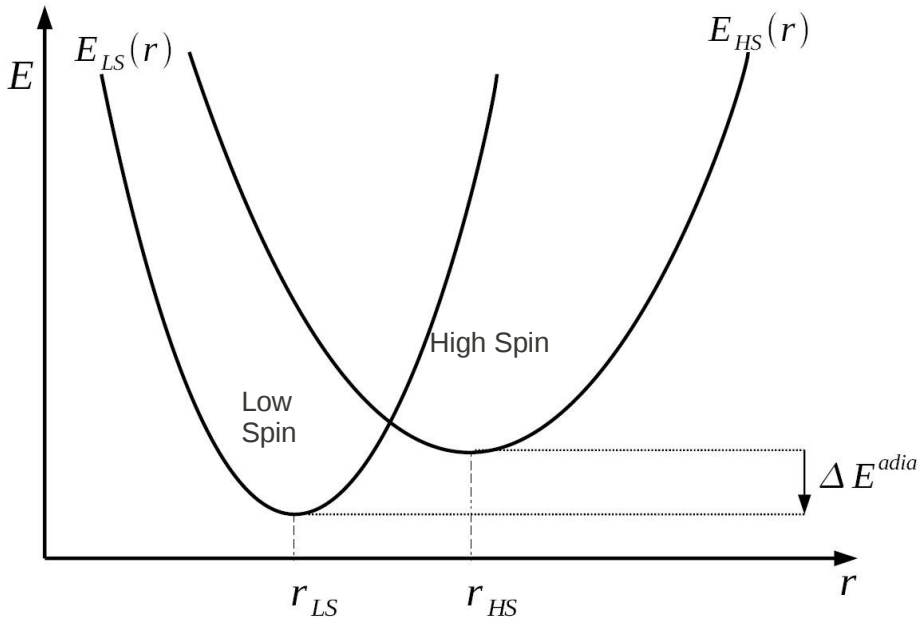
Temperature-induced spin-crossover

$$\Delta G = G_{HS} - G_{LS} = \Delta E^{adia} - T\Delta S$$

$$\Delta E^{adia} > 0 \quad \Delta S > 0$$

G Gibbs free energy
S Entropy
T Temperature

$$T_C = \frac{\Delta E^{adia}}{\Delta S}$$



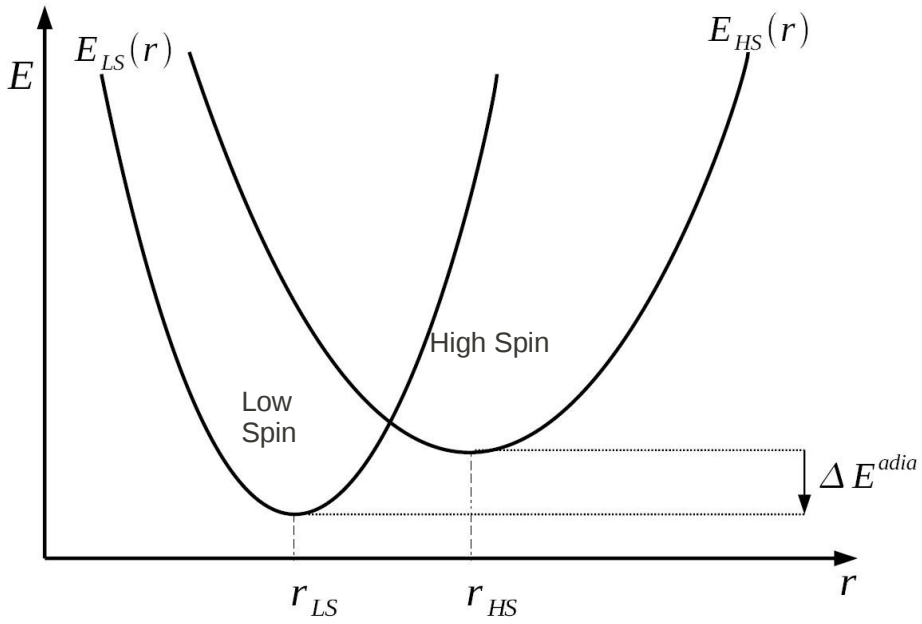
For molecules either in solutions or in crystals

Spin crossover molecules

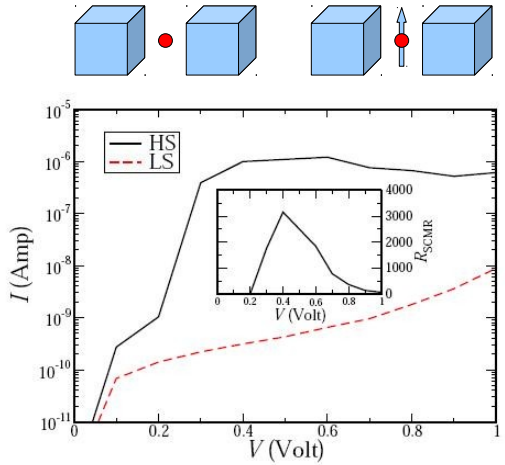
P. Gutlich & H.A. Goodwin (eds.),
Spin Crossover In Transition Metal Compounds
(Springer-Verlag, Berlin, 2004)

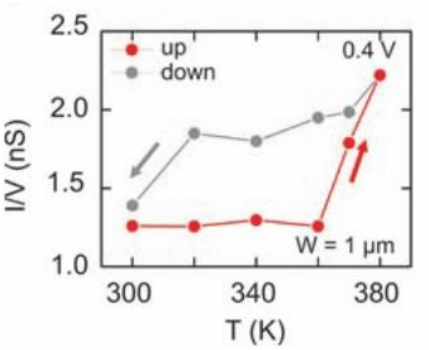
Other ways to induce the spin-crossover:

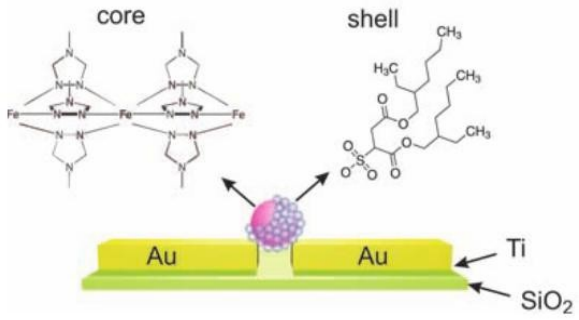
- Pressure variations
- Optical irradiation
- Static electric field (still debated)



Transport through spin-crossover molecules

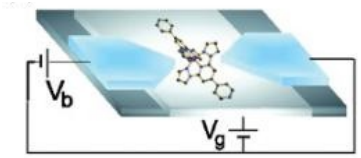


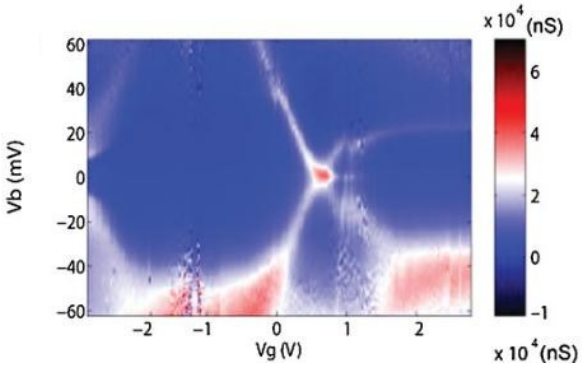




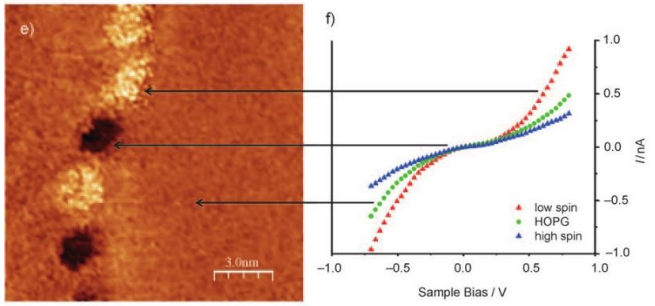
F. Prinz et al., Adv. Mat., 1545 (2011)

Theory
N. Baadji & S. Sanvito, Phys. Rev. Lett. **108**, 217202 (2012)



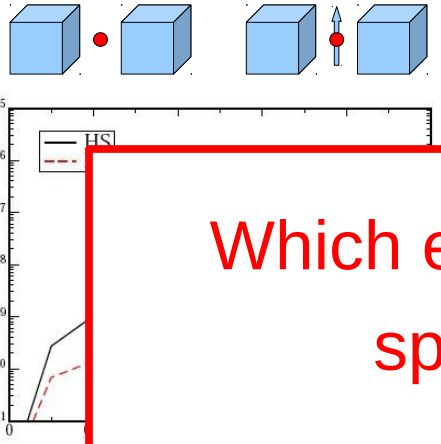


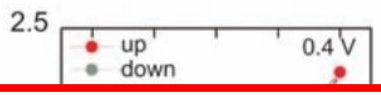
V. Meded et al., Phys. Rev. B **83**, 245415 (2011)

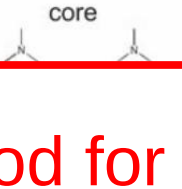


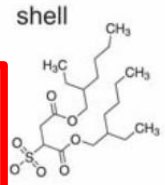
M.S. Alam et al., Angew. Chem. Int. Ed. **49**, 1159 (2010)

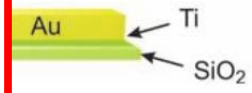
Transport through spin-crossover molecules









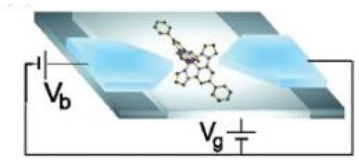


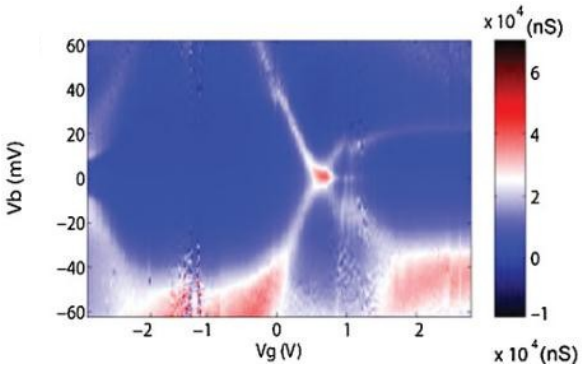
N. Baadji & S.

Which electronic structure method for spin-crossover molecules?

What about DFT?

(supposed to be accurate and scales as *O(N)*)





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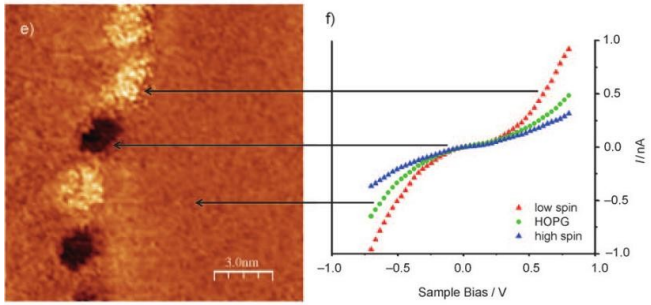

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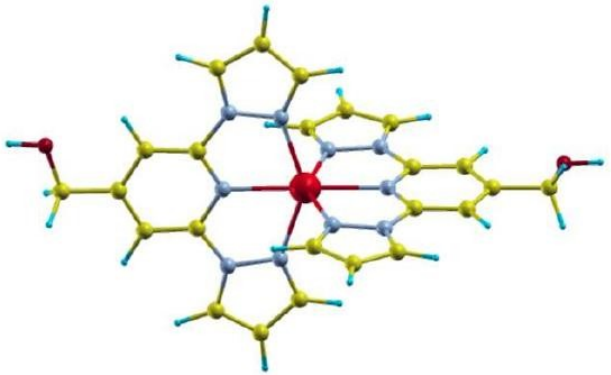
Spin-crossover molecules – a tricky problem for DFT



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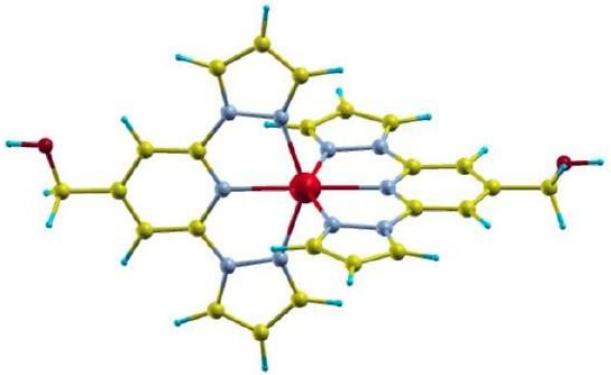
Spin-crossover molecules – a tricky problem for DFT

Oxidation state



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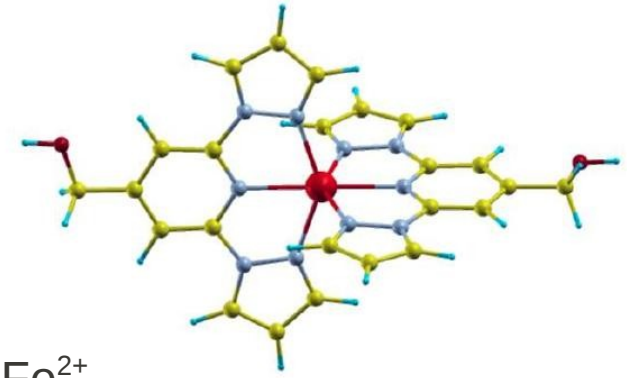
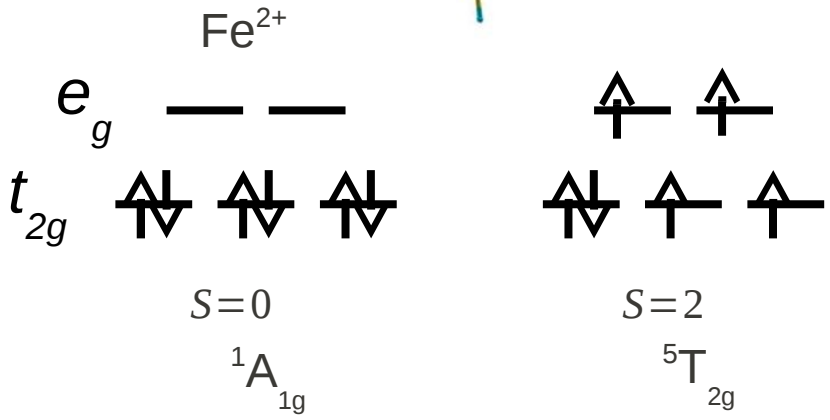


Ground state spin



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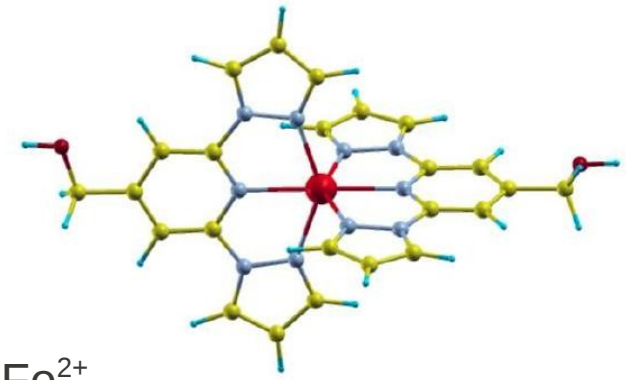
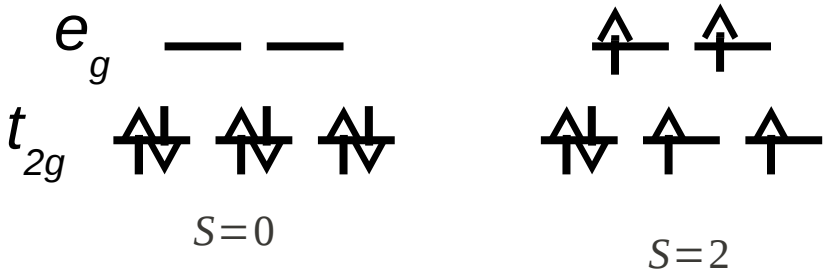


Fe^{2+}

Ground state spin



Adiabatic energy gap

$$\Delta E^{adia} = E_{HS}(r_{HS}) - E_{LS}(r_{LS})$$

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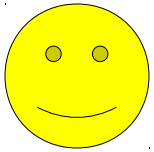
Spin-crossover molecules – a tricky problem for DFT

Oxidation state  (LDA, GGA, metaGGA, hybrids...)

Ground state spin  debatable

Adiabatic energy gap  debatable

See, for example:
M. Swart et al., J. Chem. Phys. A, **108,** 5479 (2004)
S. Zein et al., J. Chem. Phys., **126**, 014105 (2007)

Spin-crossover molecules

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Spin-crossover molecules – a tricky problem for DFT

Ground state spin  debatable

Adiabatic energy gap  debatable

These quantities are not easy to address experimentally

- depend on the phase (condensed, solution, gas)
- depend on the chemical groups attached to the molecules

...

Spin-crossover molecules

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These quantities are not easy to address experimentally

- depends on the phase (crystalline, solution, gas)
- depends on the chemical group attached to the molecules

...

Strategy:
Benchmark DFT with Diffusion Monte Carlo (DMC)

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Introduction and motivation

- Molecular spintronics
- Spin-crossover molecules

Model systems

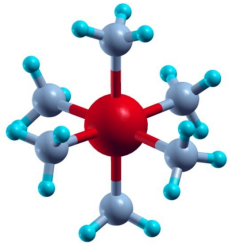
- Assessment of density functionals

Spin-crossover molecules

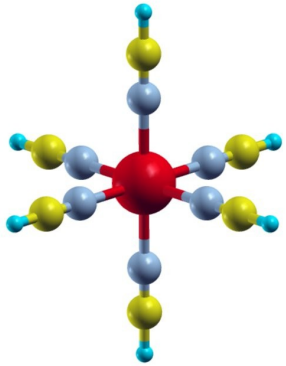
- Gas phase vs condensed phase

Model systems

$[Fe(H_2O)_6]^{2+}$



$[Fe(NH_3)_6]^{2+}$



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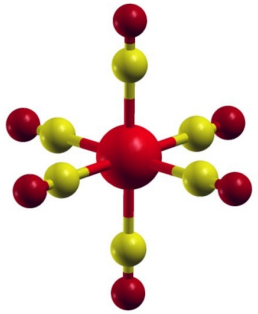


$[Fe(CO)_6]^{2+}$

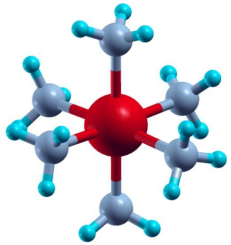
lower crystal field

higher crystal field

Spectrochemical series

Model systems

$[Fe(H_2O)_6]^{2+}$



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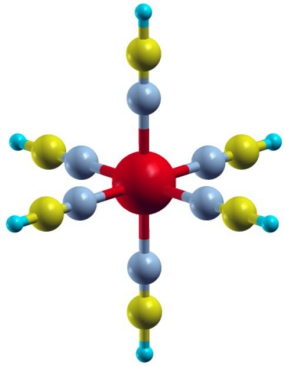

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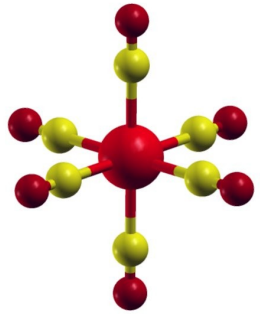


$[Fe(CO)_6]^{2+}$

lower crystal field — higher crystal field

Expected ground state:

$S=2$	$S=2$	$S=2$	$S=0$
$\Delta E^{adia}<0$	$\Delta E^{adia}<0$	$\Delta E^{adia}<0$	$\Delta E^{adia}>0$

Computational details

CRANN

DFT:

- NWCHEM code [1].
- All-electron.
- Ahlrichs triple-zeta polarized basis set [2].
- Functionals: LDA [3], BP86 (GGA) [4], various hybrids...B3LYP(20% exact exchange) [5], PBE0 (25%) [6], Half-Half (50%) [7].

[1] M. Valiev et al., Comput. Phys. Commun. **181**, 1477 (2010)
[2] A. Shafer et al., J. Chem. Phys. **100**, 5829 (1994)
[3] S.J. Vosko et al. Can. J. Phys. **58**, 1200s (1980)
[4] J.P. Perdew, Phys. Rev. B **33**, 8822 (1986);
A.D. Becke, Phys. Rev. A **38**, 3098 (1988)
[5] P.J. Stephens et al., J. Phys. Chem. 98, 11623 (1994)
[6] M. Ernzerhof & G.E. Scuseria., J. Chem. Phys., **110**, 5029 (1999);
C. Adamo & V. Barone, J. Chem. Phys. **110**, 6158 (1999)
[7] A.D. Becke, J. Chem. Phys. **98**, 5648 (1993)

Computational details

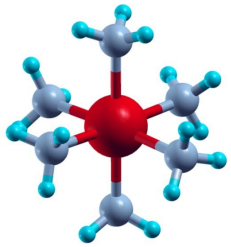
DMC:

- CASINO code [1].
- Slater-Jastrow trial wave-functions (Jastrow factor including electron-nucleus, electron-electron and electron-electron-nucleus terms - optimized minimizing the VMC energy variance).
- Single-particle orbitals obtained by DFT-LDA calculations (Quantum Espresso [2]). Plane-waves re-expanded in terms of B-splines [3].
- Dirac-Fock pseudo-potential [4] (potential-localization approximation [5]).
- Time-step of 0.0125 a.u., 0.005 a.u and 0.001 a.u. (energy differences already converged for time-steps of 0.0125 a.u.).
- 10,000 and 20,000 walkers.
- Geometry of the molecules obtained by DFT optimization (DMC error bars are usually not small enough to establish which functional returns the lowest energy geometry).

[1] R.J. Needs et al. J. Phys.: Condens. Matter **22**,023201 (2010)
[2] P. Giannozzi et al. J. Phys.: Condens. Matter, **21**, 395502 (2009)
[3] D. Alfe' & M.J. Gillian, Phys. Rev. B **70**, 161101(R) (2004)
[4] J. R. Trail et al. J. Chem. Phys. **122**, 174109 (2005); **122**, 014112 (2005)
[5] L. Mitas et al., J. Chem. Phys. **95**, 3467 (1991)

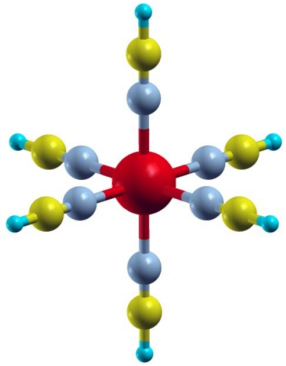
$[Fe(H_2O)_6]^{2+}$

	ΔE (eV)
LDA	-0.49
GGA	-1.04
B3LYP	-1.37
PBE0	-1.74
HH	-2.26
DMC	**-2.54(1)**



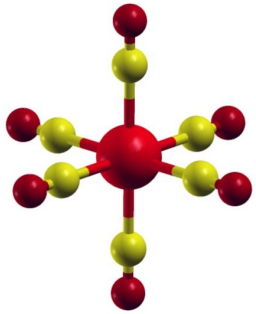
$[Fe(NH_3)_6]^{2+}$

	ΔE (eV)
LDA	0.96
GGA	0.08
B3LYP	-0.59
PBE0	-0.88
HH	-1.68
DMC	**-1.59(1)**



$[Fe(NCH)_6]^{2+}$

	ΔE (eV)
LDA	2.37
GGA	1.04
B3LYP	-0.20
PBE0	-0.44
HH	-1.49
DMC	**-1.37(3)**

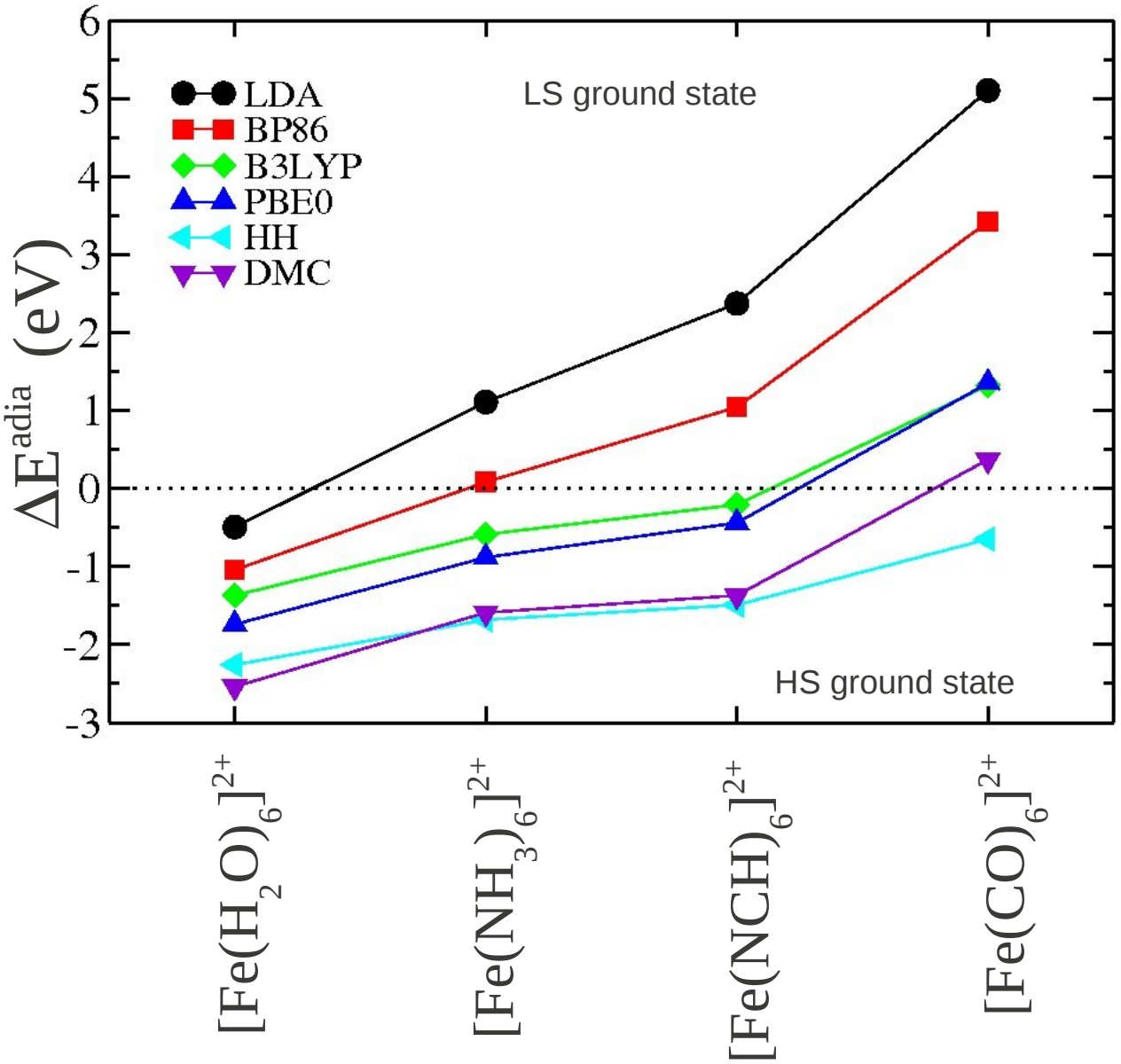


$[Fe(CO)_6]^{2+}$

	ΔE (eV)
LDA	5.10
GGA	3.41
B3LYP	1.32
PBE0	1.35
HH	-0.64
DMC	**0.37(3)**

$$\Delta E > 0 \rightarrow E_{S=2} > E_{S=0}$$

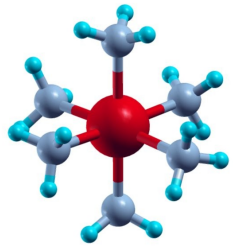
Model systems: results



Comparison with CASPT results

$[Fe(H_2O)_6]^{2+}$

	ΔE (eV)
DMC	-2.54(1)
CASSCF(12,10) [1]	-2.63
CASPT2(12,10) [1]	-2.01
CASPT2(12,10) [2]	-2.02



$[Fe(NH_3)_6]^{2+}$

	ΔE (eV)
DMC	-1.59(1)
CASSCF(12,10) [1]	-2.55
CASPT2(12,10) [1]	-1.60
CASPT2(12,10) [2]	-0.88

[1] A. Fouqueau et al., J. Chem. Phys. **120**, 9473 (2004); **122**, 044110 (2005)
[2] K. Pierloot & S. Vancoilie, J. Chem. Phys. **125**, 124303 (2006)

Comparison with CASPT results

CRANN

CASPT2

- Results far from being converged with respect to the basis set.

DMC

- LDA orbitals used in the Slater part of the trial wave-function,
- Multi-determinant trial wave-functions have not been considered so far (any suggestion for a more appropriate trial wave-function?).

Conclusions

CRANN

Fe(II) molecules – a tricky problem for DFT

Oxidation state — (LDA, GGA, metaGGA, hybrids...)

Ground state spin — Hybrid functionals with more than 20% of exact exchange, GGA with improved exchange part (e.s. OLYP)

Adiabatic energy gap — Hybrid functionals with a fraction of exact exchange between 30 and 50%

A. Droghetti et al., arXiv:1206.1293

Introduction and motivation

- Molecular spintronics
- Spin-crossover molecules

Model systems

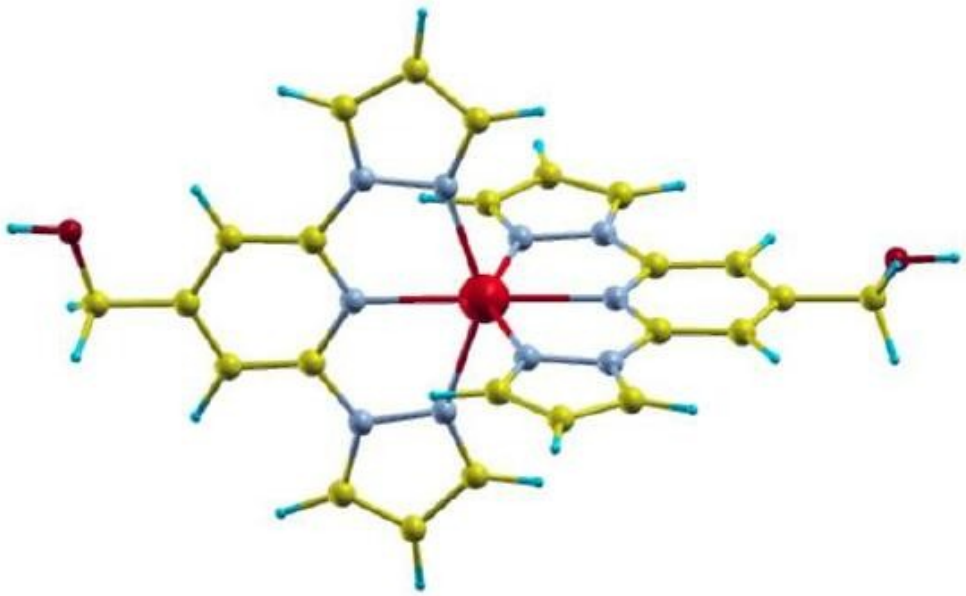
- Assessment of density functionals

Spin-crossover molecules

- Gas phase vs condensed phase

Spin Crossover

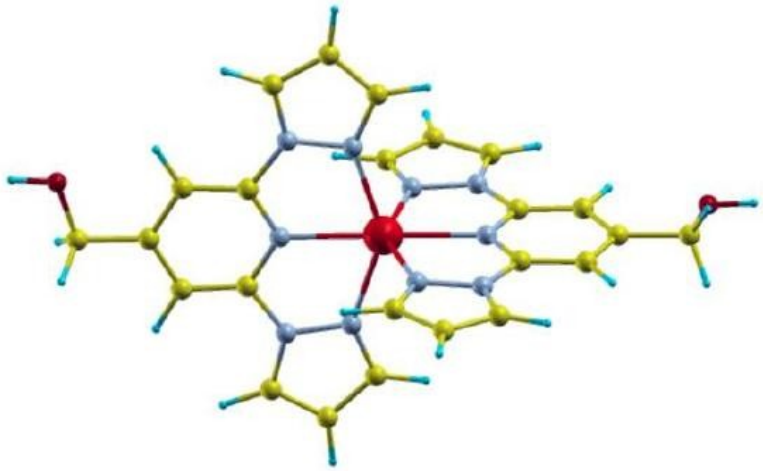
$Fe[L]^{2+}$ (L= 2-6-dypirazol-1-yl-4-hydroxymethylpyridine)



LS to HS transition **in crystals** @ 271K

V.A. Money *et al.*, Dalton Trans. **10**, 1516 (2004)

DFT vs DMC



$Fe[L]^{2+}$ (L= 2-6-dypirazol-1-yl-4-hydroxymethylpyridine)

	ΔE (eV)
GGA	1.24
B3LYP	0.01
PBE0	-0.23
HH	-1.33
DMC	**-1.21(4)**

	ΔE^{adia} (eV)
DMC	**-1.21(4)**

$$E_{HS} < E_{LS}$$

	ΔE^{adia} (eV)
DMC	**-1.21(4)**

$$E_{HS} < E_{LS}$$

Experimental structure

(condensed phase)

- the average Fe-N bond length decreases of about 0.03 Ang.

- the symmetry of the molecule is reduced

	ΔE^{adia} (eV)
DMC	**-1.21(4)**

$E_{HS} < E_{LS}$

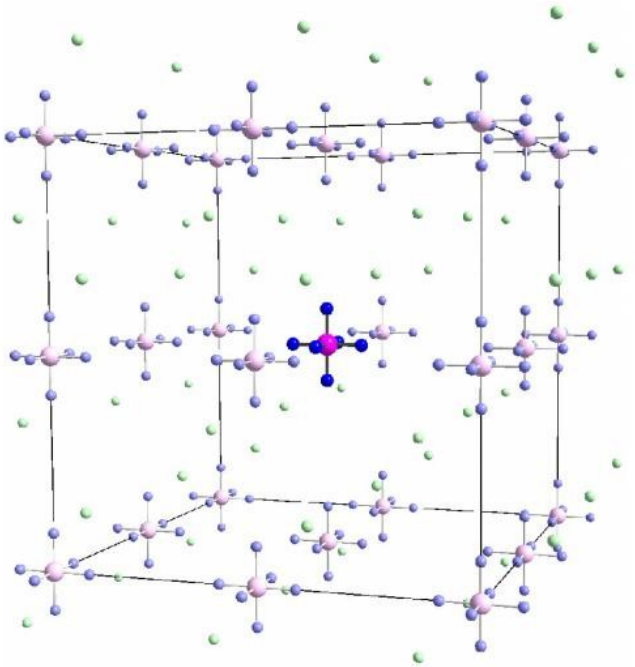
Experimental structure

	ΔE^{adia} (eV)
DMC	**-0.36(4)**

$E_{HS} < E_{LS}$

	ΔE^{ad} (eV)
DMC	**-1.21**

	ΔE^{ad} (eV)
DMC	**-0.36**



Madelung field corrections

$$E_i \approx Q_i \sum_j \frac{Q_j}{r_{ij}} \approx 0.5\,eV$$

M. Kepenekian *et al.*,

Phys. Rev. B, **79**, 094428 (2009)

JACS **131**, 11498 (2009)

	ΔE^{adia} (eV)
DMC	**-1.21(4)**

$E_{HS} < E_{LS}$

Experimental structure

	ΔE^{adia} (eV)
DMC	**-0.36(4)**

$E_{HS} < E_{LS}$

Madelung field corrections

$\sim 0.5\, eV$

$\Delta E^{adia} \approx 0.14\, eV$

	ΔE^{adia} (eV)
DMC	**-1.21(4)**

$$E_{HS} < E_{LS}$$

Experimental structure

	ΔE^{adia} (eV)
DMC	**-0.36(4)**

Mac

$$\Delta E^{adia} \approx 0.14\,eV$$

Experimental estimates

$$\Delta E^{adia} \approx 0.1 \div 0.3\,eV$$

G. Ganzenmuller et al., J. Chem. Phys., **122**, 234321 (2005)

Conclusions

- The molecule is not intrinsically spin crossover.
- Ground state in the gas phase is high spin.
- Ground state in the condensed phase is low spin and the molecule can undergo a spin-crossover transition.
- The puzzle of the spin state of spin-crossover molecules in the gas/condensed phase has been solved thanks to DMC.

A. Droghetti, D. Alfe' and S. Sanvito, arXIv 1024.5336

Acknowledgments

- Science Foundation Ireland and European Union for financial support
- Trinity Center for High Performance Computing
- Irish Center for High End Computing

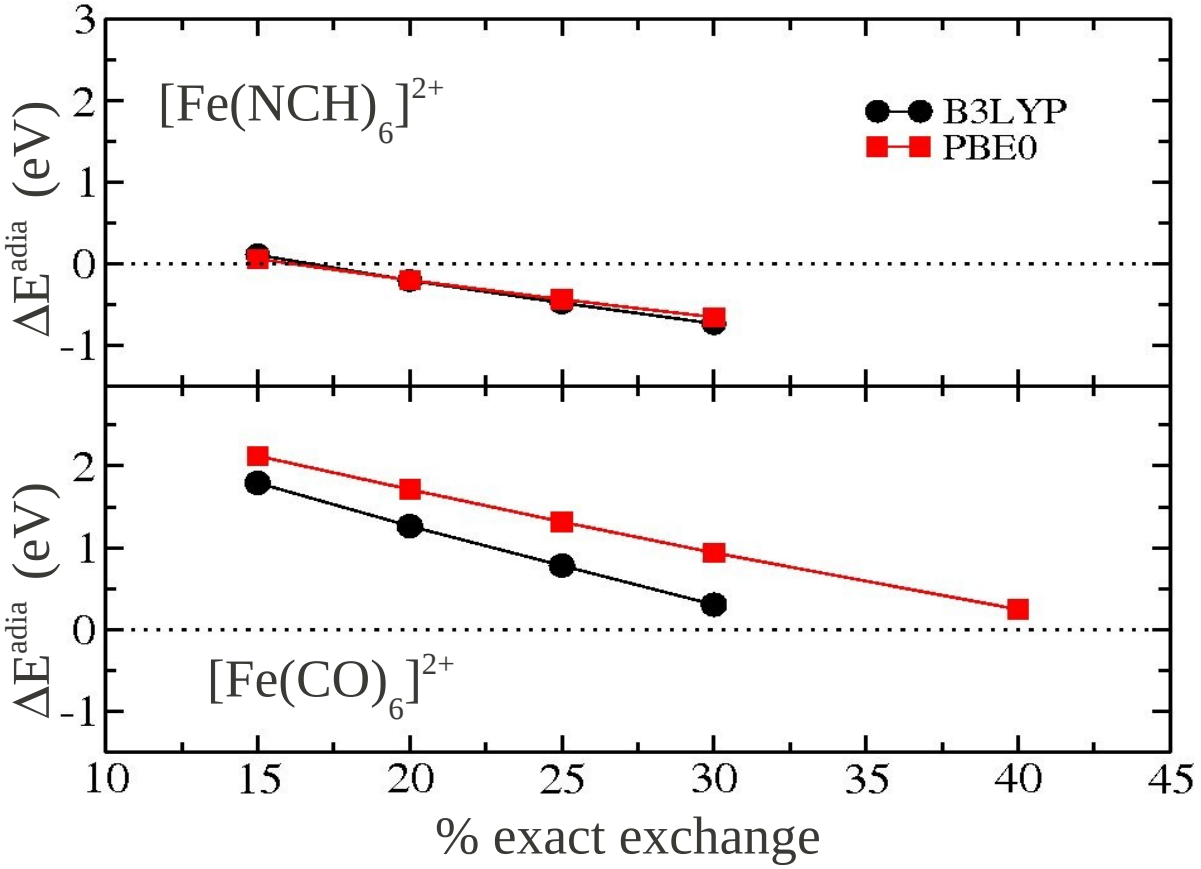
Acknowledgments

- Science Foundation Ireland and European Union for financial support
- Trini ng
- Irish

Thank you

Model systems: results

Ionic vs covalent Bond



Model systems: results

Ionic vs covalent Bond