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1 Introduction

For a long time theory has tried to match experiments, reproducing their results and trying to understand the mechanism at the origin of the different properties studied.

2 Model Hamiltonian

2.1 Spin Hamiltonian

The most well-know Spin Hamiltonian used to describe the magnetic interaction between a pair of spin located on different magnetic centres is the Heisenberg-Dirac-Van Vleck (HDVV) Hamiltonina, written as:

$$\hat{H}_{HDVV} = - \sum_{i,j} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \quad (2.1)$$

where $J_{i,j}$ is the coupling constant, $\hat{\mathbf{S}}_i$ and $\hat{\mathbf{S}}_j$ are the spin operators working on site i and j . Several conventions exist for this Hamiltonian, with negative sign and/or a factor of 2 in front. The coupling constant J can be either positive or negative depending on the magnetic properties of the system, a positive value indicate ferromagnetism with magnetic moment aligned while negative indicate antiferromagnetism with opposite alignment of magnetic moments. This Hamiltonian is regarded as a Spin Hamiltonian as it only invoke the spin degree of freedom of the system and is still to this day used in the description of the isotropic coupling in magnetic systems.

The J constant is defined as an effective integral as it involves several mechanisms:

- 1- Direct exchange originating from the exchange integral K .
- 2- Indirect exchange involving ionic determinants.
- 3- Super-exchange where a diamagnetic bridging ligand open new pathway for exchange mechanisms.

The origins and contributions of these mechanisms to the effective integral can be understood from the Hubbard Hamiltonian in the case of two electrons in two orbitals. Up to the second order perturbation theory, the following expression can be obtained for the effective integral J :

$$J = 2K - \frac{4t^2}{U} \quad (2.2)$$

Where K is the exchange integral which is always positive, t the hopping integral between the two orbitals and U the on site Coulomb repulsion. This expression shows

the competition between a ferromagnetic component (direct exchange $K>0$) and an antiferromagnetic one (indirect exchange). The contribution of super-exchange cannot be estimated at second-order and requires going up to fourth-order perturbation giving a similar expression:

$$J = 2K - \frac{4t_{eff}^2}{U} \quad (2.3)$$

Where t_{eff} is now an effective hopping integral involving the bridging ligand, the hopping term between metallic to ligand being much larger than the metallic to metallic one, the t term is usually neglected in this expression.

Ising Hamiltonian

The eigenfunctions of the Heisenberg Hamiltonian are eigenfunctions of the $\hat{\mathbf{S}}^2$ operator, making them mostly multi-determinantal functions which can only be obtained via specific computation method. To draw an easier picture, it is possible to restrict the spin vector to its component along the z axis alone.

$$H_{ising} = - \sum_{i,j} J \hat{\mathbf{S}}_{z,i} \hat{\mathbf{S}}_{z,j} \quad (2.4)$$

The magnetic moment of each lattice site are now considered to align themselves with the z axis at all time, taking a ± 1 value. The main advantage of this approximation is that the eigenfunctions of this Hamiltonian are now mono-determinantal functions opening up the extraction to new computation methods. It also reduces the analytical derivation allowing to work on larger systems without the need to diagonalize large matrices.

2.2 Mononuclear Anisotropy

Effects such as Spin-Orbit-Coupling (SOC) tend to create anisotropy in the system that cannot be described only by eq(2.1). More specifically on mononuclear systems (only one magnetic centre) with a ground state of spin larger or equal to one, a lift of degeneracy between the different M_S component of a same S state can be observed even in the absence of magnetic field, this phenomenon is called Zero-Field-Splitting. The associated Spin Hamiltonian is written:

$$\hat{H}_{ZFS} = \hat{\mathbf{S}} \cdot \overline{\overline{\mathbf{D}}} \cdot \hat{\mathbf{S}} \quad (2.5)$$

Where $\hat{\mathbf{S}}$ is the spin vector of the ground state and $\overline{\overline{D}}$ is a two rank symmetric tensor, in an arbitrary frame it is composed of six different parameters.

$$\overline{\overline{D}} = \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{xy} & D_{yy} & D_{yz} \\ D_{xz} & D_{yz} & D_{zz} \end{pmatrix} \quad (2.6)$$

This tensor can be reduced to three parameters by diagonalization, *i.e* expressing them in the the tensor principal axes that define the magnetic anisotropy axes. Going further as to work with traceless tensor allow us to use only two parameters, by convention the z-axis is taken as the main magnetic axis with D the axial parameter:

$$D = D_{zz} - \frac{1}{2}(D_{xx} + D_{yy}) = \frac{3}{2}D_{zz} \quad (2.7)$$

and the rhombic term:

$$E = \frac{1}{2}(D_{xx} - D_{yy}) \quad (2.8)$$

With $|D| \geq 3E \geq 0$. The ZFS Hamiltonian can then be written:

$$\hat{H}_{ZFS} = D(\hat{S}_z^2 - \frac{1}{3}\hat{S}^2) + E(\hat{S}_x^2 - \hat{S}_y^2) \quad (2.9)$$

A positive value of D indicates that the ground state is mainly composed of the $M_S=0$ component meaning that the projection of the spin moment along the z-axis is close to zero resulting in a easy-plane magnetism. On the contrary if $D<0$, the ground state is formed from the $M_S=\pm M_{Smax}$ components with a maximum projection of spin moment along the z-axis resulting in an easy-axis magnetism. For a ground state with spin larger than one and a half, other terms may appear but will not be reported in this work.

In the case of a triplet $S=1$ ground stat such as a nickel Ni (II) complex, the matrix representation of hamiltonian (2.5) in a random set of axis:

H_{ZFS}	$ 1, -1\rangle$	$ 1, 0\rangle$	$ 1, 1\rangle$
$\langle 1, -1 $	$\frac{1}{2}(D_{xx} - D_{yy}) + D_{zz}$	$-\frac{\sqrt{2}}{2}(D_{xz} + iD_{yz})$	$\frac{1}{2}(D_{xx} - D_{yy} + 2iD_{xy})$
$\langle 1, 0 $	$-\frac{\sqrt{2}}{2}(D_{xz} - iD_{yz})$	$D_{xx} + D_{yy}$	$\frac{\sqrt{2}}{2}(D_{xz} + iD_{yz})$
$\langle 1, 1 $	$\frac{1}{2}(D_{xx} - D_{yy} - 2iD_{xy})$	$\frac{\sqrt{2}}{2}(D_{xz} - iD_{yz})$	$\frac{1}{2}(D_{xx} + D_{yy}) + D_{zz}$

In the magnetic frame, this matrix becomes:

H_{ZFS}	$ 1, -1\rangle$	$ 1, 0\rangle$	$ 1, 1\rangle$
$\langle 1, -1 $	$\frac{1}{2}(D_{XX} + D_{YY}) + D_{ZZ}$	0	$\frac{1}{2}(D_{XX} - D_{YY})$
$\langle 1, 0 $	0	$D_{XX} + D_{YY}$	0
$\langle 1, 1 $	$\frac{1}{2}(D_{XX} - D_{YY})$	0	$\frac{1}{2}(D_{XX} + D_{YY}) + D_{ZZ}$

Removing the trace from the tensor and applying the convention from eq(2.7) and eq(2.8) we get:

$$\begin{array}{c|ccc} H_{ZFS} & |1, -1\rangle & |1, 0\rangle & |1, 1\rangle \\ \hline \langle 1, -1| & \frac{1}{3}D & 0 & E \\ \langle 1, 0| & 0 & \frac{2}{3}D & 0 \\ \langle 1, 1| & E & 0 & \frac{1}{3}D \end{array}$$

2.3 Polynuclear Anisotropy

Opening the study to multiple magnetic center introduces weak couplings between the magnetic moments of each center. This coupling between two sites A and B with a least of magnetic electron each, is called exchange interaction and is described by the following Giant Spin Hamiltonian.

$$\hat{H}_{AB} = \hat{\mathbf{S}}_A \cdot \overline{\overline{\mathbf{D}}} \cdot \hat{\mathbf{S}}_B \quad (2.10)$$

The spin-spin interaction tensor $\overline{\overline{\mathbf{D}}}$ behaves the same way as the D tensor from Zero Field Splitting and two parameters D and E can be defined similarly. This Hamiltonian is suitable for system with a ground state of spin larger or equal to one. It is also possible to study cases where mixing with low-lying excited states occurs by decomposing the tensor $\overline{\overline{\mathbf{D}}}$ in three component in the case of two unpaired electrons.

$$\hat{H}_{AB} = J(\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B) + \hat{\mathbf{S}}_A \cdot \overline{\overline{\mathbf{D}}}_{AB} \cdot \hat{\mathbf{S}}_B + \mathbf{d}_{AB} \cdot (\hat{\mathbf{S}}_A \times \hat{\mathbf{S}}_B) \quad (2.11)$$

Where the first term is the isotropic exchange, extending this coupling to more than two center this term becomes equivalent to the HDVV Hamiltonian from (2.1). The two following terms describe the anisotropic exchange with the symmetric tensor of exchange $\overline{\overline{\mathbf{D}}}_{AB}$ and the antisymmetric exchange \mathbf{d}_{AB} also called Dzyaloshinskii-Moriya pseudo-vector interaction. The matrix representation of two Cu^{2+} ions interacting is the following:

$$\begin{array}{c|cccc} H_{MS} & |1, -1\rangle & |1, 0\rangle & |1, 1\rangle & |0, 0\rangle \\ \hline \langle 1, -1| & \frac{J}{4} + \frac{D_{zz}}{4} & \frac{D_{xz}-iD_{yz}}{2\sqrt{2}} & \frac{(D_{xx}-D_{zz}-2iD_{xy})}{4} & \frac{d_y+id_x}{2\sqrt{2}} \\ \langle 1, 0| & \frac{D_{xz}+iD_{yz}}{2\sqrt{2}} & \frac{J}{4} - \frac{D_{zz}}{4} + \frac{(D_{xx}+D_{yy})}{4} & -\frac{D_{xz}-iD_{yz}}{2\sqrt{2}} & -\frac{id_z}{2} \\ \langle 1, 1| & \frac{(D_{xx}-D_{zz}+2iD_{xy})}{4} & -\frac{D_{xz}+iD_{yz}}{2\sqrt{2}} & \frac{J}{4} + \frac{D_{zz}}{4} & \frac{d_y-id_x}{2\sqrt{2}} \\ \langle 0, 0| & \frac{d_y-id_x}{2\sqrt{2}} & \frac{id_z}{2} & \frac{d_y+id_x}{2\sqrt{2}} & -\frac{3J}{4} - \frac{D_{zz}}{4} - \frac{(D_{xx}+D_{yy})}{4} \end{array}$$

From this matrix we notice that the Dzyaloshinskii-Moriya interaction create a coupling between the singlet with the three M_S components of the triplet state. As

for the symmetric tensor of anisotropic exchange, it only couples the three component of the triplet which undergo a splitting in energy. At the isotropic level, the difference between the triplet and singlet state is given by $\Delta E = J$, but with the inclusion of the anisotropic terms this becomes much more complex. As opposed to the Zero-Field Splitting mechanism, it is impossible to obtain values for these interactions from the energy spectrum only, as such they will be extracted from effective Hamiltonian theory. Note that now the application of this Hamiltonian is not restricted to a ground state with $S \geq 1$ but can be used for a singlet or doublet case. So far, we have assumed the colinearity of spin moments, the introduction of the antisymmetric exchange now favor a *spin canting* where the spin moment are no longer parallel or antiparallel resulting in weak ferromagnetism in otherwise antiferromagnetic systems.

For couplings involving more than one unpaired electron per site, local tensor are introduced:

$$\hat{H}_{AB} = J(\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B) + \hat{\mathbf{S}}_A \cdot \bar{\bar{\mathbf{D}}}_{AB} \cdot \hat{\mathbf{S}}_B + \mathbf{d}_{AB} \cdot (\hat{\mathbf{S}}_A \times \hat{\mathbf{S}}_B) \hat{\mathbf{S}}_A \cdot \bar{\bar{\mathbf{D}}}_A \cdot \hat{\mathbf{S}}_A + \hat{\mathbf{S}}_B \cdot \bar{\bar{\mathbf{D}}}_B \cdot \hat{\mathbf{S}}_B \quad (2.12)$$

All of these considerations are only possible in the strong exchange limit where the isotropic coupling is strong compared to the anisotropic interactions.

3 Methodology

All types of calculations discussed here after have for purpose to solve, in some way, the Schrodinger Equation:

$$\hat{H}\Psi_i = E_i\Psi_i \quad (3.1)$$

Where \hat{H} is an Hamiltonian used to describe the system studied, E_i is the energy associated to the wave-function Ψ_i . The solutions E_i of this problem are obtained pretty straightforwardly by diagonalizing the Hamiltonian except that in most cases, the Ψ_i vector are not known beforehand. The Hamiltonian discussed before is called exact electronic Hamiltonian as it encapsulate all the electronic and nuclear interaction of the system, it is written as follow in atomic units:

$$\hat{H} = -\sum_{i=1}^N \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|r_i - R_A|} + \sum_{i=1}^N \sum_{j<i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{|R_A - R_B|} \quad (3.2)$$

Where r_i is the position vector of the i th electron, R_A the position vector of the A th nucleus with atomic number Z_A and mass M_A . This Hamiltonian can be simplified in the context of the Born-Oppenheimer approximation, the electrons are considered

to adapt instantly to the movement of the nuclei, the latter's position can be fixed and taken out of the Hamiltonian. This approximation is justified with the fact that the electrons are much lighter than the nuclei.

$$\hat{H}_{elec} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|r_i - R_A|} + \sum_{i=1}^N \sum_{j<i}^N \frac{1}{|r_i - r_j|} \quad (3.3)$$

This Hamiltonian describes the electronic problem while the nuclei contribution is set aside in a constant, having for only effect a shift in the overall energy spectrum. While this greatly simplify the equations, it is still not solvable analytically and several approximations were developed to tackle this problem. One common point to all the methods that were used in this work rely on the construction of molecular orbitals (**MO**) as expansions of atomic orbitals (**AO**).

$$\psi_k = \sum_i c_i \phi_i \quad (3.4)$$

Where ψ_k is the k th MO built from the AO ϕ_i with the coefficient c_i . This expansion rely on a supposedly infinite number of AO but in real case application this is not achievable and will thus be restricted to a finite number of basis functions. As the electronic Hamiltonian does not include any information about spin, it will be included within a so called spin orbital with the introduction of two orthonormal function $\alpha(\omega)$ and $\beta(\omega)$, *i.e* spin up or down function, with ω an unspecified spin variable. From each spatial molecular orbital, two spin orbital can be created such that:

$$\chi_i = \begin{cases} \psi_i(r)\alpha(\omega) \\ or \\ \psi_i(r)\beta(\omega) \end{cases} \quad (3.5)$$

This definition for the spin orbital is well adapted for closed shell systems where all molecular orbitals are doubly occupied, the spatial part for any spin orbital is the same for both spin function defining the restricted formalism. Such definition changes when working with open shell system, *i.e* some orbitals are singly occupied necessitating the application of unrestricted formalism.

3.1 Hartree-Fock Method

The cornerstone of *ab initio* calculation in quantum chemistry is the Hartree-Fock method which is usually the initial step for computing a first approximation of the wave function in molecules. It is a variational approach that aims to treat the N-electron problems as problem of N non interacting electrons in the presence of an

average potential replicating interactions between them, it is in this sense a mean-field theory. This wave-function is constructed on the optimisation of a single Slater determinant Ψ :

$$\Psi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & \vdots & & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix} \quad (3.6)$$

Where χ_i are spin orbitals and the variable $x_i = \{r_i, \omega_i\}$, it involves all combination of all N electrons in all k spin orbitals. We introduce the shorthand notation for such determinant $\Psi(x_1, x_2, \dots, x_N) = |\chi_1 \chi_2 \dots \chi_k\rangle$ showing only the diagonal elements of the determinant.

The way to obtain the best adapted Hartree-Fock wave function comes through the resolution of the Roothan's equation:

$$FC = SC\epsilon \quad (3.7)$$

S is the overlap matrix of the basis function, ϵ the matrix of orbital energies and C is the matrix of the trial vector. The Fock operator F is defined as:

$$\hat{F}(i) = \hat{h}(i) + \sum_j^{N/2} [2\hat{J}_j(i) - \hat{K}_j(i)] \quad (3.8)$$

The core-Hamiltonian $\hat{h}(i)$ is a mono-electronic operator that contains the kinetic energy operator of the i th and coulomb repulsion with the fixed nuclei. The two bielectronic operator $\hat{J}_j(i)$ and $\hat{K}_j(i)$ describe the coulomb repulsion and exchange mechanism between the i th electron and the rest. These operator carry a direct dependance on the trial vectors from eq 3.7 as such, the Roothan's equation are non-linear and will be solved iteratively following a *Self Consistent Field* (SCF) procedure.

3.2 Complete Active Space Self Consistent Field

For most of magnetic systems, a single reference wave function is not enough as the system is usually not closed-shell and present one or more unpaired electron. Hence, its ground state is described by a wave function composed of several determinants. One of the most used method to introduce multiple reference in the wave function is called *Complete Active Space Self Consistent Field* (CASSCF). Compared to the Hartree-Fock theory where two types of orbitals (occupied and unoccupied) were considered, in CASSCF theory orbitals are separated in three sub-space. The

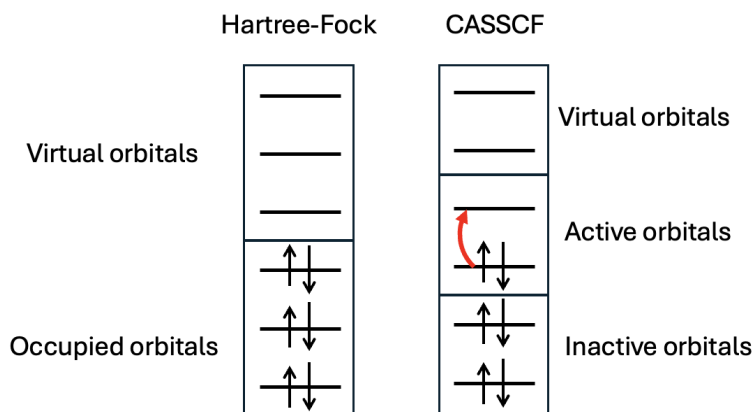


Figure 1: Difference between the orbitals space in Hartree-Fock and CASSCF Theory

inactive orbitals are doubly occupied throughout the calculation, virtual orbitals will stay empty while the active orbitals have a variable occupancy ranging from zero to two electrons. These active orbitals define the active space into which a configuration interaction will be realised computing all the determinants possible within this sub-space. As the number of determinant grows significantly with the number of orbitals included in the active space, this method is quite costly and its size becomes a limiting factor for the calculations. The new wave functions is now written as an expansion of Slater determinant which is obtained via a SCF procedure where both the expansion coefficients and orbitals are optimised as to minimize the Schrodinger Equation. This double optimisation scheme can render the convergence troublesome, as such the definition of the active space and the choice of the starting orbitals becomes crucial. One usually starts from a set of orbitals previously obtained via an Hartree-Fock calculation. For computation of magnetic properties in metallic systems, the minimum active space should consists of the magnetic orbitals, *i.e* the singly occupied d-orbitals of the metallic centers, this can later be extended to all of the 3-d orbitals of the metal as well as some orbitals of the ligands. As a result of the CASSCF method we obtain the energies of all states included in the calculation and a new set of orbitals into which they are expressed. This calculation takes into account the correlation between the electrons inside the active space in the mean field created by the other electrons. While this method provides the non-dynamical correlation, it fails to capture the correlation with the inactive electron and their reponse to excitations, called dynamic-correlation and the need to look further appears.

3.3 Perturbation Theory

Perturbative treatment can be applied to extract the dynamical correlation of the mono and diexcitations that is left out from simple CASSCF calculation. For such calculation, one can use the CASPT (Complete Active Space Perturbation theory) or the NEVPT (N-electron valence state perturbation theory). Both of these methods rely on the assumption that the Hamiltonian can be partitioned into a zeroth order term and a perturbation with the parameter λ :

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \lambda^2 \hat{H}^{(2)} + \dots \quad (3.9)$$

The wave function and energy are expanded in a similar way and the zeroth order term $\Psi_{(0)}^0$ is chosen to be the CASSCF wave function. The effect of the configurations outside of the active space on the energy and the wave function is estimated through perturbation theory and the expansions of the equations allows one to obtain the corrected energies usually at second order of perturbation with CASPT2 or NEVPT2. These two methods mainly differ from their choice of zeroth-order Hamiltonian, CASPT2 relies on a monoelectronic Hamiltonian built from a one electron Fock operator that falls back to the Moller-Plesset Hamiltonian in single reference case. This treatment may lead to what is called "intruder states" where low-lying states induce divergence in the denominator of the correction term where a difference of energy is taken. Several approaches have been adapted such as the introduction of a *level shift*, real or imaginary, as to fix this divergence. In case of NEVPT2, the zeroth-order Hamiltonian is a bi-electronic Dyal Hamiltonian which in itself includes a shift in energy between states from inside or outside the active space preventing the appearance of intruder states. One should add that this correlation is considered contracted as these methods do not act upon the coefficients inside the wave functions but only on the energies.

3.4 Difference dedicated configurational interaction

To get a full picture of the dynamic correlation one has to go to Multi-Referential-Configuration-Interaction (MRCI) methods. This method allows to introduce new determinants in the wave-function that do not belong to the CASSCF space, this way not only the energies but the wavefunction itself is revised. While very promising this method is not applicable to any real systems because of the number of determinants to include in the CI expansion, the cost of calculation becoming too high one has to truncate the MRCI space. Restricting the CI to all the simple and double excitations is still not feasible as they are too numerous, but some of them can be left out of the calculations. These excitations are classified into eight categories depending on the number of hole/particle created. A hole is an excitation from an inactive orbital to an

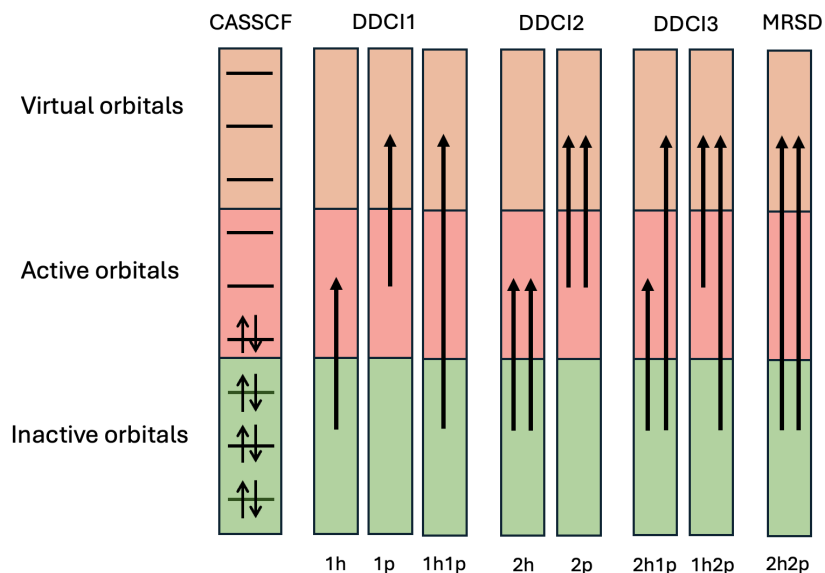


Figure 2: Classes of excitations and associated DDCI method

active or virtual orbital, while a particle is an excitation from an active or inactive orbital to a virtual one.

The most troublesome excitations are the one generating two holes and two particles (2h-2p) as they are the most numerous, but it can be shown at second order of perturbation that they do not contribute to the energy difference but only act as a shift of the diagonal energies. As such they can be neglected giving rise to a variant of MRCI called Difference-Dedicated-Configurational-Interaction (DDCI). Three sub-variant of DDCI exists taking into account different classes of excitation as pictured on fig... It has been established that the extraction of magnetic coupling involving bridging ligand requires the use of the DDCI3 method to provide good estimates.

3.5 Density functional theory

Another way to get a description of the electronic structure of is through density functional theory (DFT). The main interest of such method is the description of the ground state properties through the determination of the ground state energy E_0 following the variationl theorem

$$E_0 = \min \langle \Psi | \hat{H} | \Psi \rangle \quad (3.10)$$

Here, the electronic wavefunction of the molecule Ψ is approximated to a single Slater determinant obtained from the determination of the electronic density $\rho(\mathbf{r})$:

$$\rho(\mathbf{r}) = N \int |\Psi(\mathbf{x}_1 \dots \mathbf{x}_N)|^2 ds_1 dx_2 \dots dx_N \quad (3.11)$$

The Hamiltonian 3.3 can be written:

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ne} \quad (3.12)$$

with \hat{T} the kinetic energy operator, \hat{V}_{ee} the electron-electron interaction operator and \hat{V}_{ne} the nuclei-electron interaction operator. Solving the Shrod

by replacing $v_{ne}(\rho\mathbf{r})$ by a known external potential $v(\mathbf{r})$, one can obtain the ground state wave function Ψ by solving the Shrodinger equation giving the electron density follows. The first Hohenberg-Kohn theorem states that this external potential is an unique functional of the electron density. As such, knowing the electron density allows to determine the properties of the ground states. The second Hohenberg-Kohn gives in case of non degenerate ground state, the wave function Ψ is itself a functional of $\rho()$ which allow to define the total energy:

$$E[\rho] = F[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \quad (3.13)$$

with $F[\rho]$ an universal density functional which contain the kinetic and potential contributions. The ground state energy E_0 is the minimum of eq 3.13 which is reached when the electron density is that of the ground state $\rho_0(\mathbf{r})$. In theory the knowledge of the electron density allows to determine E_0 , however the density dependence expression of $F[\rho]$ is not known.

$$F[\rho] = T[\rho] + V_{ee}[\rho] \quad (3.14)$$

Kohn and Sham introduced new definition of this functional by replacing the interacting system with a fictitious system of N non interacting electrons. The functional becomes:

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \quad (3.15)$$

Where $T_s[\rho]$ is the non interacting kinetic energy functional of density ρ expressed in the basis of $\phi_i(\mathbf{r})$ that are built to reproduce the ground state density $\rho(\mathbf{r})$.

$$\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2 \quad (3.16)$$

$$T_s[\rho] = \sum_i^n \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle \quad (3.17)$$

The Hartree-potential $J[\rho]$ gives the coulomb repulsion between electrons pair:

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (3.18)$$

The energy expression eq 3.13 finally becomes:

$$E[\rho] = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + T_s[\rho] + J[\rho] + E_{xc}[\rho] \quad (3.19)$$

This definition gives the exact energy given that the expression of the Exchange-Correlation is known, unfortunately this is not the case. Over the years multiple attempts have been made to find an universal expression of E_{xc} in terms of ρ and its derivative. In the most basic approach, called Local Density Approximation (LDA), the system is taken to behave as a uniform electron gas where E_{xc} depends only in the density ρ . This model was later adapted to study different spin configuration with the Local Spin Density Approximation (LSDA). Other attempts tried to improve the functional by incorporating a dependance in the derivative of ρ with the Generalized Gradient Approximation (GGA) or a small portion of the Hartree-Fock exact exchange in what is called hybrid functionals.

3.6 Embedded Cluster Method

In the case of molecules, the study of magnetic anisotropy is well described by single molecule calculations as these interactions are localised between the metallic centers and ligands. The restricted size of the molecule generally allows for an explicit treatment of all the atoms involved. The same cannot be said about cristalline systems which are considred infinite but cannot be treated that way by the methods chosen in this work, as such we have to work on smaller part called "cluster" or "fragment". In theory one would want the fragment to be as large as possible to reduce the error created by cutting off the fragment of its environment, unfortunately to reduce computational cost we have to limit ourselves with small sized fragments. It then becomes crucial to chose correctly the fragment based on our knowledge of the physics we want to include. The properties of the cluster alone differ from the one inside its natural environment, to reproduce them accurately it is immersed inside an embedding. This embedding is composed of point charges that aim to replicate the electrostatic field of the crystal inside the cluster region, called Madelung Field. To keep the symmetries of the crystal, the point charges are positionned at the lattice site in a sphere of radius R_c .

Another problem in selecting fragments in ionic crystal is the overall charge of the fragment. The centre of the study is the metallic ions, charged positively, forming ionic bonds with negatively charged ligand. A correct description of these magnetic

centre requires to include all closest neighbors which makes the overall fragment negatively charged. The ions at the border of the fragment, replaced by point charges, are then positive. This induces a polarization of the electron density of the anions bordering the cluster. To avoid the electrons escaping the fragment, pseudo-potentials are placed at the lattice sites near the fragment to act as walls which prevent electrons from approaching these positive charges as if they were real atoms.

Two procedure were explored to create such embedding:

- (1) Formal charges were used in a sphere with very large R_c (around 50 Å).
- (2) Optimised point charges were obtained using Ewal Summation from formal charges, this allows to reduce the R_c to a few angstrom around the fragment.

These potentials are called Total-Ion-Potentials (TIPS) and can be either *ab initio* model potential (AIMP) or Effective Core Potential (ECP) depending on which Quantum chemistry software is used. All of this is done to ensure that the properties extracted from the fragment, *i.e* a finite system, are a good representation of the crystal properties, *i.e* an infinite system.

3.7 Effective Hamiltonian

Having ways to compute the *ab initio* multi reference wave functions usually leads to lengthy expression where the wave function is spanned along a large number of Slater determinant making its analysis complicated. On the other hand, the model Hamiltonian work in a much smaller space where a small number of electrons is used to introduce effective interactions. A way to connect the two Hamiltonians is to apply a theory developped by Bloch called Effective Hamiltonian theory. Its purpose is to build an effective Hamiltonian whose eigenvalues reproduce the energy spectrum of the *ab initio* Hamiltonian but using a much smaller number of eigenfunctions.

Starting from the Schrodinger equation with the Born-Oppenheimer Hamiltonian \hat{H} :

$$\hat{H} |\Psi_m\rangle = E_m |\Psi_m\rangle \quad (3.20)$$

Where Ψ_m are the eigenvectors with the associated eigenvalue E_m forming the space S of size N . We define a smaller space S_0 with N_0 states, this space is usually composed of the low lying state where the model Hamiltonian will be developped. An effective Hamiltonian H_{eff} is built to reproduce the energy spectrum of the exact Hamiltonian in the target space S_T using a small number of low-lying states $\tilde{\Psi}_m$ such that:

$$\hat{H}_{eff} |\tilde{\Psi}_m\rangle = E_m |\tilde{\Psi}_m\rangle \quad (3.21)$$

This target space S_T is chosen to be the same as the model space S_0 . The first step is to project the eigenfunctions Ψ_m onto the model space using the projector:

$$\hat{P}_0 = \sum_m^{N_0} |\tilde{\Psi}_m\rangle \langle \tilde{\Psi}_m| \quad (3.22)$$

$$|\tilde{\Psi}_m\rangle = \hat{P}_0 |\Psi_m\rangle \quad (3.23)$$

These eigenvectors are not necessarily orthogonal leading to a non-Hermitian Hamiltonian, this is problematic when comparing to the model Hamiltonians which are Hermitians. In this work, we apply the formalism proposed by Des Cloizeaux where the vectors are symmetrically orthonormalized from the overlap matrix S :

$$|\tilde{\Psi}_m^\perp\rangle = S^{-1/2} |\tilde{\Psi}_m\rangle \quad (3.24)$$

At this point, it is possible to check the quality of the target space by calculating the norm of the projected vectors. If too small, the interactions of the system are not captured correctly by the model space making it inadequate.

When these projections are close to one, we can consider the model space adequate, the effective Hamiltonian is then built:

$$H_{eff} = \sum_m^N |\tilde{\Psi}_m^\perp\rangle E_m \langle \tilde{\Psi}_m^\perp| \quad (3.25)$$

Once this is done, this numerical matrix H_{eff} constructed from the *ab initio* exact Hamiltonian are compared to the model Hamiltonian representation matrix. This allows for the extraction of values for the model Hamiltonian parameters as well as a test of validity. If there is too much deviation between the two matrices, it is possible that there is some missing interaction in the model.

4 Impact of the electric field on the ZFS parameter

5 Electric field on Exchange anisotropy

6 Herbertsmithite

6.1 Isotropic component

6.2 Anisotropy