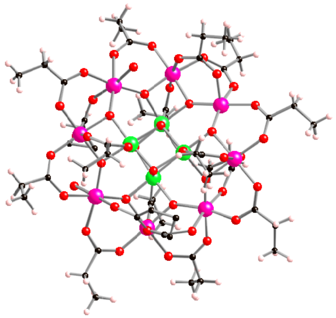
Laboratoire de Chimie et Physique Quantiques

Exchange, Super-Exchange Interaction and Magnetic Anisotropy: a Theoretical Insight



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Bangalore : 26-30 November 2018

A POSSIBLE ROLE OF QUANTUM CHEMISTRY IN MAGNETISM

$$\hat{H}\Psi = E\Psi$$

Quantum chemists work with the exact electronic Hamiltonian (and add relativistic effects):

$$\hat{H}_{BO} = \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} - \sum_i \frac{\Delta_i}{2} - \sum_{A,i} \frac{Z_A}{r_{iA}} + \sum_{i<j} \frac{1}{r_{ij}} = cste + \sum_i \vartheta_i + \boxed{\sum_{i<j} \frac{1}{r_{ij}}} \longleftarrow$$

Responsible for the difficulty

The methodological corpus developed to solve the Schrödinger equation is particularly important.
It consists in treating the electron repulsion as best as possible, i.e. to account for electron correlation.

However:
i) it cannot be applied to large magnetic systems,
ii) the interpretation of the wavefunctions is often complicated.
iii) There are by far too many interactions and configurations to model simply the properties…

In practice, both experimentalists and theoretical physicists (who add collective effects in solids) use model Hamiltonians.

The Heisenberg Hamiltonian is a model Hamiltonian
Why do we need models?

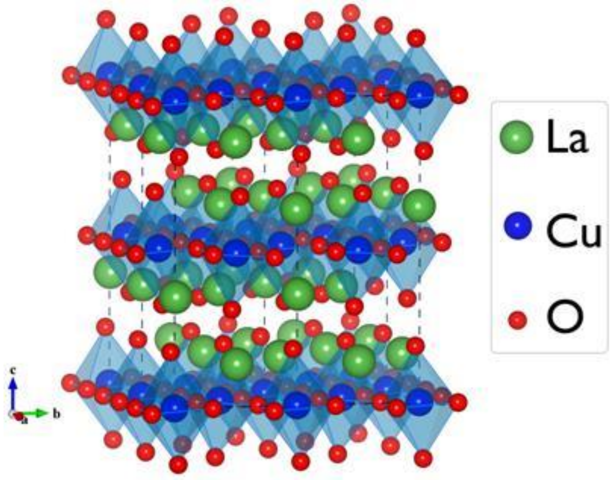
Model Hamiltonians are simpler than the exact electronic Hamiltonian:

Ex: $$\hat{H} = -\sum_{<i,j>} J_{ij}^{eff} \hat{S}_i . \hat{S}_j$$

- They only treat a few number of electrons (here 1 per copper ion)

- They only keep a few number of configurations (here spin distributions)

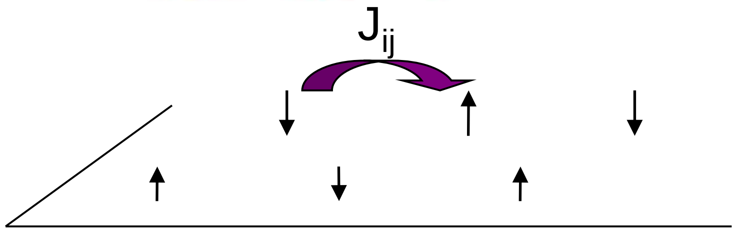
- They have effective interactions that are supposed to capture all the neglected physics



La_2CuO_4

↓

Cu^{2+}

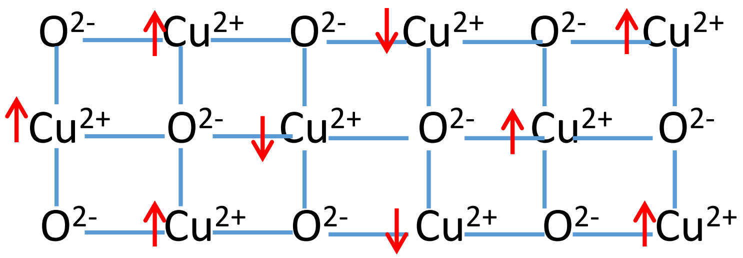


Objective : derive analytically and determine from *ab initio* calculation and the effective Hamiltonian theory the physical content of the exchange interaction and the Zero Field Splitting (magnetic anisotropy).

Magnetic systems and the Heisenberg Hamiltonian

Low-energy spectrum : states which only differ by their spin and have the same spatial configuration.

Ex : La_2CuO_4



All orbitals are doubly occupied except d_{x2-y2} of Cu^{2+} that carries a single electron.
From the different spin distributions that can be build by distributing all ↑ and ↓ on the skeleton, one can generate all the lowest states.

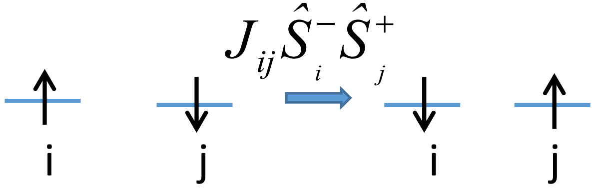
These states are generally quasi-degenerate

These states are well described by the Heisenberg Hamiltonian Dirac van Vleck (HDvV) model

$$\hat{H} = -2\sum_{i<j} J_{ij}\left(\hat{S}_i\hat{S}_j - \frac{\hat{I}}{4}\right)$$

$$with\ \hat{S}_i\hat{S}_j = \hat{S}_{Zi}\hat{S}_{Zj} + \frac{1}{2}\left[\hat{S}_i^+\hat{S}_j^- + \hat{S}_i^-\hat{S}_j^+\right]$$

The exchange integral of J_{ij} ≠0 if i and j interact :



Heisenberg model

The model space is constituted of all neutral determinants, products of local ground states, i.e. local highest spin states (due to the Hund's rule).

$$\hat{H}^{Heis.} = -\sum_{<ij>} J_{ij}\left(\hat{\vec{S}}_i.\hat{\vec{S}}_j - \frac{\hat{n}_i\hat{n}_j}{4}\right)$$

This definition ensures that the highest spin state is at zero of energy here $\hat{n}_i$ is the number of unpaired electron(s) on site i

The operator is a scalar product between the spin vectors

$$\hat{\vec{S}}_i.\hat{\vec{S}}_j = \begin{pmatrix}\hat{S}_{X_i} & \hat{S}_{Y_i} & \hat{S}_{Z_i}\end{pmatrix}\begin{pmatrix}\hat{S}_{X_j}\\ \hat{S}_{Y_j}\\ \hat{S}_{Z_j}\end{pmatrix} = \hat{S}_{X_i}\hat{S}_{X_j} + \hat{S}_{Y_i}\hat{S}_{Y_j} + \hat{S}_{Z_i}\hat{S}_{Z_j} = \hat{S}_{Z_i}\hat{S}_{Z_j} + \frac{1}{2}\left(\hat{S}_i^+\hat{S}_j^- + \hat{S}_i^-\hat{S}_j^+\right)$$

Heisenberg Hamiltonian matrix for 2 electrons in 2 orbitals : Ex: S_1=1/2, S_2=1/2

$$\hat{\mathrm{H}}^{\mathrm{Heis.}} = -\mathrm{J}_{12}\left(\hat{\mathrm{S}}_{z1}\hat{\mathrm{S}}_{z2} - \frac{\hat{\mathrm{I}}}{4}\right) - \frac{\mathrm{J}_{12}}{2}\left(\hat{\mathrm{S}}_{+1}\hat{\mathrm{S}}_{-2} + \hat{\mathrm{S}}_{-1}\hat{\mathrm{S}}_{+2}\right)$$

$$H_{21} = \langle \downarrow_1 \uparrow_2 | \hat{H} | \uparrow_1 \downarrow_2 \rangle$$

Space:

Ms=1 distribution : ↑ ↑ , Ms=1 component of the triplet
Ms =0 2 possible distributions : ↓ ↑, ↓ ↑, Ms=0 component of the triplet and one singlet state.
Ms=-1 distribution :↓ ↓ , Ms=1 component of the triplet

Diagonal elements :

$$\langle \uparrow_1 \uparrow_2 | -J\left(\hat{S}_{z1}\hat{S}_{z2} - \frac{1}{4}\right) | \uparrow_1 \uparrow_2 \rangle = -J\left(\frac{1}{4} - \frac{1}{4}\right)\langle \uparrow\uparrow \| \uparrow\uparrow \rangle = 0$$

$$\langle \uparrow\downarrow | -J\left(\hat{S}_{z1}\hat{S}_{z2} - \frac{1}{4}\right) | \uparrow\downarrow \rangle = -J\left(-\frac{1}{4} - \frac{1}{4}\right)\langle \uparrow\downarrow \| \uparrow\downarrow \rangle = \frac{J}{2}$$

Off-diagonal elements :

$$\langle \downarrow\uparrow | -\frac{J}{2}\left(\hat{S}_1^+\hat{S}_2^- + \hat{S}_1^-\hat{S}_2^+\right) | \uparrow\downarrow \rangle = \frac{-J}{2}\sqrt{s_1(s_1+1) - m_{s1}(m_{s1}-1)}\sqrt{s_2(s_2+1) - m_{s2}(m_{s2}+1)}\langle \downarrow\uparrow \| \downarrow\uparrow \rangle = -\frac{J}{2}\langle \downarrow\uparrow \| \downarrow\uparrow \rangle$$

The matrix writes :

$$(\hat{\mathrm{H}}^{\mathrm{Heis.}}) = \begin{array}{c|cc|c|c} & |\uparrow\downarrow\rangle & |\downarrow\uparrow\rangle & |\uparrow\uparrow\rangle & |\downarrow\downarrow\rangle \\ \langle\uparrow\downarrow| & \mathrm{J}/2 & -\mathrm{J}/2 & 0 & 0 \\ \langle\downarrow\uparrow| & -\mathrm{J}/2 & \mathrm{J}/2 & 0 & 0 \\ \hline \langle\uparrow\uparrow| & 0 & 0 & 0 & 0 \\ \hline \langle\downarrow\downarrow| & 0 & 0 & 0 & 0 \end{array}$$

Eigenvalues and eigenvectors

The Ms=-1 and Ms=+1 of the triplet are eigenvectors and their energy is zero

Eigenvalues in the Ms=0 subspace (2×2 matrix) :

$$\begin{array}{c|cc} & |\uparrow\downarrow\rangle & |\downarrow\uparrow\rangle \\ \hline \langle\uparrow\downarrow| & \mathrm{J}/2 & -\mathrm{J}/2 \\ \langle\downarrow\uparrow| & -\mathrm{J}/2 & \mathrm{J}/2 \end{array} \quad \Longrightarrow \quad \begin{vmatrix} \mathrm{J}/2-\mathrm{E} & -\mathrm{J}/2 \\ -\mathrm{J}/2 & \mathrm{J}/2-\mathrm{E} \end{vmatrix} = 0$$

Eigenvalues: $(\mathrm{J}/2-\mathrm{E})^2-(\mathrm{J}/2)^2=0 \quad \Leftrightarrow \quad \mathrm{E}=\begin{cases} 0 \\ \mathrm{J} \end{cases}$

Energy of the Ms=0 component of the triplet.

Energy of the singlet

$$\Delta E_{ST}=J$$

$$\hat{H}\Psi = E\Psi$$

$$\begin{pmatrix} J/2 & -J/2 \\ -J/2 & J/2 \end{pmatrix}\begin{pmatrix} C_{11} \\ C_{12} \end{pmatrix} = E_{\substack{S\\T}}\begin{pmatrix} C_{11} \\ C_{12} \end{pmatrix} \Leftrightarrow \begin{cases} (J/2)C_{11}-(J/2)C_{12}=E_S C_{11} \\ |C_{11}|^2+|C_{12}|^2=1 \end{cases} \Leftrightarrow \begin{cases} C_{11}=\pm C_{12} \\ C_{12}=\dfrac{1}{\sqrt{2}} \end{cases}$$

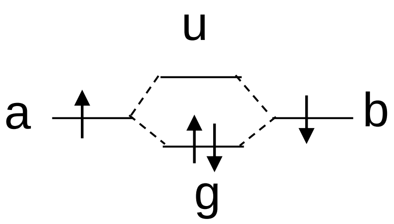
Eigenvectors:

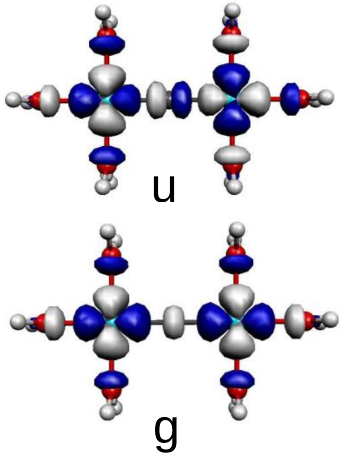
$$\boxed{|\Psi_{\mathrm{S}}\rangle=\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle\right)} \qquad \boxed{|\Psi_{\mathrm{T}}\rangle=\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle\right)}$$

Ab initio calculations : magnetic systems are correlated systems

Hückel description (monoelectronic) is not valid.

Delocalized orbitals

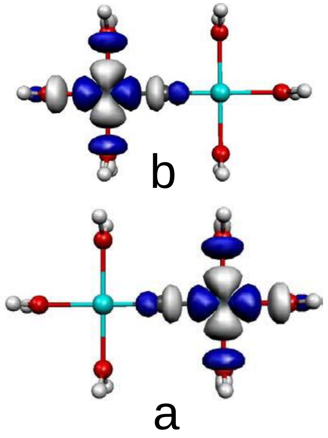




Magnetic orbitals

$$a = \frac{g+u}{\sqrt{2}} \qquad b = \frac{g-u}{\sqrt{2}}$$

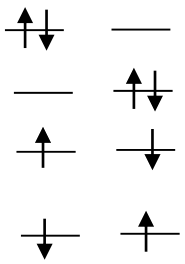
$$\langle a|b\rangle = 0$$



The single determinant function $|g\bar{g}|$ is no more a good function

$$|g\bar{g}| = \frac{1}{2}|a\bar{a} + b\bar{b} + a\bar{b} + b\bar{a}|$$

Same amount of ionic and neutral configurations



$|a\bar{a}|$

$|b\bar{b}|$

$|a\bar{b}|$

$-|b\bar{a}|$

Ionic $Cu^{3+}Cu^{+}$

Neutral $Cu^{2+}Cu^{2+}$

For strongly localized electrons : multireference wavefunctions are required to restore the correct ionic/neutral ratio

$${}^1\psi_{CAS} = \lambda|g\bar{g}| - \mu|u\bar{u}| = \left(\frac{\lambda+\mu}{2}\right)|a\bar{b} - \bar{a}b| + \left(\frac{\lambda-\mu}{2}\right)|a\bar{a} - \bar{b}b|$$

1%

$${}^3\psi_{CAS} = |gu| = |ab|$$

Covalent (or ionic) bond: $\lambda \gg \mu$

Magnetic « bond » : $\lambda \sim \mu$

Derivation of the Heisenberg model from the exact electronic Hamiltonian

Heis. works on neutral

$\left|a\bar{b}\right\rangle \qquad \left|\bar{a}b\right\rangle$

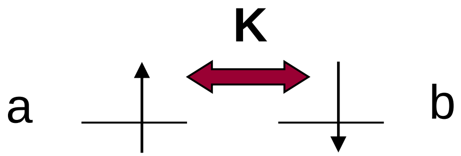
$$\begin{array}{c|cc} & \left|a\bar{b}\right\rangle & \left|b\bar{a}\right\rangle \\ \hline \left\langle a\bar{b}\right| & J_{ab} & K \\ \left\langle a\bar{b}\right| & K & J_{ab} \end{array}$$

Repulsion of the two electrons in the orbitals a and b

$$J_{ab} = \iint a(1)b(2)\frac{1}{r_{12}}b(2)a(1)\,d\tau_1 d\tau_2$$

Exchange integral of the exact electronic Hamiltonian :

$$K = \iint a(1)b(2)\frac{1}{r_{12}}b(1)a(2)\,d\tau_1 d\tau_2 > 0$$



$$\left(J_{ab}-E\right)^2-\left(K\right)^2=0 \quad \Leftrightarrow \quad E=\begin{cases} J_{ab}+K & \text{Singlet} \\ J_{ab}-K & \text{Triplet} \end{cases}$$

The triplet is lower in energy than the singlet : Hund’s rule

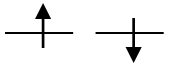
$$\Delta E_{ST} = 2K$$

If one limits to the neutral determinants, the world would be ferromagnetic !

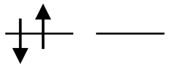
What is the microscopic origin of antiferromagnetism ?

Kinetic exchange : ionic determinants contribution to the singlet state

neutral



Ionic



$$\begin{array}{c|cccc} & |a\bar{b}\rangle & |b\bar{a}\rangle & |a\bar{a}\rangle & |b\bar{b}\rangle \\ \hline \text{neutral} & J_{ab} & K & t & t \\ & K & J_{ab} & t & t \\ \text{Ionic} & t & t & J_{aa} & K \\ & t & t & K & J_{aa} \end{array} \Longrightarrow \begin{array}{cccc} |S_N^g\rangle & |T_N^u\rangle & |S_I^g\rangle & |S_I^u\rangle \\ K & 0 & 2t & 0 \\ 0 & -K & 0 & 0 \\ 2t & 0 & U+K & 0 \\ 0 & 0 & 0 & U-K \end{array}$$

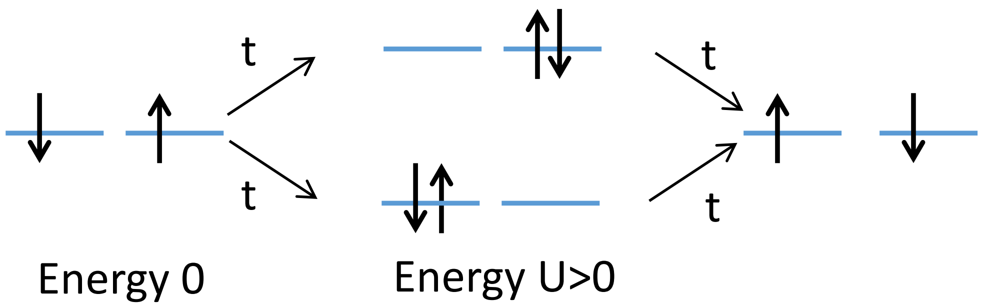
$U=J_{aa}-J_{ab}$

$t=F_{ab}$ can be seen as the hopping integral (b of Hückel)
(actually it is bielectronic)

Variationally

$$E(S^g)=\frac{U+2K-\sqrt{16t^2+U^2}}{2}$$

$$E(T)=-K$$



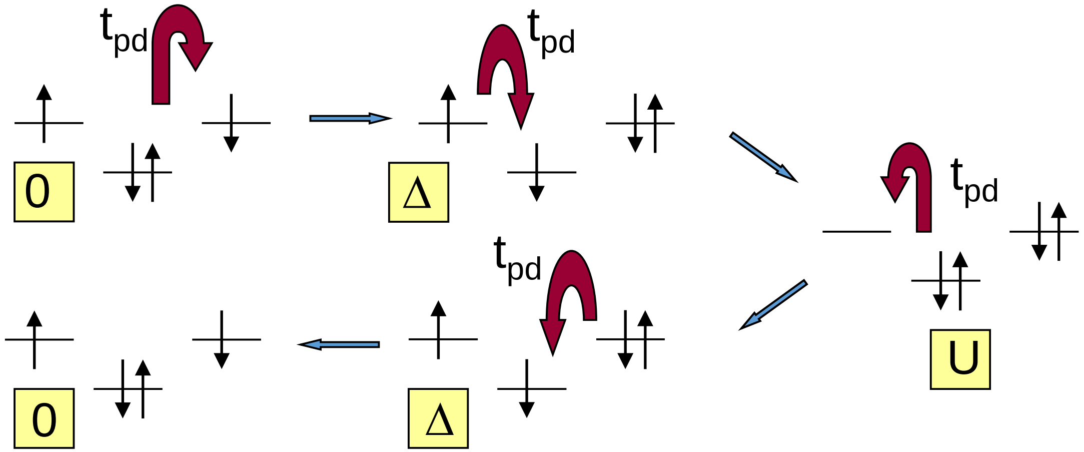
Perturbatively (2nd order) :

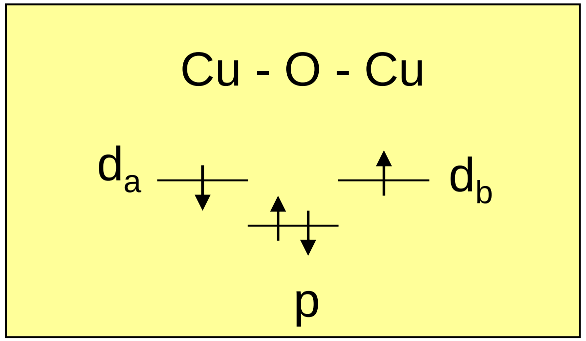
$$\left.\begin{array}{l} E\left(S_N^g\right)=K-\dfrac{4t^2}{U} \\ E\left(T_N^u\right)=-K \end{array}\right\} \Delta E_{ST}=2K-\frac{4t^2}{U}=J$$

Si K > 2t²/U ⟶ J>0 ⟶ ferromagnetism
Si K < 2t²/U ⟶ J<0 ⟶ antiferromagnetism

Role of the bridging ligands : superexchange

Superexchange : through ligand coupling





$$J = 2K - \frac{4}{U}\frac{t_{pd}^4}{\Delta^2} - 4\frac{t_{ab}^2}{U}$$

Δ : charge transfer (MLCT or LMCT) det. energy

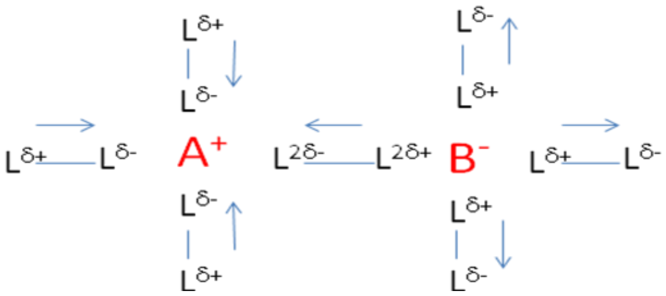
U : ionic det. energy

The coupling may also involve antibonding orbitals, for instance π^* in molecular bridge

To correlate the ML- or LM-CT configurations is necessary to describe correctly their effect

Other effects of electron correlation: charge and spin polarization

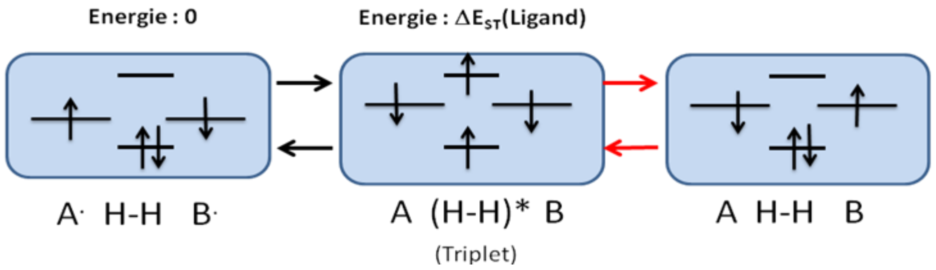
Charge polarization : The screening of U changes U by U^{eff}



$$J = \Delta E_{ST}^{\,2nd\ order} = 2K - \frac{4t_{ab}^2}{U - \sum_{i,r}\frac{\langle i|J_a - J_b|r\rangle^2}{(E_r - E_i)+U}} = 2K - \frac{4t_{ab}^2}{U^{eff}}$$

The screening of U is an antiferromagnetic contribution, it also comes from higher excitations. It is huge : J may be multiplied by 3 to 10

Spin polarization : Changes K to an effective K^{eff}=K-ΔK



$$\begin{array}{c|cc} & \big||i\bar{i}a\bar{b}|\big\rangle & \big||i\bar{i}\bar{a}b|\big\rangle \\ \hline \big\langle|i\bar{i}a\bar{b}|\big| & E_{PS} & -K_{ab} - \Delta K \\ \big\langle|i\bar{i}\bar{a}b|\big| & -K_{ab} - \Delta K & E_{PS} \end{array}$$

$$\Delta K = 2\sum_{i,r}\frac{\big\langle|i\bar{i}a\bar{b}|\big|\hat{H}\big||ir\bar{a}\bar{b}|\big\rangle\big\langle|ir\bar{a}\bar{b}|\big|\hat{H}\big||i\bar{i}\bar{a}b|\big\rangle}{\varepsilon_r - \varepsilon_i} = 2\sum_{i,r}\frac{\langle i|K_a|r\rangle\langle r|K_b|i\rangle}{\varepsilon_r - \varepsilon_i}$$

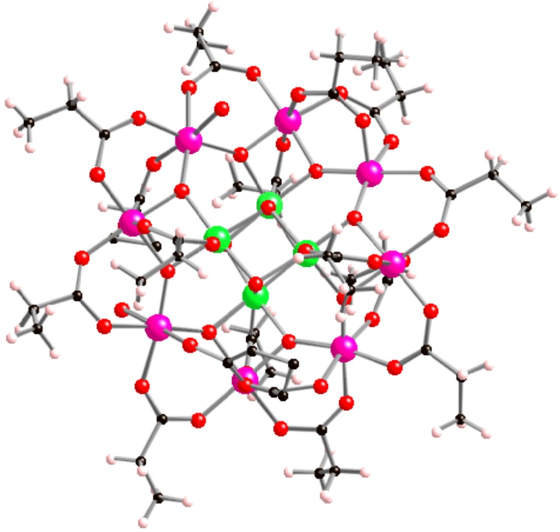
ΔK may have both signs and may therefore stabilized either the singlet or the triplet

Conclusions on the exchange and super exchange interactions : J^{eff} made of several contributions

i) Direct exchange is always positive and favors ferromagnetic couplings
ii) Kinetic exchange always favors antiferromagnetic couplings
iii) The super-exchange goes through the bridging ligands
iv) Charge polarisation favors antiferromagnetic couplings
v) Spin polarisation might either be in favor of ferro or antiferromagnetic couplings
vi) All these contributions are very sensitive to electron correlation

Magnetic Interactions in Molecules and Highly Correlated Materials: Physical Content, Analytical Derivation, and Rigorous Extraction of Magnetic Hamiltonians; Jean Paul Malrieu, Rosa Caballol, Carmen J. Calzado, Coen de Graaf, and Nathalie Guihéry; *Chem. Rev.*, 2014, *114* (1), pp 429–492 and references here in.

Magnetic anisotropy : Microscopic origin of single molecule magnet behaviour

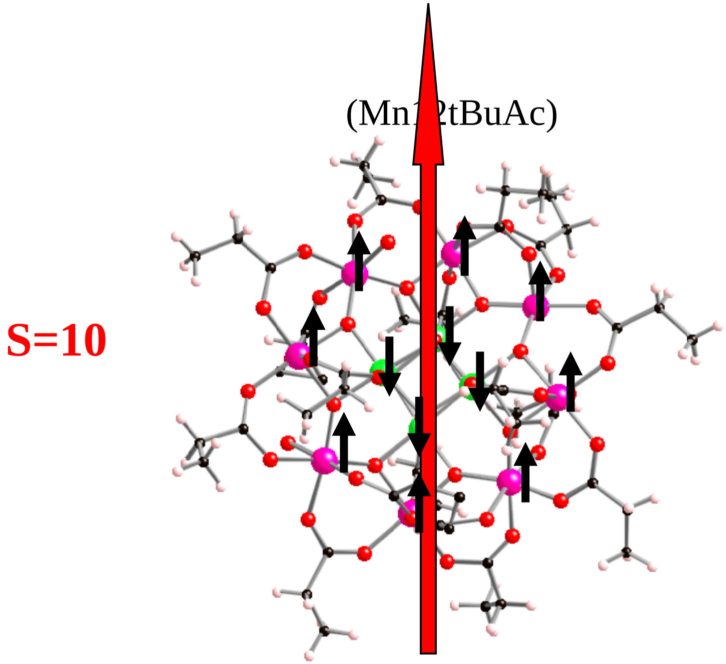


Methodology of quantum chemistry to get accurate ZFS parameters and method of extraction based on the effective Hamiltonian theory and *ab initio* results (now implemented in ORCA)

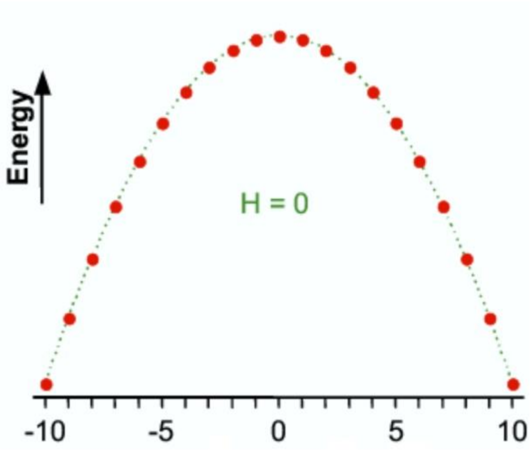
R. Maurice, N. Guihéry, R. Bastardis and C. de Graaf J. Chem. Theory Comput., 6, 55 (2010)
R. Maurice, C. de Graaf and N. Guihéry Phys. Rev. B 81, 214427 (2010)
R. Maurice, C. de Graaf and N. Guihéry J. Chem. Phys. 133, 084307 (2010)
R. Maurice, A. M. Pradipto, N. Guihéry, R. Broer, and C. de Graaf J. Chem. Theory Comput., 2010, 6 (10), pp 3092–3101
R. Maurice, K. Sivalingam, D. Ganyushin, N. Guihéry, C. de Graaf and F. Neese Inorg. Chem., 2011, 50 (13), pp 6229–6236
R. Maurice, R. Bastardis, C. de Graaf, N. Suaud, T. Mallah and N. Guihéry, J. Chem. Theory Comput., 5, 2977 (2009)

Magnetic anisotropy :Microscopic origin of single molecule magnet behaviour

Single Molecule Magnets



Spin-orbit coupling :
projection of the SO states on |S,Ms>



12 Mn : 8 Mn^{3+} (d^4), 4 Mn $^{4+}$ (d^3)
Antiferromagnetically coupled

Zero-Field Splitting:
Degeneracy lift of the Ms components of the ground spin state S=10

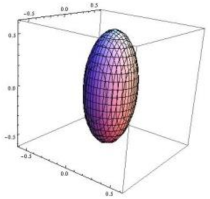
Strong axial anisotropy : slow relaxation of the magnetization
Axial anisotropy parameter D<0 (Ms=±10 ground states)

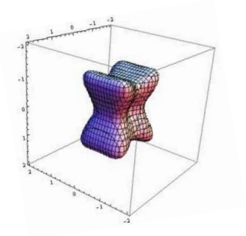
Usual models for magnetic anisotropy

Giant spin (for the ground state) either for mononuclear or polynuclear systems

Ising

$$\hat{H} = \underbrace{D\hat{S}_Z^2 + E\left(\hat{S}_X^2 - \hat{S}_Y^2\right)}_{\hat{H} = \hat{S}\,\overline{\overline{D}}\,\hat{S}} + \underbrace{C(\hat{S}_+^4 + \hat{S}_-^4) + D'\hat{O}_4^0 + E'\hat{O}_4^2}_{\text{Higher order terms}}$$

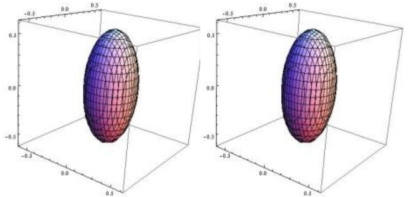




Multispin Hamiltonian (all the states of the spatial configuration) for polynuclear systems

$$\hat{H} = \underbrace{\sum_{i} \hat{S}_i \overline{\overline{D}}_i \hat{S}_i} + \underbrace{\sum_{<i,j>} \hat{S}_i \overline{\overline{D}}_{ij} \hat{S}_j + \sum_{<i,j>} \bar{d}_{ij} \hat{S}_i \wedge \hat{S}_j} + \underbrace{\sum_{<i,j>} J_{ij} \hat{S}_i . \hat{S}_j}$$

Local anisotropies. An. of the interaction Magnetic coupling



→ ?

Extraction of the ZFS tensor and magnetic axes in mononuclear complexes

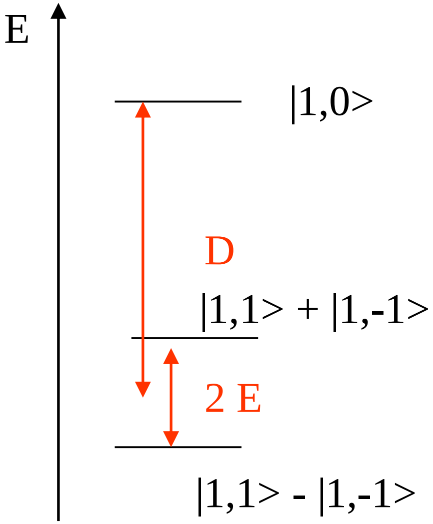
Phenomenological Hamiltonian :

$$\hat{\mathbf{H}}^{\mathrm{model}} = \hat{\mathbf{S}}.\overline{\overline{\mathbf{D}}}.\hat{\mathbf{S}} = D\left[\mathbf{S}_{\mathbf{Z}}^{2} - \frac{1}{3}S(S+1)\hat{\mathbf{I}}\right] + E\left[\mathbf{S}_{\mathbf{X}}^{2} - \mathbf{S}_{\mathbf{Y}}^{2}\right]$$

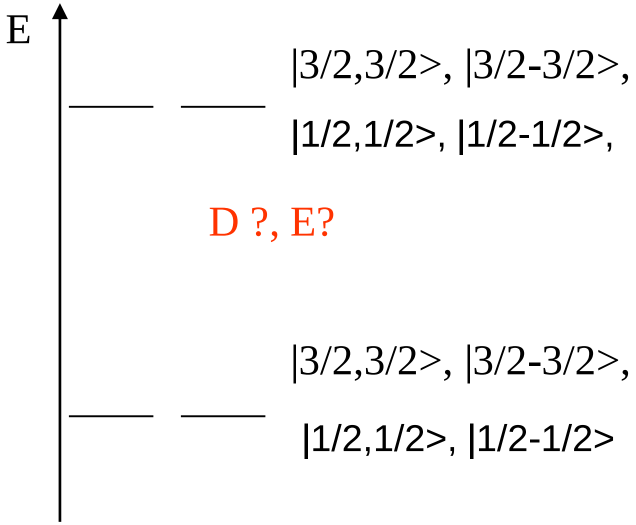
$$(\mathbf{D}) = \begin{pmatrix} D_{11} & D_{12} & D_{13} \\ D_{12} & D_{22} & D_{23} \\ D_{13} & D_{23} & D_{33} \end{pmatrix} \Rightarrow (\mathbf{D}) = \begin{pmatrix} D_{XX} & 0 & 0 \\ 0 & D_{YY} & 0 \\ 0 & 0 & D_{ZZ} \end{pmatrix}$$

D = 3/2 D_{zz} : axial parameter E = 1/2 (D_{xx} – D_{yy}) : rhombic parameter

Extraction of D and E from the energies only : possible for integer spin systems



Extraction of D and E from the energies only : Impossible for half-integer spin systems

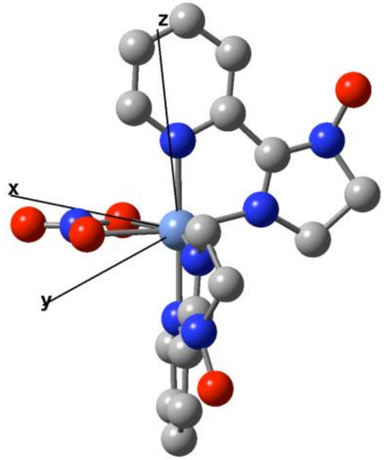


Determination of the effective matrix from both the energies and the wavefunctions

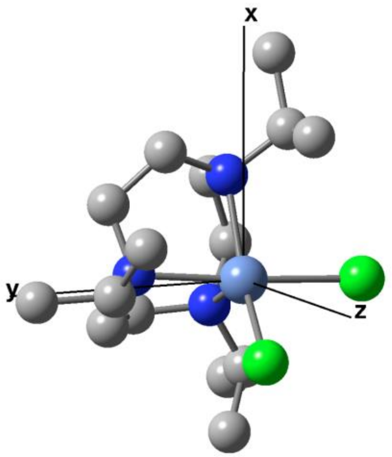
⇒ **Universal method + extraction of the magnetic axes**

Mono-nuclear Complexes: Methodological Tests

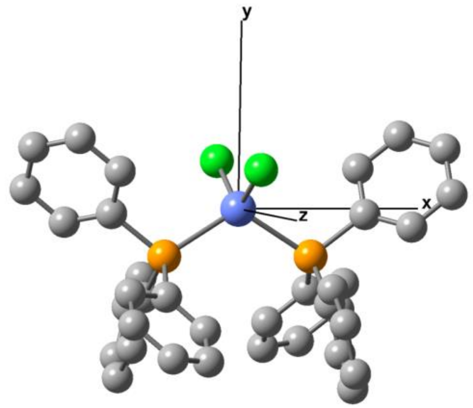
1. $[Ni(HIM2\text{-}py)_2NO_3]^+$



2. $[Ni(iPrtacn)Cl_2]$



3. $[CoCl_2(PPh_3)_2]$

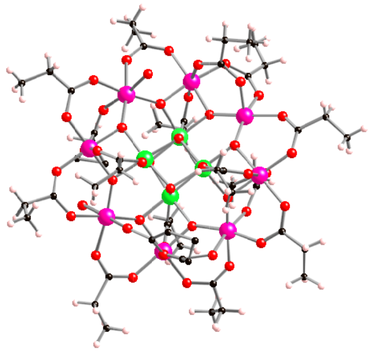


- ⇒ Good agreement theory-experiment
- Dynamic correlation plays a non-negligible role
- ZFS dominated by a small number of excited states
- Metal-to-Ligand charge transfer excitations must be taken into account

Time and energy consuming *ab initio* calculations

Comp.	ZFS (cm^{-1})	PT2 (12/12)	Exp. (HF-EPR)
1	D	-10.60	-10.15
	E	0.76	0.10
2	D	+16.45	+15.70
	E	3.82	3.40
3	D	-14.84	-14.76
	E	0.54	1.14

Microscopic origin of magnetic anisotropy



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Physical origin of magnetic anisotropy : example of Ni $^{2+}$

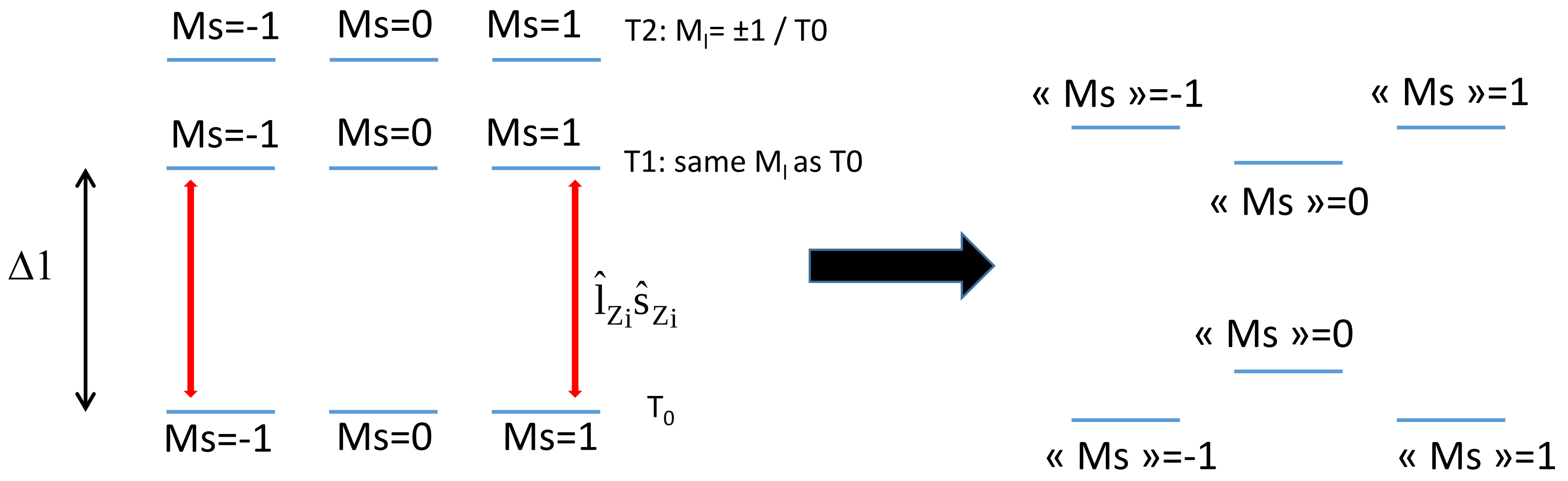
Relativistic effects : Spin-orbit coupling with excited states

$$\hat{H}_{SO} = \sum_i \zeta_i(r)\hat{l}_i.\hat{s}_i = \sum_i \zeta_i(r)\left(\underbrace{\hat{l}_{X_i}\hat{s}_{X_i} + \hat{l}_{Y_i}\hat{s}_{Y_i}}_{} + \underbrace{\hat{l}_{Z_i}\hat{s}_{Z_i}}_{}\right) = \sum_i \zeta_i(r)\left[\frac{1}{2}\left(\hat{l}_i^+\hat{s}_i^- + \hat{l}_i^-\hat{s}_i^+\right) + \hat{l}_{Z_i}\hat{s}_{Z_i}\right]$$

Electronic states

Same Ml
same Ms

Spin-orbit states



Ms=-1 Ms=0 Ms=1 T2: M_l= ±1 / T0

Ms=-1 Ms=0 Ms=1 T1: same M_l as T0

$\Delta 1$

$\hat{l}_{Z_i}\hat{s}_{Z_i}$

Ms=-1 Ms=0 Ms=1 T_0

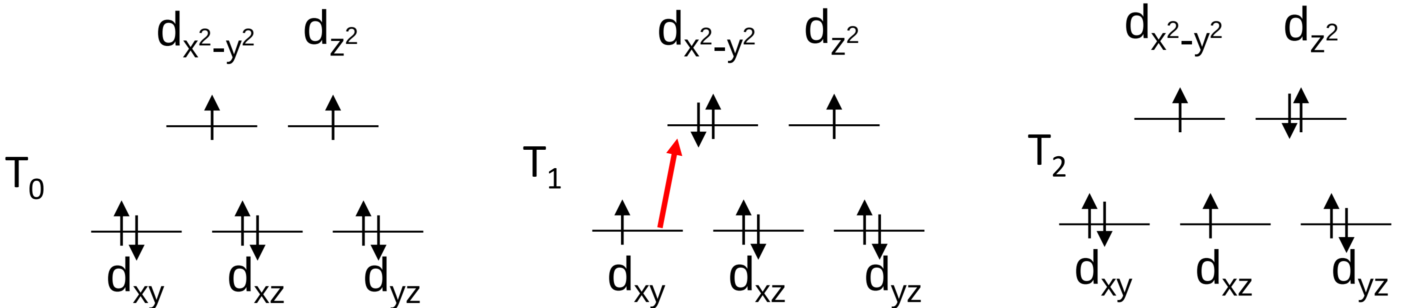
« Ms »=-1 « Ms »=1

« Ms »=0

« Ms »=0

« Ms »=-1 « Ms »=1

D<0



Ni $^{2+}$: d^8
triplet

$\{d_{x^2-y^2}, d_{xy}\} = \{d_{2+}, d_{2-}\}$

$\{d_{xz}, d_{yz}\} = \{d_{1+}, d_{1-}\}$

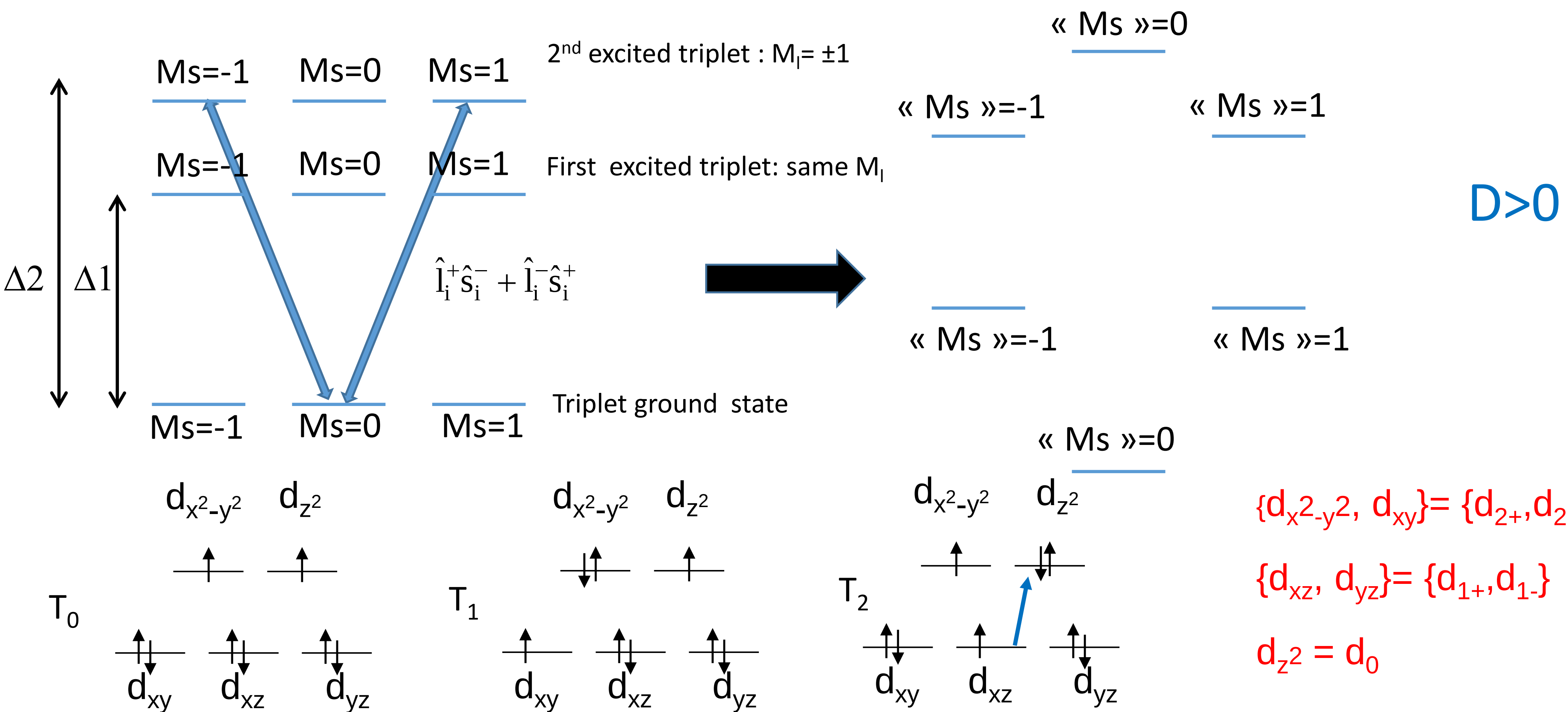
$d_{z^2} = d_0$

Physical origin of magnetic anisotropy

Relativistic effects : Spin-orbit coupling with excited states

$$\hat{H}_{SO} = \sum_i \zeta_i(r)\hat{l}_i.\hat{s}_i = \sum_i \zeta_i(r)\left(\underbrace{\hat{l}_{X_i}\hat{s}_{X_i} + \hat{l}_{Y_i}\hat{s}_{Y_i}}_{} + \underbrace{\hat{l}_{Z_i}\hat{s}_{Z_i}}_{}\right) = \sum_i \zeta_i(r)\left[\frac{1}{2}\left(\hat{l}_i^+\hat{s}_i^- + \hat{l}_i^-\hat{s}_i^+\right) + \hat{l}_{Z_i}\hat{s}_{Z_i}\right]$$

Electronic states **Spin-orbit states**



$\{d_{x^2-y^2}, d_{xy}\} = \{d_{2+}, d_{2-}\}$

$\{d_{xz}, d_{yz}\} = \{d_{1+}, d_{1-}\}$

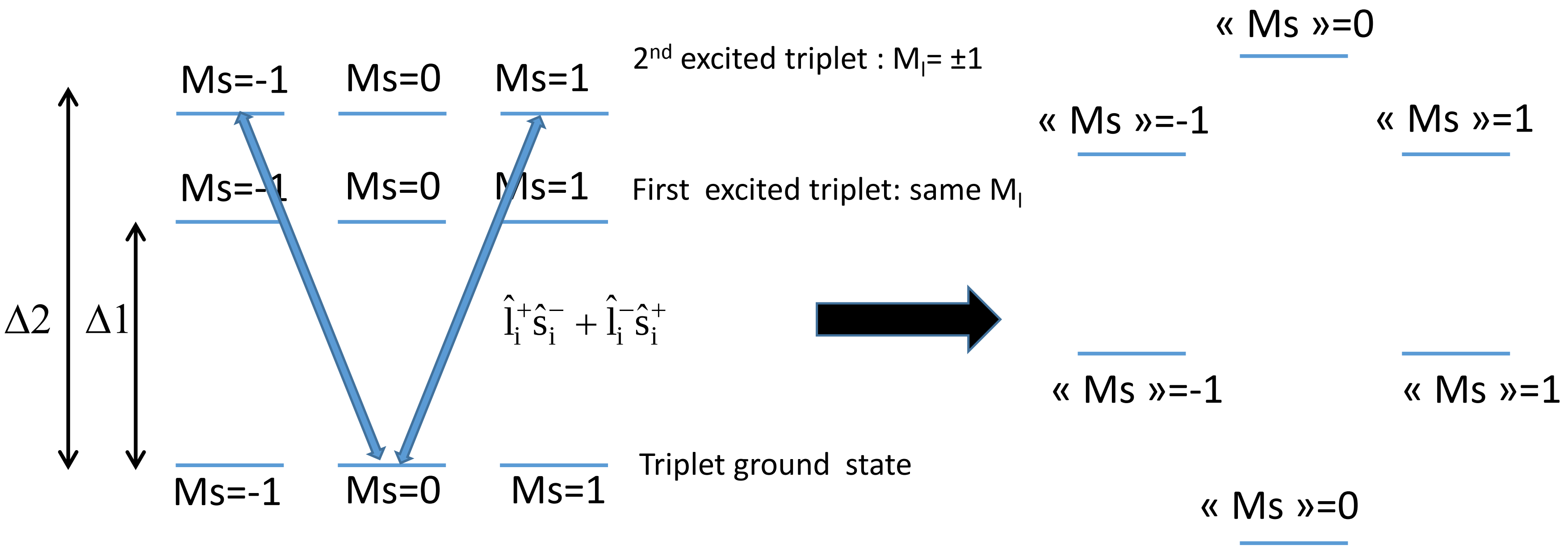
$d_{z^2} = d_0$

Physical origin of magnetic anisotropy

Relativistic effects : Spin-orbit coupling with excited states

$$\hat{H}_{SO} = \sum_i \zeta_i(r)\hat{l}_i.\hat{s}_i = \sum_i \zeta_i(r)\left(\underbrace{\hat{l}_{Xi}\hat{s}_{Xi} + \hat{l}_{Yi}\hat{s}_{Yi}} + \underbrace{\hat{l}_{Zi}\hat{s}_{Zi}}\right) = \sum_i \zeta_i(r)\left[\frac{1}{2}\left(\hat{l}_i^+\hat{s}_i^- + \hat{l}_i^-\hat{s}_i^+\right) + \hat{l}_{Zi}\hat{s}_{Zi}\right]$$

Electronic states **Spin-orbit states**



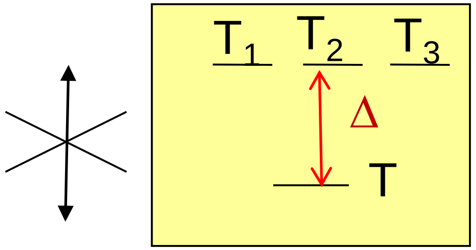
Second-order perturbation treatment

$$\langle \phi_I | \hat{H}^{eff} | \phi_I \rangle = E_i + \sum_{\alpha \notin S} \frac{\langle \phi_I | \hat{H}_{SOC} | \phi_\alpha \rangle^2}{E_I^0 - E_\alpha^0} \propto \frac{coef.\zeta^2}{\Delta}$$

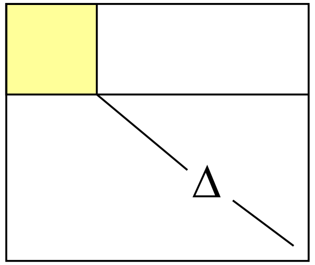
Δ1 versus Δ2 ? → Correlation with Ligand field

More details in *Inorg. Chem.*, 2017, 56, 4601-4608

Rationalization : 2nd order of perturbation
First test : No ZFS in O_h symmetry



$$
\begin{array}{ccc|ccc|ccc|ccc}
T_+ & T_0 & T_- & T_1^+ & T_2^+ & T_3^+ & T_1^0 & T_2^0 & T_3^0 & T_1^- & T_2^- & T_3^- \\
\hline
0 & 0 & 0 & i\zeta & 0 & 0 & 0 & \frac{i\zeta}{\sqrt{2}} & \frac{-\zeta}{\sqrt{2}} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{i\zeta}{\sqrt{2}} & \frac{-\zeta}{\sqrt{2}} & 0 & 0 & 0 & 0 & \frac{-i\zeta}{\sqrt{2}} & \frac{\zeta}{\sqrt{2}} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i\zeta}{\sqrt{2}} & \frac{\zeta}{\sqrt{2}} & -i\zeta & 0 & 0
\end{array}
$$



$$
\begin{array}{c|ccc}
 & |T_+\rangle & |T_0\rangle & |T_-\rangle \\
\langle T_+| & \frac{-2\zeta^2}{\Delta} & 0 & 0 \\
\langle T_0| & 0 & \frac{-2\zeta^2}{\Delta} & 0 \\
\langle T_-| & 0 & 0 & \frac{-2\zeta^2}{\Delta}
\end{array}
$$

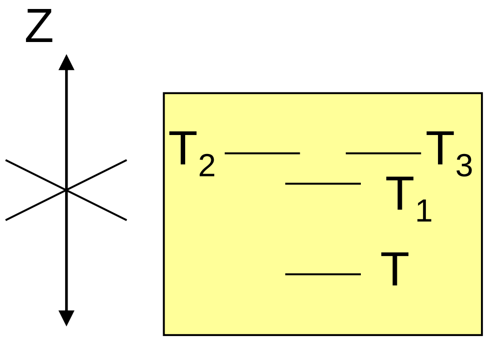
Energy of the first triplet state $T_{1,2,3,}$ $=\Delta$

$$
\langle \phi_I | \hat{H}^{eff} | \phi_J \rangle = \langle \phi_I | \hat{V} | \phi_J \rangle + \sum_{\alpha \notin S} \frac{\langle \phi_I | \hat{V} | \phi_\alpha \rangle \langle \phi_\alpha | \hat{V} | \phi_J \rangle}{E_J^0 - E_\alpha^0}
$$

The three components are degenerate

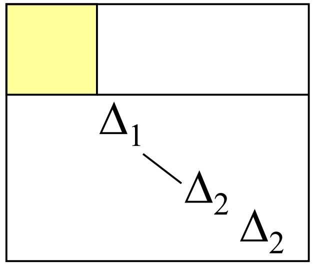
ZFS results from a symmetry lowering + Spin orbit coupling

Rationalization of the D sign : Axial deformation : ZFS in D_{4h} symetry



H_{eff} for a D_{4h} geom. In the magnetic axes frame:

H_{eff}	$\|T_+\rangle$	$\|T_0\rangle$	$\|T_-\rangle$
$\langle T_+\|$	$-\frac{\zeta^2}{\Delta 1}-\frac{\zeta^2}{\Delta 2}$	0	0
$\langle T_0\|$	0	$-\frac{2\zeta^2}{\Delta 1}$	0
$\langle T_-\|$	0	0	$-\frac{\zeta^2}{\Delta 1}-\frac{\zeta^2}{\Delta 2}$

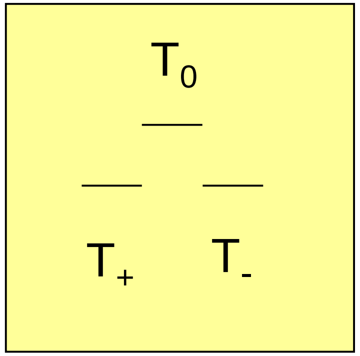


$$\Delta_1 = E(T_1) = \Delta$$

$$\Delta_2 = E(T_2) = \Delta + \frac{35}{4} D_T$$

Lift of degeneracy « axial »
btween Ms=0 and Ms=1 and Ms=-1

No tunnel splitting



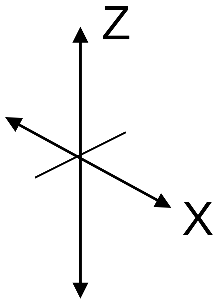
$$D = -\frac{\zeta^2}{\Delta_1} + \frac{\zeta^2}{\Delta_2}$$

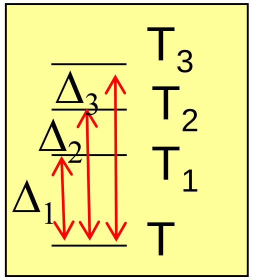
Proposed by Abragam

Rationalization of the D sign

Elongation along Z : Δ2<Δ1 D<0
Compression along Z : Δ2>Δ1 D>0

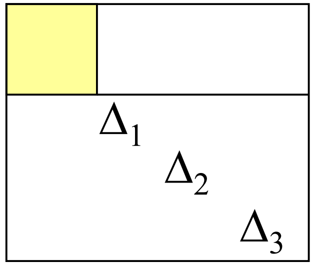
Rationalization of the rhombic component E : deformation in the (X,Y) plane : ZFS in D_{2h} symmetry





H_{eff} pour une géométrie D_{2h} et dans le système d'axes propres

H_{eff}	$\|T_+>$	$\|T_0>$	$\|T_->$
$<T_+\|$	$\frac{\zeta^2}{\Delta 1}+\frac{1}{2}\cdot\frac{\zeta^2}{\Delta 2}+\frac{1}{2}\cdot\frac{\zeta^2}{\Delta 3}$	0	$\frac{1}{2}\cdot\frac{\zeta^2}{\Delta 2}-\frac{1}{2}\cdot\frac{\zeta^2}{\Delta 3}$
$<T_0\|$	0	$\frac{\zeta^2}{\Delta 2}+\frac{\zeta^2}{\Delta 3}$	0
$<T_-\|$	$\frac{1}{2}\cdot\frac{\zeta^2}{\Delta 2}-\frac{1}{2}\cdot\frac{\zeta^2}{\Delta 3}$	0	$\frac{\zeta^2}{\Delta 1}+\frac{1}{2}\cdot\frac{\zeta^2}{\Delta 2}+\frac{1}{2}\cdot\frac{\zeta^2}{\Delta 3}$

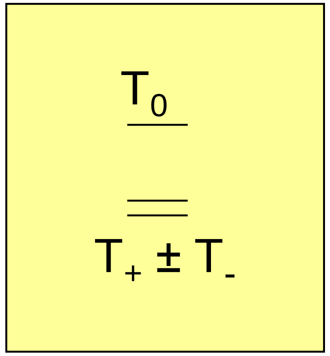


$$\Delta_1 = E(T_1) = \Delta$$

$$\Delta_2 = E(T_2) = \Delta + \frac{35}{4}D_T - D_R$$

$$\Delta_3 = E(T_3) = \Delta + \frac{35}{4}D_T + D_R$$

Spectrum



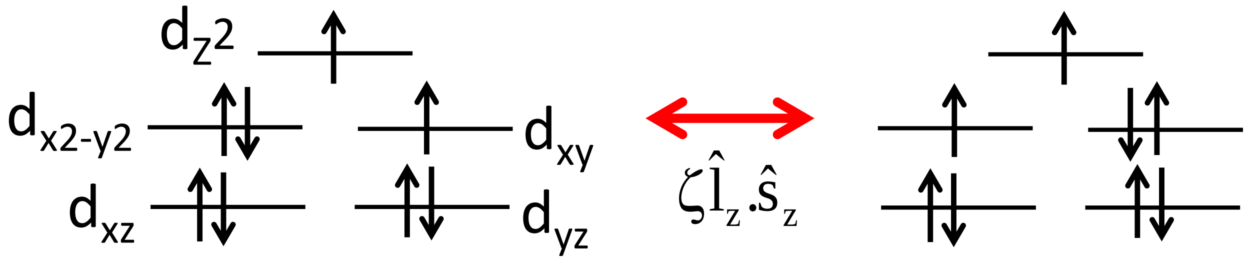
Axial D and rhombic E parameters

$$\left\{\begin{array}{l} D = -\frac{\zeta^2}{\Delta_1}+\frac{\zeta^2}{2\Delta_2}+\frac{\zeta^2}{2\Delta_3} \\ E = \frac{\zeta^2}{2\Delta_2}-\frac{\zeta^2}{2\Delta_3} \end{array}\right.$$

Looking for large uniaxial magn. anis. in mononuclear complex

1) Use heavy elements (Important SOC) instead of transition metals

2) Play with first-order SOC: degenerate ground state:

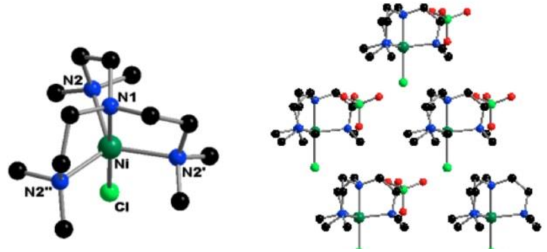


$(d_{x2\text{-}y2}, d_{xy})$=linear combinations of (d_{2+}, d_{2-})

Degenerate ground term components coupled by SOC

→ large splitting of Ms=±1 and Ms=0 components.

Problem: The Jahn-Teller distortion removes the ground term degeneracy : with exotic coordination (penta- and hepta-coordination).

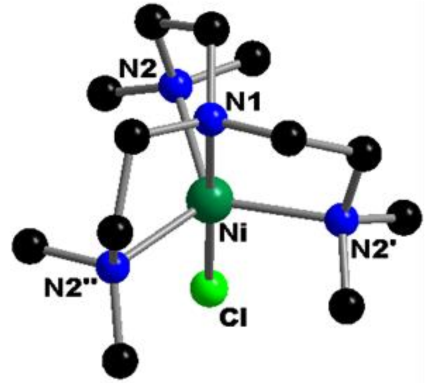


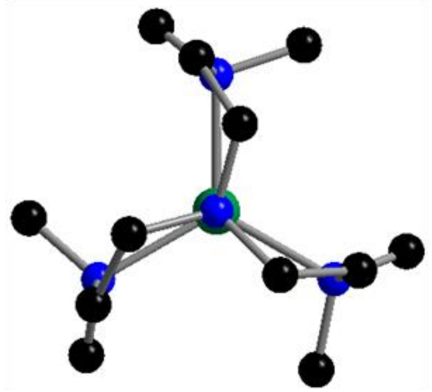
More details in *JACS* 135 3017-3026 (2013)

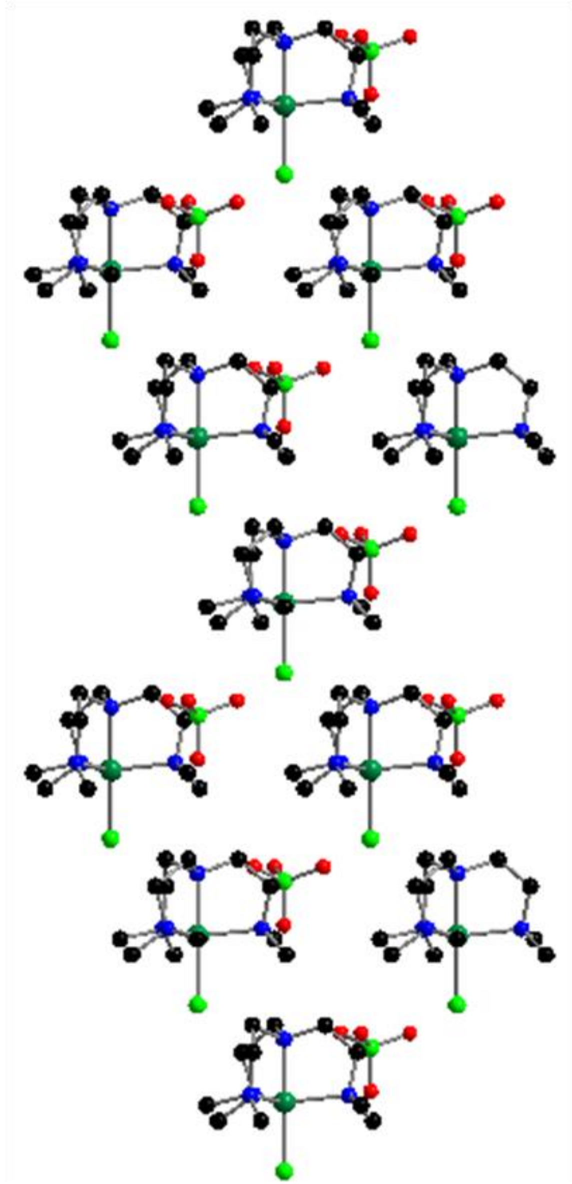
Studied complexes: Cl or Br, ligand

The complex is found of symmetry C_3 experimentally :

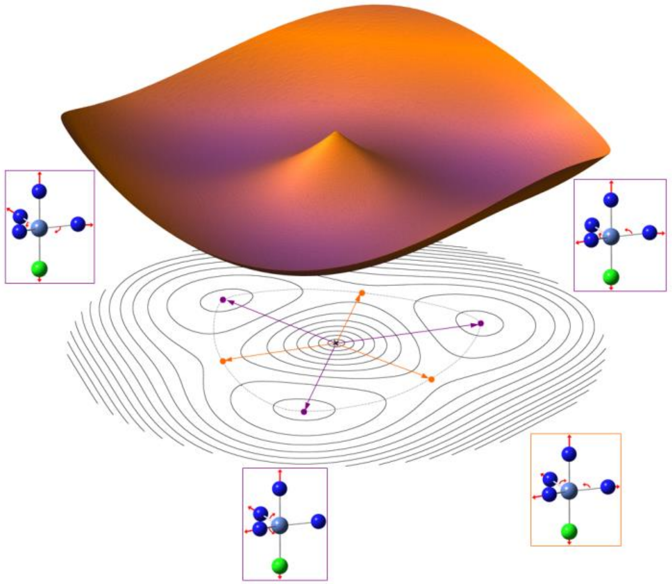
Means that d_{xy} and d_{x2-y2} are degenerate !!!

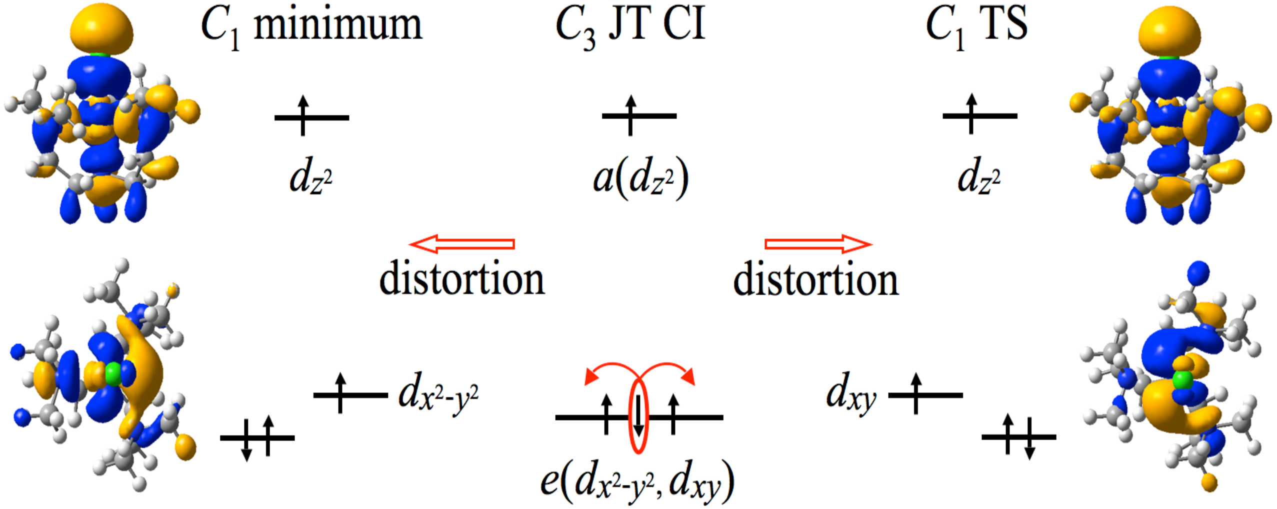






DFT Results
on the Cl compound:
minima and saddle point
a moat around the
conical intersection





Energy barrier including ZPE (well bottom to the saddle point): 70 cm^{-1}

This small value rationalizes the X-Ray observation of a C_3 molecule at room temperature

Modelization of the Spin orbit potential energy curve along the Jahn Teller distortion

Model Hamiltonian matrix describing the interactions resulting from the SOC and the electronic coupling due to the Jahn teller distortion:*

$$
\begin{array}{cc}
 & \begin{array}{cccccc} |d_{xy},-1\rangle & |d_{x^2-y^2},-1\rangle & |d_{xy},0\rangle & |d_{x^2-y^2},0\rangle & |d_{xy},1\rangle & |d_{x^2-y^2},1\rangle \end{array} \\
\begin{array}{c} \langle d_{xy},-1| \\ \langle d_{x^2-y^2},-1| \\ \langle d_{xy},0| \\ \langle d_{x^2-y^2},0| \\ \langle d_{xy},1| \\ \langle d_{x^2-y^2},1| \end{array} &
\begin{pmatrix}
-\Delta+\delta_1 & \delta_2+i\zeta & 0 & 0 & 0 & 0 \\
\delta_2-i\zeta & -\Delta-\delta_1 & 0 & 0 & 0 & 0 \\
0 & 0 & -\Delta+\delta_1 & \delta_2 & 0 & 0 \\
0 & 0 & \delta_2 & -\Delta-\delta_1 & 0 & 0 \\
0 & 0 & 0 & 0 & -\Delta+\delta_1 & \delta_2-i\zeta \\
0 & 0 & 0 & 0 & \delta_2+i\zeta & -\Delta-\delta_1
\end{pmatrix}
\end{array}
$$

$$
\left\{\begin{aligned}
E_{1,2}(Ms=\pm1) &= -\Delta-\sqrt{\delta^2+\zeta^2} \\
E_{3,4}(Ms=0) &= -\Delta\pm\delta \\
E_{5,6}(Ms=\pm1) &= -\Delta+\sqrt{\delta^2+\zeta^2}
\end{aligned}\right.
$$

$$
\nearrow \quad \left\{\begin{aligned}
E_{\substack{1,2\\5,6}}(Ms=\pm1) &= \mp\zeta\,; \\
E_{3,4}(Ms=0) &= 0
\end{aligned}\right.
$$

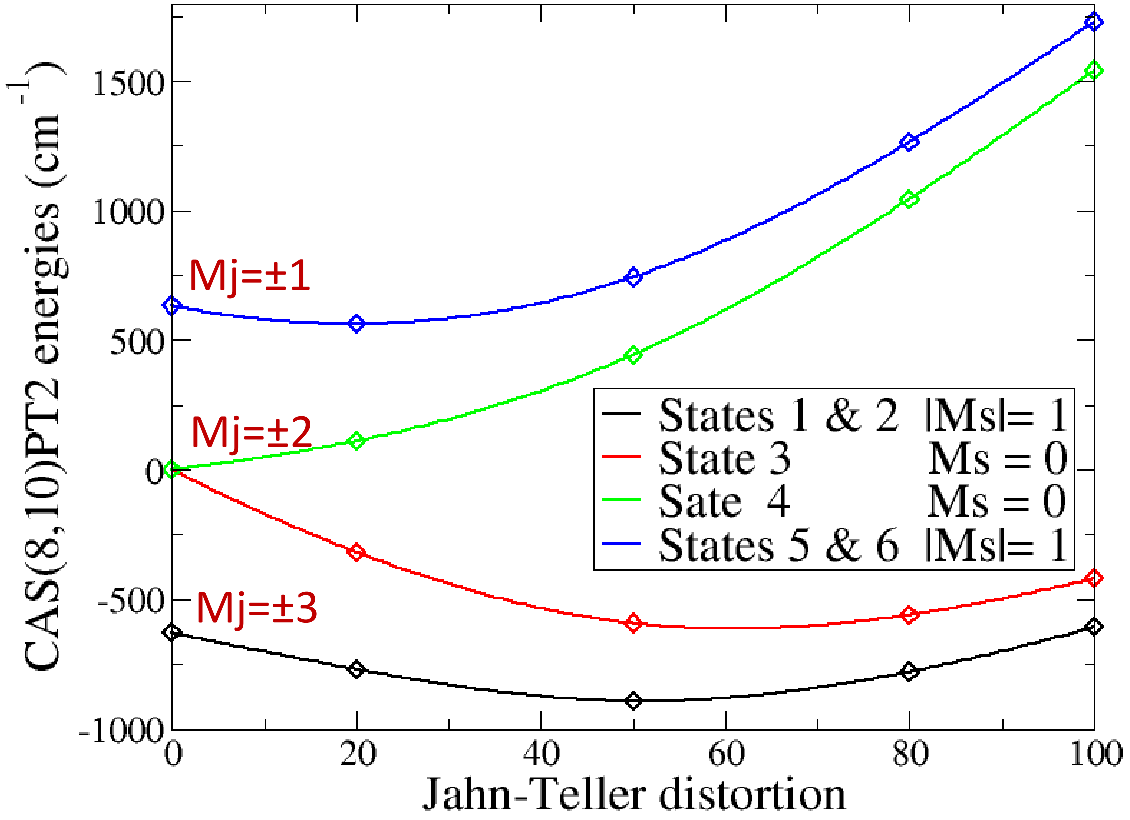
No distortion

$$
\searrow \quad \left\{\begin{aligned}
E_{1,2,3}(Ms=0,\pm1) &= -\Delta-\delta \\
E_{4,5,6}(Ms=0,\pm1) &= -\Delta+\delta
\end{aligned}\right.
$$

Strongly distorted

*Atanasov; M., et al. *Inorg. Chem.* . 2008, **47**, 8112.

2 states SOSI-CASPT2 potential energy curves



Low energy spectrum computed at the two-state SOSI-CAS(8,10)PT2 level of correlation. The *x* axis represents a linear distortion between the C_3 (0) and DFT C_1 minimum (100).

* Symmetry C_3 : the splitting is around 635 cm^{-1}. It is reduced by the distortion.

* At this level of calculation, the minimim does not coincide with the DFT minimum, The SO-SI CASPT2 minimum is less distorted .

* Note that the ground state is degenerate. One should introduce the second order SOC (other excited states).

Summary

* The reduction of the splitting due to the Jahn-Teller distortion is quite important : $\Delta E = -635\ cm^{-1}$ at the C_3 point ; $-300 cm^{-1} < D < -200 cm^{-1}$ at the various C_1 studied geometries.

* Including higher excited states reduces the values of D in all considered distorted structures $-200 cm^{-1} < D < -100 cm^{-1}$

* The better agreement with experiment for the magnetic suceptibility is obtained for the SO-SI CASSCF minimum : $D = -152 cm^{-1}$

* This work reports the largest uniaxial magnetic anisotropy observed in mononuclear complex.

HF-HFRPE: $D_{exp.}$ between $-120\ cm^{-1}$ and $-180\ cm^{-1}$

These extremely large values show that the Jahn-Teller distortion is not large enough to completely eliminate the large impact of the spin-orbit coupling between the two lowest states. The rigidity of the ligand preventing strong deformations is probably responsible for this result.

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Thank you for your kind attention !