Laboratoire de Chimie et Physique Quantiques

AGENCE NATIONALE DE LA RECHERCHE ANR

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Université de Toulouse

Université Paul Sabatier TOULOUSE III

Model Hamiltonians :
i) Analytical Derivation,
ii) Extraction from the effective and intermediate Hamiltonian Theories and ab initio Calculations
iii) Limits and Refinements

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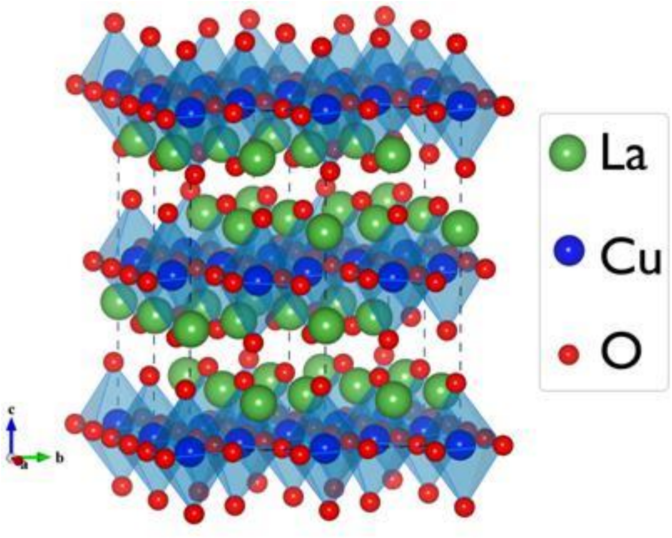
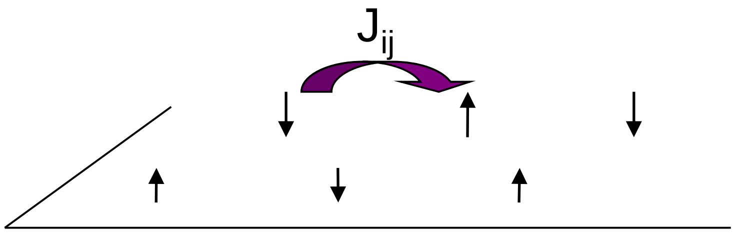
I. What is a model Hamiltonian ? Why do we need them?

Model Hamiltonians are simpler than the exact electronic Hamiltonian:

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

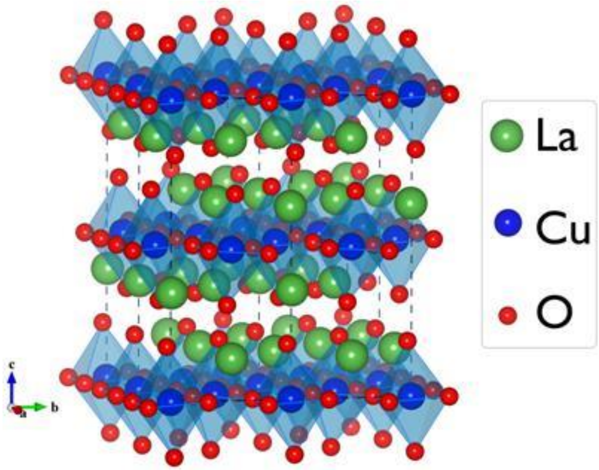
- They only treat a few number of electrons (here 1 per copper(II) ion)
- They only keep a few number of configurations (here spin distributions)
- They allow the treatment of collective effects as they can be used on larger systems (eventually infinite)





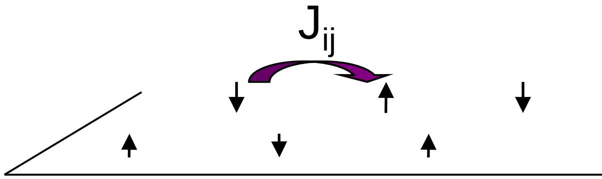
I. How model Hamiltonians are usually anticipated from chemical intuition ?

1. Reduction of dimensionality : here from 3D to 2D Based on the crystallography (large distance between the planes)



2. Reduction of the number of treated electrons:
La^{3+}, O^{2-} (rare gaz electronic structures)
La_2CuO_4 : $2(+3)+x+4(-2)=0$ ⇨ $x=+2$
Cu^{2+}: $[Ar]3d^9$ ⇨ 1 unpaired electron

3. Orbital order: Crystal field theory: the SOMO is d_{x2-y2}



4. Reduction of the number of configurations:

- Large distance between the copper centers :

⇨ The unpaired electrons are essentially localized
⇨ The single degree of freedom is the spin component $m_s = \pm 1/2$
⇨ The model space is constituted of products of atomic ground states:

$$\left|\uparrow\downarrow\uparrow\downarrow\ldots\right\rangle;\left|\uparrow\uparrow\downarrow\downarrow\ldots\right\rangle;\left|\downarrow\uparrow\downarrow\uparrow\ldots\right\rangle;\ldots$$

5. Possible appropriate model : The Heisenberg Dirac van Velck model applied to a 2D system

$$\hat{H} = \sum_{<i,j>} J_{ij} \hat{S}_i . \hat{S}_j$$

Experiment

Magnetic susceptibility
Relaxation time of magnetization,
Blocking temperature,
EPR, FDMRS spectroscopy etc.

« Exact »
Full System

« Assume » a certain H$^{\text{model}}$

Theory

Spectrum and wavefunctions
of H$^{\text{exact}}$, using sophisticated methods
(correlated, relativistic …)
or DFT energies

« Approximate »
Only fragments WFT
Periodic calculations DFT

« deduce» H$^{\text{model}}$ (Local int.)

$$\hat{\mathbf{H}}^{\text{model}} = \sum_{\langle i,j\rangle} J_{ij}\hat{\mathbf{S}}_i.\hat{\mathbf{S}}_j + \sum_{\langle i,j\rangle}\lambda_{ij}\left(\hat{\mathbf{S}}_i.\hat{\mathbf{S}}_j\right)^2 + \sum_i \hat{\mathbf{S}}_i.\overline{\overline{\mathbf{D}}}_i.\hat{\mathbf{S}}_i + \sum_{\langle i,j\rangle}\hat{\mathbf{S}}_i.\overline{\overline{\mathbf{D}}}_{ij}.\hat{\mathbf{S}}_j + \sum_{\langle i,j\rangle}\overline{\mathbf{d}}_{ij}\hat{\mathbf{S}}_i \wedge \hat{\mathbf{S}}_j$$

« Fitting » of electronic interactions J, λ,
tensors D (Zero-Field splitting) and g etc.

?

Validity of H$^{\text{model}}$
Understanding of
microscopic origins

Propose new models
and rationalizations

From microscopic to macroscopic treatments : a multi-scale approach

All electron Hamiltonian on fragments

$$H = H_{BO} + SO$$

Density Functional Theory (DFT) and Wave Function Theory (WFT)

All electrons → DFT dynamic correlations

WFT (MRCI or MRPT2) non-dynamic and dynamic correlations

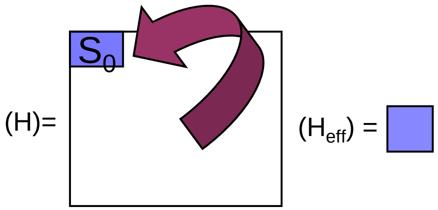
Spin-orbit Coupling → SO-RASSI Method

Model Hamiltonian on fragments

$$H = J S_1 . S_2 + \ldots$$

Extraction of dominant interactions

Effective Hamiltonian theory



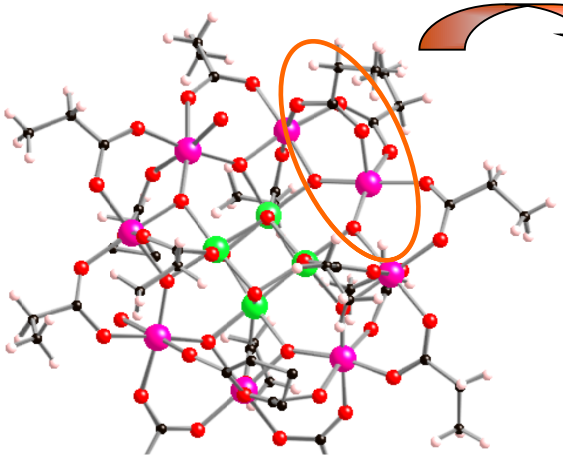
Information: reduction S_0

Model Hamiltonian on the whole system

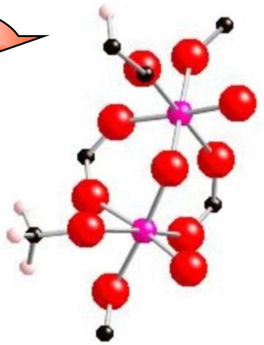
$$H = J \sum_{<i,j>} S_i . S_j + \ldots$$

Collective effects

- -Exact diagonalization + extrapolation
- - RSRG-EI
- - DCM
- - QMC
- - CC
- - PT…

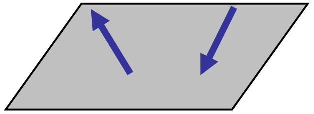


Whole real system

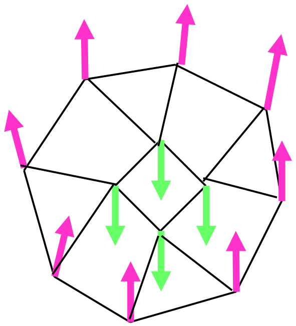


Charges +TIPS

Embedded real fragment



Model Fragment



Whole model system

II. Presentation and some derivations of simple model Hamiltonians

II.a Prerequisite:

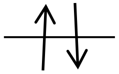
Exact Hamiltonian in the Born Oppenheimer approximation in a.u. :

$$\hat{H}_{BO}^{Exact} = \left(\sum_{A<B} \frac{Z_A Z_B}{R_{AB}} \right) - \sum_{i} \frac{\Delta_i}{2} - \sum_{A,i} \frac{Z_A}{r_{iA}} + \sum_{i<j} \frac{1}{r_{ij}} = \vartheta_1 + \vartheta_2$$

Slater determinants for 2 electrons in two spin orbitals:

$$\boxed{\psi_{12}^{Slater}(x_1, x_2) = \frac{1}{\sqrt{2}} \left[\varphi_1(x_1)\varphi_2(x_2) - \varphi_1(x_2)\varphi_2(x_1) \right]}$$

Ex : H_2



$$\varphi_1 = g.\alpha = g \quad \varphi_2 = g.\beta = \bar{g}$$

Some important integrals :

Repulsion of two e- in orbital a:

Repulsion of two e- in orbitals a and b:

Exchange integrals between e- in a and b:

$$\boxed{\begin{aligned} \langle a\bar{a} | \vartheta_2 | a\bar{a} \rangle &= J_{aa} \\ \langle b\bar{a} | \vartheta_2 | b\bar{a} \rangle &= J_{ab} \\ \langle a\bar{b} | \vartheta_2 | b\bar{a} \rangle &= K_{ab} \\ \langle a\bar{a} | \vartheta_2 | b\bar{b} \rangle &= K_{ab} \end{aligned}}$$

II.a Prerequisite

Perturbation theory (Rayleigh- Schrödinger):

$$\hat{H} = \hat{H}_0 + \hat{V} \longleftarrow \text{perturbation}$$

The eigenvalues and normalized eigenfunctions of $\hat{H}_0$ are known:

$$\hat{H}_0 \Psi_i^{(0)} = E_i^{(0)} \Psi_i^{(0)} \qquad \left\langle \Psi_i^{(0)} \middle| \Psi_i^{(0)} \right\rangle = 1$$

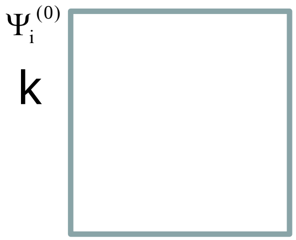
Perturbation theory is a procedure which aims at systematically improve the calculated eigenvalues and eigenfunctions of the Hamiltonian $\hat{H}$.

Note that the perturbation might diverge or oscillate.

It considers that the perturbation can be written as a function of an ordering parameter λ, that will later be set to unity:

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}$$

The eigenvalues and eigenfunctions are expanded in Taylor's series in λ:



Energy : $E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \ldots$

Wave function : $\Psi_i = \Psi_i^{(0)} + \lambda \Psi_i^{(1)} + \lambda^2 \Psi_i^{(2)} + \ldots$

The wave function can be written as (in intermediate normalization) : $\left\langle \Psi_i^{(0)} \middle| \Psi_i \right\rangle = 1$

$$\left\langle \Psi_i^{(0)} \middle| \Psi_i \right\rangle = \left\langle \Psi_i^{(0)} \middle| \Psi_i^{(0)} \right\rangle + \lambda \left\langle \Psi_i^{(0)} \middle| \Psi_i^{(1)} \right\rangle + \lambda^2 \left\langle \Psi_i^{(0)} \middle| \Psi_i^{(2)} \right\rangle + \ldots = 1$$

which means that the corrections are all orthogonal to the zeroth order wave function:

$$\left\langle \Psi_i^{(0)} \middle| \Psi_i^{(n)} \right\rangle = 0 \quad \forall\, n \qquad \left| \Psi_i^{(n)} \right\rangle = \sum_{k \neq \Psi_i^{(0)}} C_{k,i}^{(n)} \left| k \right\rangle = \sum_{k \neq \Psi_i^{(0)}} \left| k \right\rangle \left\langle k \middle\| \Psi_i^{(n)} \right\rangle$$

Solving the equation $\hat{H}\Psi_i = E_i\Psi_i$ order by order:

$$\left(\hat{H}_0+\lambda\hat{V}\right)\left|\Psi_i^{(0)}+\lambda\Psi_i^{(1)}+\lambda^2\Psi_i^{(2)}+\dots\right\rangle = \left(E_i^{(0)}+\lambda E_i^{(1)}+\lambda^2 E_i^{(2)}+\dots\right)\left|\Psi_i^{(0)}+\lambda\Psi_i^{(1)}+\lambda^2\Psi_i^{(2)}+\dots\right\rangle$$

order 0 $\quad \hat{H}_0\left|\Psi_i^{(0)}\right\rangle = E_i^{(0)}\left|\Psi_i^{(0)}\right\rangle$

order 1 $\quad \hat{H}_0\left|\Psi_i^{(1)}\right\rangle + \hat{V}\left|\Psi_i^{(0)}\right\rangle = E_i^{(0)}\left|\Psi_i^{(1)}\right\rangle + E_i^{(1)}\left|\Psi_i^{(0)}\right\rangle$

order 2 $\quad \hat{H}_0\left|\Psi_i^{(2)}\right\rangle + \hat{V}\left|\Psi_i^{(1)}\right\rangle = E_i^{(0)}\left|\Psi_i^{(2)}\right\rangle + E_i^{(1)}\left|\Psi_i^{(1)}\right\rangle + E_i^{(2)}\left|\Psi_i^{(0)}\right\rangle$

Etc.

Projecting each of these equations on $\left\langle\Psi_i^{(0)}\right|$, one gets:

$$E_i^{(0)} = \left\langle\Psi_i^{(0)}\middle|\hat{H}_0\middle|\Psi_i^{(0)}\right\rangle \qquad E_i^{(3)} = \left\langle\Psi_i^{(0)}\middle|\hat{V}\middle|\Psi_i^{(2)}\right\rangle$$

$$E_i^{(1)} = \left\langle\Psi_i^{(0)}\middle|\hat{V}\middle|\Psi_i^{(0)}\right\rangle$$

Etc.

$$E_i^{(2)} = \left\langle\Psi_i^{(0)}\middle|\hat{V}\middle|\Psi_i^{(1)}\right\rangle$$

From the equation of the first order, it comes :

$$\left(\hat{H}_0 - E_i^{(0)}\right)\left|\Psi_i^{(1)}\right\rangle = \left(E_i^{(1)} - \hat{V}\right)\left|\Psi_i^{(0)}\right\rangle = \left(\left\langle\Psi_i^{(0)}\middle|\hat{V}\middle|\Psi_i^{(0)}\right\rangle - \hat{V}\right)\left|\Psi_i^{(0)}\right\rangle$$

Expanding the correcting wavefunctions in the basis in which the Hamiltonian is working :

$$\left|\Psi_i^{(1)}\right\rangle = \sum_{k\neq\Psi_i^{(0)}} C_{k,i}^{(1)}\left|k\right\rangle = \sum_{k\neq\Psi_i^{(0)}}\left|k\right\rangle\left\langle k\middle|\Psi_i^{(1)}\right\rangle$$

Projecting the equation of the first order on <k| : $\left(E_k^{(0)} - E_i^{(0)}\right)\left\langle k\middle|\Psi_i^{(1)}\right\rangle = -\left\langle k\middle|\hat{V}\middle|\Psi_i^{(0)}\right\rangle$

The second order correction
to the energy is:

$$E_i^{(2)} = \sum_{k\neq\Psi_i^{(0)}} \frac{\left\langle\Psi_i^{(0)}\middle|\hat{V}\middle|k\right\rangle^2}{E_i^{(0)} - E_k^{(0)}}$$

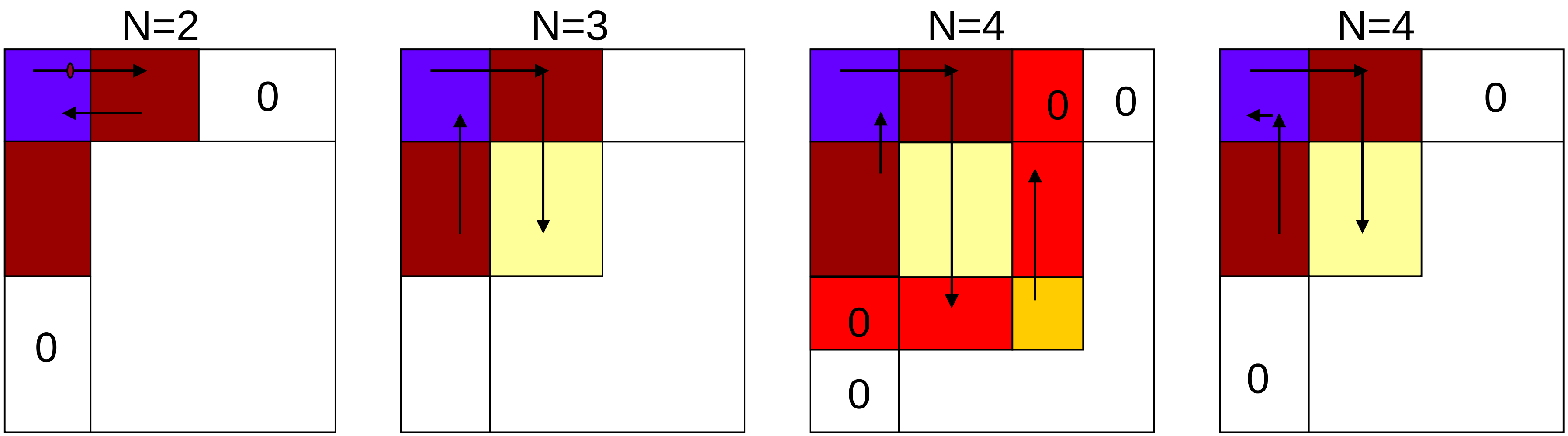
There is no guarantee that at a given order the energy is an upperbound of the exact energy,

Prerequisite : Model H can be derived from the quasi-degenerate perturbation theory

- Electronic effective interactions should be physically based

  Model Hamiltonian should provide rationalizations (identify electronic mechanisms)

  → can be analytically derived from quasi-degenerate perturbation theory



$$
\begin{aligned}
\langle \Phi_I|\hat{H}^{eff}|\Phi_J\rangle &= \langle \Phi_I|\hat{H}|\Phi_J\rangle - \sum_{r}\frac{\langle \Phi_I|\hat{V}|\Phi_r\rangle\langle \Phi_r|\hat{V}|\Phi_J\rangle}{E_r-E_J}\\
&+\sum_{r,s}\frac{\langle \Phi_I|\hat{V}|\Phi_r\rangle\langle \Phi_r|\hat{V}|\Phi_s\rangle\langle \Phi_s|\hat{V}|\Phi_J\rangle}{(E_r-E_J)(E_s-E_J)} - \sum_{r,K}\frac{\langle \Phi_I|\hat{V}|\Phi_r\rangle\langle \Phi_r|\hat{V}|\Phi_K\rangle\langle \Phi_K|\hat{V}|\Phi_J\rangle}{(E_r-E_J)(E_r-E_K)}\\
&-\sum_{r,s,t}\frac{\langle \Phi_I|\hat{V}|\Phi_r\rangle\langle \Phi_r|\hat{V}|\Phi_s\rangle\langle \Phi_s|\hat{V}|\Phi_t\rangle\langle \Phi_t|\hat{V}|\Phi_J\rangle}{(E_r-E_J)(E_s-E_J)(E_t-E_J)}\\
&+\sum_{r,s,K}\frac{\langle \Phi_I|\hat{V}|\Phi_r\rangle\langle \Phi_r|\hat{V}|\Phi_s\rangle\langle \Phi_s|\hat{V}|\Phi_K\rangle\langle \Phi_K|\hat{V}|\Phi_J\rangle}{(E_r-E_J)(E_s-E_J)(E_s-E_K)}\\
&+\sum_{r,s,K}\frac{\langle \Phi_I|\hat{V}|\Phi_r\rangle\langle \Phi_r|\hat{V}|\Phi_K\rangle\langle \Phi_K|\hat{V}|\Phi_s\rangle\langle \Phi_s|\hat{V}|\phi_J\rangle}{(E_r-E_J)(E_r-E_K)(E_s-E_J)}\\
&-\sum_{r,K,L}\frac{\langle \Phi_I|\hat{V}|\Phi_r\rangle\langle \Phi_r|\hat{V}|\Phi_K\rangle\langle \Phi_K|\hat{V}|\Phi_L\rangle\langle \Phi_L|\hat{V}|\Phi_J\rangle}{(E_r-E_J)(E_r-E_K)(E_r-E_L)}
\end{aligned}
$$

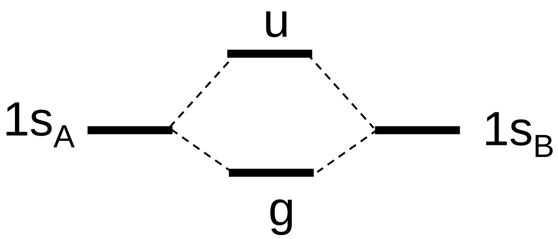
N infinite

⬇

Effective hamiltonian theory

Model Hamiltonians work in local orbitals (orthogonal Valence Bond basis)

Most methods of quantum chemistry work with symmetry-adapted MOs as they are orthogonal.



$$g = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B); \quad u = \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B)$$

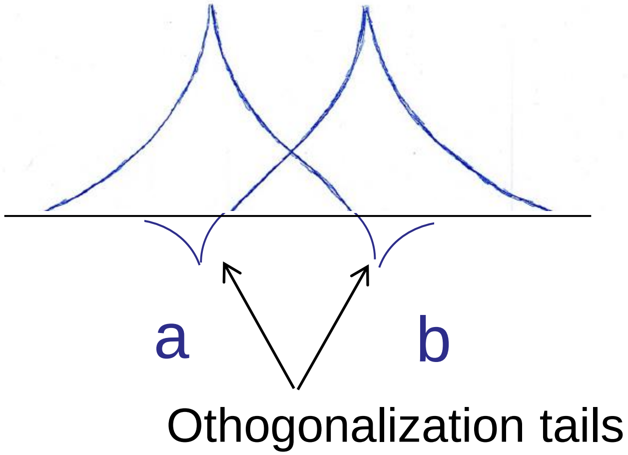
$$\langle 1s_A | 1s_B \rangle \neq 0$$

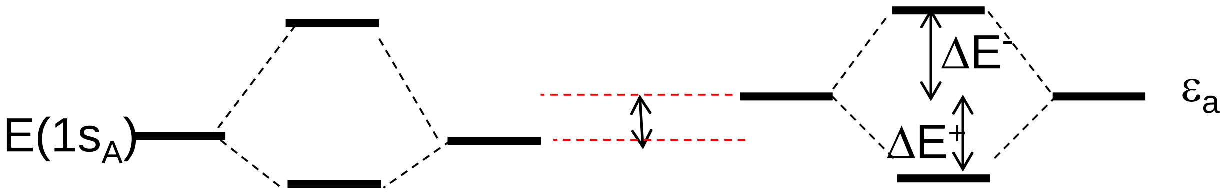
AOs are not orthogonal. But it is possible to get orthogonal local orbitals by rotating the SA MOs.

$$a = \frac{1}{\sqrt{2}}(g+u); \quad b = \frac{1}{\sqrt{2}}(g-u) \qquad \langle a | b \rangle = 0$$

$$\varepsilon_a = \langle a | \hat{h} | a \rangle = \left\langle \frac{g+u}{\sqrt{2}} \middle| \hat{h} \middle| \frac{g+u}{\sqrt{2}} \right\rangle = \frac{1}{2}(\varepsilon_g + \varepsilon_u) > E(1s_A)$$

$$\varepsilon_b = \langle b | \hat{h} | b \rangle = \left\langle \frac{g-u}{\sqrt{2}} \middle| \hat{h} \middle| \frac{g-u}{\sqrt{2}} \right\rangle = \frac{1}{2}(\varepsilon_g + \varepsilon_u) > E(1s_B)$$





$$\Delta E^+ = \Delta E^-$$

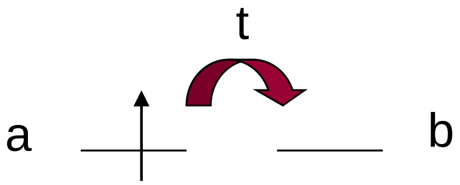
II.b The simplest Hückel model : expression and physical content

Hückel Hamiltonian in second quantization :

$$\hat{H} = \sum_{a} \varepsilon_a a_a^{+} a_a + \sum_{<ab>} t_{ab} \left(a_a^{+} a_b + a_b^{+} a_a \right)$$

$a_b^{+} a_a$ is a hopping operator and $t=t_{ab}$ is the hopping integral between the magnetic orbitals a and b

For a 1 el. / 2 centers : Hamiltonian matrix, energies, wavefunctions



$$\begin{array}{cc} a & b \\ \left(\begin{matrix} \varepsilon_a & t \\ t & \varepsilon_b \end{matrix}\right) \end{array}$$

If $\varepsilon_a=\varepsilon_b$ then $E(D_+)=|t|$

$E(D_-)=-|t|$

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

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

The sign of t is opposite to the overlap between the AO from which are built the OAO a and b

Physical content of t for a one-electron system :

$$\langle a | \hat{H}^{\text{Huckel}} | b \rangle = \langle a | \hat{H}^{\text{exact}} | b \rangle = t_{ab} = \langle a | \overline{\vartheta}_1 | b \rangle$$

where $\hat{\vartheta}_1$ is the single-electron part of $\hat{H}^{\text{exact}}$

Physical content of t between neutral and ionic forms in polyelectronic systems:

$$\left\langle \left| \uparrow_i \downarrow_j \uparrow_k \downarrow_l \ldots \right| \left| \hat{H}^{\text{Hückel}} \right| \left| +_i -_j \uparrow_k \downarrow_l \ldots \right| \right\rangle = \left\langle \left| \Psi \right| \left| \hat{H}^{\text{exact}} \right| a_j^{+} a_i \left| \Psi \right| \right\rangle$$

$$= t_{ij} = \langle i | \overline{\vartheta}_1 | j \rangle + \sum_r \langle ir \| jr \rangle = \langle i | \overline{\vartheta}_1 | j \rangle + \sum_r \langle ir | jr \rangle - \langle ir | rj \rangle = \langle i | \hat{f} | j \rangle$$

Interaction between

$\left| \underset{\curvearrowleft}{\uparrow\downarrow} \uparrow\downarrow \ldots \right\rangle$ and $\left| +-\uparrow\downarrow \ldots \right\rangle$

II.c Treatment of non-dynamic correlation : the Hubbard Hamiltonian

One way to account for non-dynamic correlation is to introduce an energetic penalty to ionic determinants. This will increase the weigth of neutral determinants in comparison to ionic ones.

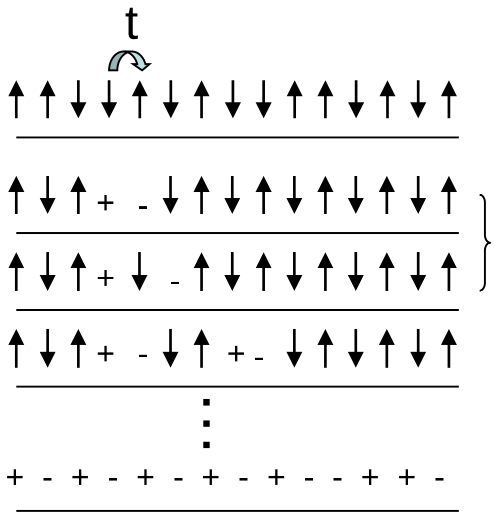
Hamiltonian in second quantization :

$$\hat{H} = \sum_{ij} t_{ij}\left(a_i^+ a_j + a_j^+ a_i\right) + U \sum_i a_i^+ a_{\bar{i}}^+ a_{\bar{i}} a_i$$

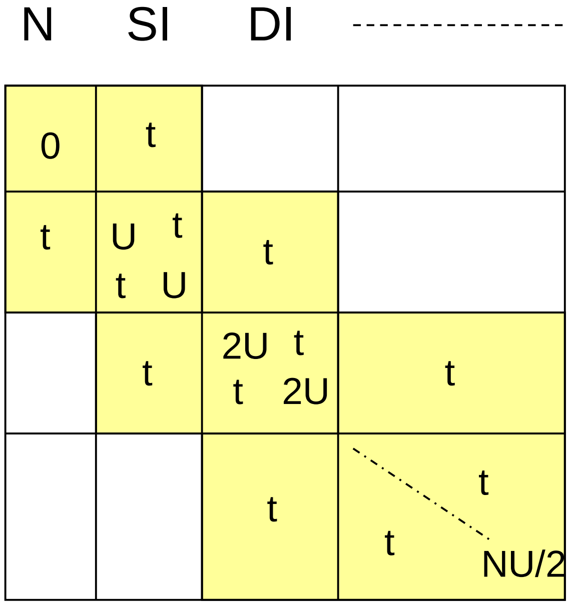
t_{ij}=Hopping integral (β of Hückel)
U=Energetic penalty of ionic forms

Example at half-filling:

Its model space is the CASSCF space : $\mathrm{Dim}(S_0) = \left(C_N^{N/2}\right)^2$



	Energy
neutral	0
singly-ionic	U
di-ionic	$2U$
fully-ionic	$\frac{N}{2}U$



N	SI	DI	---------------
0	t		
t	U t t U	t	
	t	2U t t 2U	t
		t	t t NU/2

Physical content of the interactions of the generalized Hubbard model

Between neutral forms : one may eventually introduce exchange integrals K_{ij}

Examples : 2 determinants differing by the m_s of two interacting centers I and J may interact through K_{ij}

Interaction between

$$\left|\underset{\longleftrightarrow}{\uparrow\downarrow}\uparrow\downarrow\ldots\right\rangle \text{and} \left|\underset{\longleftrightarrow}{\downarrow\uparrow}\uparrow\downarrow\ldots\right\rangle$$

$$\left\langle\left|\uparrow\downarrow\right|\left|\hat{H}^{\text{Hubbard}}\right|\left|\downarrow\uparrow\right|\right\rangle = \left\langle\left|i\bar{j}\right|\left|\hat{H}^{\text{exact}}\right|\left|\bar{i}j\right|\right\rangle = -\left\langle\left|i\bar{j}\right|\left|\hat{H}^{\text{exact}}\right|\left|j\bar{i}\right|\right\rangle = -K_{ij}$$

$$= -\iint i(1)\alpha(1)\,j(2)\beta(2)\frac{1}{r_{12}}\,j(1)\alpha(1)i(2)\beta(2)dr_1dr_2 = -\iint i(1)\,j(2)\frac{1}{r_{12}}\,j(1)i(2)dr_1dr_2$$

Between neutral and ionic forms or between ionic forms: t_{ij}

Examples : neutral and ionic determinants may interact through a hopping integral

Interaction between

$$\left|\underset{\curvearrowright}{\uparrow\downarrow}\uparrow\downarrow\ldots\right\rangle \text{ and } \left|\underset{\curvearrowright}{+-}\uparrow\downarrow\ldots\right\rangle$$

$$\left\langle\left|\uparrow_i\downarrow_j\uparrow_k\downarrow_l\ldots\right|\left|\hat{H}^{\text{Hubbard}}\right|\left|+_i -_j \uparrow_k\downarrow_l\ldots\right|\right\rangle = \left\langle\left|\Psi\right|\left|\hat{H}^{\text{exact}}\right|a_j^+a_i\left|\Psi\right|\right\rangle$$

$$= t_{ij} = \left\langle i\left|\overline{\vartheta}_1\right|j\right\rangle + \sum_r \left\langle ir\|jr\right\rangle = \left\langle i\left|\overline{\vartheta}_1\right|j\right\rangle + \sum_r \left\langle ir|jr\right\rangle - \left\langle ir|rj\right\rangle = \left\langle i\left|\hat{f}\right|j\right\rangle$$

Physical content of : U

$$\left\langle\left|+_i -_j \uparrow_k\downarrow_l\ldots\right|\left|\hat{H}^{\text{Hubbard}}\right|\left|+_i -_j \uparrow_k\downarrow_l\ldots\right|\right\rangle - \left\langle\left|\uparrow_i\downarrow_j\uparrow_k\downarrow_l\ldots\right|\left|\hat{H}^{\text{Hubbard}}\right|\left|\uparrow_i\downarrow_j\uparrow_k\downarrow_l\ldots\right|\right\rangle$$

$$= \left\langle\left|+_i -_j\right|\left|\hat{H}^{\text{exact}}\right|\left|+_i -_j\right|\right\rangle - \left\langle\left|\uparrow_i\downarrow_j\right|\left|\hat{H}^{\text{exact}}\right|\left|\uparrow_i\downarrow_j\right|\right\rangle = J_{jj} - J_{ij}$$

Energy difference between

$$\left|\underset{\curvearrowright}{\uparrow\downarrow}\uparrow\downarrow\ldots\right\rangle \text{ and } \left|\underset{\curvearrowright}{+-}\uparrow\downarrow\ldots\right\rangle$$

II.d Heisenberg-Dirac-van Vleck (HDvV) model

For very large U values, one may keep only the neutral determinants :
the single degree of freedom is the spin.

$$\hat{H}^{Heis.} = -\sum_{<ij>} J_{ij} \hat{\vec{S}}_i . \hat{\vec{S}}_j$$

J : effective exchange

$\mathrm{Cu_a}$ $\mathrm{Cu_b}$ $\mathrm{Cu_a}$ $\mathrm{Cu_b}$

$$|\varphi_1| = |a\bar{b}| \overset{J}{\longleftrightarrow} |\varphi_2| = |\bar{a}b| \longrightarrow$$

Singulet (S)
Triplet (T)

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

$$\hat{\vec{S}}_i . \hat{\vec{S}}_j = \begin{pmatrix} \hat{S}_{X_i} & \hat{S}_{Y_i} & \hat{S}_{Z_i} \end{pmatrix} \begin{pmatrix} \hat{S}_{X_j} \\ \hat{S}_{Y_j} \\ \hat{S}_{Z_j} \end{pmatrix} = \hat{S}_{X_i}\hat{S}_{X_j} + \hat{S}_{Y_i}\hat{S}_{Y_j} + \hat{S}_{Z_i}\hat{S}_{Z_j}$$

2. Spin operators

$\hat{S}$: Spin kinetic momentum

$\hat{S}_Z$: projection of $\hat{S}$ onto the quantization axis (OZ)

$$\boxed{\hat{S}^2|s, m_S\rangle = \hbar^2 s(s+1)|s, m_S\rangle}$$

$$\boxed{\hat{S}_Z|s, m_S\rangle = \hbar\, m_S|s, m_S\rangle}$$

For one electron : s=1/2, m_s=±1/2

* m_s=1/2 : |↑>= |1/2, 1/2 > = |+ >

* m_s=-1/2 : |↓>= |1/2, -1/2 > = |- >

$$\hat{S}^2|\pm\rangle = \frac{3}{4}\hbar^2|\pm\rangle \text{ et } \hat{S}_Z|\pm\rangle = \pm\frac{1}{2}\hbar|\pm\rangle$$

The eigenvectors of $\hat{S}^2$ and $\hat{S}_z$ are not eigenvectors of $\hat{S}_x$ and $\hat{S}_y$: $\left[\hat{S}_x, \hat{S}_y\right] = i\hbar\hat{S}_z$

In practice, one introduces the operators step up and step down :

$$\boxed{\begin{aligned}\hat{S}_+ &= \hat{S}_x + i\hat{S}_y \\ \hat{S}_- &= \hat{S}_x - i\hat{S}_y\end{aligned}}$$

which are such that : $\hat{S}_\pm|s, m_s\rangle = \hbar\sqrt{S(S+1) - m_s(m_s \pm 1)}|s, m_s \pm 1\rangle$

For one electron : s=1/2, m_s=±1/2

$$\hat{S}_+|-\rangle = \hbar|+\rangle; \quad \hat{S}_+|+\rangle = 0; \quad \hat{S}_-|-\rangle = 0; \quad \hat{S}_-|+\rangle = \hbar|-\rangle$$

Note that:

$$\boxed{\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \hat{S}_z^2 + \frac{1}{2}\left[\hat{S}_+\hat{S}_- + \hat{S}_-\hat{S}_+\right]}$$

« Easy » manipulation of Heisenberg

Coupling two kinetic moments

$S=s_1+s_2,\ s_1+s_2-1, \ldots, |s_1-s_2|$
$M_S=-S,-S+1, \ldots, S$

Ex : $s_1=1/2$, $s_2=1/2$

S =1/2+1/2, 1/2-1/2

* S=1, Ms=-1,0,1 → Spin Multiplicity $g_s=2S+1=3$
* S=0, Ms=0 → Spin Multiplicity $g_s=2S+1=1$

Generalization to n spins :

One couples the moments 2 by 2 :

Ex : $s_1=1/2$, $s_2=1/2$, $s_3=1/2$

$S' = s_1+s_2=1/2+1/2,\ 1/2-1/2$
$s_1=1/2$, $s_2=1/2$

* S'=1, Ms=-1,0,1 → Spin Multiplicity $g_s=2S+1=3$
* S'=0, Ms=0 → Spin Multiplicity $g_s=2S+1=1$

$S=S'+s_3$: S'=1,0, $s_3=1/2$

* S=1+1/2=3/2 Ms=-3/2,-1/2,1/2,3/2 → Spin Multiplicity $g_s=2S+1=4$
* S=1-1/2=1/2 Ms=-1/2, 1/2 → Spin Multiplicity $g_s=2S+1=2$
* S=0+1/2 Ms=-1/2, 1/2 → Spin Multiplicity $g_s=2S+1=2$

Numbering the spin states from the spin distributions:

- One numbers the spin distributions for each possible Ms starting from Ms_{max}
- In each subspace of $Ms<Ms_{max}$ one removes the K highest spin states which were found in the sub-spaces of higher Ms. It remains N-K spin states of S=Ms .
- One determines all the spin states that can be generated from m electrons in M orbitals.

The Hamiltonian does not mix spin distributions of different Ms: $\left[\hat{H},\hat{S}_z\right]=0$

Ex : $s_1=1/2$, $s_2=1/2$, $s_3=1/2$

Ms=3/2 distribution : ↑↑↑, is the Ms=3/2 of a quadruplet state (2S+1=4)
Ms =1/2 3 possible distributions : ↓↑↑, ↑↓↑, ↑↑↓ ,
From which one may buid the Ms=1/2 component of the quadruplet state. It remains 3-1=2 states which have an Ms=1/2 component, they must be doublet states.

Ex : $s_1=1/2$, $s_2=1/2$, $s_3=1/2$, $s_4=1/2$

Ms=2 distribution : ↑↑↑↑ , is the Ms=2 component of a quintuplet state
Ms =1 4 possible distributions : ↓↑↑↑, ↑↓↑↑, ↑↑↓↑ , ↑↑↑↓
From which one may build the Ms=1 component of the quintuplet. It remains 4-1=3 states having an Ms=1 component. They must be triplet states.
Ms=0 6 possible distributions : ↓↓↑↑ , ↓↑↓↑ , ↓↑↑↓ , ↑↓↓↑ ,↑↓↑↓ , ↑↑↓↓
From which one may build the Ms=0 of one quintuplet and of 3 triplets.
It remains 6-1-3=2 states. They must be singlet states.

Heisenberg Hamiltonian matrix for 2 electrons in 2 orbitals :

Ex: $S_1=1/2$, $S_2=1/2$

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

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

Diagonal elements :

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

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

Off-diagonal elements :

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

The matrix writes :

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

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) :

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

$$(J/2-E)^2-(J/2)^2=0 \quad \Leftrightarrow \quad E=\begin{cases} 0 & \text{Energy of the Ms=0 component of the triplet.} \\ J & \text{Energy of the singlet} \end{cases}$$

Eigenvectors:

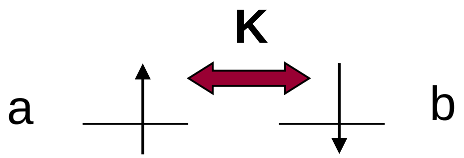
$$\begin{pmatrix} J/2 & -J/2 \\ -J/2 & J/2 \end{pmatrix}\begin{pmatrix} C_{11} \\ C_{12} \end{pmatrix} = E_S\begin{pmatrix} C_{11} \\ C_{12} \end{pmatrix} \Leftrightarrow \begin{cases} (J/2)C_{11}-(J/2)C_{12}=E_S C_{11} \\ |C_{11}|^2+|C_{12}|^2=1 \end{cases} \Leftrightarrow \begin{cases} C_{11}=-C_{12}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

$$\begin{pmatrix} J/2 & -J/2 \\ -J/2 & J/2 \end{pmatrix}\begin{pmatrix} C_{21} \\ C_{22} \end{pmatrix} = E_T\begin{pmatrix} C_{21} \\ C_{22} \end{pmatrix} \Leftrightarrow \begin{cases} (J/2)C_{21}-(J/2)C_{22}=E_T C_{21} \\ |C_{21}|^2+|C_{22}|^2=1 \end{cases} \Leftrightarrow \begin{cases} C_{21}=C_{22} \\ C_{21}=\dfrac{1}{\sqrt{2}} \end{cases}$$

$$\boxed{|\Psi_S\rangle=\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle-|\downarrow\uparrow\rangle\right)} \qquad \boxed{|\Psi_T\rangle=\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle\right)}$$

Derivation of the Heisenberg model from the Hubbard model

Direct exchange :



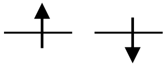
Exchange integral of the exact electronic Hamiltonian :

$$\mathrm{K} = \iint \mathrm{a}(1)\mathrm{b}(2)\frac{1}{\mathrm{r}_{12}}\mathrm{b}(1)\mathrm{a}(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \quad > 0$$

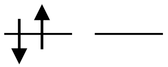
The triplet is lower in energy than the singlet : Hund's rule

Kinetic exchange : ionic determinant contribution to the singlet state

neutral



Ionic



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

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

Variationally

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

$$\mathrm{E}(\mathrm{T}) = -\mathrm{K}$$

$$\mathrm{S}^g = \lambda(\mathrm{a}\bar{\mathrm{b}} + \mathrm{b}\bar{\mathrm{a}}) - \mu(\mathrm{a}\bar{\mathrm{a}} + \mathrm{b}\bar{\mathrm{b}})$$

$\lambda > \mu$ positive

$$T^u = \frac{1}{\sqrt{2}}(a\bar{b} - b\bar{a})$$

Perturbatively (2nd order) :

$$E(S_N^g) = K - \frac{4t^2}{U}$$

$$E(T_N^u) = -K$$

$$\frac{\Delta \mathrm{E}_{\mathrm{ST}}}{2} = \mathrm{K} - \frac{2\mathrm{t}^2}{\mathrm{U}} = \frac{\mathrm{J}}{2}$$

$$\mathrm{J} < 0 \text{ if } \mathrm{K} < \frac{2\mathrm{t}^2}{\mathrm{U}}$$

$$\mathrm{J} > 0 \text{ if } \mathrm{K} > \frac{2\mathrm{t}^2}{\mathrm{U}}$$

$\mathrm{S}^t < \mathrm{T}^t$

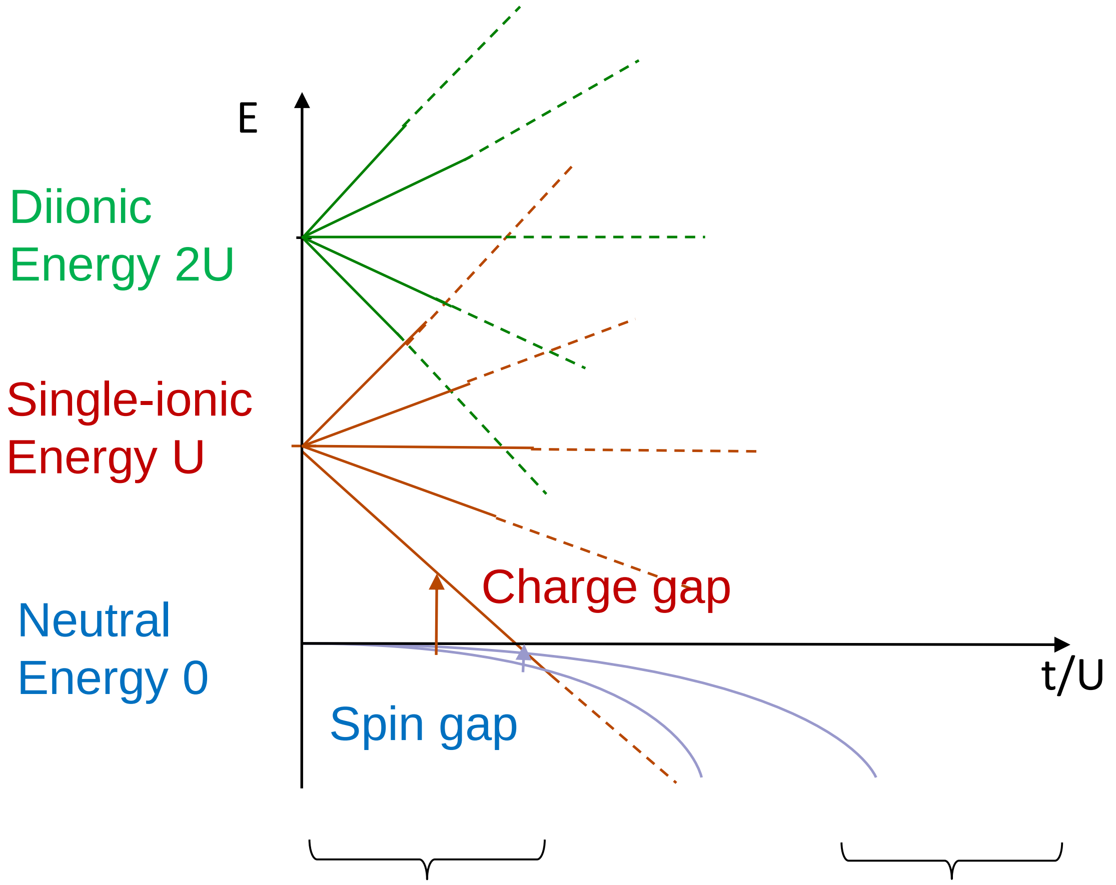
Antiferromagnetic system

Ferromagnetic system

$\mathrm{T}^t < \mathrm{S}^t$

Validity domain of the model Hamiltonians

The Mott –Hubbard diagram



Heisenberg limit

$U \longrightarrow \infty$

Strongly correlated

Hückel limit

$U \longrightarrow 0$

Uncorrelated

Conclusions

- Model Hamiltonians can be analytically derived from the exact electronic Hamiltonian (or Hubbard Ham.) including SOC and the perturbation theory
  1. The physical content of effective interactions is known
  2. An order of magnitude of the interactions can be anticipated from the perturbation theory order to which they appear and the number of contributing mechanisms

- Owing to the effective Hamitonian theory, all these interactions can be extracted from the energies and wavefunctions computed *ab initio*
  1. The extraction is controlled: one knows the magnitude of the projections and all the matrix elements of the model Ham : the relevance of both the model space and the operator of the model can be rationally deduced..
  2. Model (effective) Hamiltonian can involve more than two-body operators.

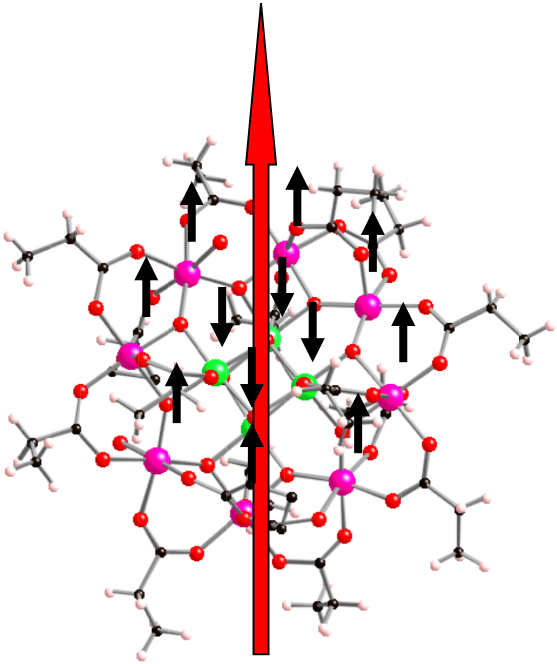
- Model Hamiltonian are versatile, they can mimick different physics

Thank you for you kind attention !

II. e Anisotropic Spin Hamiltonian for transition metal complexes

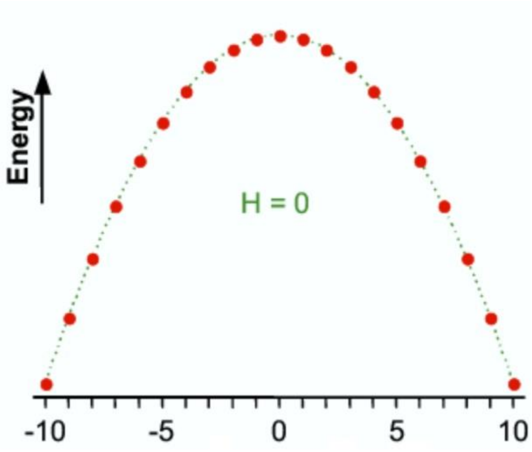
Single Molecule Magnets

S=10



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

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



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)

Interlude

Various couplings of two spin momenta : scalar, vector and tensorial products

- The scalar product gives a scalar : 1 number

$$\vec{V}_1.\vec{V}_2 = \begin{pmatrix} V_{x1} \\ V_{y1} \\ V_{z1} \end{pmatrix} \begin{pmatrix} V_{x2} \\ V_{y2} \\ V_{z2} \end{pmatrix} = V_{x1}.V_{x2} + V_{y1}.V_{y2} + V_{z1}.V_{z2} = J$$

Example : J
is the magnetic
coupling

- The vector product gives a vector : 3 numbers

$$\vec{V}_1 \times \vec{V}_2 = \begin{pmatrix} V_{x1} \\ V_{y1} \\ V_{z1} \end{pmatrix} \times \begin{pmatrix} V_{x2} \\ V_{y2} \\ V_{z2} \end{pmatrix} = \begin{pmatrix} V_{y1}V_{z2} - V_{z1}V_{y2} \\ V_{z1}V_{x2} - V_{x1}V_{z2} \\ V_{x1}V_{y2} - V_{y1}V_{x2} \end{pmatrix} = \vec{d}$$

Example : $\vec{d}$
is the dzyaloshinski-
Moriya (pseudo)vector

- The tensorial product gives a second order tensor : a matrix of 9 numbers

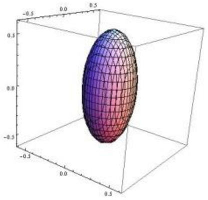
$$\vec{V}_1 \otimes \vec{V}_2 = \begin{pmatrix} V_{x1} \\ V_{y1} \\ V_{z1} \end{pmatrix} \begin{pmatrix} V_{x2} \\ V_{y2} \\ V_{z2} \end{pmatrix} = \begin{pmatrix} V_{X_1}V_{X_2} & V_{X_1}V_{Y_2} & V_{X_1}V_{Z_2} \\ V_{Y_1}V_{X_2} & V_{Y_1}V_{Y_2} & V_{Y_1}V_{Z_2} \\ V_{Z_1}V_{X_2} & V_{Z_1}V_{Y_2} & V_{Z_1}V_{Z_2} \end{pmatrix} = \overline{\overline{D}}$$

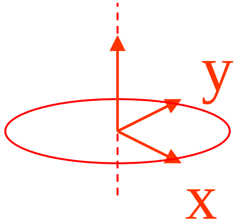
Example : $\overline{\overline{D}}$
is the Zero-Field
Splitting tensor

Usual model for magnetic anisotropy

The projections of the spin operator onto the x, y and z components are different

$$\hat{S} = \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix}$$





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

Phenomenological Hamiltonian :

Magnetic axes

Ising

$$\hat{\mathbf{H}}^{\text{model}} = \hat{\mathbf{S}}.\overline{\overline{\mathbf{D}}}.\hat{\mathbf{S}} = D\left[\mathbf{S}_Z^2 - \frac{1}{3}S(S+1)\hat{\mathbf{I}}\right] + E\left[\mathbf{S}_X^2 - \mathbf{S}_Y^2\right]$$

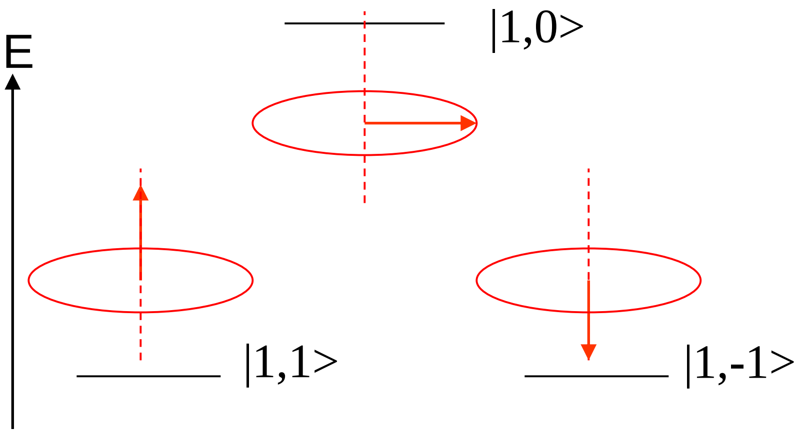
$$(\mathbf{D}) = \begin{pmatrix} D_{11} & D_{12} & D_{13} \\ D_{12} & D_{22} & D_{23} \\ D_{13} & D_{23} & D_{33} \end{pmatrix} \Rightarrow (\mathbf{D}) = \begin{pmatrix} D_{XX} & 0 & 0 \\ 0 & D_{YY} & 0 \\ 0 & 0 & D_{ZZ} \end{pmatrix}$$

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

This Hamiltonian should reproduce the energy difference between the spin orbit states

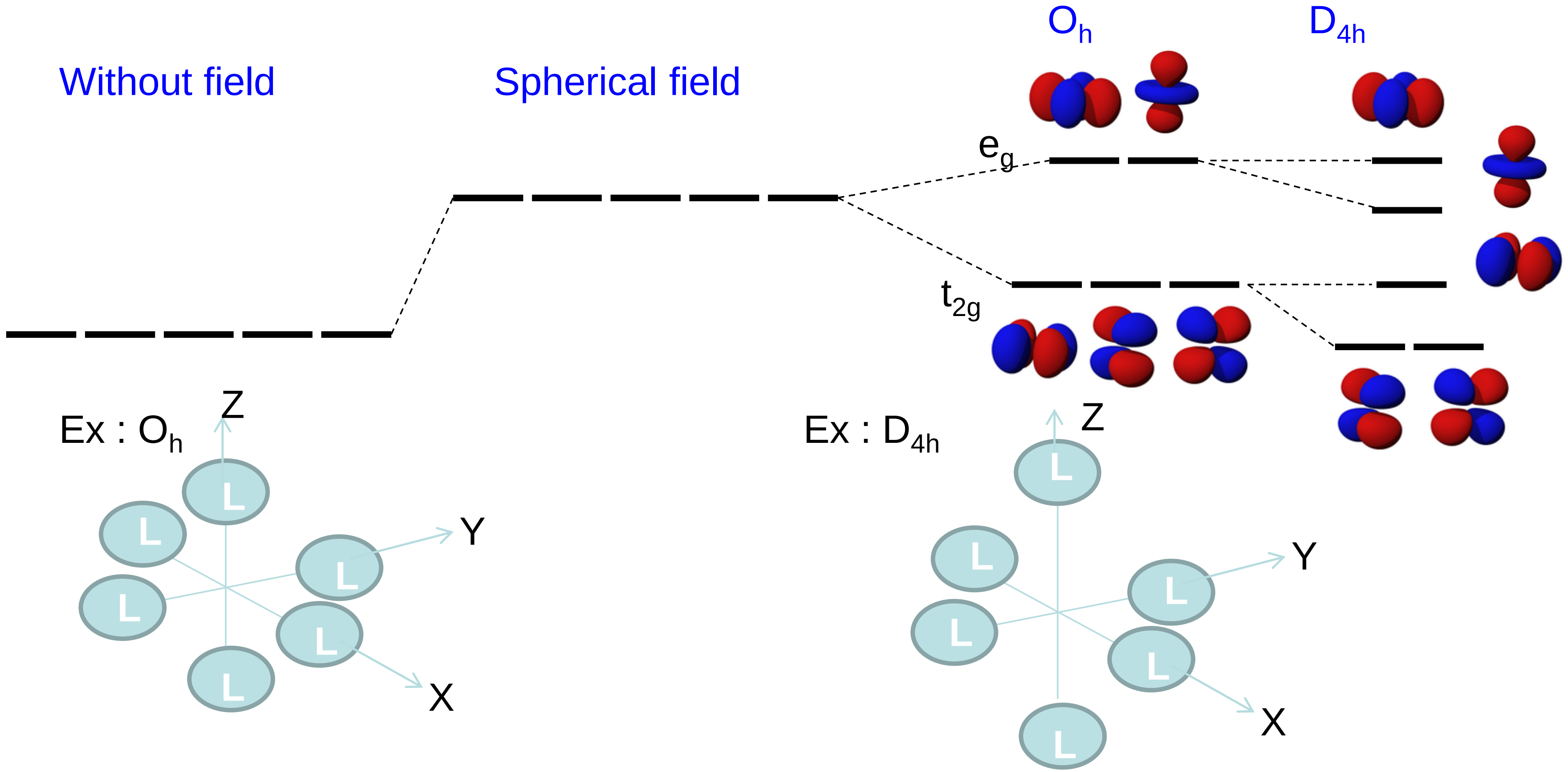
Example for a 2-electron system : S=1

$$\left(\hat{\mathbf{H}}^{\text{model}}\right) = \begin{array}{ccc} |M_S=-1\rangle & |M_S=0\rangle & |M_S=1\rangle \\ \left(\begin{array}{c} (D_{11}+D_{22})/2+D_{33} \\ -(D_{13}+iD_{23})/\sqrt{2} \\ (D_{11}-D_{22})/2+iD_{12} \end{array} \right. & \begin{array}{c} -(D_{13}-iD_{23})/\sqrt{2} \\ D_{11}+D_{22} \\ (D_{13}+iD_{23})/\sqrt{2} \end{array} & \left. \begin{array}{c} (D_{11}-D_{22})/2-iD_{12} \\ (D_{13}-iD_{23})/\sqrt{2} \\ (D_{11}+D_{22})/2+D_{33} \end{array} \right) \end{array}$$



Other interlude. Basic elements of crystal field theory

The first theory has been developed to explain the properties of metal ions in ionic crystals
According to this theory, the free doublet of a ligand is considered as a negative charge which repels the electrons of the d-orbitals of the metal ion.

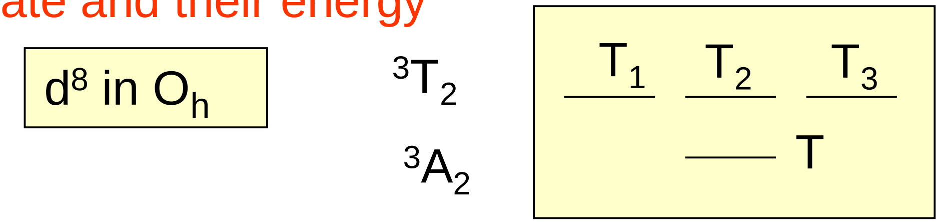


d_{x2-y2} and d_{z2} pointing through the ligands are more destabilized than the orthers. An elongation (or compression) may lift their degeneracy.

Beyond numbers : analytical derivation of the ZFS tensor components : example in a Ni(II) model complex

Approximation : To consider all the states would be too complex and unecessary

States can be selected according to the magnitude of their spin-orbit coupling with the ground state and their energy



d^8 in O_h

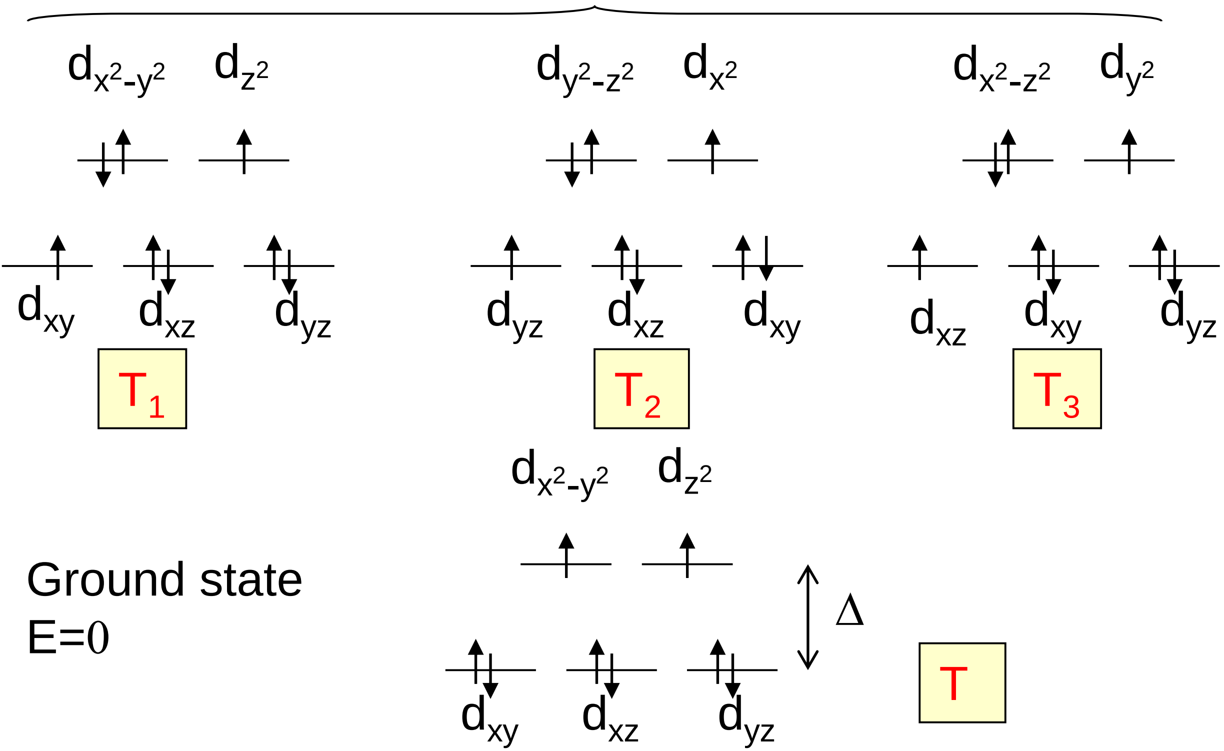
$^3T_2$

$^3A_2$

T_1 T_2 T_3

T

Different orbital sets



Excited states
E=Δ

$d_{x^2-y^2}$ d_{z^2}

d_{xy} d_{xz} d_{yz}

T_1

$d_{y^2-z^2}$ d_{x^2}

d_{yz} d_{xz} d_{xy}

T_2

$d_{x^2-z^2}$ d_{y^2}

d_{xz} d_{xy} d_{yz}

T_3

Ground state
E=0

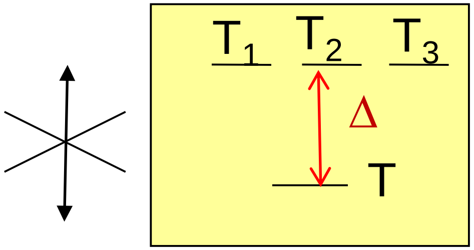
$d_{x^2-y^2}$ d_{z^2}

Δ

d_{xy} d_{xz} d_{yz}

T

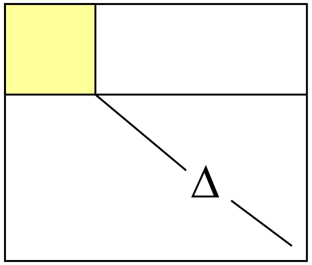
First test : No ZFS in O_h symmetry



$$\langle \phi_I | \hat{H}^{eff} | \phi_J \rangle = \langle \phi_I | \hat{H}_0 + \hat{V} | \phi_J \rangle + \sum_{\alpha \notin S} \frac{\langle \phi_I | \hat{V} | \phi_\alpha \rangle \langle \phi_\alpha | \hat{V} | \phi_J \rangle}{E_J^0 - E_\alpha^0}$$

$$V = \sum_i \zeta_i \hat{l}_i . \hat{S}_i$$

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



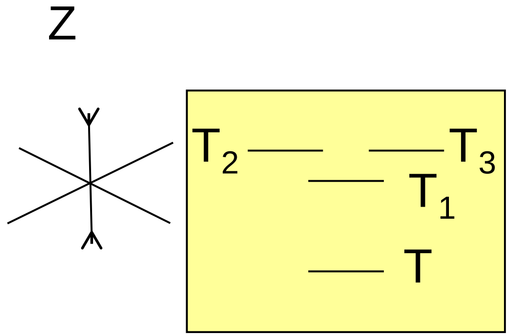
$$\begin{array}{cccc}
 & |T_+\rangle & |T_0\rangle & |T_-\rangle \\
\langle T_+| & \frac{-2\zeta^2}{\Delta} & 0 & 0 \\
\langle T_0| & 0 & \frac{-2\zeta^2}{\Delta} & 0 \\
\langle T_-| & 0 & 0 & \frac{-2\zeta^2}{\Delta}
\end{array}$$

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

The three components are degenerate

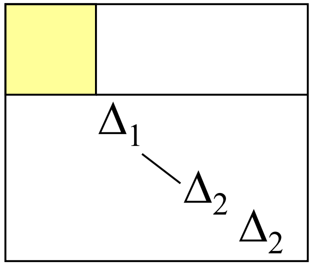
ZFS results from a symmetry lowering + spin-orbit coupling

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

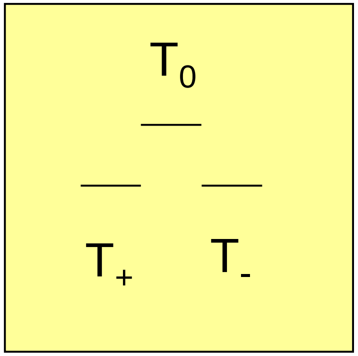


$$\Delta_1 = E(T_1) = \Delta$$

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

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

No tunnel splitting



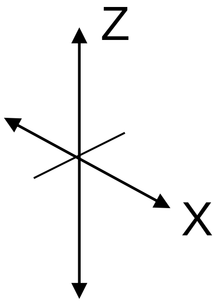
$$\boxed{D = -\frac{\zeta^2}{\Delta_1} + \frac{\zeta^2}{\Delta_2}}$$

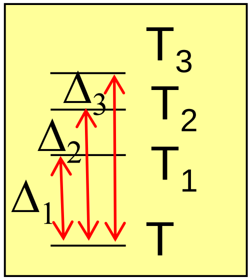
Proposed by Abragam

Rationalization of the D sign

Compression along Z : $\Delta 1<\Delta 2$ $D<0$
Elongation along Z : $\Delta 1>\Delta 2$ $D>0$

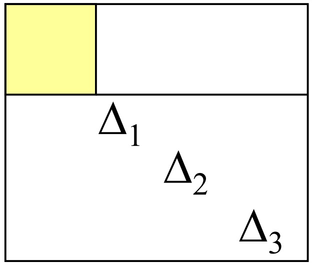
Rationalization of the rhombic component E : deformation in the (X,Y) plane : ZFS in D_{2h} symmetry



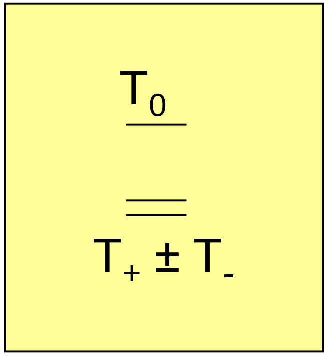


H_{eff} pour une géométrie D_{2h} et dans le système d'axes propres

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	$\frac{\zeta^2}{\Delta 1}+\frac{1}{2}\cdot\frac{\zeta^2}{\Delta 2}+\frac{1}{2}\cdot\frac{\zeta^2}{\Delta 3}$



Spectrum



Axial D and rhombic E parameters

$$\begin{cases} D = -\dfrac{\zeta^2}{\Delta_1} + \dfrac{\zeta^2}{2\Delta_2} + \dfrac{\zeta^2}{2\Delta_3} \\ E = \dfrac{\zeta^2}{2\Delta_2} - \dfrac{\zeta^2}{2\Delta_3} \end{cases}$$

III. Extraction of model Hamiltonians interactions from the effective Hamiltonian theories and *ab initio* calculations

III.a **Rational reduction of information : the effective and intermediate Hamiltonian theory**

Bloch, Nucl.Phys **8** 91 (1958); J. de Cloizeaux Nucl. Phys. 20, 321 1960

Choice of the target space :

$$S = \{\Psi_i\} \quad S \subset S' \quad \dim(S) = N_m$$

Biunivocal relation

Choice of the model space

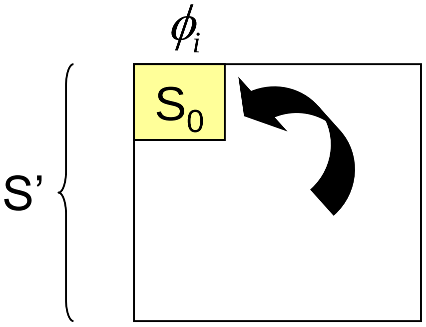
$$S_0 = \{\phi_i\} \qquad \dim(S_0) = N_m$$

Projector onto the model space

$$\hat{P}_0 = \sum_i |\phi_i\rangle\langle\phi_i|$$

Low lying states of H exact

$$\hat{\mathrm{H}}^{\mathrm{Exact}}|\Psi_i\rangle = \mathrm{E}_i|\Psi_i\rangle$$



Low lying states of the H effective

$$\hat{H}^{eff}|\tilde{\Psi}_i\rangle = E_i|\tilde{\Psi}_i\rangle$$

where $|\tilde{\Psi}_i\rangle$: Orthogonal projections

$$\hat{\mathrm{H}}^{\mathrm{eff}} = \sum_{i=1}^{N_m} |\tilde{\Psi}_i\rangle\langle\tilde{\Psi}_i| \mathrm{E}_i$$

Controlled Extraction : The quality of H^{eff} can be appreciated by the weight of the model function in the ab initio wavefunction $\sum_{i=1}^{N_m} \|\tilde{\Psi}_i\|$ max

The effective Hamiltonian for a two-dimension model space : des Cloizeaux formalism

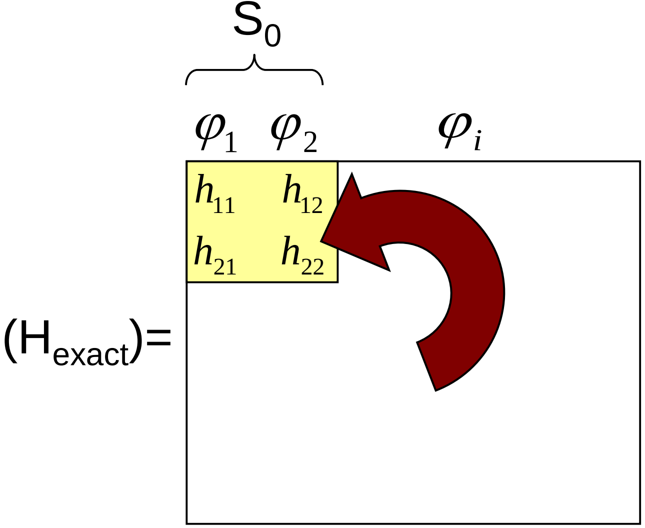
Target space S

$$\left\{\begin{array}{l} \Psi^1 = \underbrace{\boxed{C_1^1\varphi_1 + C_2^1\varphi_2 + \ldots}}_{\tilde{\Psi}^i} + C_i^1\varphi_i + C_n^1\varphi_n \quad \text{of energy } E^1 \\ \Psi^2 = \boxed{C_1^2\varphi_1 + C_2^2\varphi_2 + \ldots} + C_i^2\varphi_i + C_n^2\varphi_n \quad \text{of energy } E^2 \end{array}\right.$$

In localized orbitals

$\tilde{\Psi}^i$: The projections onto the model space S_0 are orthonormalized

H^{eff} is dressed under the effect of the external space



$$\hat{H}^{eff} = \sum_{i=1}^{N_m} \left|\tilde{\Psi}_i\right\rangle\left\langle\tilde{\Psi}_i\right| E_i$$

numbers

$$(H_{model}) = (H^{eff}) = \begin{array}{cc} \varphi_1 & \varphi_2 \\ \left(\begin{array}{cc} h'_{11} & h'_{12} \\ h'_{21} & h'_{22} \end{array}\right) & \end{array}$$

$\{E^i;\Psi^i\}$

Diagonalization

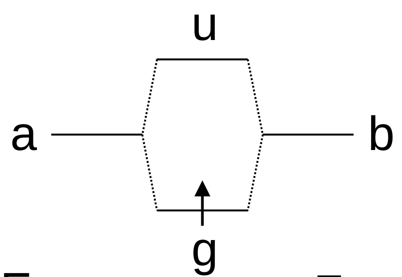
$\{E^i;\tilde{\Psi}^i\}$

$$\hat{H}^{eff} = \hat{P}_0\hat{H}\hat{\Omega}\hat{P}_O$$

The wave operator : $\hat{\Omega}\left|\tilde{\Psi}_i\right\rangle = \left|\Psi_i\right\rangle$ → QDPT up to an infinite order

III.b Extraction of the Hückel parameters for both symmetric and non-symmetric systems

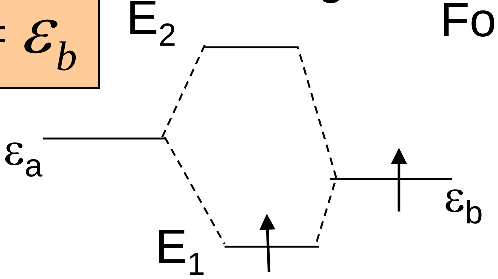
$\text{if } \varepsilon_a = \varepsilon_b$



$$t = (E(D_g) - E(D_u))/2$$

From symmetry-adapted solutions !

$\textit{if } \varepsilon_a \neq \varepsilon_b$



For orthonormalized projections

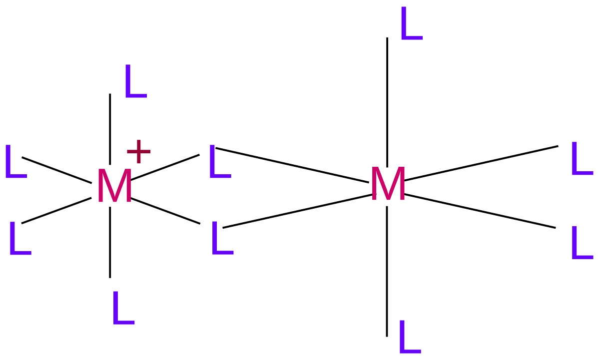
$$E_1 : \ \psi_1 = \cos\varphi \, \phi_a + \sin\varphi \, \phi_b$$
$$E_2 : \ \psi_2 = -\sin\varphi \, \phi_a + \cos\varphi \, \phi_b$$

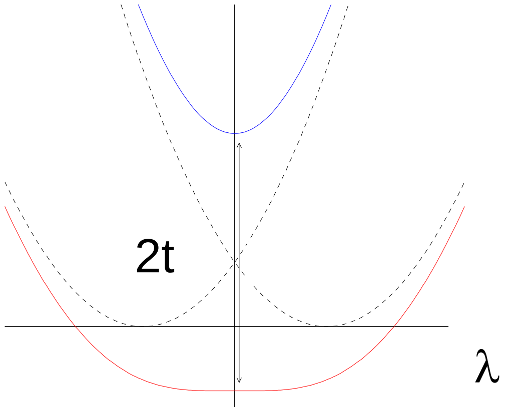
$$t = \cos\varphi \sin\varphi (E_2 - E_1)$$
$$\varepsilon_a - \varepsilon_b = \sqrt{(E_2 - E_1)^2 - 4t^2}$$

For a bi-metallic complex where the metal is surrounded by a coordination sphere of ligands

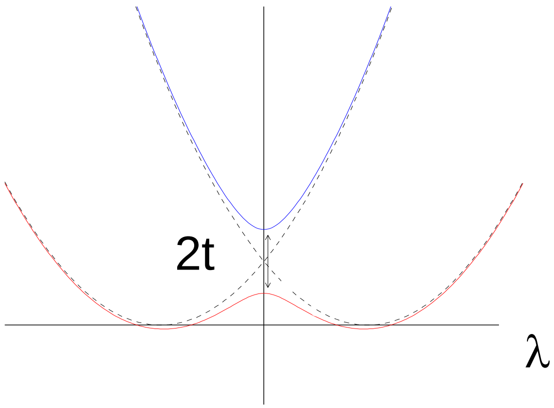
Q : the antisymmetric combination of the coordination sphere stretchings

$$(H) = \begin{pmatrix} \Delta(\lambda - 1)^2 & t \\ t & \Delta(\lambda + 1)^2 \end{pmatrix}$$





Delocalized

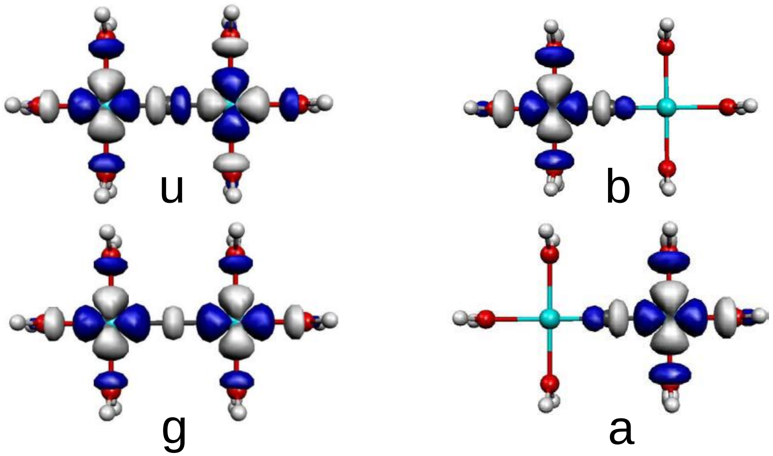


Localized

Bistability condition : t< 2Δ

III.c Extraction of Heisenberg model from both SA and BS solutions

1) Using energies & SA wavefunctions (WFT)



§ Escher : symétrie 70 (papillons)

$$(H)=\begin{array}{cc} \uparrow\downarrow & \downarrow\uparrow \\ \left(\begin{array}{cc} J/2 & -J/2 \\ -J/2 & J/2 \end{array}\right) \end{array}$$

$$E(S=0)-E(S=1)=J$$

MRCI solutions are eigenfunctions of S^2 : The anatycal expression of J can be obtained from the energies computed at the correlated level of calculation

$$\hat{H}^{eff}=\sum_{i=1}^{N_m}\left|\tilde{\Psi}_i\right\rangle\left\langle\tilde{\Psi}_i^{\perp}\right|E_i$$

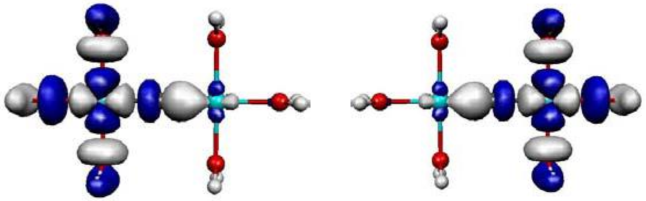
➡ More information can be obtained from the wavefunctions as we will see later on.

2) Using the energies of broken symmetry DFT solutions and the derivation from Hubbard

As DFT gives single determinants, one needs to match with single spin distribution: Ising Hamiltonian

$$\hat{H}^{\mathrm{eff}} = J\hat{\vec{S}}_{Z_1}.\hat{\vec{S}}_{Z_2}$$

BS MOs $\begin{cases} a'_1 = a_1 \cos\varphi + a_2 \sin\varphi \\ a'_2 = a_1 \sin\varphi + a_2 \cos\varphi \end{cases}$



Remembering that the Hubbard matrix (from which HDvV H is derived) writes:

$$\begin{array}{c} \langle\uparrow \quad \uparrow| \\ \langle\uparrow \quad \downarrow| \\ \langle\uparrow\downarrow \quad +| \\ \langle+ \quad \uparrow\downarrow| \end{array} \left(\begin{array}{cc|cc} -K & 0 & 0 & 0 \\ 0 & 0 & t & t \\ \hline 0 & t & U & K \\ 0 & t & K & U \end{array}\right) \Rightarrow \quad E\left(|\uparrow\downarrow\rangle_{BS}\right) = \frac{-2t^2}{U}$$

One may attribute a value to the effective exchange from the two BS solutions from the Ising Hamiltonian :

Perturbative evaluation

$$E\left(|\uparrow\downarrow\rangle_{BS}\right) - E\left(|\uparrow\uparrow\rangle_{BS}\right) = \frac{-2t^2}{U} + K = J/2$$

It might be necessary to spin decontaminate these solutions, as $|\uparrow\uparrow\rangle$ is not a real triplet and $|\uparrow\downarrow\rangle$ is not half a singlet and half a triplet.

III. d. Extraction of anisotropic spin Hamiltonians in mononuclear and binuclear complexes

Mono nuclear complexes : giant spin Hamiltonian :

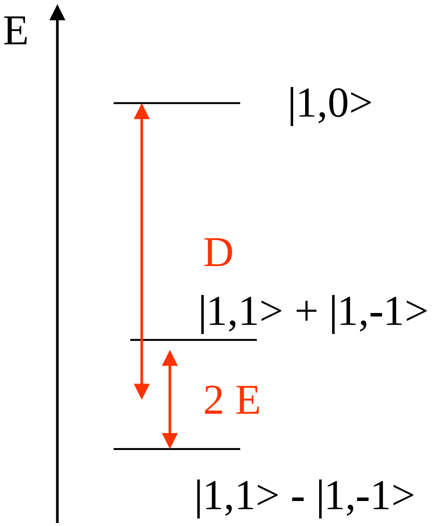
$$\hat{\mathbf{H}}^{\text{model}} = \hat{\mathbf{S}}.\overline{\overline{\mathbf{D}}}.\hat{\mathbf{S}} = D\left[\mathbf{S}_{\mathbf{Z}}^{2} - \frac{1}{3}S(S+1)\hat{\mathbf{I}}\right] + E\left[\mathbf{S}_{\mathbf{X}}^{2} - \mathbf{S}_{\mathbf{Y}}^{2}\right]$$

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

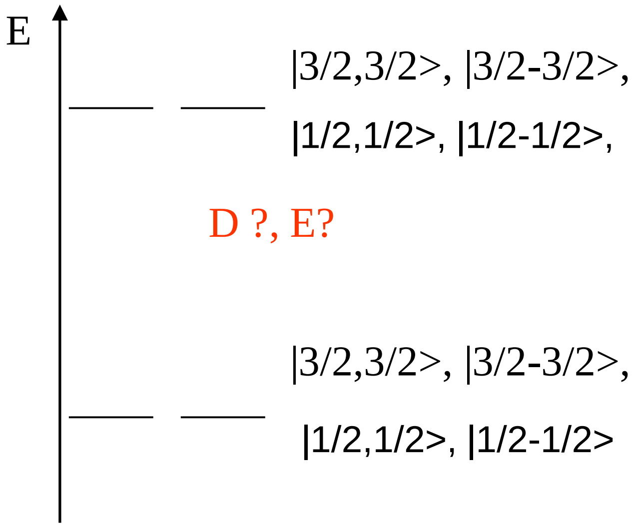
$D = 3/2\ D_{zz}$: axial parameter $E = 1/2\ (D_{xx} - D_{yy})$: rhombic parameter

For half-integer spins, the extraction cannot be performed from the energies only. One uses the effective Hamiltonian theory and therefore the wavefunctions.

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



- Example: $[\mathrm{Ni(HIM_2\text{-}py)_2NO_3}]^+$

$$\left(\hat{\mathrm{H}}^{\mathrm{model}}\right)=\begin{pmatrix}(D_{11}+D_{22})/2+D_{33} & -(D_{13}-iD_{23})/\sqrt{2} & (D_{11}-D_{22})/2-iD_{12}\\ -(D_{13}+iD_{23})/\sqrt{2} & D_{11}+D_{22} & (D_{13}-iD_{23})/\sqrt{2}\\ (D_{11}-D_{22})/2+iD_{12} & (D_{13}+iD_{23})/\sqrt{2} & (D_{11}+D_{22})/2+D_{33}\end{pmatrix}$$

Analytical expression of the model Hamiltonian matrix

$$\updownarrow$$

$$\left(\hat{\mathrm{H}}^{\mathrm{eff.}}\right)=\begin{pmatrix}6.386 & -0.690+0.376i & -3.734+3.134i\\ -0.690-0.376i & 0.125 & 0.690-0.376i\\ -3.734-3.134i & 0.690+0.376i & 6.386\end{pmatrix}$$

Numerical expression of the effective Hamiltonian matrix

$$\downarrow$$

$$(\mathrm{D})=\begin{pmatrix}D_{11} & D_{12} & D_{13}\\ D_{12} & D_{22} & D_{23}\\ D_{13} & D_{23} & D_{33}\end{pmatrix}=\begin{pmatrix}-3.671 & 3.134 & 0.976\\ 3.134 & 3.797 & -0.532\\ 0.976 & -0.532 & 6.323\end{pmatrix}$$

Numerical expression of the ZFS tensor

$$\downarrow$$

Rotation matrix : **R** → Magnetic Axes

$$(\mathrm{D})=\begin{pmatrix}D_{XX} & 0 & 0\\ 0 & D_{YY} & 0\\ 0 & 0 & D_{ZZ}\end{pmatrix}=\begin{pmatrix}6.449 & 0 & 0\\ 0 & 4.920 & 0\\ 0 & 0 & -4.920\end{pmatrix} \longrightarrow \boxed{D=-10.60\,\mathrm{cm}^{-1},\ E=0.76\,\mathrm{cm}^{-1}}$$

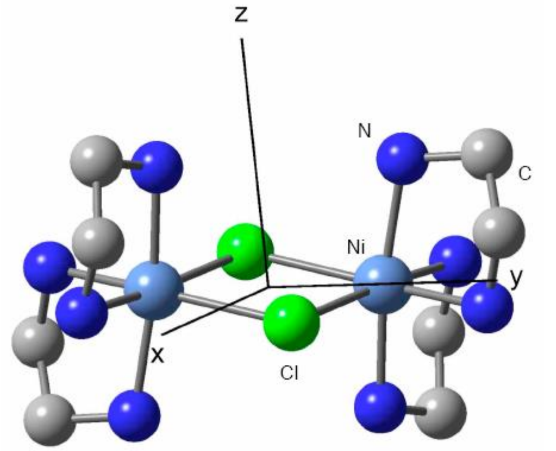
Not traceless

Bi-nuclear complexes : Giant-Spin and Multi-Spin Hamiltonians in the weak exchange limit

Giant-Spin Hamiltonian Reproduces the energy of a single spin state (ex: quintuplet)

$$\hat{H}^{GS} = \underbrace{\hat{\vec{S}}.\overline{\overline{D}}.\hat{\vec{S}}}_{} + \sum_{k=0,2,4} B_4^k \hat{O}_4^k = B_2^0\hat{O}_2^0 + B_2^2\hat{O}_2^2 + B_4^0\hat{O}_4^0 + B_4^2\hat{O}_4^2 + B_4^4\hat{O}_4^4$$

$$D = 3B_2^0 \text{ and } E = B_2^2$$



Multi-Spin Hamiltonian : reproduces the energy of all spin states of a spatial configuration Singlet, Triplet, Quintuplet

$$\hat{\mathbf{H}}^{MS} = \underbrace{J\hat{\mathbf{S}}_a.\hat{\mathbf{S}}_b}_{\text{Exchange Integral}} + \underbrace{\hat{\mathbf{S}}_a.\overline{\overline{\mathbf{D}}}_a.\hat{\mathbf{S}}_a + \hat{\mathbf{S}}_b.\overline{\overline{\mathbf{D}}}_b.\hat{\mathbf{S}}_b}_{\text{Local anisotropies}} + \underbrace{\hat{\mathbf{S}}_a.\overline{\overline{\mathbf{D}}}_{ab}.\hat{\mathbf{S}}_b}_{\text{Anisotropy of exchange}} + \cancel{\underbrace{\overline{\mathbf{d}}_{ab}\hat{\mathbf{S}}_a \wedge \hat{\mathbf{S}}_b}_{\text{Antisymmetric anisotropy}}}$$

Objectives:- to check the validity of these Hamiltonians for bi-nuclear complexes

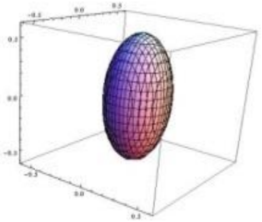
Main results concerning the Giant-Spin Hamiltonian ?

Stevens operators

$$\hat{H} = \underbrace{\hat{\vec{S}}.\overline{\overline{D}}.\hat{\vec{S}}}_{D = 3B_2^0 \text{ et } E = B_2^2} + \underbrace{\sum_{k=0,2,4} B_4^k \hat{O}_4^k}_{\text{Spin mixing ?}} = B_2^0 \hat{O}_2^0 + B_2^2 \hat{O}_2^2 + B_4^0 \hat{O}_4^0 + B_4^2 \hat{O}_4^2 + B_4^4 \hat{O}_4^4$$

I. The Giant Spin Hamiltonian for a bi-nuclear complex of Ni(II) can be used in the strong exchange limit (i.e. spin mixing is negligible, J is large).

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



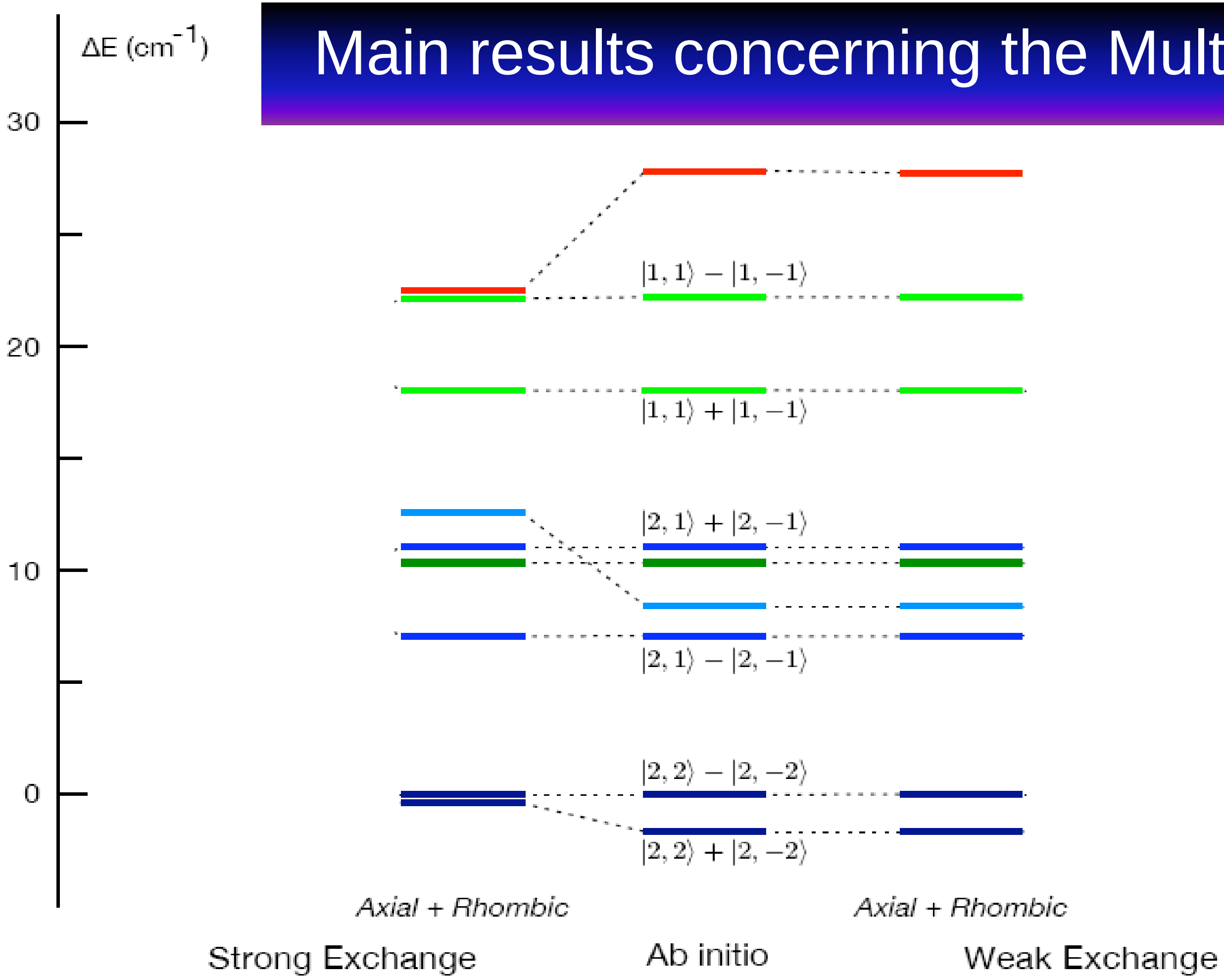
$D = 3/2\ D_{zz}$: axial parameter $E = 1/2\ (D_{xx} - D_{yy})$: rhombic parameter

In the proper magnetic axes frame, the ZFS tensor is diagonal:

→ Extraction of the easy or hard axes (or plane) of magnetization

This model can be used safely but the additional Stevens operator are not only necessary for treating the spin mixing with excited states!

Main results concerning the Multi- Spin Hamiltonian



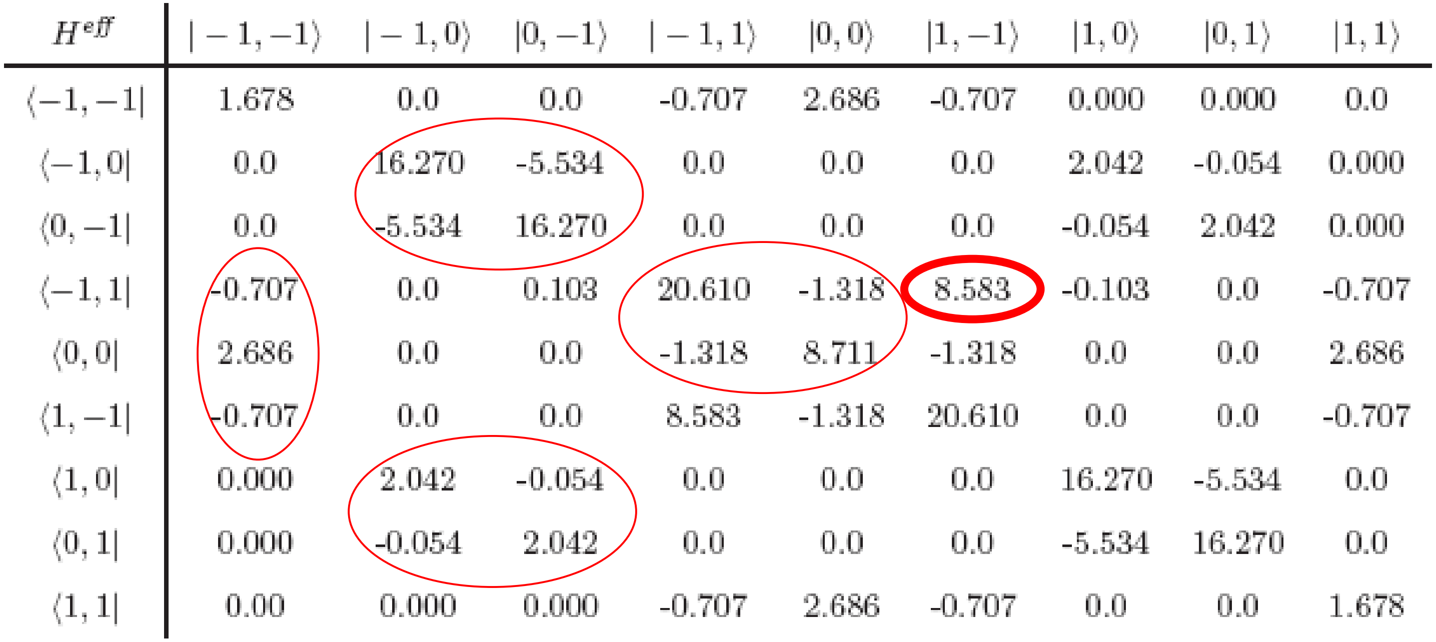
« fitted » parameters
from the spectrum only

(cm^{-1})	Axial + Rhombic	EPR	D_a fixed; J, D_{ab} fitted
J	+5.41	+9.66	+7.86
D_a,E_a	-9.43, 2.04	-4.78	-4.82
D_{ab},E_{ab}	0.36, -0.05	-0.64	-1.54
Errors %	0.07	-	7.1

Multi-spin Hamiltonian

|M_{Sa},M_{Sb}>	|-1,-1>	|-1,0>	|0,-1>	|-1,1>	|0,0>	|1,-1>	|1,0>	|0,1>	|1,1>
<-1,-1|	J+2/3D_a +2/3D_{ab}	0	0	E_a	E_{ab}	E_a	0	0	0
<-1,0|	0	-1/3D_a	J-1/3D_{ab}	0	0	0	E_a	E_{ab}	0
<0,-1|	0	J-1/3D_{ab}	-1/3D_a	0	0	0	E_{ab}	E_a	0
<-1,1|	E_a	0	0	-J+2/3D_a -2/3D_{ab}	J-1/3D_{ab}	0	0	0	E_a
<0,0|	E_{ab}	0	0	J-1/3D_{ab}	-4/3D_a	J-1/3D_{ab}	0	0	E_{ab}
<1,-1|	E_a	0	0	0	J-1/3D_{ab}	-J+2/3D_a -2/3D_{ab}	0	0	E_a
<1,0|	0	E_a	E_{ab}	0	0	0	-1/3D_a	J-1/3D_{ab}	0
<0,1|	0	E_{ab}	E_a	0	0	0	J-1/3D_{ab}	-1/3D_a	0
<1,1|	0	0	0	E_a	E_{ab}	E_a	0	0	J+2/3D_a +2/3D_{ab}

(cm^{-1})



H^{eff}	$\lvert -1,-1\rangle$	$\lvert -1,0\rangle$	$\lvert 0,-1\rangle$	$\lvert -1,1\rangle$	$\lvert 0,0\rangle$	$\lvert 1,-1\rangle$	$\lvert 1,0\rangle$	$\lvert 0,1\rangle$	$\lvert 1,1\rangle$
$\langle -1,-1\rvert$	1.678	0.0	0.0	-0.707	2.686	-0.707	0.000	0.000	0.0
$\langle -1,0\rvert$	0.0	16.270	-5.534	0.0	0.0	0.0	2.042	-0.054	0.000
$\langle 0,-1\rvert$	0.0	-5.534	16.270	0.0	0.0	0.0	-0.054	2.042	0.000
$\langle -1,1\rvert$	-0.707	0.0	0.103	20.610	-1.318	8.583	-0.103	0.0	-0.707
$\langle 0,0\rvert$	2.686	0.0	0.0	-1.318	8.711	-1.318	0.0	0.0	2.686
$\langle 1,-1\rvert$	-0.707	0.0	0.0	8.583	-1.318	20.610	0.0	0.0	-0.707
$\langle 1,0\rvert$	0.000	2.042	-0.054	0.0	0.0	0.0	16.270	-5.534	0.0
$\langle 0,1\rvert$	0.000	-0.054	2.042	0.0	0.0	0.0	-5.534	16.270	0.0
$\langle 1,1\rvert$	0.00	0.000	0.000	-0.707	2.686	-0.707	0.0	0.0	1.678

Proposition of an appropriate Multi-Spin Hamiltonian

- Confrontation of $\mathbf{H}^{\mathrm{eff}}$ to $\mathbf{H}^{\mathrm{mod}}$: invalidates $\mathbf{H}^{\mathrm{model}}$

$$\hat{H} = J\vec{S}_a.\vec{S}_b + \vec{S}_a\overline{\overline{D}}_a\vec{S}_a + \vec{S}_b\overline{\overline{D}}_b\vec{S}_b + \vec{S}_a\overline{\overline{D}}_{ab}\vec{S}_b + \vec{S}_a \otimes \vec{S}_a.\overline{\overline{\overline{\overline{D}}}}_{aabb}.\vec{S}_b \otimes \vec{S}_b$$

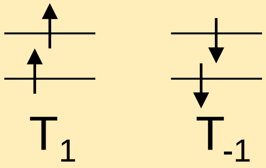
- Reproduces all differences between the effective and model Hamiltonians.
- The four-rank tensor matrix a priori has 81 elements.
- All tensors have their own magnetic axes frame. The extraction requires to introduce rotation matrices to reduce the number of parameters (proper axes of the tensor)
- The extraction of all relevant parameters is particularly difficult…

III. e Heisenberg Hamitonian for S=1

$$\hat{H} = \sum_{<ij>} J_{ij} \hat{\vec{S}}_i . \hat{\vec{S}}_j$$

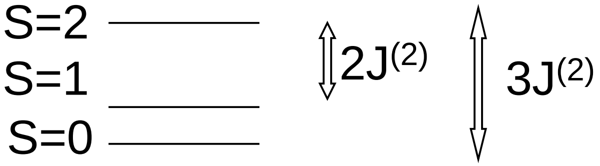
Model space constituted of products of atomic ground state

Ex: S=1



$S_0 = \{T_0 T_0 \;,\; T_{+1} T_{-1} \;,\; T_{-1} T_{+1}\}$

Spectre :


S=2

S=1

S=0

$2J^{(2)}$

$3J^{(2)}$

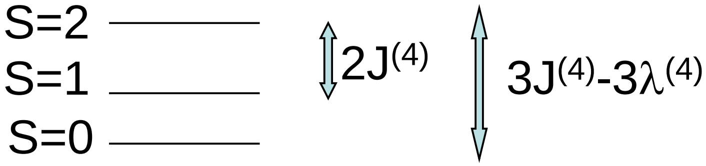
In come cases, one observes deviations to these spacings due to Higher order effects :

$$\hat{H} = J^{(4)} \hat{\vec{S}}_i . \hat{\vec{S}}_j + \lambda^{(4)} \left(\hat{\vec{S}}_i . \hat{\vec{S}}_j \right)^n$$

For S=1 : Biquadratic term

$$\hat{H} = J^{(4)} \hat{\vec{S}}_i . \hat{\vec{S}}_j + \lambda^{(4)} \left(\hat{\vec{S}}_i . \hat{\vec{S}}_j \right)^2$$

Spectre :


S=2

S=1

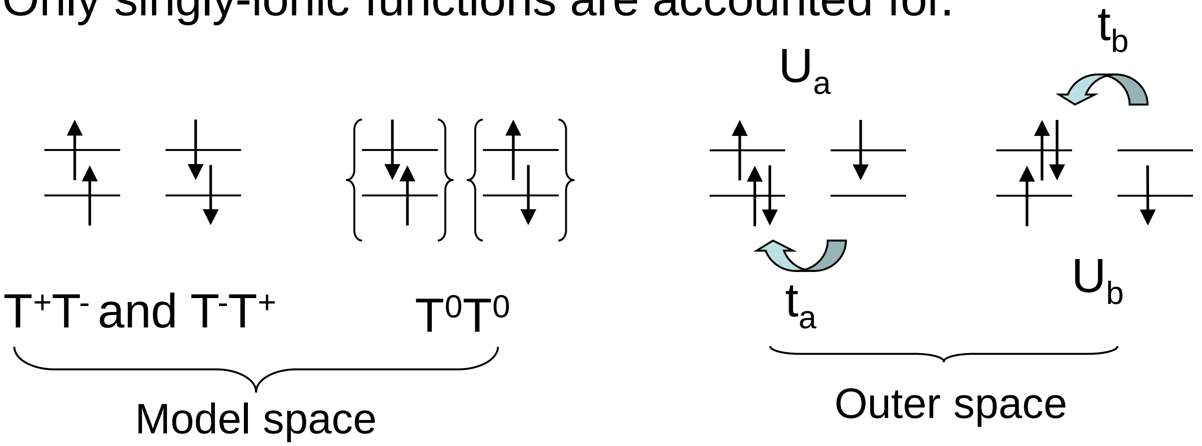
S=0

$2J^{(4)}$

$3J^{(4)}-3\lambda^{(4)}$

Physical content of the exchange integral at the 2nd order perturbation

Only singly-ionic functions are accounted for.



U_a t_b

t_a U_b

T^+T^- and T^-T^+ T^0T^0

Model space

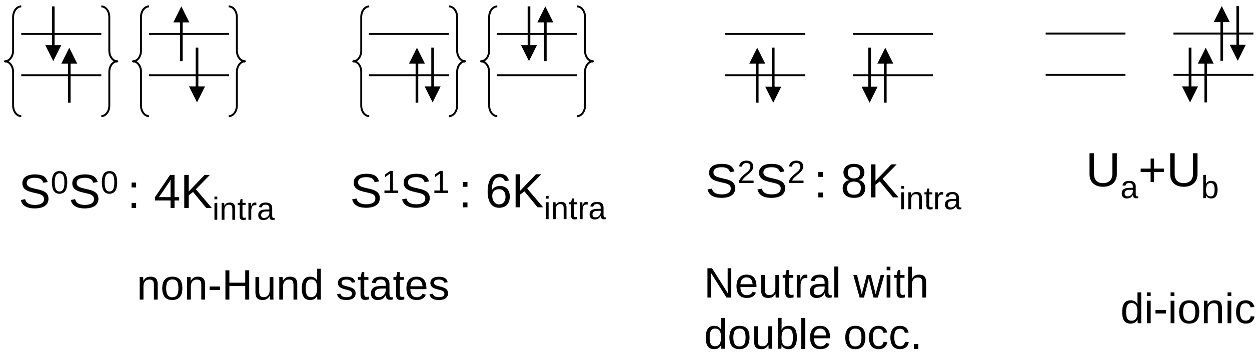
Outer space

$$J = -K^{eff} + \sum_i \frac{t_i^2}{U_i}$$

Where $K^{eff} = \sum_{\substack{i \in a_1, b_1 \\ j \in a_2, b_2}} K_{ij}$

Physical content of both the exchange integral and the biquadratic term : 4th order

The analytical derivation of the biquadratic operator requires to go up to the fourth order: It accounts for the coupling of the model space with ionic, neutral local non-Hund states and di-ionic functions



$S^0S^0 : 4K_{intra}$ $S^1S^1 : 6K_{intra}$

non-Hund states

$S^2S^2 : 8K_{intra}$

Neutral with double occ.

U_a+U_b

di-ionic

$$J = -K^{eff} + \left(\frac{t_a^2}{U_a} + \frac{t_b^2}{U_b} \right)$$

$$B = \left(\frac{t_a^2}{U_a} - \frac{t_b^2}{U_b} \right)$$

$$\left(\begin{array}{ccc|ccccccc|cccccccc|cc}
Q & T & S & N_1^{+*} & N_1^{-*} & N_2^{*} & N_3^{-*} & N_4^{*} & N_5^{*} & N_3^{+*} & I_{b1}^{+} & I_{b1}^{-} & I_{b2}^{+} & I_{b2}^{-} & I_{a1}^{+} & I_{a1}^{-} & I_{a2}^{+} & I_{a2}^{-} & DI^{+} & DI^{-} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -t_b & 0 & -t_b & 0 & -t_a & 0 & -t_a & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\sqrt{\frac{3}{2}}t_b & 0 & \sqrt{\frac{3}{2}}t_b & 0 & -\sqrt{\frac{3}{2}}t_a & 0 & \sqrt{\frac{3}{2}}t_a & 0 & 0 \\
\hline
0 & 0 & 0 & 2k & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 2k & 0 & 0 & 0 & 0 & 0 & t_b & 0 & t_b & 0 & -t_a & 0 & -t_a & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 4k & 0 & 0 & 0 & 0 & 0 & \frac{t_b}{\sqrt{2}} & 0 & -\frac{t_b}{\sqrt{2}} & 0 & \frac{t_a}{\sqrt{2}} & 0 & -\frac{t_a}{\sqrt{2}} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 4k & 0 & 0 & 0 & 0 & -\frac{t_a}{\sqrt{2}} & 0 & \frac{t_a}{\sqrt{2}} & 0 & -\frac{t_b}{\sqrt{2}} & 0 & \frac{t_b}{\sqrt{2}} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 6k & 0 & 0 & t_a & 0 & -t_a & 0 & -t_b & 0 & t_b & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6k & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 8k & 0 & -\frac{t_a}{\sqrt{2}} & 0 & \frac{t_a}{\sqrt{2}} & 0 & -\frac{t_b}{\sqrt{2}} & 0 & \frac{t_b}{\sqrt{2}} & 0 & 0 \\
\hline
0 & -t_b & 0 & 0 & t_b & 0 & 0 & t_a & 0 & 0 & U_b & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -t_a \\
0 & 0 & -\sqrt{\frac{3}{2}}t_b & 0 & 0 & \frac{t_b}{\sqrt{2}} & -\frac{t_a}{\sqrt{2}} & 0 & -t_a & -\frac{t_a}{\sqrt{2}} & 0 & U_b & 0 & 0 & 0 & 0 & 0 & 0 & -t_a & 0 \\
0 & -t_b & 0 & 0 & t_b & 0 & 0 & -t_a & 0 & 0 & 0 & 0 & U_b & 0 & 0 & 0 & 0 & 0 & 0 & t_a \\
0 & 0 & \sqrt{\frac{3}{2}}t_b & 0 & 0 & -\frac{t_b}{\sqrt{2}} & \frac{t_a}{\sqrt{2}} & 0 & 0 & \frac{t_a}{\sqrt{2}} & 0 & 0 & 0 & U_b & 0 & 0 & 0 & 0 & t_a & 0 \\
0 & -t_a & 0 & 0 & -t_a & 0 & 0 & -t_b & 0 & 0 & 0 & 0 & 0 & 0 & U_a & 0 & 0 & 0 & 0 & -t_b \\
0 & 0 & -\sqrt{\frac{3}{2}}t_a & 0 & 0 & \frac{t_a}{\sqrt{2}} & -\frac{t_b}{\sqrt{2}} & 0 & 0 & -\frac{t_b}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & U_a & 0 & 0 & -t_b & 0 \\
0 & -t_a & 0 & 0 & -t_a & 0 & 0 & t_b & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & U_a & 0 & 0 & t_b \\
0 & 0 & \sqrt{\frac{3}{2}}t_a & 0 & 0 & -\frac{t_a}{\sqrt{2}} & \frac{t_b}{\sqrt{2}} & 0 & 0 & \frac{t_b}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & U_a & t_b & 0 \\
\hline
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -t_a & 0 & t_a & 0 & -t_b & 0 & t_b & U_a+U_b & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -t_a & 0 & t_a & 0 & -t_b & 0 & t_b & 0 & 0 & U_a+U_b
\end{array}\right)$$

Physical content of the Hamiltonian at the fourth order of perturbations

$$\hat{H} = J^{(4)}\hat{S}_1\hat{S}_2 + \lambda^{(4)}\left(\hat{S}_1\hat{S}_2\right)^2$$

$$\begin{cases} J^{(4)} = J + \dfrac{B^2}{K} \quad \text{where} \quad J = J^{(2)} \\ \lambda^{(4)} = \dfrac{J^2}{2U_a} + \dfrac{J^2}{2U_b} + \dfrac{JB}{2U_a} + \dfrac{JB}{2U_b} + \dfrac{B^2}{K} - \dfrac{J^2}{4K} \end{cases}$$

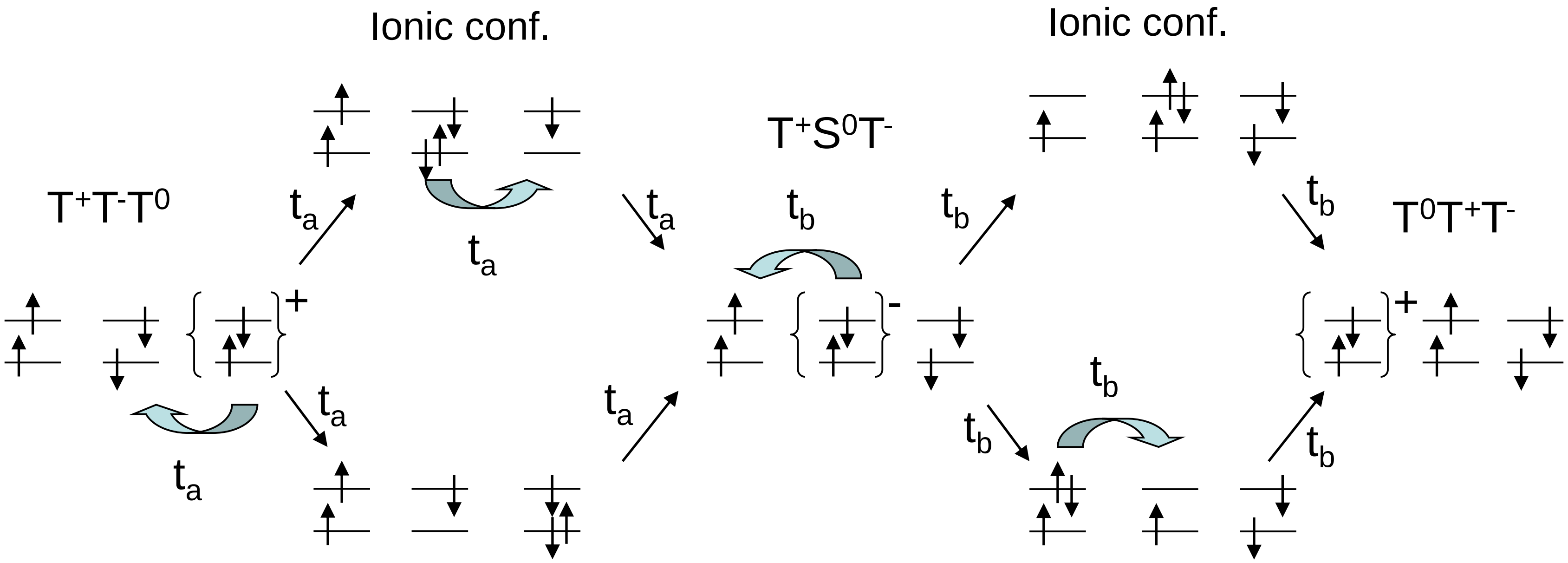
This Hamiltonian in only valid for bi-nuclear systems!

No transferability for the treatment of larger systems (materials) !

Hamiltonian for the treatment of larger systems : role of the three-body operator

$$\hat{H} = \sum_{<ij>} \left[\left(J_{ij} + \frac{B_{ij}^2}{K} \right) \hat{S}_i \hat{S}_j + \left(\frac{J_{ij}^2}{2U_a} + \frac{J_{ij}^2}{2U_b} + \frac{J_{ij} B_{ij}}{2U_a} + \frac{J_{ij} B_{ij}}{2U_b} + \frac{B_{ij}^2}{K} - \frac{J_{ij}^2}{4K} \right) \left(\hat{S}_i \hat{S}_j \right)^2 + \sum_{i,<jk>} \frac{B_{ij} B_{jk}}{2K} \left(\left(\hat{S}_i \hat{S}_j \right)\left(\hat{S}_i \hat{S}_k \right) + \left(\hat{S}_i \hat{S}_k \right)\left(\hat{S}_i \hat{S}_j \right) - \left(\hat{S}_i \hat{S}_i \right)\left(\hat{S}_j \hat{S}_k \right) \right) \right]$$

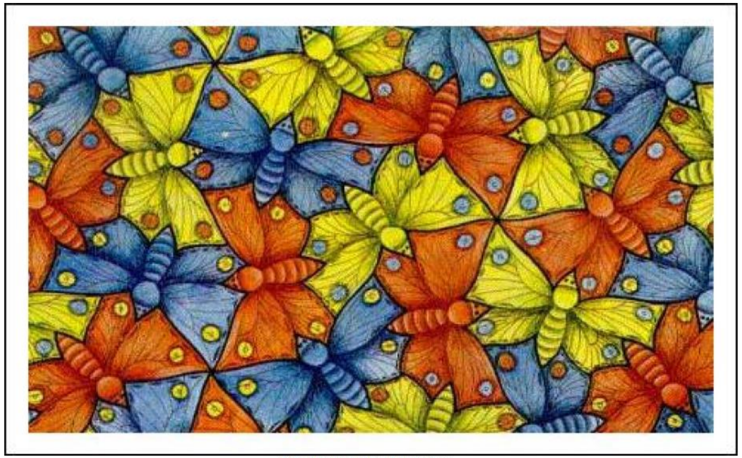
Physical content of the three-body operator introduces coupling such that :



4th order of perturbation but the essential contribution to the deviation

Extraction of magnetic Hamitonian for S=1 from WFT and DFT calculations

1) Using energies & wavefunctions (WFT)



§ Escher : symétrie 70 (papillons)

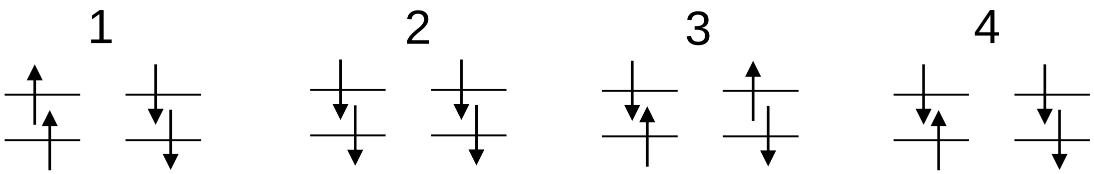
MRCI solutions are eigenfunctions of S^2

1. Calculation of the analytical model matrix (7*7 for a trimer of Ni)
2. Calculation of the numerical effective Hamiltonian matrix from both energies and wavefunctions.
3. Identification of the matrix elements
4. Resolution of the system of equations

→ Provide a value for all interactions, J, λ and B

Extraction of complex interactions from DFT calculations S=1 systems

2) Using the energies of broken symmetry DFT solutions and the derivation from Hubbard

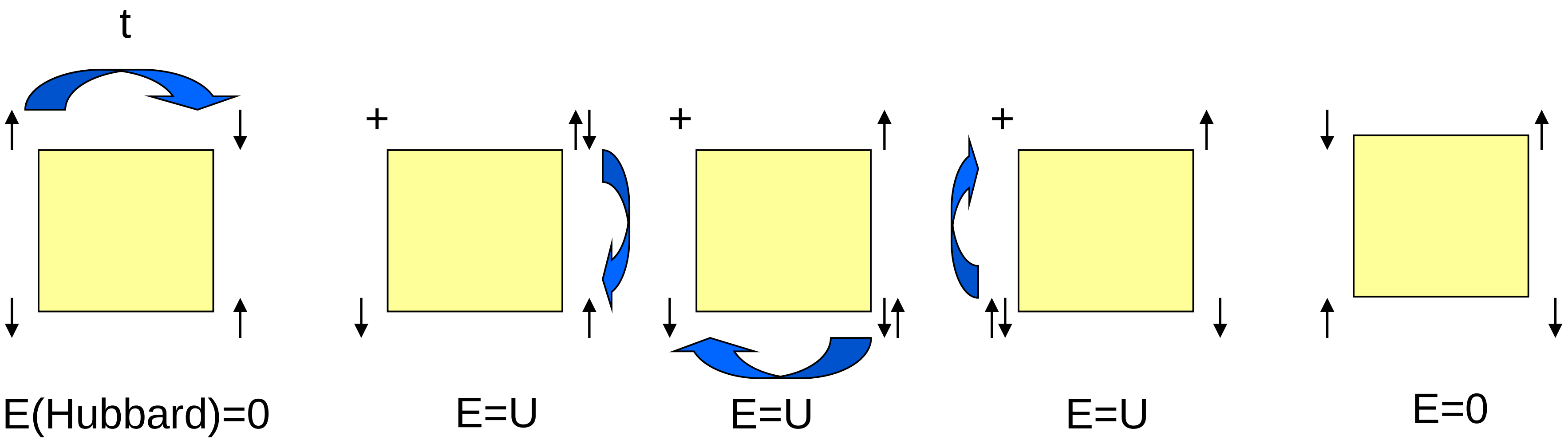


$$\left\{\begin{aligned} E_1 &= -2\frac{t_a^2}{U} - 2\frac{t_b^2}{U} \\ E_2 &= 0 \\ E_3 &= 2K \\ E_4 &= K - 2\frac{t_a^2}{U-K} \end{aligned}\right.$$

$$\left\{\begin{aligned} J &= -\frac{t_1^2}{U} - \frac{t_2^2}{U} - \frac{B^2}{K} \\ \lambda &= \frac{B^2}{K} - \frac{1}{K}\left(\frac{t_a^2}{U} + \frac{t_b^2}{U}\right)^2 \\ B &= \frac{t_a^2}{U} - \frac{t_b^2}{U} \end{aligned}\right.$$

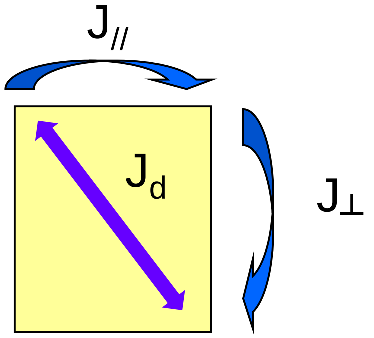
From the energy differences between the different solutions and the analytical equations all the interactions can be extracted except de spin polarization.

III. f Four-body spin mechanism



$$j_{ring} \propto 80 \frac{t^4}{U^3}$$

4th order of perturbation but numerous ! Same physical origin than the aromatic contribution in benzene rings!



Expression of the Hamiltonian

$$\hat{H} = -J\sum_{<ij>}^{NN}(\hat{S}_i\hat{S}_j - \frac{\hat{I}}{4}) - J_d\sum_{<ij>}^{NNN}(\hat{S}_i\hat{S}_j - \frac{\hat{I}}{4}) - J_r^{ijkl}\sum_{<ij>}^{NNN}\left[(\hat{S}_i\hat{S}_j)(\hat{S}_k\hat{S}_l) + (\hat{S}_i\hat{S}_l)(\hat{S}_j\hat{S}_k) - (\hat{S}_i\hat{S}_k)(\hat{S}_j\hat{S}_l) - \frac{\hat{I}}{16}\right].$$

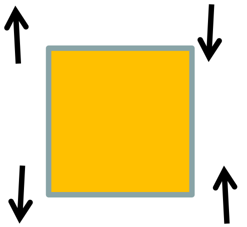
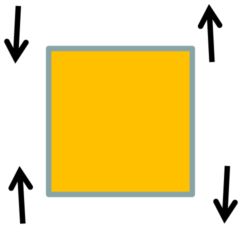
$$J_{r1} = J^{abcd}; J_{r2} = J^{adbc}; J_{r1} = J^{acdb}; A = (J_{r1} + J_{r2} - J_{r3})/8; B = (J_{r1} - J_{r2} + J_{r3})/8; C = (-J_{r1} + J_{r2} + J_{r3})/8$$

Extraction of the four-body spin interaction from WFT

J Escher : symétrie 70 (papillons)

1. Determination of the model matrix

$$\begin{array}{c}\langle|a\bar{b}c\bar{d}|| \\ \langle|\bar{a}b\bar{c}d|| \\ \langle|ab\bar{c}\bar{d}|| \\ \langle|\bar{a}\bar{b}cd|| \\ \langle|a\bar{b}\bar{c}d|| \\ \langle|\bar{a}bc\bar{d}||\end{array}\begin{pmatrix} J_{//}+J_{\perp} & \boxed{-J_{r1}/2} & -J_{//}/2+A & -J_{//}/2+A & -J_{//}/2+B & -J_{//}/2+B \\ & J_{//}+J_{\perp} & -J_{//}/2+A & -J_{//}/2+A & -J_{//}/2+B & -J_{//}/2+B \\ & & J_{//}+J_{d} & -J_{r2}/2 & -J_{d}/2+C & -J_{d}/2+C \\ & & & J_{//}+J_{d} & -J_{d}/2+C & -J_{d}/2+C \\ & & & & J_{d}+J_{\perp} & -J_{r3}/2 \\ & & & & & J_{d}+J_{\perp} \end{pmatrix}$$

Main coupling between :  and 

2. Calculation of the numerical matrix from the effective Hamiltonian theory and ab initio energies and wavefunctions.

3. Identification of the matrix elements → numerical values of the interactions

The largest interaction is J_{r1} (10 to 20% of the AF magnetic coupling for cuprate ladders).even if this is a 4th order effect

→ Crucial to conciliate experimental data in ladders

Extraction of the four-body spin interaction from DFT

1. Broken symmetry DFT solutions are computed for Ms=2, Ms=1, Ms=0
2. From the analytical expression of the energies of the different solutions all the interactions can be extracted.

$$E_{|abcd|} - E_{|abc\bar{d}|} = \frac{J_{//} + J_{\perp} + J_{d}}{3} + \frac{J_{r1}}{8}$$

$$E_{|abcd|} - E_{|a\bar{b}c\bar{d}|} = J_{//} + J_{\perp}$$

$$E_{|abcd|} - E_{|ab\bar{c}\bar{d}|} = J_{//} + J_{d}$$

$$E_{|abcd|} - E_{|a\bar{b}\bar{c}\bar{d}|} = J_{\perp} + J_{d}$$

3. Resolution of the system of equations

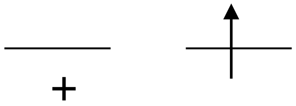
The DFT results are in agreement with WFT extraction in cuprate ladders for 33% of exact Fock exchange.in the B3JYP functional.

III. g Doping magnetic systems of spin s=1/2 with hole: t-J model Hamiltonians

Doped materials : a fraction x of n-valent counterions are substituted by n'-valent counterions

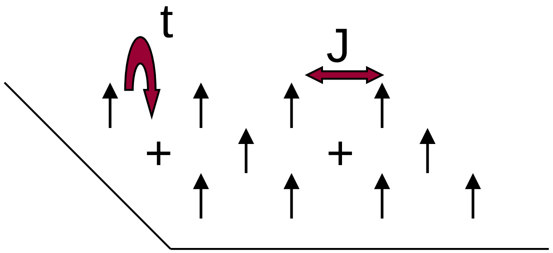
La_2CuO_4 : 2.(3+) +y +4.(2-)=0 $\longrightarrow$ y=2+ $\longrightarrow$ Formal oxydation degree : Cu(2+), Cu(II)

$La_{2-x}Ca_xCuO_4$: (2-x).(3+) +x(2+)+y +4.(-2)=0, if x=0.5 then Cu(2.5+)

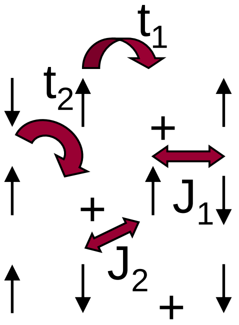


Introduction of holes in the lattice :

$$\hat{H} = \sum_{<ij>} t_{ij}\left(a_i^+ a_j + a_j^+ a_i\right) + J_{ij}\delta(\hat{n}_i + \hat{n}_j, 2)\hat{\vec{S}}_i\hat{\vec{S}}_j$$

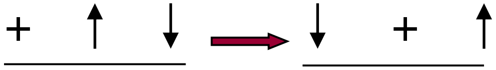


A refined t-J model has been extracted for cuprates which introduces additional operato

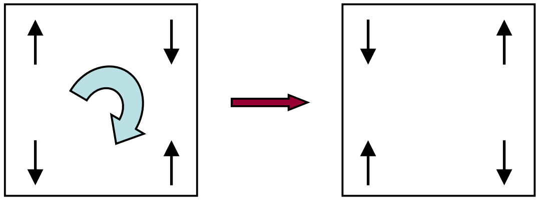


Hole-hole repulsion V, second neighbour interaction

Three body-operator : exchange transfer or singlet propagation



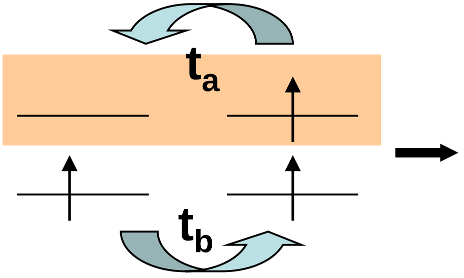
Four-body operator :

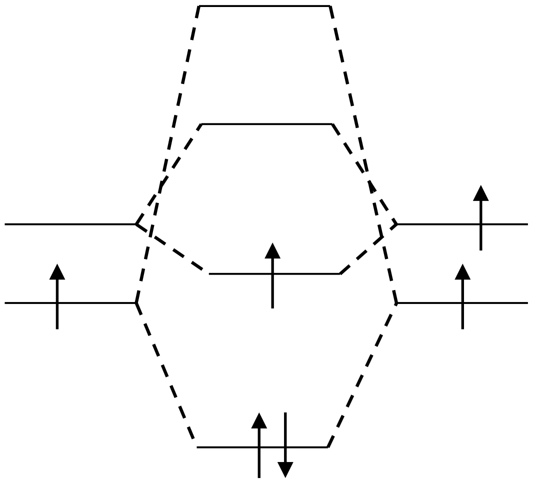


Dependance of the interactions on the position of the + charges of the surrounding…

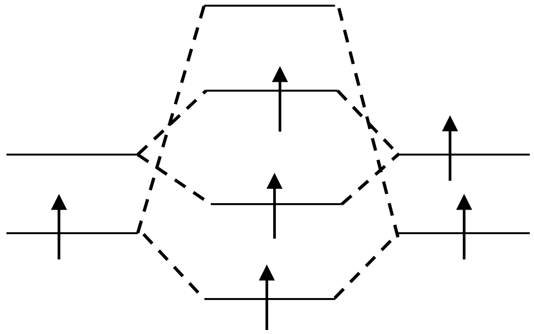
III. h Doping magnetic systems of spin s>1/2: the double exchange model :

Mixed valence system involving magnetic centers with several open shells



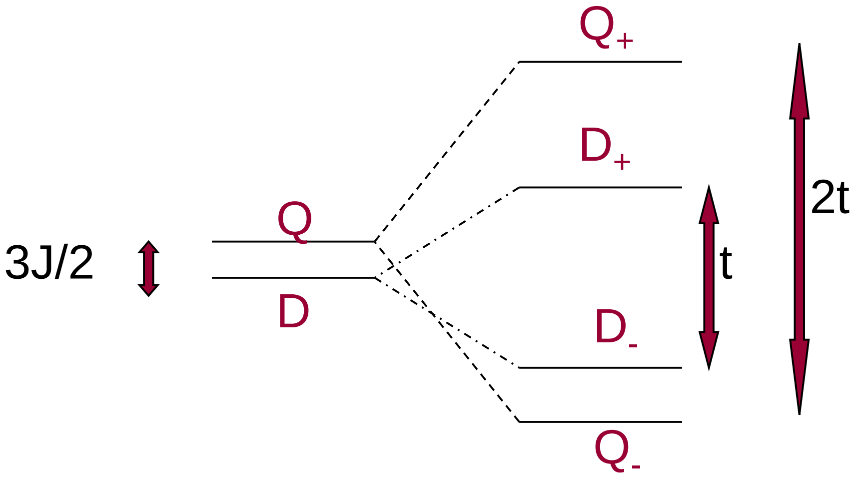


For strongly interacting centers one would expect a doublet ground state



For weakly interacting centers one gets a quadruplet ground state

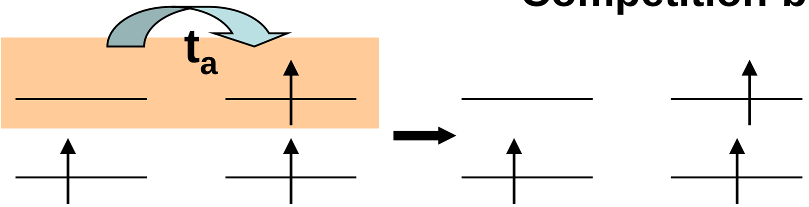
The spectrum contains 4 states, 2 quartet and 2 doublet states



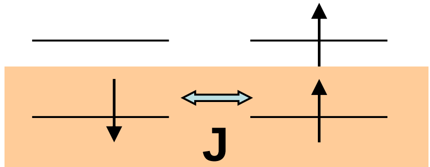
Doping magnetic systems of spin s>1/2 with holes : the usual double exchange model : Zener +Girerd Papefthymiou

Mixed valence system involving magnetic centers with several open shells

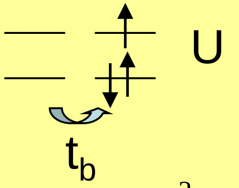
Model space constituted of products of atomic ground states
Competition between t and J



Due to the Hund's rule, the hopping induces a ferromagnetic order



The exchange integral (>0) favors an antiferromagnetic order



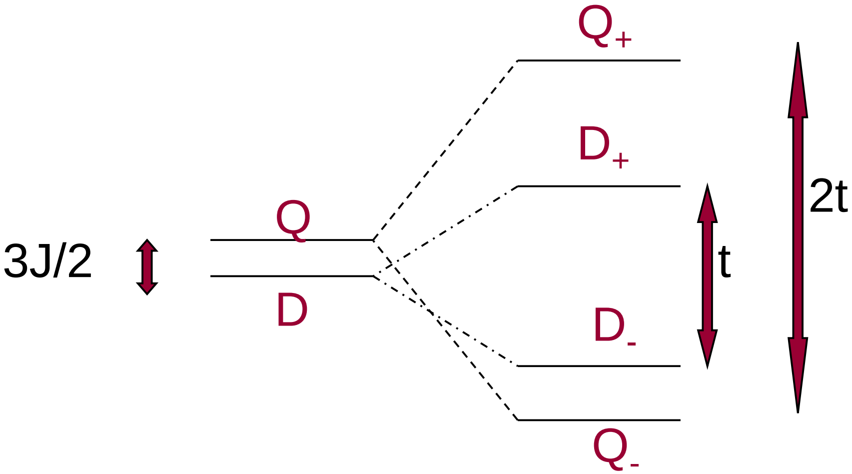
$$J \approx -\frac{2t_b^2}{U}$$

Solution for a dimer :

$$E_{S\neq S_{max}}(S,\pm) = \pm t\frac{(S+1/2)}{S_{max}+1/2} - \frac{J}{2}\left(S_{max}\left(S_{max}+1\right)-S\left(S+1\right)\right)$$

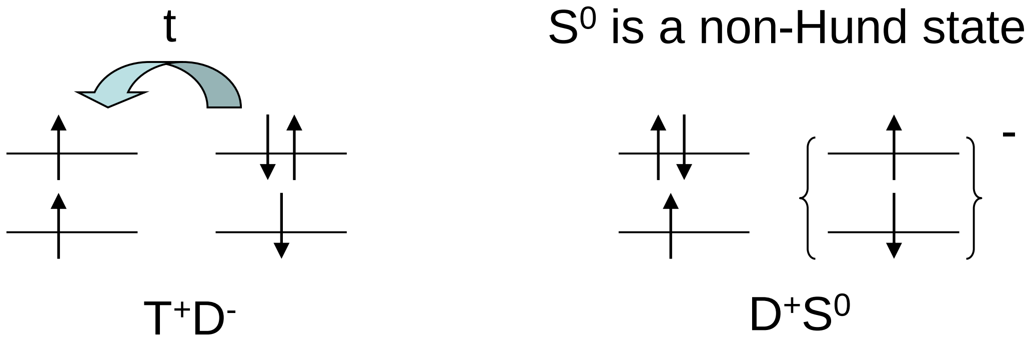
$$E_{S_{max}} = \pm t$$

The spectrum contains
4 states, 2 quartet and
2 doublet states



A double exchange model which combines the Anderson Hasegawa model and the antiferromagnetic contribution of Girerd and Papaefthymiou

Anderson and Hasegawa model considers the non-Hund states. The model space is enlarged to products of an excited atomic state by an atomic ground state.



S^0 is a non-Hund state

D^+S^0 is directly coupled to the model space of the usual DE model by a term proportional to t

$$E(S \neq S_{max}, \pm) = \frac{1}{2}\left[\Delta - \sqrt{\Delta^2 + 4t\left(t \mp \frac{S+1/2}{S_{max}+1/2}\Delta\right)}\right] - \frac{J}{2}\left[S(S+1) - S_{max}(S_{max}+1)\right] \qquad E(S_{max}, \pm) = \pm|t|$$

Δ is the energy of the non-Hund state functions

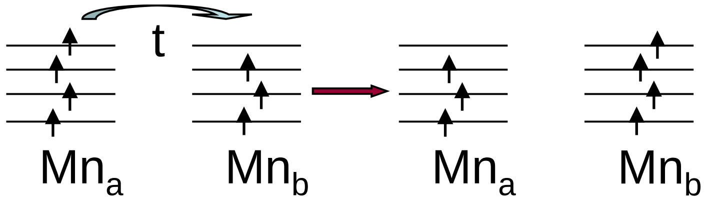
The usual model is inconsistent : $\Delta = 2K < U$

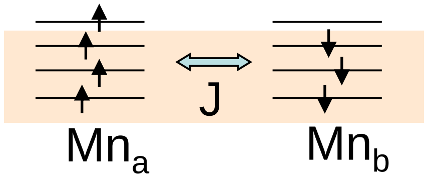
Here again it is possible to extract all the interactions from WFT (symmetry adapted solutions) and DFT (broken solutions)

III. i Versatility of model Hamiltonians : double exchange versus Heisenberg

1. Holes are localized on Mn sites

$Mn^{3.5+}O^{2-}Mn^{3.5+}$



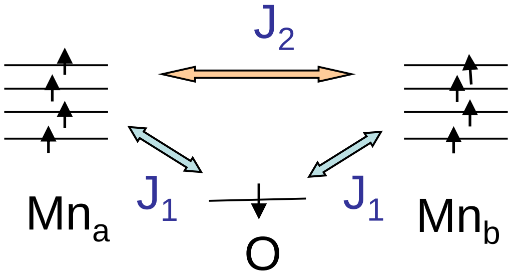


Double exchange :

$$E(S,\pm) = \pm t \frac{(S+1/2)}{S_{max}+1/2} - \frac{J}{2}\left(S_{max}(S_{max}+1) - S(S+1)\right)$$

2. Holes are localized on the bridging oxygens

$Mn^{3+}O^{-}Mn^{3+}$



J_1 : exchange integral between Mn and O

J_2 : exchange integral between 2 Mn sites

Heisenberg :

$$E(S,\pm) = \frac{(J_1 - J_2)}{2}\left[\frac{1}{2} \pm \left(S + \frac{1}{2}\right)\right] - \frac{J_2}{2}\left[S(S+1) - \frac{1}{2}(S^{H}_{max} - \frac{1}{2})^2 - \frac{3}{4}\right]$$

The two models lead to the same spectrum (except for the S=9/2 state which is not described in the double exchange model) !

Conclusions

- Model Hamiltonians can be analytically derived from the exact electronic Hamiltonian (or Hubbard Ham.) including SOC and the perturbation theory
  1. The physical content of effective interactions is known
  2. An order of magnitude of the interactions can be anticipated from the perturbation theory order to which they appear and the number of contributing mechanisms

- Owing to the effective Hamitonian theory, all these interactions can be extracted from the energies and wavefunctions computed *ab initio*
  1. The extraction is controlled: one knows the magnitude of the projections and all the matrix elements of the model Ham : the relevance of both the model space and the operator of the model can be rationally deduced..
  2. Model (effective) Hamiltonian can involve more than two-body operators.

- Model Hamiltonian are versatile, they can mimick different physics

Thank you for you kind attention !

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