Spin-crossover molecules: puzzling systems for electronic structure methods

Andrea Droghetti
School of Physics and CRANN, Trinity College Dublin

Introduction

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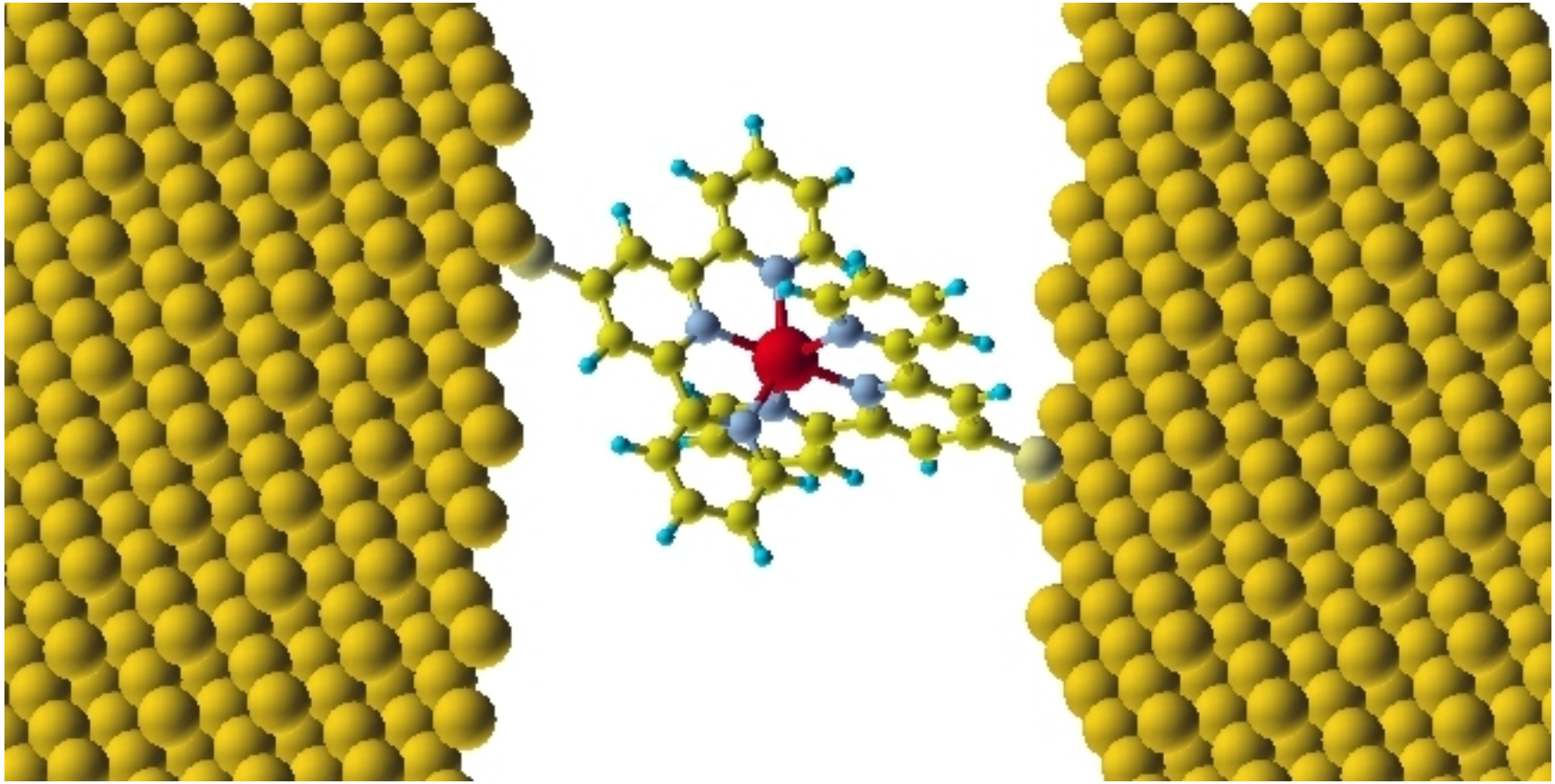
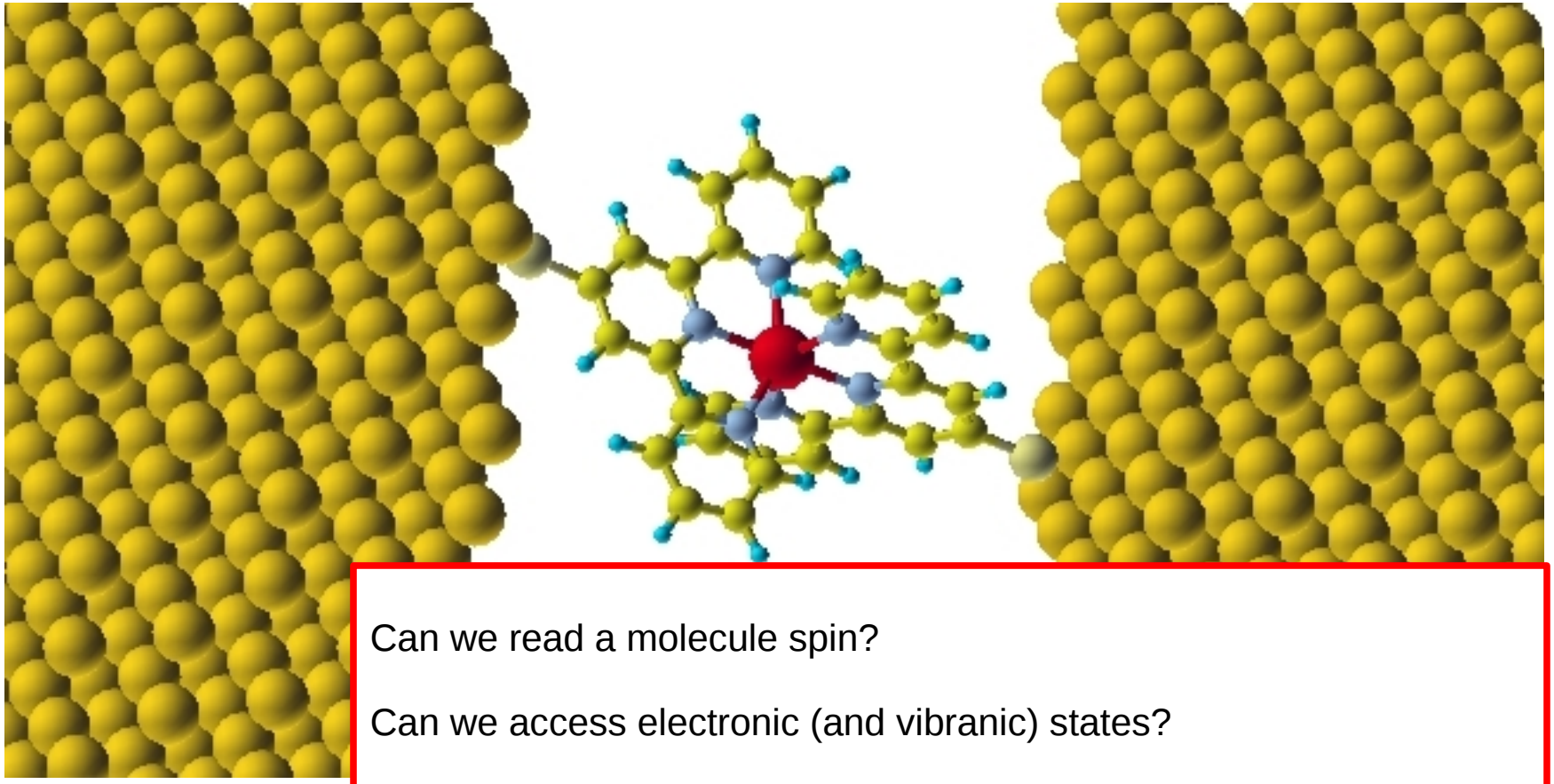


Introduction



Can we read a molecule spin?

Can we access electronic (and vibranic) states?

Can we write and read information in the spin state of a molecule?

Introduction

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Electronic structure of the molecule

Electronic structure of the device (equlibrium properties)

Transport properties of the device (out-of-equilibrium properties)

Introduction

Electronic structure of the molecule

DFT DMC CASSCF

Electronic structure of the device (equlibrium properties)

DFT beyond-DFT

Transport properties of the device (out-of-equilibrium properties)

DFT

Beyond-DFT (?)
(TDDFT, MDPT ?)

Introduction

Electronic structure of the molecule

DFT **DMC** CASSCF

1- Accurate results (?)

Electronic structure of the device (equlibrium properties)

DFT beyond-DFT

Transport properties of the device (out-of-equilibrium properties)

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Beyond-DFT (?)
(TDDFT, MDPT ?)

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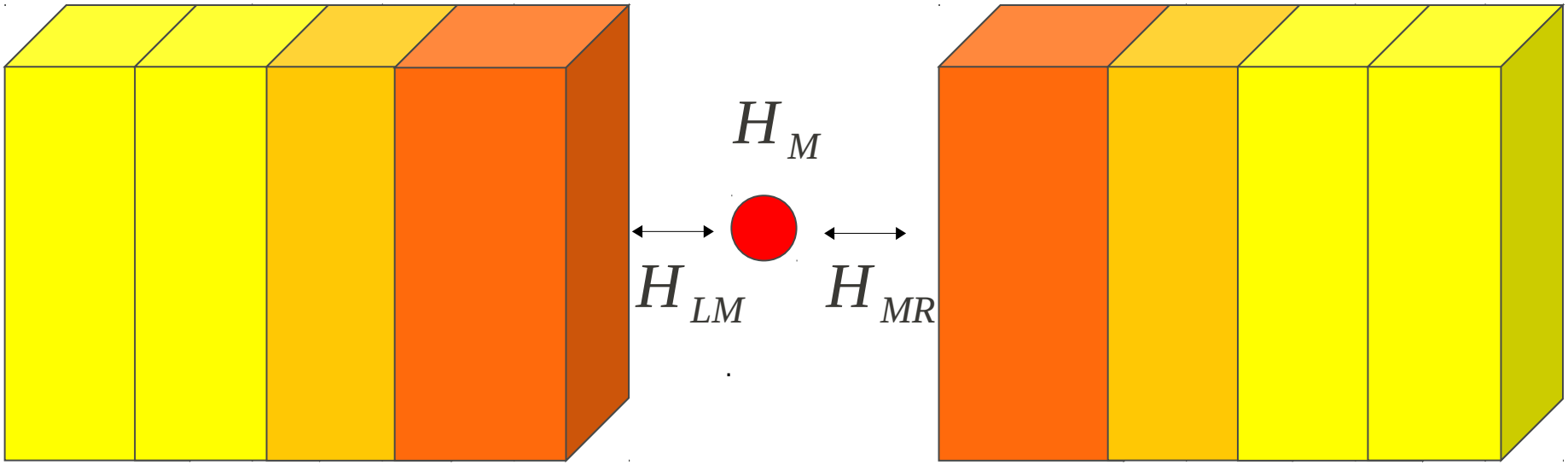
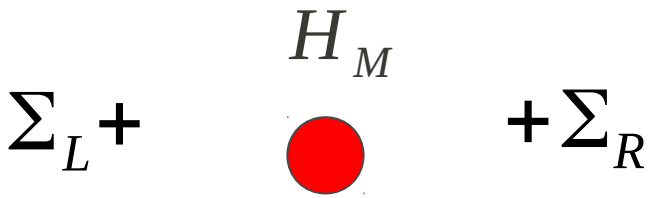
Beyond-DFT (?)
(TDDFT, MDPT ?)

DFT for infinite systems



H_L H_R

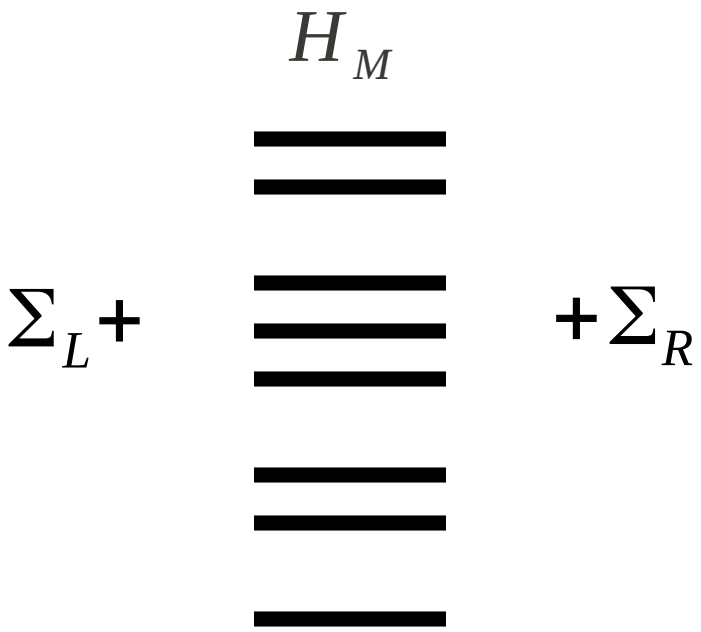
DFT for infinite systems



Smeagol
Non-equilibrium Electronic Transport

www.smeagol.tcd.ie

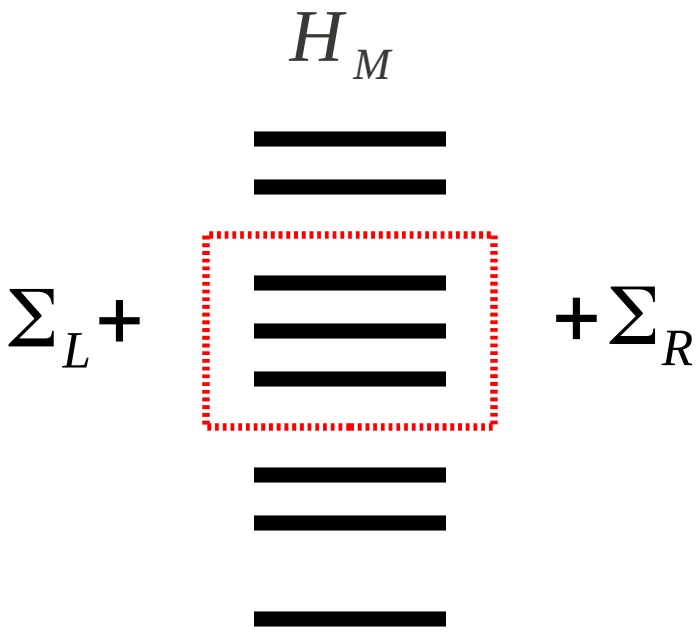
DFT for infinite systems



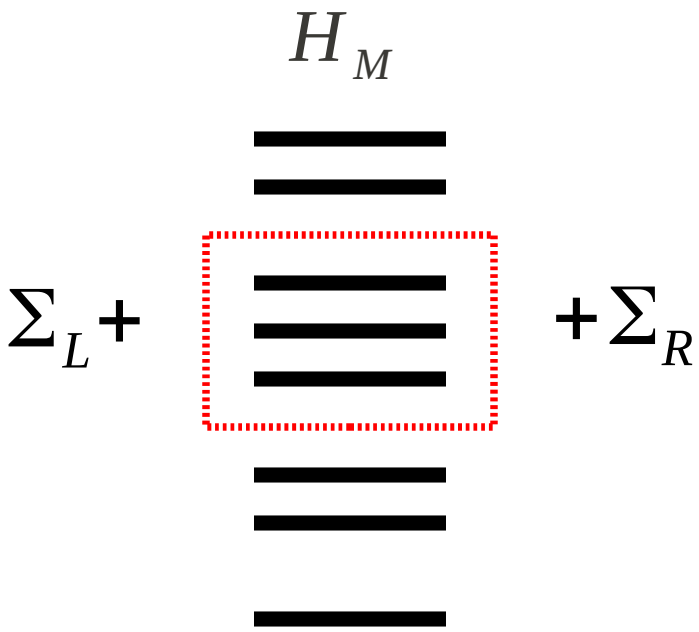
Smeagol
Non-equilibrium Electronic Transport

www.smeagol.tcd.ie

The Theoretical Method



The Theoretical Method



The Theoretical Method

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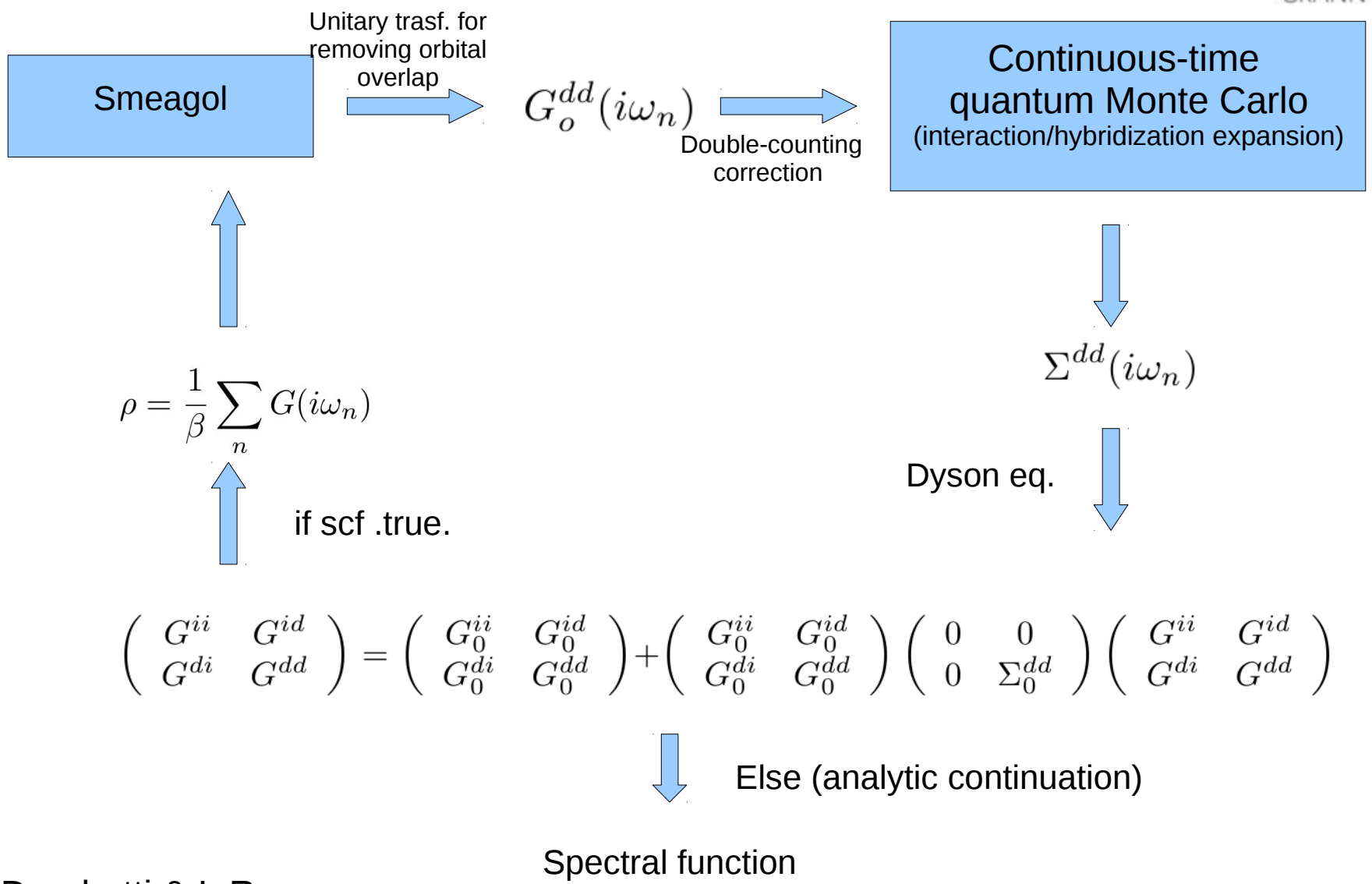
$$H'_M = H_0 + V_{ee}$$

$$\Sigma_L + \quad \equiv \quad + \Sigma_R$$

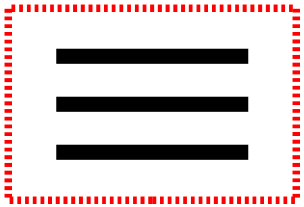
.



A. Droghetti & I. Rungger

The Theoretical Method

$$H'_M = H_0 + V_{ee}$$



.

DMC two-particle density matrix = model two-particle density matrix

(Lucas Wagner)

Electronic structure of the molecule

DFT **DMC** CASSCF

1- Accurate results (?)
2- Allow to extract “first-principles” model Hamiltonians

Electronic structure of the device (equlibrium properties)

DFT beyond-DFT

Transport properties of the device (out-of-equilibrium properties)

DFT Beyond-DFT (?)
(TDDFT, MDPT ?)

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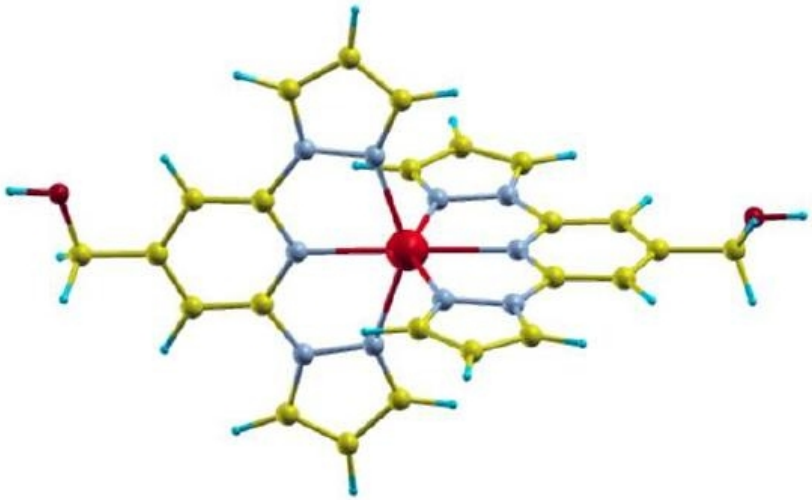
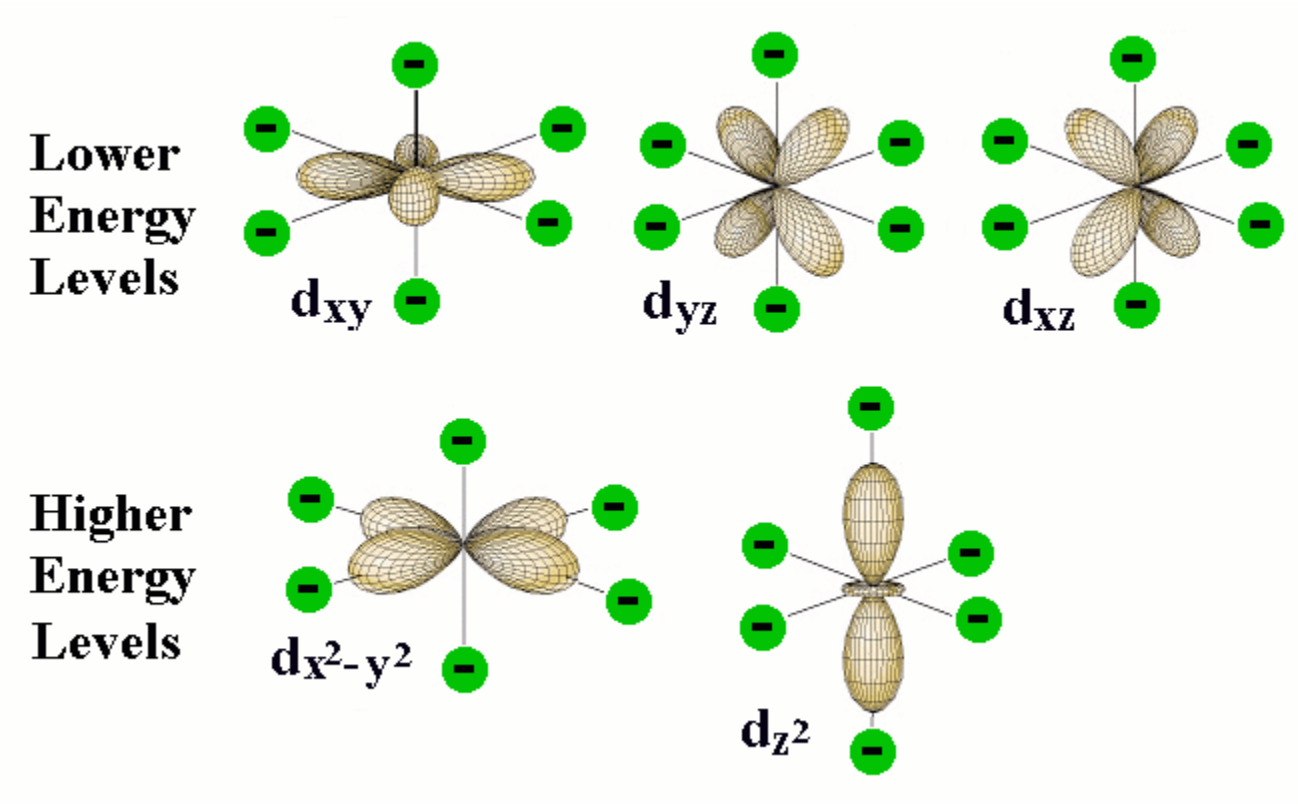
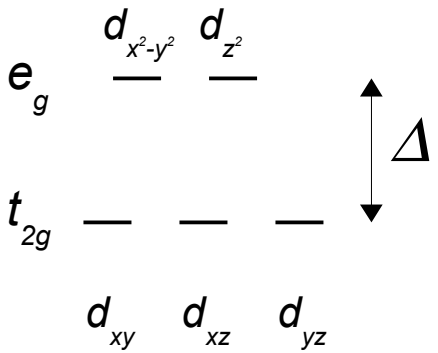
Spin-Crossover molecules

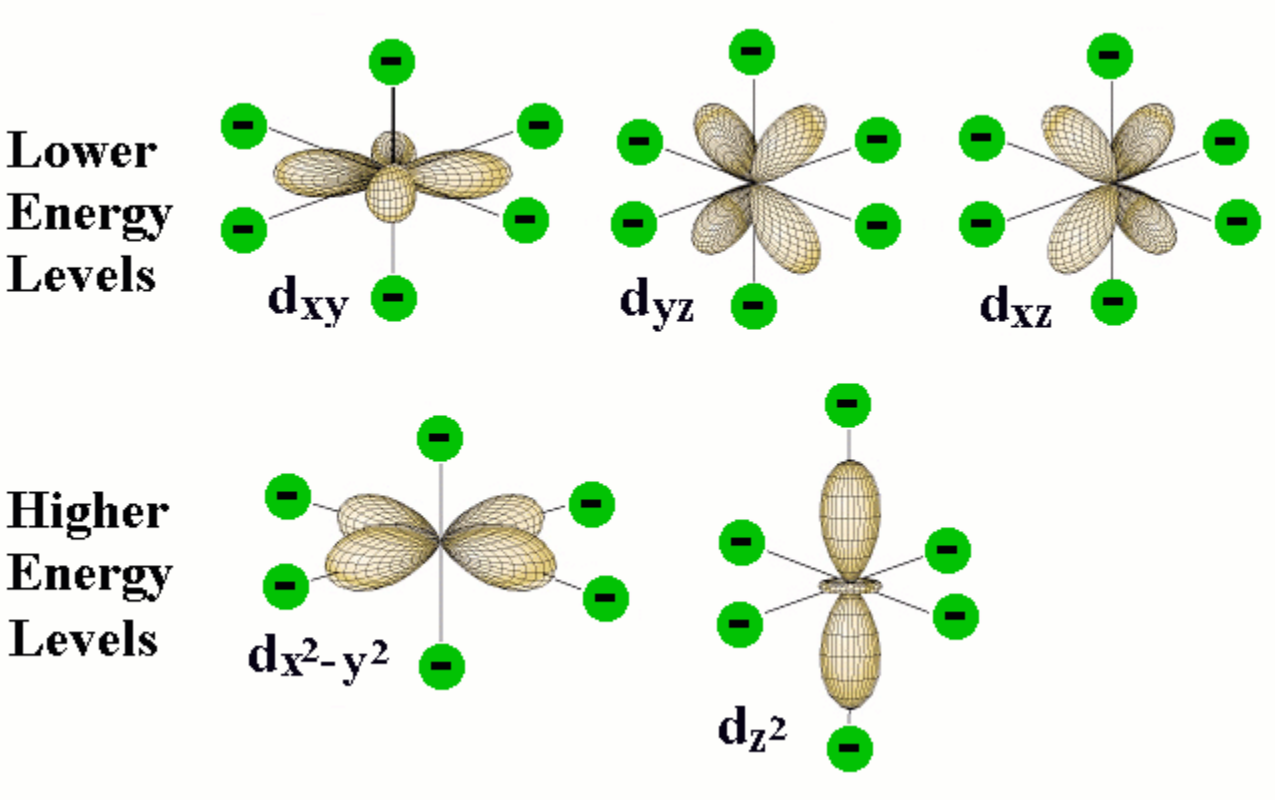


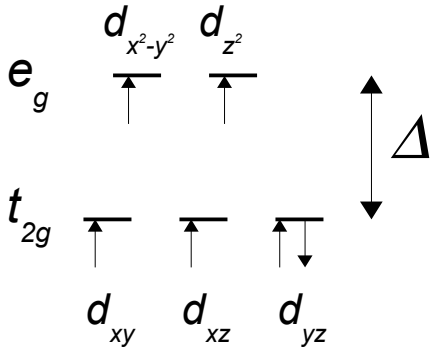
Spin-crossover molecules



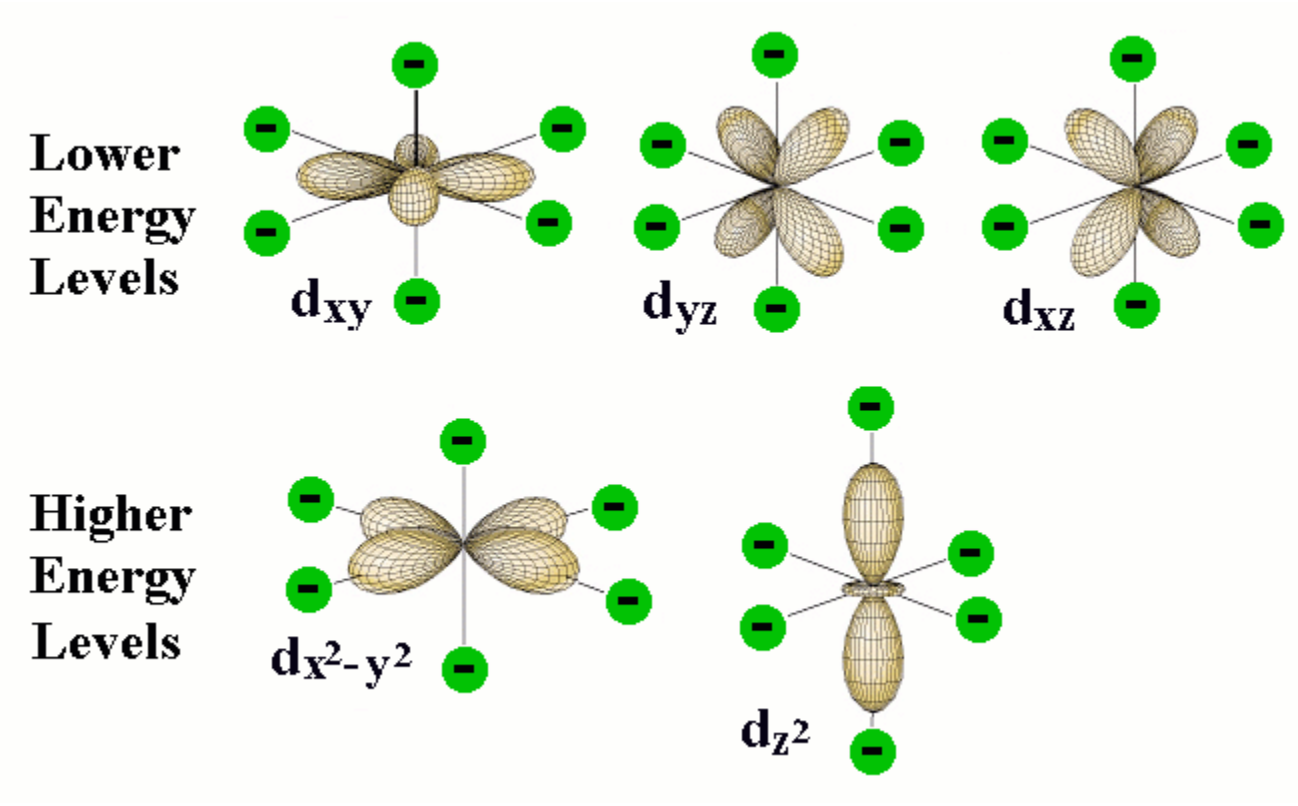


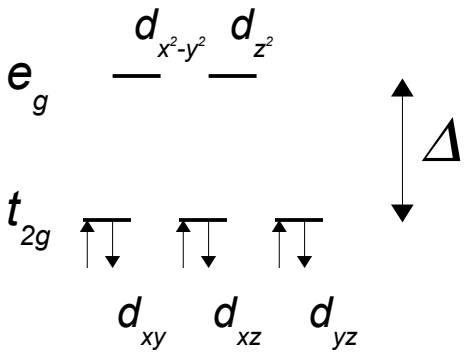
Spin-crossover molecules



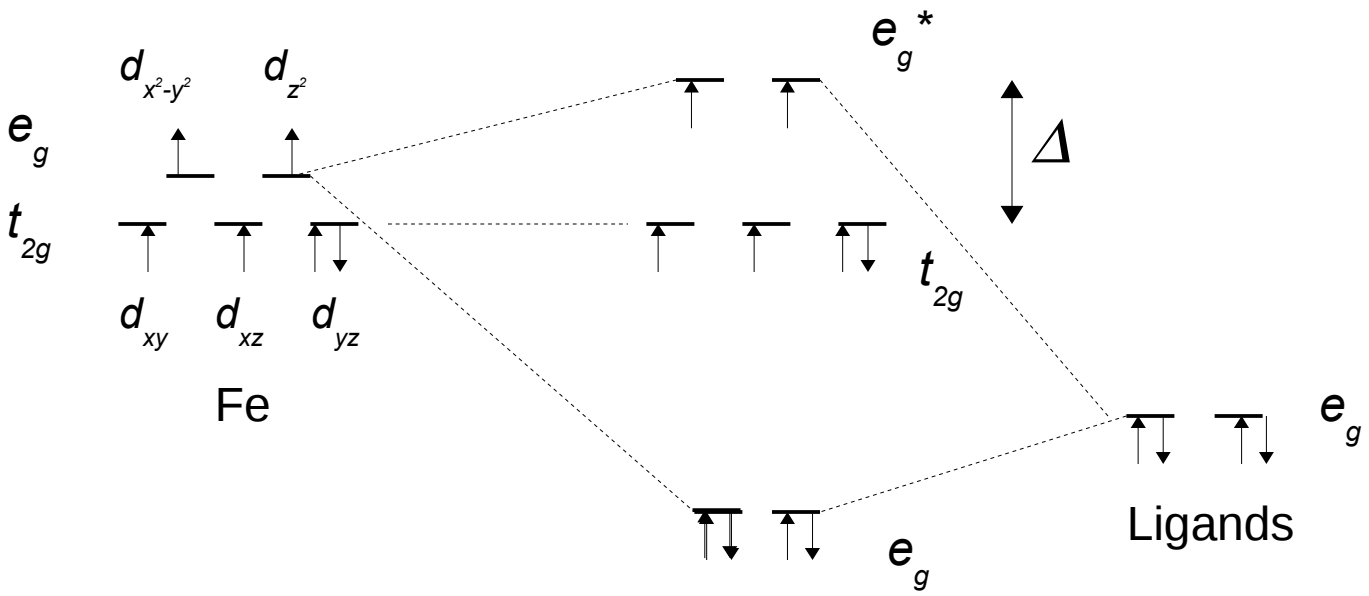


Spin-crossover molecules

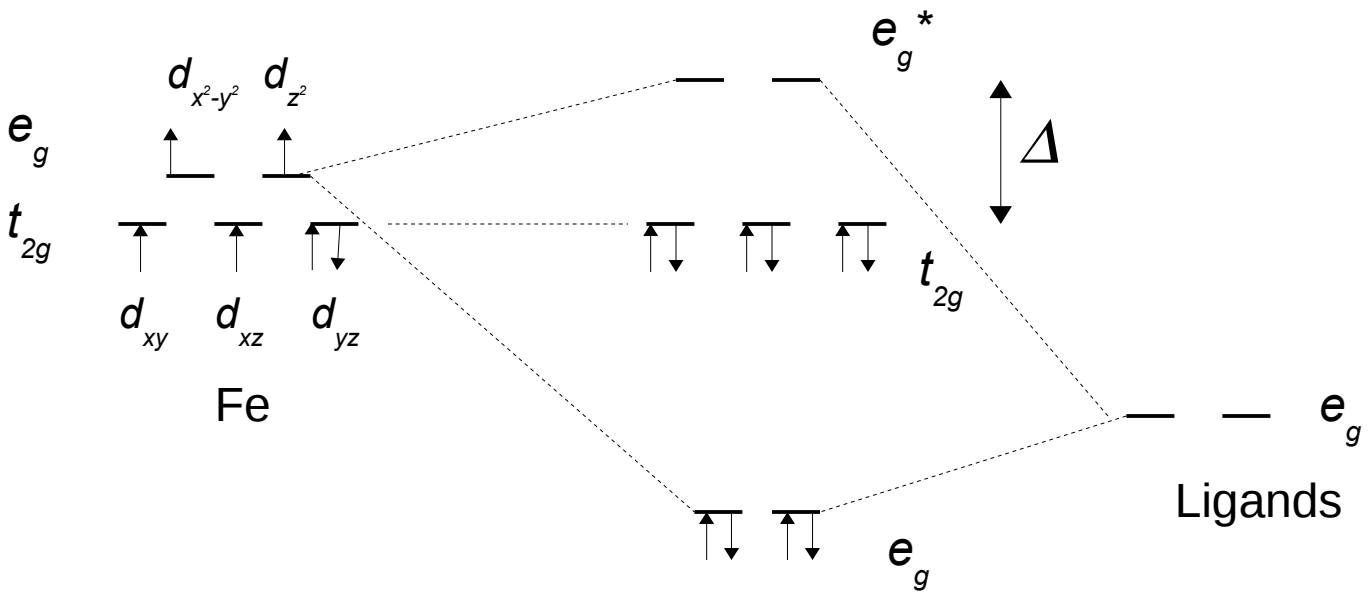




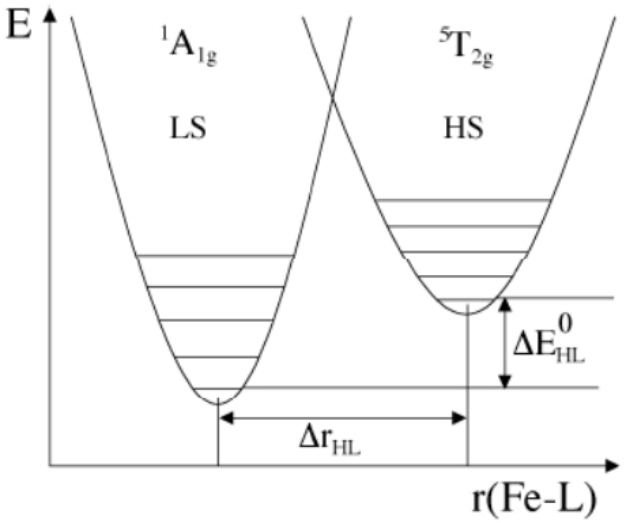
Spin-crossover molecules



Spin-crossover molecules



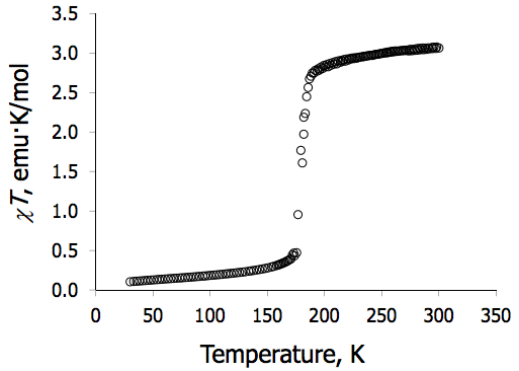
Magnetic molecules



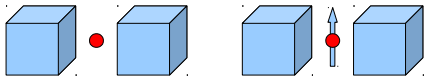
$$\Delta G = G_{HS} - G_{LS} = \Delta E - T\Delta S$$

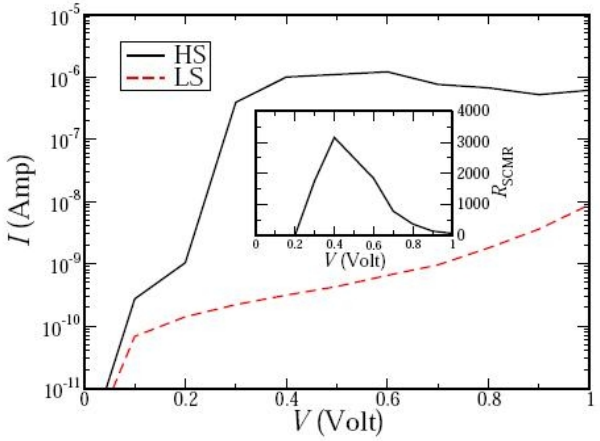
$$\Delta E > 0 \qquad \Delta S > 0$$

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

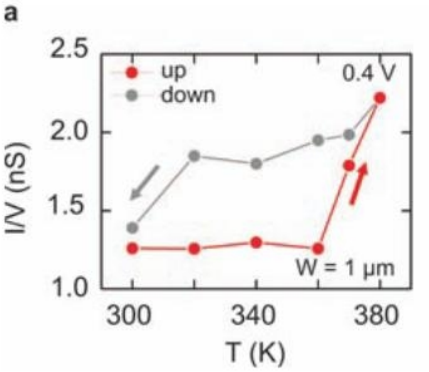


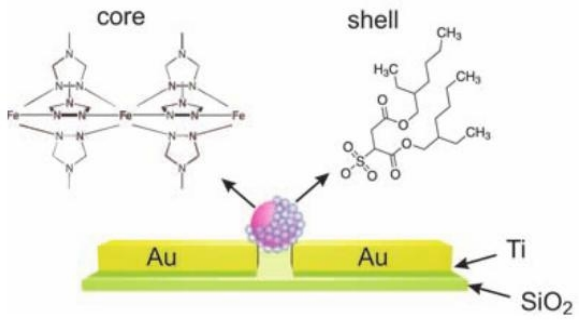
Transport through SCMs



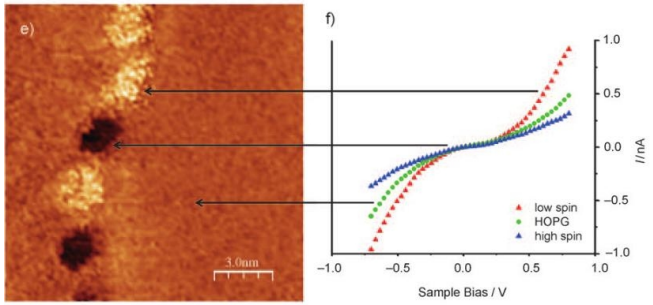


N. Baadji & S. Sanvito,
Phys. Rev. Lett. **108**, 217201 (2012)



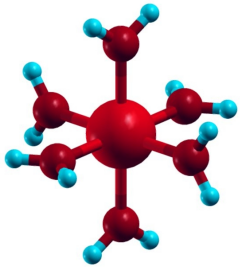


F. Prinz et al., Adv. Mat., **23**, 1545 (2011)

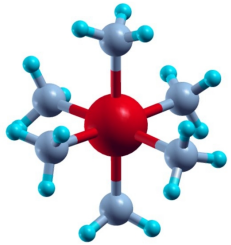


M.S. Alam et al., Angew. Chem. Int. Ed., **49**, 1159 (2010)

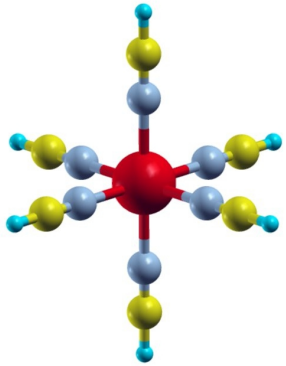
Model systems



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



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



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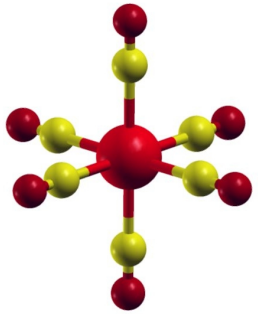


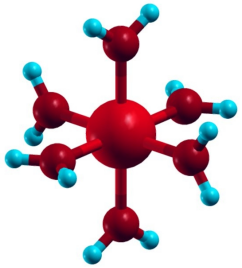
$[Fe(CO)_6]^{2+}$

lower crystal field

higher crystal field

Spectrochemical series

Model systems



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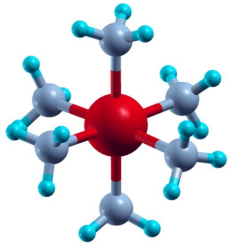

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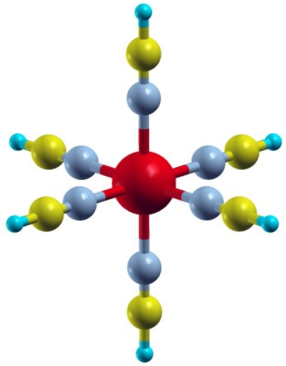

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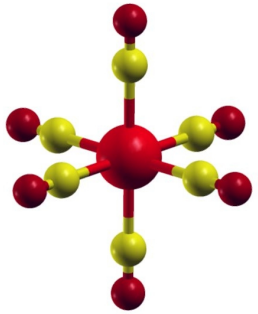


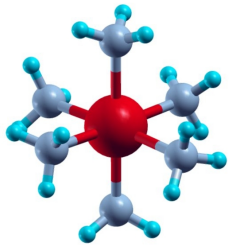
$[Fe(CO)_6]^{2+}$

lower crystal field — higher crystal field

Expected ground state:

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

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



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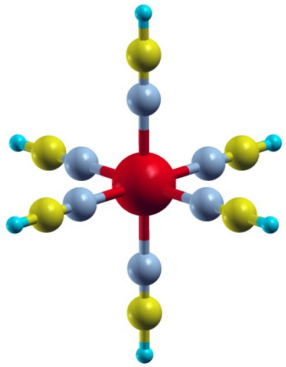

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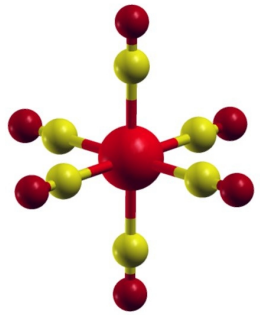


$[Fe(CO)_6]^{2+}$

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

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

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

	ΔE^{adia} (eV)
LDA	5.18
GGA	3.42
B3LYP	1.27
PBE0	1.32
HH	0.24
DMC	**0.37(3)**

$$\Delta E^{adia} > 0 \rightarrow E_{HS} > E_{LS}$$

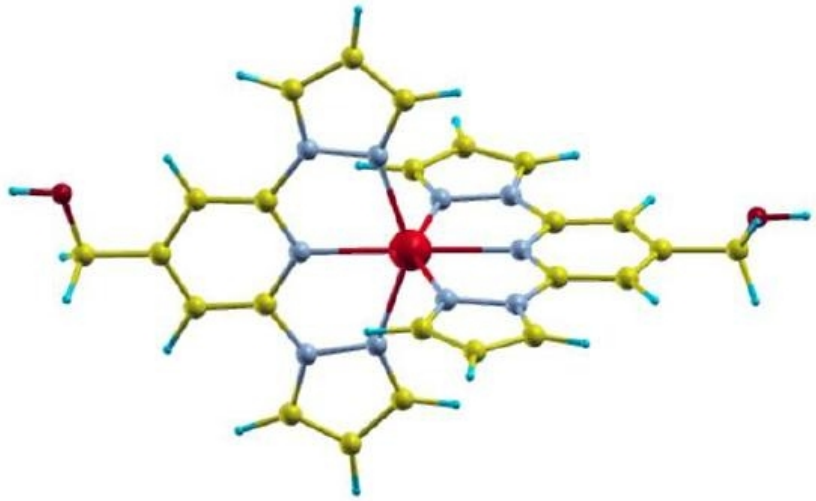
Caculations with CASINO
Dirac-Fock Trail-Needs PP (small core for Fe)
Slater-Jastrow (LDA orbitals)

A. Droghetti & S. Sanvito and in collaboration with D. Alfe' (UCL)

Spin Crossover

$[FeL_2](BF_4)_2$
(L=2,6-dypirazol-1-yl-4-hydroxymethylpyridine)

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

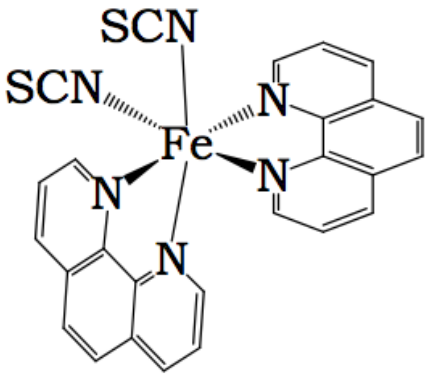


	ΔE^{adia} (eV)
GGA	1.24
B3LYP	0.01
PBE0	-0.23
HH	-1.33
DMC	**-1.21(4)**

A. Droghetti, D. Alfe' and S. Sanvito, J. Chem. Phys. **137**, 124303 (2012)

A. Droghetti, D. Alfe' and S. Sanvito, Phys. Rev. B **87**, 205114 (2013)

Spin Crossover

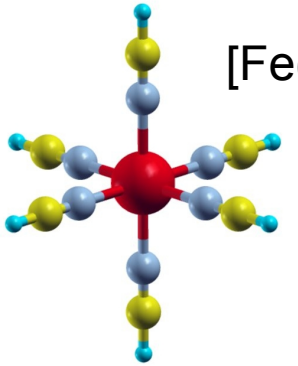


	ΔE^{adia} (eV)
GGA	**0.44**
B3LYP	**-0.33**
PBE0	**-0.54**
DMC	**-0.69(8)**
CASPT2	**0.10**

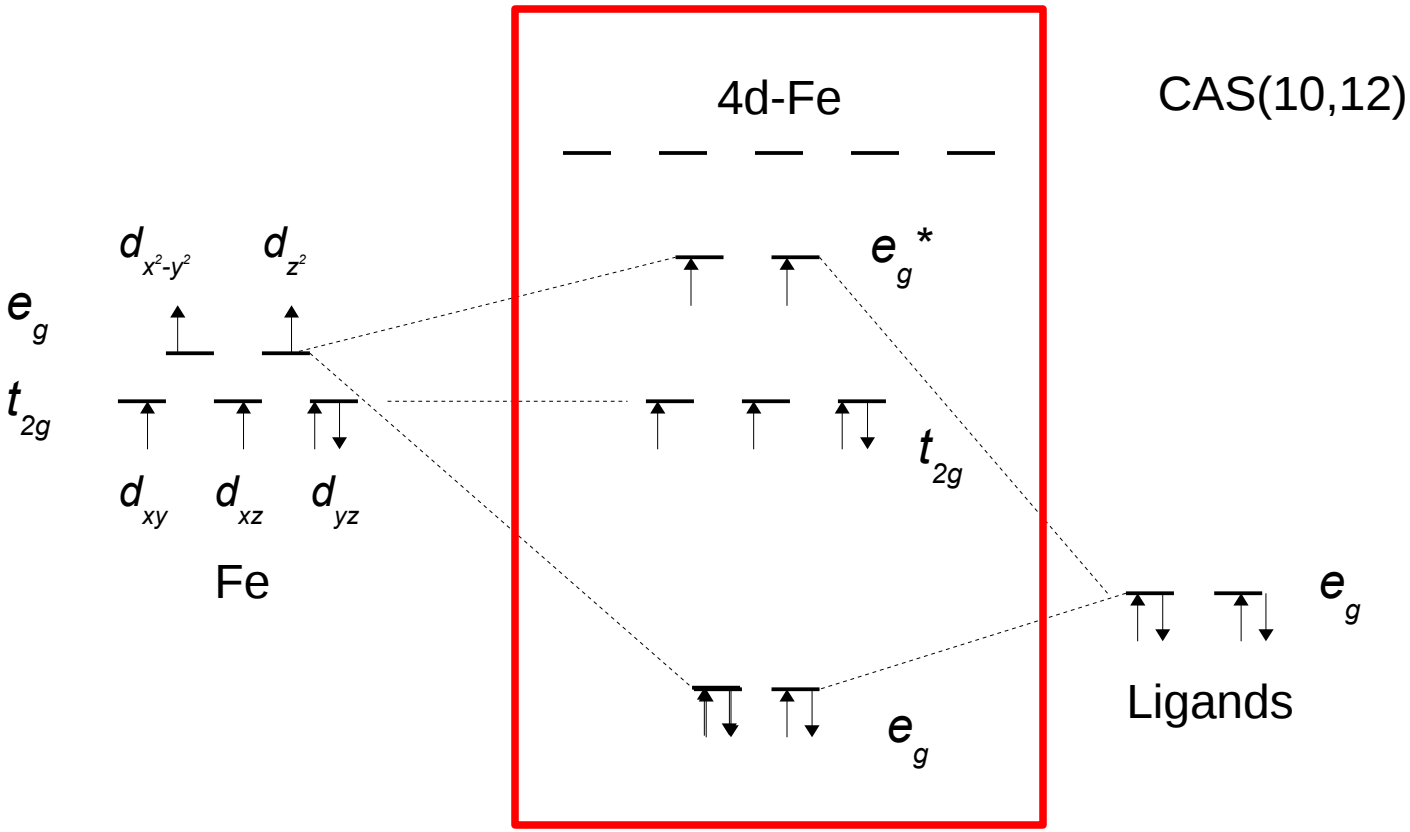
DMC with QWALK,
(new) Burkatzki-Filippi-Dong PP
Slater-Jastrow

Calculations performed by A. Droghetti and M. Fumanal (Barcelona)
Thanks to Lucas Wagner for the code and technical support

Spin Crossover

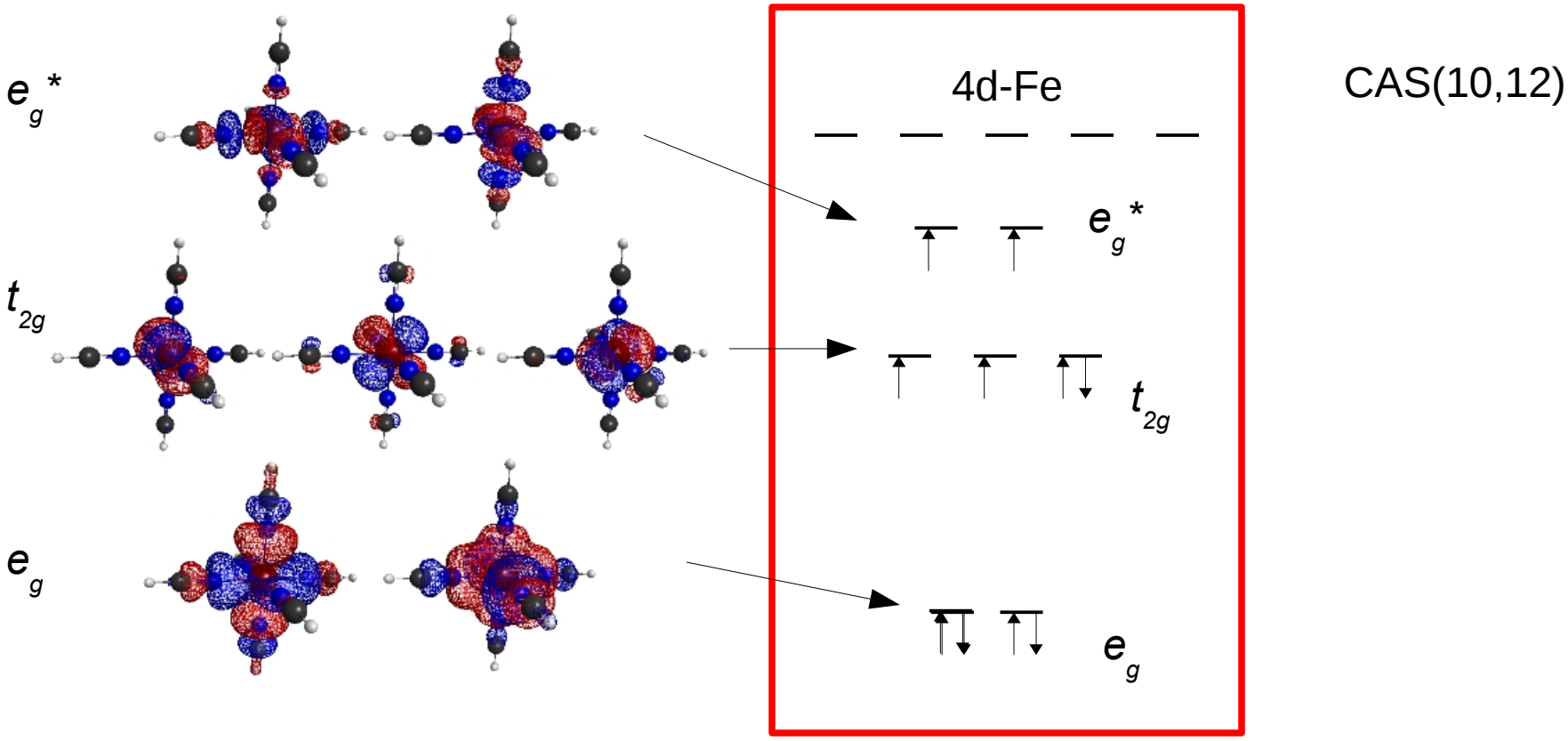


$[Fe(NCH)_6]^{2+}$



Spin Crossover

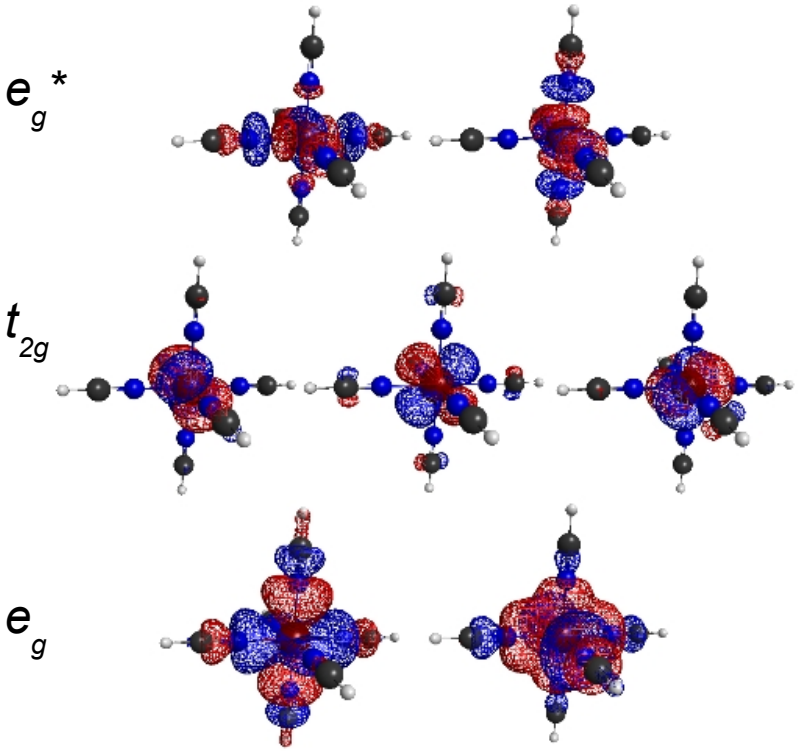
$[Fe(NCH)_6]^{2+}$

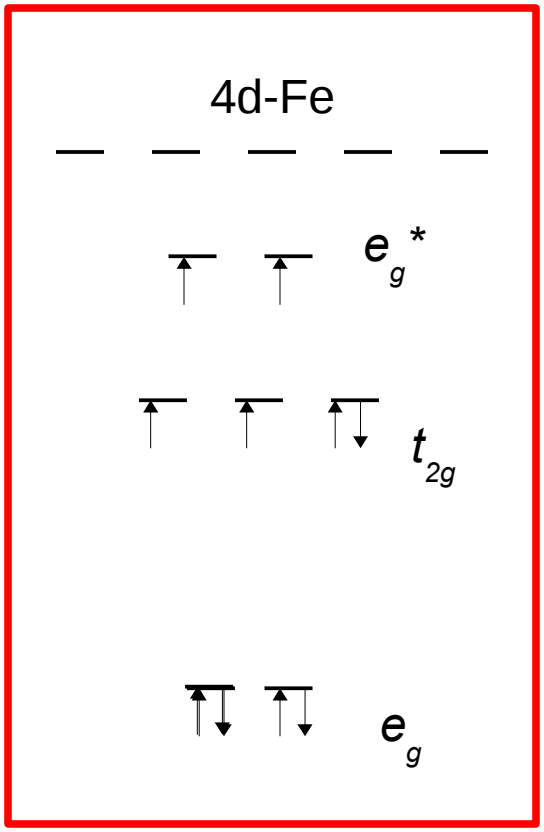


CAS(10,12)

Spin Crossover

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





CAS(10,12)

	ΔE^{adia}
HF	**-3.82 eV**
CASSCF	**-1.96 eV**
CASPT2	**-0.33 eV**

Spin Crossover

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

	ΔE^{adia}
HF	-3.82 eV
B3LYP	-0.29 eV
PBE	0.76 eV
CASSCF	-1.96 eV
CASPT2	-0.33 eV

	ΔE^{adia}
DMC (HF)	-1.16(5) eV
DMC (B3LYP)	-1.05(5) eV
DMC (PBE)	-0.87(4) eV

DMC (Slater-Jastrow)

Spin Crossover

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HS CAS(10,7)					
CSF 1 (1 det)	a a 2 a a 2 2				
CSF 3 (3 det)	a a 2 a a 2 2	a a a 2 a 2 2	a a a a 2 2 2		
CSF 15 (15 det)	a a 2 a a 2 2	a a a 2 a 2 2	a a a a 2 2 2	2 a 2 a a a 2	2 a 2 a a 2 a
	a 2 2 a a a 2	a 2 2 a a 2 a	2 a a 2 a a 2	2 a a 2 a 2 a	a 2 a 2 a a 2
	a 2 a 2 a 2 a	2 a a a 2 a 2	2 a a a 2 2 a	a 2 a a 2 a 2	a 2 a a 2 2 a
CSF 21 (21 det)	a a 2 a a 2 2	a a a 2 a 2 2	a a a a 2 2 2	2 a 2 a a a 2	2 a 2 a a 2 a
	a 2 2 a a a 2	a 2 2 a a 2 a	2 a a 2 a a 2	2 a a 2 a 2 a	a 2 a 2 a a 2
	a 2 a 2 a 2 a	2 a a a 2 a 2	2 a a a 2 2 a	a 2 a a 2 a 2	a 2 a a 2 2 a
	a a 2 2 a 2 a	a a 2 2 a a 2	a a 2 a 2 2 a	a a 2 a 2 a 2	a a a 2 2 2 a
	a a a 2 2 a 2				

CI space HS

2: doubly occupied
0: empty
a: spin up
b: spin down

Energy (a.u)

CSF1	**-220.698(1)**
CSF7	**-220.700(1)**
CSF13	**-220.706(1)**
CSF21	**-220.700(1)**

Spin Crossover

LS CAS(10,7)					
CSF 1 (1 det)	00 222 22				
CSF 7 (7 det)	00 222 22	20 220 22	02 220 22	20 202 22	02 202 22
	20 022 22	02 022 22			
CSF 13 (15 det)	00 222 22	20 220 22	02 220 22	20 202 22	02 202 22
	20 022 22	02 022 22	20 222 20	20 222 02	02 222 20
	02 222 02	20 222 ab	20 222 ba	02 222 ab	02 222 ba
CSF 23 (43 det)	00 222 22	20 220 22	02 220 22	20 202 22	02 202 22
	20 022 22	02 022 22	20 222 20	20 222 02	02 222 20
	02 222 02	20 222 ab	20 222 ba	02 222 ab	02 222 ba
	ab 222 20	ba 222 20	ab 222 02	ba 222 02	ab 220 22
	ba 220 22	ab 202 22	ba 202 22	ab 022 22	ba 022 22
	ab 2ab 22	ba 2ab 22	ab 2ba 22	ba 2ba 22	ab a2b 22
	ba a2b 22	ab b2a 22	ba b2a 22	ab ab2 22	ba ab2 22
	ab ba2 22	ba ba2 22	ab 222 ab	ba 222 ab	ab 222 ba

CI space LS

2: doubly occupied
0: empty
a: spin up
b: spin down

Energy (a.u)

CSF1	**-220.645(1)**
CSF7	**-220.648(1)**
CSF13	**-220.647(1)**
CSF23	**-220.649(1)**

Conclusions

CRANN

- DFT, DMC and CASPT return different results (different order of magnitude!!)
- CASPT2 – chemsists say that we should trust it as reference
- DMC...trial wave-function seems not to matter much
- Pseudo-potential...hard to say...but can a “bad pseudo-potential” be responsible for an systematic error of about more than 0.5 eV on an energy difference?
- What else?

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