



Treball Final de Grau

Spin-crossover transition metal complexes as candidates to single-molecule devices.

Complexes metà·lics amb transició d'espí com a candidats per a dispositius electrònics unimoleculars.

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It is not the possession of truth, but the success which attends the seeking after it, that enriches the seeker and brings happiness to him.

Max Plank

I would like to express my very great appreciation:

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And last, but not least, to my father, who has always had faith in me.

REPORT

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1. SUMMARY

Recently, spin-crossover complexes have been especially appealing due to their electron transport ability amongst other useful properties. By switching its spin state this conductance can be modified, even cancelled. Thus, SCO complexes can be used in new electronic and spintronic devices, such as memories, nanoparticle electronics and single-molecule devices by changing their spin state by many external stimuli, such as temperature, pressure or light, which are truly easy controllable parameters. This work focuses on mononuclear coordination complexes taking into consideration different metallic centres (Fe^{II} , Co^{II} , Cr^{II} , Mn^{III} and Mn^{II}) to gather information about their conducting ability. The study has been performed using Density Functional Theory (DFT) methods with six different exchange-correlation functionals (B3LYP, B2PLYP, TPSSh, OPBE, M06 and ω B97x) in order to compare their accuracy in the estimation of the energy difference between high- and low-spin states. Hence, a universal functional for any metallic complex can be defined, as until now only Fe^{II} systems have been exhaustively studied in the spin transition field. Results obtained show that for the thirteen compounds studied, the functional that has best performed is the hybrid TPSSh. One of the Fe^{II} compounds studied, $[\text{Fe}(\text{amp})_2\text{Cl}_2]$, has been found to be the best candidate to become a single-molecule device, generating a β -polarised current when a differential of potential is applied. Otherwise, the other compounds researched showed a mediocre conducting ability. Therefore, further research is required in order to obtain more potential candidates to become single-molecule devices.

Keywords: DFT, spin-crossover, molecular electronics, coordination chemistry.

2. RESUM

Recentment, els compostos de coordinació que presenten transició de spin han esdevingut un tema de gran interès degut a la seva infinitat d'aplicacions en el camp del transport electrònic, entre altres. El fet de canviar la multiplicitat del sistema pot aportar grans canvis a la conductivitat elèctrica fins al punt d'arribar a suprimir-la. Aquests canvis de comportament aporten un gran ventall d'aplicacions diferents, com ara en memòries, nanopartícules i dispositius monoelectrònics on un estímul extern pot generar la transició del sistema. Aquest treball es basa en complexos metàl·lics mononuclears que poden canviar la seva configuració mitjançant canvis de temperatura. Degut a què fins ara només s'han estudiat en profunditat els nuclis de Fe (II), en aquest estudi es contemplen diferents nuclis metàl·lics: a més de Fe^{II}, Co^{II}, Cr^{II}, Mn^{III} i Mn^{II}. Els càlculs d'estimació energètica entre els sistemes d'spin alt i spin baix s'han dut a terme mitjançant sis funcionals de correlació-intercanvi del mètode del Funcional de la Densitat (DFT) (B3LYP, B2PLYP, TPSSh, OPBE, M06 i ωB97X) per tal de realitzar també un estudi comparatiu de la precisió i l'eficiència d'aquests funcionals amb complexos de coordinació mononuclears diferents al Fe^{II}, doncs fins l'actualitat compostos amb aquest centre metàl·lic han estat àmpliament estudiats, però no hi ha un únic funcional òptim definit per a qualsevol nucli metàl·lic en compostos de coordinació que presenten transició de spin. Els resultats obtinguts a l'estudi mostren que el funcional que millor ha funcionat pels cinc diferents nuclis ha estat el TPSSh, un funcional híbrid amb baixa contribució tipus Hartree-Fock. De tots els sistemes estudiats, el compost [Fe(amp)₂Cl₂] és el que presenta millor conductivitat, el qual genera una corrent polaritzada β quan una diferència de potencial és aplicada. Pel contrari, sistemes amb un nucli metàl·lic diferent presenten una capacitat per a conduir mediocre, tot i que acceptable, amb el qual es proposa seguir investigant en aquesta línia per tal de trobar més candidats potencials per a esdevenir dispositius unimoleculars.

Paraules clau: DFT, spin-crossover, molecular electronics, coordination chemistry.

3. INTRODUCTION

3.1. SPIN CROSSOVER

In some cases, coordination compounds show a special molecular diagram with small energy differences between ground and excited states, consequently causing a wide set of singularities in their chemical and physical behaviour that other kinds of molecules do not present. For instance, coordination of one or more ligands to a metallic central ion implies a loss of degeneration on the d orbitals of the metallic ion. This splitting caused by the interaction with ligands is usually indicated as Δ_0 or as $10Dq$ in compounds with octahedral geometry.¹ One of these special features of coordination compounds is spin crossover (SCO) or spin transition. (See Fig. 1) The existence of a first excited state with a spin multiplicity different of the ground state generates a switching phenomenon where the central transition-metal ion changes its spin state due to a rearrangement of the electrons in its molecular orbitals.

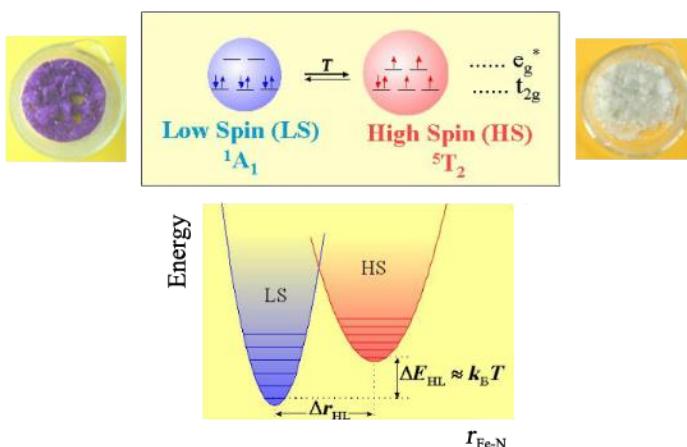


Figure 1. (Top) Change of electron configuration between LS and HS states of an octahedral Fe(II) coordination compound exhibiting thermal SCO. The orbitals are consequence of a splitting of the 3d orbitals in an octahedral ligand field. Depletion of charge in the antibonding e_g^* orbitals during HS to LS transition shortens the metal-to-ligand bond distances. SCO presents a change in colour. (Bottom) Representation of HS and LS ground states. (Image taken from Gütlich *et al.*, ref. 5).

Therefore, the electronic configuration of the metallic centre changes, implying a modification of many other structural features such as bond distances and angles, colour, magnetic and electronic behaviour, etc. In other words, this property allows having two molecules with different parameters in one, that is, a bistable system. There are many ways of inducing changes of spin state. The most common is the variation of the temperature, commonly known as thermally induced SCO, but many other external stimuli can be easily controlled in order to get the same result, such as changes in pressure or irradiating the molecule with light. As a consequence, many physical features of the molecule become modified. Bond distances and angles, magnetic properties, physical appearance as colour, etc. are the most notable and important changes. An increase in temperature favours the stability of the high-spin state in electronic (higher multiplicity, Hund's rule) and vibrational entropic terms (weaker metal-ligand bonds), namely the entropic contributions compensate the enthalpic contribution favourable to a low-spin state. The temperature where this bistable system reaches the equilibrium is known as $T_{1/2}$, therefore corresponds to the transition of half of the molecules.² Also, it is worth noting that electric fields (or currents) can also induce the spin transition. This feature is especially important in Molecular Electronics because, in order to design devices from the technical point of view, as the switching can be easily controlled while using magnetic fields or light, is not possible a single-molecule control.³

SCO compounds were discovered on the early 1930s by Cambi and co-workers, who reported an unusual behaviour of magnetic properties in iron(III) complexes.⁴ The occurrence of spin transition relies on the strength of the ligand field and the mean spin-pairing energy. Octahedral complexes of d^{4-7} ions can be either high spin or low spin compounds, depending on the crystal field strength Δ_0 . However, this value differs for the same transition metal due to the effect of the ligands coordinated to it. The ability a ligand has for splitting the degenerated d orbitals of the metal ion will determine its spin state. In the same manner, the metal itself has a strong dependence with its spin state, as its oxidation state and its effective attraction force can increase or decrease the ligand field strength. Therefore, there are practically no SCO examples of 4d and 5d metals, as Δ_0 increases up to 50% from 3d to 4d elements, but spin-pairing energy does not change that roughly. On that way, 4d and 5d transition-metal complexes tend to adopt LS states, having no possibility of switching their spin state. Another fact that should be taken into consideration is that tetrahedral SCO complexes of 3d elements are not known. The reason why this happens is that the ligand field strength of Td complexes is

about the half of Oh complexes ($2\Delta_T \approx \Delta_0$) and hence Td compounds tend to adopt HS states. All in all, these leaves us with the fact that only 3d transition-metal cores with d⁴⁻⁷ configuration with an octahedral geometry present this bistable behaviour, as there exists a favourable competition between the ligand field stabilization energy and the mean spin-pairing energy.¹⁴ Spin transitions are categorized in terms of magnetic susceptibility χ or molar fraction of high spin molecules γ_{HS} as a function of temperature. Therefore, the transition can be gradual, abrupt, with hysteresis (that is, with two different transition temperatures for the back and forth paths), step-wise or even incomplete.⁵

Gradual transitions occur when the ground state and the first excited state energies are very similar when due to the inclusion of a magnetic field. Therefore, the gradual scheme is due to the change of population between both states while the spin is switching. Abrupt transitions take place when the transition energy between the ground state and the first excited state equals the spin isomerism enthalpy between both spinomers. On the other hand, hysteresis cycles occur when a strong cooperativity exist between a given transition-metal core with other molecules, that is to say, when an intense communication is present between neighbouring metal compounds. Hysteresis reflects a remarkable structural change of the compound in solid state, as it exists a tendency to maintain the same spin state that neighbouring molecules have (cooperativity). If a given system has a strong cooperativity, it presents a wide hysteresis loop, since there is a lack of space between the changing molecule and the nearest neighbouring molecules. This means the systems requires more energy in order to convert all of its molecules, as there is no space enough for them to swap their spins and, therefore, rearrange their structure at the same temperature. In general terms, gradual transitions appear in solution, whereas abrupt transitions have a different dependence with temperature due to the cooperative interactions. Actually, great difference in shape between HS state and LS state can be kinetically inhibited, hence, these compounds won't show SCO even though their electronic structure allows it.³

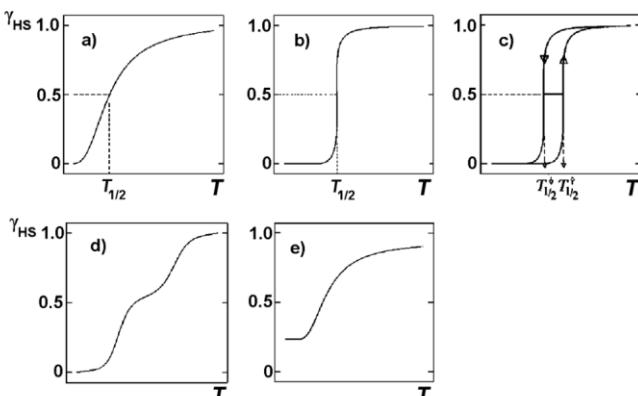


Figure 2. Different kinds of spin transition curves in terms of the molar fraction of HS molecules as a function of temperature. (a) Gradual, (b) abrupt, (c) with hysteresis, (d) step-wise and (e) incomplete curves are plotted. (Image taken from Gütlich *et al*, ref. 5).

3.1.1. State-of-art in SCO compounds

Due to the interest of the scientific community, these compounds have been widely studied for almost a century. Complexes of iron(III), iron(II) and cobalt(II) are the ones that have been studied the most. Other SCO octahedral systems such as chromium(II) and manganese(III) have been studied mainly by Y. Garcia and P. Gütlich;⁶ tetrahedral HS to square planar LS nickel(II) transitions in solution are being studied by Tuczek and Herges; cobalt(III) systems are being studied by W. Kläui with compounds that commonly present LS behaviour due the oxidation state of the metal,⁷ etc. Iron(III) complexes have been fully characterised by Van Koningsburggen with plenty of different ligands. Six-coordinated iron(II) complexes have also been exhaustively studied, as the Mössbauer spectroscopy provides an accurate description of the electronic configuration of such centre. The reason why iron complexes have been fully studied is because this phenomenon is particularly prevalent in these compounds in any of its phases. They do not have an only spin transition curve: they can be gradual, abrupt, stepwise and with or without hysteresis in room temperatures. What's more, iron(II) compounds show favourable cooperative interactions.³

The most commonly known applications studied in SCO systems are memory devices made of spin transition polymers, electrical and electroluminescent devices, etc. Studies of photomagnetic features with LIESTS (Light-Induced Excited Spin-State Trapping) versus TIESTS effects (thermally-induced excited spin state trapping) are also being investigated.

LIESST is a photophysical phenomenon triggered by a light irradiation that converts LS to a HS state in a solid SCO compound, providing a metastable HS state at low temperatures, whereas TIESST would be the conventional thermal conversion in SCO compounds. Other interesting research areas are the combination of SCO behaviour with other physical phenomena that covers up from liquid crystalline properties to fluorescence or electrical conductivity, which is being studied with this work. The most desirable complexes to perform these works are those that present transition temperatures ($T_{1/2}$) near room conditions, so their manipulation can be plain and easy and, therefore, more applicable in routinely conditions tasks.²⁻⁵

3.1.2. Molecular Electronics

In the last decades, a great amount of research has been done in the molecular electronics field. As its name indicates, this scientific branch consists in the study and application of single molecules for the fabrication of electronic components in order to take advantages of the molecular dimensional scale and take profit of quantum effects, hence smaller electronic devices can be designed. Transistors, wires and rectifiers have already been developed. These studies are usually focused on highly conjugated organic molecules, as an easy electronic circulation is possible due to the aromatic delocalization. However, molecules that can swap their spin state have become very appealing on this field, firstly because this switching can change the conducting ability of the molecule, and secondly because this switching can be promoted by easily controllable stimuli, converting them to handy molecular devices.⁸

In order to provide a channel to the electron transmission, the molecular MO must be near the Fermi level of the electrode and the electrode energy levels must interact with the MO of the molecule. Studies are usually carried out considering gold electrodes, but other metallic elements or grapheme can be used. Most of these studies calculate the density of states, DOS, which considers this orbital splitting and provides qualitative and quantitative information about electronic conductance. Broad bands in DOS represent molecular orbitals that highly interact with the electrodes and, thereby, electronic transportation can take place. On the other hand, narrow bands on DOS are molecular orbitals that do not split with the levels of the electrode and conductivity will not be provided. Also, the transmission spectra are calculated in order to know if such levels represented in the DOS are useful for transport properties (see Fig. 3). Alpha and beta MO are usually represented separately for open shell systems in order to set the polarity of the current. The use of DOS for the analysis of transport properties is performed in the following

way: In Figure 3, Aravena *et al.*⁹ studied the conductivity ability of the spin-crossover system $[\text{Fe}(\text{tzpy})_2(\text{NCS})_2]$. HS β molecular orbitals present a broad band close to the Fermi level (noted as 0 eV). On the contrary, α molecular orbitals from the same state presents narrower bands and further from the Fermi level of the electrode, so as a consequence its intensity generated is negligible. Thereby, the HS state generates a β -polarized current. On the contrary, both α and β molecular orbitals from the LS state, even presenting quite broad bands, their energies are not close to the Fermi level of the electrode, so conduction will not be expected for the LS configuration. The transmission spectra $T(E)$ also reveal that HS state will have larger conductance due to the existence of broad peaks close to the Fermi level, especially those of the β orbitals (one filled t_{2g}) and four empty d orbitals of HS Fe^{II} are close to the Fermi level while for the LS configuration the molecular orbitals are far of the Fermi level. In order to calculate $T(E)$ it is required to perform DFT + NEG (non equilibrium Green functions) calculations. These are very complex and limit the number of compounds to study. Due this fact, in this study molecular DFT calculations with no electrodes have been performed, and these do not allow to determine $T(E)$.

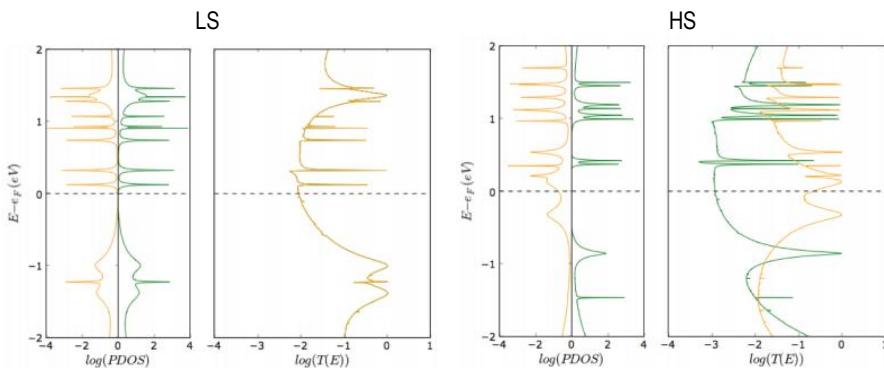


Figure 3. Logarithm of density of states of $[\text{Fe}(\text{tzpy})_2(\text{NCS})_2]$ (S5) (left) and transmission spectra (right) for LS (left) and HS (right) states when the Au-S bond distance was kept constant. Green and orange colours correspond to the α and β contributions, respectively. LS state presents identical α and β MO, therefore its DOS and transmission spectra are identical. (Image taken from Aravena *et al.*, ref. 9).

Many scientific branches involving physics, chemistry and materials, among others, have performed researches with different kinds of techniques in both experimental and computational branches. These experiments require conductance measurements to assess the conductivity ability. In order to get these values in solid state, the wide majority of these studies use the STM (Scanning Tunneling Microscope) technique. By a statistic treatment of a wide number of

conductance measures, a general conductance value for a single molecule can be extrapolated. This conductance refers to dI/dV and is expressed in units of conductance quantum or G_0 , which is equivalent to $2e^2/h$ (e = electron charge, h = Planck constant). Moreover, 1 G_0 refers to the value of the conductance of a metallic wire of a thickness of one atom. Thereby, the conductance of a single molecule will always be less than 1 G_0 . Going back to the experimental techniques, the same STM can be used to prepare the device: the molecule presenting the switching activity ability is deposited to a surface and the current it can generate by changing its electronic rearrangement is studied again with the STM. As the interaction between the molecule and the STM tip generates a difference of potential, this current can be detected and measured. One of the main problems of such experiments is to be sure that the molecule is really placed between the two electrodes. Thus, it is particularly useful in the case of magnetic molecules the existence of the Kondo effect that is an unusual high conductance that appears at very low temperature due to the strong coupling between the unpaired electrons of the molecules and those of the electrodes. Such special behaviour allows corroborating that the molecule is well connected to the electrodes.^{2,10} Notable examples of studies employing the STM technique are the ones performed by Gopakumar *et al.*¹¹, who used STM at 5 K with $[\text{Fe}(\text{H}_2\text{Bpz})_2(\text{bipy})]$ molecules deposited on an Au(111) surface and were able to switch from low- to high-spin state by applying current to the STM tip. They also found out that HS to LS transitions from a second layer of molecules could also generate current with a more intense current. Another outstanding example for these kind of experiments comes from Miyamachi *et al.*¹², who have also performed STM studies at low temperatures with another Fe^{II} molecule, $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, this time deposited on Cu(001) surfaces with an interfacial CuN layer. The direct deposition of these particles on the Cu surface triggered the loss of SCO behaviour. The addition of the CuN layer prevented the loss of the property and the system provided excellent conductivity.

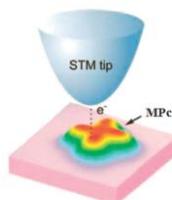


Figure 4. Representations about the STM technique in conductivity measurements in molecular electronics.

Another recent technique introduced in the past years is nanolithography. The different components of the conducting device are created and grouped step by step by lithography printing. A nanowire is deposited and posteriorly a break junction is opened by electromigration. This gap created electrochemically is where the conducting molecule is deposited. A peak of conductivity is generated when the conducting MO of the molecule are aligned to the Fermi level of the electrodes. Measurements of currents generated are simple to perform, as the components of the device resemble a conventional transistor.^{2,13} Studies with nanoparticles of ($[Fe(trz)_3](BF_4)_2$) have been developed by Prins and coworkers.¹⁴ These particles were adsorbed to an electrode with an equidistant Coulomb blockade step, and built a single-nanoparticle device that could generate current at 10 K.

Finally, the mechanically controllable break junctions (MCBJ) technique has also been employed. This technique is based on mechanical elongation and rupture of a metallic wire by measurements of conductivity to control the break junction distance. The deposition of the molecule can be done while the elongation is done by putting in contact such cable and a solution with the molecule of interest, or it can also be deposited after de junction is created. Devices created with these techniques are tested with STM, as commented before.¹⁵ Wulfhekel and co-workers carried out such measurements of a spin-switching molecule on a Co island that was on a Cu(111) substrate. Differences in the differential conductance of the spin-switching molecules between the tip and substrate were found to be dependant on the relative alignment of the tip and surface magnetization. More recently, experiments using spin-polarized scanning tunnelling microscopy in combination with scanning tunnelling spectroscopy have been performed.¹⁶ It is important to remark that nowadays exist plenty of research groups that are trying to merge the properties of spin-crossover and electrical conductance in bulk materials. Moreover, great interest exists in merging these two properties with the LIESST effect, as by irradiating the molecule conductivity could be promoted.

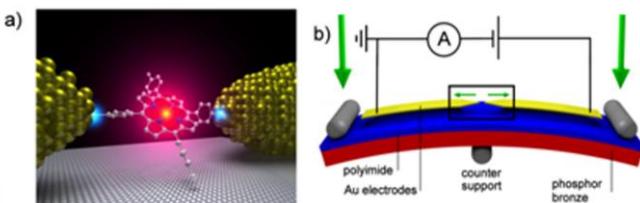


Figure 5. Representations about the MCBJ technique: a) Artistic impression of a single molecule three – terminal device. b) Lay-out of the mechanically controllable break junction (MCBJ) set up. (Image taken from Mickael L. Perrin et al. Beilstein J. Nanotechnol. 2011, 2, 714-719)

3.2. ELECTRONIC STRUCTURE CALCULATIONS

Studies involving spin transition are also performed by computational calculations apart from the experimental methods already stated. Theoretical studies with DFT methods have successfully provided coherent results and faithful correlation between results and computational efficiency. They have allowed the gathering of very valuable information that enables designing synthetic SCO compounds and materials with tailored properties. Nevertheless, the comparison of theoretical results with experimental data is not an easy task to conduct. In order to create SCO systems, it would be essential to determine $T_{1/2}$, which is normally found empirically in solid samples rather than in discrete isolated molecules. Computational determination of this parameter requires the calculation of vibrational spectra of the system, which are found using DFT methods, fact that becomes this task arduous, as the calculation of energy differences between configurations of different multiplicity is problematic. However, different functionals have been developed in order to overcome the obstacles presented.² More accurate post Hartree-Fock methods, i.e. CASSCF or CASPT2 are computationally too demanding to handle such systems if calculation of the vibrational contributions wants to be performed. Thus, such methods are mainly employed to calculate excited states providing a larger accuracy than DFT methods. Nevertheless, modifications to the DFT method are usually applied to circumvent these problems. Bučko and co-workers¹⁷ succeeded in studying $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ in both molecular and crystalline state by periodic dispersion corrected DFT calculations, finding reasonable results with the experimental information already known of the compound. Energetic difference between the isolated molecule and the crystalline lattice was found to be 3.8 kcal mol⁻¹, being the LS state the most stable. The crystal lattice showed to more stable than the isolated molecule due to London forces.

The Density Functional Theory or DFT methods have become very useful to nowadays calculations. In order to approach the study of a system with a large number of electrons, the direct resolution of the mono and bielectronic densities matrixes gives plenty of advantages. This method is based on the Hohenberg-Kohn theorem (1964), which announces that the Hamiltonian from a polyelectronic system is directly determined by its ground state electronic density.¹⁸ At the same time, that ground state energy satisfies a minimum condition and it depends on the monoelectronic density, the same condition as the variational principle complies:

$$E = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \quad (1)$$

where the minimization is over all antisymmetric wavefunctions with N particles.

This condition is used to determine the electronic density of the system, and thus other ground state properties.

3.2.1. Hohenberg-Kohn theorems

The theorems start with a Null Theorem or #0 Theorem, which states that the best wavefunction for a given system cannot be the best wavefunction of another given system, so two different ground states of different ground systems cannot be described by the same wavefunction.¹⁹

Given this first statement, the following theorems can be described. The first one, also known as the Variacional Hohenberg and Kohn theorem, states that two different systems cannot have the same electronic density on their ground state, and that the energy is a universal functional of the electronic density:

$$E_0 = E[\rho_0] \quad (2)$$

$$E[\rho] \equiv F[\rho] + \int_{R^3} v_{ne}(\vec{r})\rho(\vec{r})d\vec{r} \quad (3)$$

where $F[\rho]$ is an unknown universal functional of the electron density. So,

$$E[\rho_0] = \langle \Psi | \hat{H} | \Psi \rangle = T[\rho_0] + V_{ne}[\rho_0] + V_{ee}[\rho_0] \quad (4)$$

The second theorem enunciates that the extern potential of a polyelectronic system is determined by monoelectronic density of its ground state. The Hamiltonian determines the electronic wavefunctions of every state of a system; therefore, any other property of this system will be given by its ground state monoelectronic density.^{19,20}

These theorems were described for the ground state, but they can be easily generalized for any other electronic state of a system with the lowest energy of any spatial or/and spin symmetry.

3.2.2. Kohn-Sham methods

In order to simplify the resolution of the previous theorems described, W. Kohn and L.J. Sham propounded a method with the aim of approximating the $F[\rho]$ functional.²¹ This method

consists of creating a Hamiltonian describing a hypothetical system with n electrons that do not interact with the rest of electrons in the same system, and with a monoelectronic density for its ground state with the same value for the real system that is being studied:

$$\rho_0^{\text{KS}} = \rho_0 \quad (5)$$

In this way, the electronic energy is described as:

$$E[\rho] \equiv \int \rho_0(\vec{r}) v_{ne}(\vec{r}) d\vec{r} + \frac{1}{2} \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + T^{\text{KS}}[\rho_0] + E_{xc}[\rho_0] \quad (6)$$

where the first part describes the interaction with the external potential, the second term describes the classic Coulombic repulsion, $T^{\text{KS}}[\rho_0]$ is the kinetic energy for a system with no-interacting electrons with the same monoelectronic density for the interacting system, and $E_{xc}[\rho_0]$ is the correlation and exchange functional, which is unknown in a given system.

Iterative cycles are required in order to resolve the Kohn-Sham equation. With an initial monoelectronic density $\rho_0^{(0)}$ an external potential $v^{KS(0)}$ can be found, and it is described as:

$$v^{KS}(\vec{r}_1) = v_{ne}(\vec{r}_1) + \int_{\vec{r}_2} \frac{\rho_0(\vec{r}_2)}{r_{12}} d\vec{r}_2 + v_{xc}(\vec{r}_1) \quad (7)$$

$$v_{xc}(\vec{r}) = \left(\frac{\delta E_{xc}[\rho]}{\delta \rho} \right)_{\rho=\rho_0} \quad (8)$$

then, the eigenfunctions of the KS operator (\hat{h}^{KS}) are found. With these equations, a new value for the monoelectronic density is newly calculated, in order to start a new iterative cycle. Autoconsistence is reached once the \hat{h}^{KS} eigenvectors reproduce the external potential v^{KS} of the same operator. As commented before, once the ϕ^{KS} are found, other properties besides the ground state energy can be obtained.

3.2.3. Exchange-Correlation Functionals

With the purpose of obtaining a more valid exchange-correlation energy value, plenty of Exchange-Correlation Functionals have been described during the past century. Their main properties are the energy functional should be self-interaction-free, when the monoelectronic density becomes constant; the uniform electron gas result should be recovered (even though it is not very relevant for chemical applications); the coordinate scaling of the exchange energy should be linear; etc.^{20,22}

In the initial phase of DFT development, where only LDA and GGA methods existed, Perdew and Schmidt proposed the *Jacob's ladder of approximations to the exact exchange-correlation functional*, which consists of the ladder of functionals that progresses from the Hartree world, without non-local exchange, towards the highest rung with full accuracy designed as the “heaven” of chemical accuracy. Therefore, Perdew and Schmidt suggested a constant development of methods in order to improve in the accuracy of DFT methods, as each rung up the ladder would imply an improvement on the performance of the methods used in the previous rungs. Therefore, until then computational chemistry had stayed on the first and second rung, with LDA and GGA functionals. Then, meta-GGA methods appeared, providing a step forward to the ladder of approximations, and it continues with hybrid and double hybrid methods. Thereby, this ladder implies an evolution from semilocal to nonlocal functionals in the computational chemistry world.

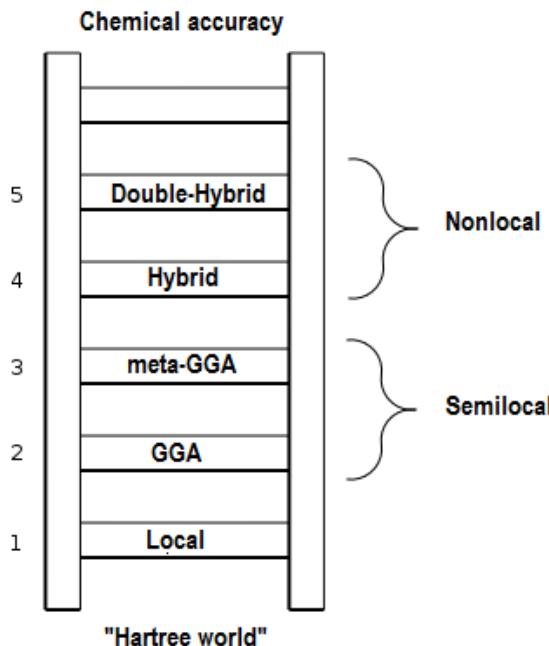


Figure 6. Representation of the Jacob's Ladder of Density Functional Approximations for the exchange-correlation energy proposed by Perdew and Schmidt in 2001.

3.2.3.1. LDA or Local Density Approximation

As E_{xc} is expressed as a function of the monoelectronic density, it can be treated as a uniform electron gas, which means that the density is a slowly varying function. Monte Carlo simulations of this uniform gas were used to parameterize interpolations between the known forms in the high-density and low-density limits. This functional is adequate for optimizing the geometry of solids, but is also included in the rest of the DFT functional as an explicit component. Vosko and Perdew developed a wide range of LDA functionals. It is important to remark the LSDA or Local Spin Density Approximation, a functional that is used for cases where α and β densities are not equal.^{20,22,23}

3.2.3.2. GGA or Generalized Gradient Approximation

Even though the great simplicity in the model described in the LDA correlation functionals, atomic or molecular systems have a huge different density respect the uniform electron gas model. Thus, a new dependence factor is added, the density gradient ∇p , along with other conditions, which provide a more realistic model that takes into consideration the position of the nucleus. Whereas LDA does not provide valid energy gaps for insulators, conductors and semiconductors (or molecular properties), GGA methods provide improved results in comparison with LDA. The most common GGA methods are the B or B88 (usually the acronym is the first character of the family new of the authors of the functional, i.e. Becke), OPTX, OPBE and LYP.^{20,22,24}

3.2.3.3. Meta-GGA or Higher order gradient methods

These methods are more developed extensions of GGA functionals and include higher order derivatives of electron density, where the laplacian $\nabla^2 p$ is its second order term. There is a more used version where, instead of having the second-order gradient of the monoelectronic density, the function can be dependent on the orbital kinetic energy density τ as its calculation is numerically easier than the laplacian term. Also, functionals that in general use orbital information may also be considered as meta-GGA methods. BR (Becke and Roussel), M06-L (Truhlar) and TPSS (Tao-Perdew-Staroverov-Scuseria) methods are notable examples.^{20,23}

3.2.3.4. Hybrid or Hyper-GGA methods

These methods add an inclusion of the Hartree-Fock (HF) exchange energy E_{x}^{HF} , which wave function consists in a single Slater determinant composed of KS orbitals. This HF-type

exchange energy is not included on its totality, but only a percentage portion of it, so the general form of the functional can be described as

$$E_{XC} = E_{XC}^{DFA} + c_X E_{XC}^{DFA} \quad (9)$$

where the first summand is the energy provided by the density functional approximations, and the second term corresponds a fraction of the exact HF-type exchange energy. The inclusion of the HF-type exchange solves the main problem of pure DFT methods, the self-interaction error. This error is introduced because in the calculation of the electron-electron interactions, each electron interacts with the total electron density. Thus, there is a spurious self-interaction error that causes a wrong asymptotic behaviour of the potential at long distances resulting for instance in wrong energy gap values, as previously noticed.^{19,20}

The most notable example of this method is the famous B3LYP, introduced by Becke, which includes a 20% of HF-type exact exchange.^{20,25} There are other methods known as *hybrid meta-GGA* functionals that combine both characteristics of hybrid and meta-GGA functions. Some examples are TPSSh, with a 10% of E_{X}^{HF} , and Truhlar's M06, which contains a 27% of contribution.^{25,26}

3.2.3.5. Double hybrid methods

These methods consist of a fraction of non-local HF-type exact exchange energy, as the conventional Hyper-GGA methods presented before, but also a non-local perturbation contribution to dynamic correlation composed of the Moller-Plesset method, which is a second order many-body perturbation theory. The dynamic correlation is in principle introduced by pure DFT methods but dispersion terms are not included. Thereby, the inclusion of the dispersion contribution through the MP2 method improves the description of van der Waals interactions that are neglected in common DFT functionals. The most known functional is B2PLYP, and has a 53% of E_{X}^{HF} .^{27,28}

3.2.3.6. Long-range corrected methods

The goal of such functionals is to introduce a correction to the self-interaction error depending of the region of the space. As previously mentioned, such error is larger at long distances, thus, we can divide the space around the atoms and to use different expressions for the functional in the short and long-range regions. Hence, at long distances the expression of the exchange corresponds to the Hartree-Fock-type term and consequently, is free of self-

interaction error. In this work, the long-range corrected method is ω B97x and contains full exact exchange for the conditions established.²⁹⁻³²

3.3. DFT IN SPIN CROSSOVER

Theoretical studies involving spin crossover systems have a long history behind. Hartree-Fock-based methods lack of electron correlation for electrons with unlike spins, driving to optimize molecules in the high-spin state, therefore has no predictive power in SCO field.³³⁻³⁵ Thereby, the Density Functional Theory became a solution. The main goal of the first studies that were carried out with DFT methods was to reproduce the experimental energy difference values between high- and low-spin states for the $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$] complex, a system that has widely been studied in this field. On the initial phase of SCO studies, standard pure functionals like LDA and GGA methods systematically favour low-spin over high-spin states, for which they are not very reliable. Thereby, new functionals appeared. As Hartree-Fock-based methods tend to present the contrary result (favouring the HS-state) due to the lack of electron correlation for electrons with unlike spins, hybrid functionals were designed to take advantage of both facts by combining both methods, providing a compensation on the biases, so more reliable results were able to gather. B3LYP, the most famous DFT hybrid method, came out to be a very successful tool and has provided a great amount of valuable information. However, this functional also provides biased results to the HS state, so, in consequence, a B3LYP* functional was proposed, which only differed from the previous B3LYP method in the amount of E_{X}^{HF} (15% instead of 20% from the original B3LYP functional).^{2,22} Six-coordinate Fe^{II} mononuclear compounds with donor-atom ligands have been the most characterised systems, since spin transition seems to occur predominantly, and have been reviewed many times in the literature.^{3,5,22,36}

Nowadays, it has been shown that almost all DFT methods can predict correctly the ground-state spin multiplicity for complexes containing strong-field ligands. Nevertheless, weak-field complexes tend to be over-stabilized in the LS state when calculated with GGA methods. This happens in cases where energies between both spin states differ little. Also B2PLYP appears to be slightly biased in favour of high-spin states. Therefore, it is assumed that the HS-LS energy differences calculated by the B2PLYP functional in a range of -6 to 0 kcal/mol should be taken as being indicative of SCO complexes. These values have been selected considering the magnitude of the entropic terms until room temperature that will compensate the larger stabilization of LS state at 0 K. Anyway, more reliable results can be harvested using the def2-

QZVPP basis.^{33,37} Ground-state energy calculations have also been long studied, and it is widely known that hybrid functionals tend to fail in low-spin states. Recent studies show that newer functionals such as X3LYP and M06 also show this tendency to provide wrong values. However, OPBE is shown again to gather reliable results, altogether with the TPSSh functional.^{2,34}

For the estimation of energy difference between HS and LS states and geometry optimization, many studies suggest different functionals. Swart states in his study that OPBE has provided the best performance, whereas Ye and Neese obtained accurate results using the B2PLYP double-hybrid functional. On the other hand, Jensen and Cirera gathered balanced results using the TPSSh functional.^{33,34,38} Nevertheless, all the information exposed previously refers to studies involving Fe^{II} compounds. There are very few studies involving other metallic cores, and there is not a defined DFT functional that can be used for any SCO compound independently of the metal present in the structure.

4. OBJECTIVES

One of the aims of this work is undertaking a quantitative comparative study of the accuracy in molecular optimization of various DFT exchange-correlation methods for 13 mononuclear systems that present the spin-crossover feature in order to determine which of these methods would be the best in defining the properties for any SCO system. Five different metallic cores are studied in this project: Fe^{II}, Cr^{II}, Mn^{II}, Mn^{III} and Co^{II}, with six different exchange-correlation functionals: OPBE, B3LYP, TPSSh, ωB97x, B2PLYP and M06.

The second goal is to determine which of the studied compounds would become a potential single-molecule good electronic conductor by analysing the disposition of the alpha and beta σ molecular orbitals, as they will be the ones to interact with the MO of a gold electrode when entering in contact with it. The MO rearrangement that occurs when both electrode and molecule enter in contact has not been studied as the frequency calculations needed for the study consume a great amount of computational time.

5. COMPUTATIONAL DETAILS

5.1. SELECTION AND PREPARATION OF CANDIDATE SYSTEMS IN ELECTRONIC CONDUCTION

Metallic systems with Fe^{II}, Cr^{II}, Mn^{II}, Mn^{III} and Co^{II} centres were searched in published literature. Spin transition temperature $T_{1/2}$ has been the main criteria in the selection of molecules to study, as it is an important parameter when talking about bringing these species into real life applications. The molecules to be studied are shown in the table below.

System	Compound	Name	Picture	$T_{1/2}$ [K]
S1 ^{5,34}	[Fe(phen) ₂ (NCS) ₂]	cis-bis(Isothiocyanato)-bis(1,10-phenanthroline-N,N')-iron(II)		175
S2 ^{5,34}	[Fe(amp) ₂ Cl ₂] ^(a)	trans-Dichloro-bis(2-pyridylmethylamine-N,N')-iron(II)		20
S3 ³⁴	[Fe(phen) ₃] ²⁺	tris(1,10-Phenanthroline)-iron(II)		300
S4 ³	[Fe(H ₂ Bpz ₂) ₂](bipy)] ^(b)	(2,2'-Bipyridyl)-bis(dihydrogen bis(pyrazol-1-yl)borate)-iron(II)		159,5
S5 ^{9,39}	[Fe(tzpy) ₂ (NCS) ₂] ^(c)	Pyridyl)(1,2,3)triazolo(1,5-a)pyridine)-bis(isothiocyanato)-iron(II)		118
S6 ⁶	[Cr(I ₂)(depe) ₂] ^(d)	trans-bis(1,2-bis(Diethylphosphinoethane-P,P')-diiodo-chromium(II)		170
S7 ⁶	[(Ind ^{3Me-2,4,7}) ₂ Cr] ^(e)	bis(2,4,7-Trimethylindenyl)-chromium(II)		200

System	Compound	Name	Picture	T _{1/2} [K]
S8 ⁶	[Mn(pyrol) ₃ (tren)]	tris(1-(2-Azoly)-2-azabuten-4-yl)-amino-manganese(III)		44
S9 ^{40,41}	[Mn(3,5-diBr-sal ₂ 323)] ⁺	(2,2'- <i>o</i> ,6,9,13-Tetraazatetradeca-1,13-diene-1,14-diyi)bis(4,6-dibromophenolato))-manganese(III)		150
S10 ^{6,42}	[Mn(Cp) ₂]	Decamethylmanganocene		184–314
S11 ⁴³	[Mn((tBu)Cp) ₂]	bis(h ₅ -t-Butyl-cyclopentadienyl)-manganese		200
S12 ⁴⁴	[Co(terpy) ₂] ²⁺	bis(2,2':6',2"-Terpyridyl)-cobalt(II)		200
S13 ⁴⁴	[Co(terpyridone) ₂] ²⁺	bis(4'-Hydroxy-2,2':6',2"-terpyridine)-cobalt(II)		172,4

(a) amp = 2-pyridylmethylaniline

(b) H₂Bp₂ = bis(pyrazoly)borate

(c) Izpy = 3-(2-pyridyl)[1,2,3]triazolo[1,5-a]pyridine

(d) depe = 1,2-bis(diethylphosphino)ethane

(e) Ind^{3Me-2,4,7} = (2,4,7-Me₃ bis(indenyl)₂

Table 1. Images of the full structures studied are shown in Appendix 1. Classification of the systems studied in this work.

Their structures were obtained by X-Ray crystallography data available in Conquest (Cambridge Structural Database) and later taking their molecular Cartesian matrix using CrystalMaker 8.7. These matrixes were used to prepare the Gaussian input for calculations with Gaussian g09d1 version for the B3LYP functional. The geometry obtained from this optimization was used as an initial point for the rest of the DFT exchange-correlation functionals already commented: B2PLYP, M06, ωB97x, OPBE and TPSSh. The final geometries from the optimized structures are attached to this project in a CD.

5.2. ANALYSIS OF THE FRONTIER ORBITALS

Conditions of these calculations are at 0 K and vibrations have not been taken into consideration. The ground state of the molecule at these conditions should be the low-spin state. HS state should not differ much from the energy of the LS state, as it is stabilized by its entropic (vibrational and electronic) terms, and this difference should not be extremely high, since if it does not the spin swapping would not occur. Complexes have been considered to adopt a pseudo-octahedral structure. Thereby the nomenclature used to name the MO is the one established for octahedral geometries.

5.2.1. Iron(II) complexes

Spin transition in iron(II) systems is between configurations $t_{2g}^6 e_g^0$ ($1A_{1g}$, LS, $S=2$) $\leftrightarrow t_{2g}^4 e_g^2$ ($5T_{2g}$, HS, $S=0$).^{3,5,45} This implies, for the high spin state, five α and one β occupied molecular orbitals, whereas for the low spin state three α and three β occupied molecular orbitals are required.

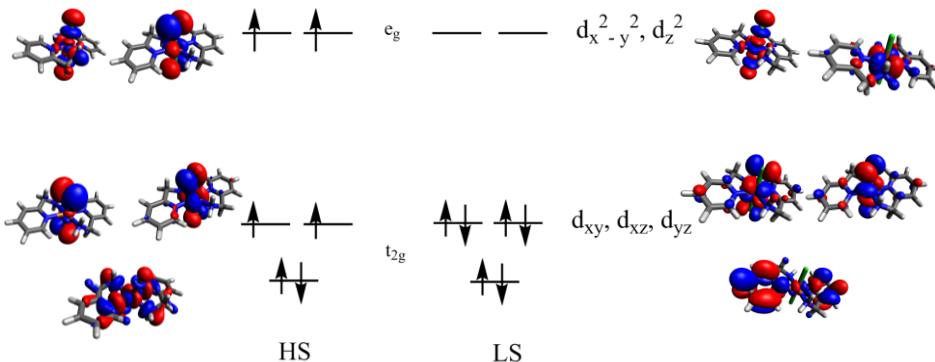


Figure 7. Diagram of splitted d molecular orbitals for pseudo-octahedral Fe^{II} coordination compounds. Molecular orbitals obtained for $[Fe(amp)_2Cl_2]$ are represented. Ligand contributions are present in the pictures.

5.2.2. Chromium(II) and Manganese(III) complexes

In both cases studied, spin transition occurs between configurations $t_{2g}^4 e_g^0$ ($3T_{1g}$, LS, $S=1$) $\leftrightarrow t_{2g}^3 e_g^1$ ($5E_g$, HS, $S=2$)^{3,6,46} which implies four occupied α MO for high spin states, while three α and one β occupied MO are required for low spin states. Mn^{III} complexes show the same spin transition as Cr^{II} since both present identical electronic configurations (both are d^4 ions).^{3,6,41} Therefore, their molecular orbitals are studied in the same way.

5.2.3. Manganese(II) complexes

These systems exhibit a $t_{2g}^3 e_g^2$ (LS, S=1/2) \leftrightarrow $t_{2g}^5 e_g^0$ (HS, S=5/2) transition, which implies five α occupied MO for HS and three α with two β occupied MO for LS states.^{42,43}

5.2.4. Cobalt(II) complexes

As found in the literature, these complexes show a $t_{2g}^6 e_g^1$ (2E_g, LS, S=1/2) \leftrightarrow $t_{2g}^5 e_g^2$ (4T1g, HS, S=3/2) transition which implies the whole five α MO and two β MO occupied for a HS state. For LS, four α and three β occupied MO are required.^{3,44,47,48}

6. DFT RESULTS

In order to perform a faster comparison, energy difference between high-spin state and low-spin state are shown to continuation. As explained in the previous section, low spin state should be the most stable of both states at 0 K, since otherwise spin swap would not occur. A guideline value has been established in order to discern accurate from biased results. Neese and Shengfa proposed this difference to be between 0 and -6 kcal/mol, but they did not take into consideration the interaction between molecules, which favours the stability of the lattice. (As said before, Bučko *et al.* obtained differences between 2-3 kcal/mol resulted from the theoretical study of both isolated and crystalline compounds).^{17,33} Thus, the guideline is merely indicative. Nevertheless, higher differences disfavours the SCO phenomena, as the energetic barrier between both spin states becomes extremely high, therefore spin swap becomes a minor effect. Thus, negative low values are taken as a criterion of selection for the best DFT method, that is, the method that provides more reliable results. Among the others, the only method that accomplishes the criterion established previously is TPSSh. The rest show a tendency to stabilize HS ground states rather than the LS state (differences of energy greater than 20 kcal/mol in many cases). Therefore, the molecular orbitals obtained with this method are used to perform the electron transport studies.

Initially, OPBE was expected to become the best DFT method for geometry optimizations, since it was indicated in most of the literature used for this work. Against the odds, TPSSh has turned out to be the most efficient for this SCO study for compounds with a large variety of

metals. OPBE is a GGA method and TPSSh is a hybrid or hyper-GGA method. An important fact can be concluded from this statement: TPSSh, as a hybrid method, has a Hartree-Fock-type exact exchange contribution, whereas GGA methods do not have any of it, only considering electronic density and its gradient. Intuitively, one could consider that, as higher stabilization is given for lower multiplicity states by HF-type functionals, methods containing a slightly HF-type contribution should present a tendency in overstabilizing these lower multiplicity systems. However, as TPSSh has a very optimal amount of this kind of contribution it performs better than OPBE.

System	B3LYP	OPBE	B2PLYP	TPSSh	M06	ω B97x
S1	3.7	-3.4	—	-9.5	—	7.1
S2	12.9	8.3	45.2	2.0	22.6	16.0
S3	-3.4	—	—	-17.5	—	—
S4	0.78	-2.1	38.0	-11.9	9.7	3.2
S5	3.0	-1.7	—	-9.5	—	10.2
S6	9.2	5.5	—	-0.73	12.7	7.5
S7	9.2	3.3	—	0.93	11.3	5.0
S8	0.24	—	18.8	-7.2	11.6	0.69
S9	0.13	0.30	17.3	-7.6	12.6	0.71
S10	-0.66	-10.9	48.9	-16.5	—	-8.8
S11	7.1	-5.2	55.0	-9.0	20.6	1.7
S12	-1.5	-12.4	22.8	-4.7	0.93	1.4
S13	2.1	—	22.8	—	—	—

Table 2. Differences of energies obtained between LS and HS states for each system studied in kcal mol^{-1} . Systems with less than 6 kcal mol^{-1} of difference are thought to be able to transitate, as their entropic term is compensable. Energies obtained from calculations are shown in Appendix 2. The results indicated as dash corresponds to non yet converged calculations.

On the other hand, TPSSh and B3LYP are both hybrid methods (TPSSh is hybrid meta-GGA), but, as seen in Table 2, Becke's hybrid method tends to overestimate the stability of the high spin state, favouring the low spin state. Therefore, both hybrid methods provide different results. The reason why relies on the amount of Hartree-Fock exact exchange: as commented before, as Hartree-Fock based functionals tend to stabilize systems with lower multiplicity, the

more exact exchange a hybrid method has, bigger is the tendency in overestimating the stability of the higher multiplicity system. B3LYP has a 20% of exact exchange, whilst TPSSh only contains a 10%. This decrease of contribution provides remarkably better results. This deviation had already been reported for Fe^{II} systems and was the main reason of the creation of the B3LYP* functional (15% of HF-type exchange instead of 20% from B3LYP). The M06 functional is also biased in favour of HS states. Again, this tendency can be produced by the HF-type exchange contribution. M06 is a hybrid meta-GGA method, like TPSSh, but their main difference is, again, the amount of HF-type exchange: M06 has a bigger percentage of this non-local contribution (27%) against the only 10% of TPSSh has. M06 shows similar results with B3LYP (hybrid, 20% HF-type exchange), but its performance is considerably better rather the Minnesota class functional M06.

The double hybrid B2PLYP functional has proved to be the less exact and efficient method. As a double hybrid it has a slightly fraction of HF-type exact exchange and a Moller-Pleset perturbation correction part. With all these factors to be calculated, its running time has been estimated to be around 2 weeks and a half (depending on the system it has taken a whole month for its calculation). Moreover, it overstabilizes HS states amongst LS states. Shengfa and Neese reported this HS-biased tendency in their work, but qualitative and reliable results were obtained when changing the basis set used: in their study they claimed the use of the def2-QZVPP basis, as in consequence B2PLYP provided accurate energies between both spin states. In this study, the basis set used has been QZVP (for metals), which is a smaller and less flexible base in comparison with the larger and more flexible basis set they used.³³ Generally, DFT is not a basis-dependant method, but in their research, differences of energy for [Fe(phen)₂(NCS)₂] (S1) differ from the ones obtained in this work (-9 kcal/mol against 3.7 kcal/mol obtained in this study using the B3LYP functional in both cases). Using the def2-QZVPP basis set the best outstanding functional were OPBE and B2PLYP, whereas TPSSh provided enormous energy differences, not only for [Fe(phen)₂(NCS)₂], but for all their systems studied (Fe compounds). Hence, the combination of the functionals with the basis set used in Shengfa and Neese's study worked well, but a clear conclusion can not be drawn, as in this work not all the functionals have converged, hence not all the results are available for a comparison.

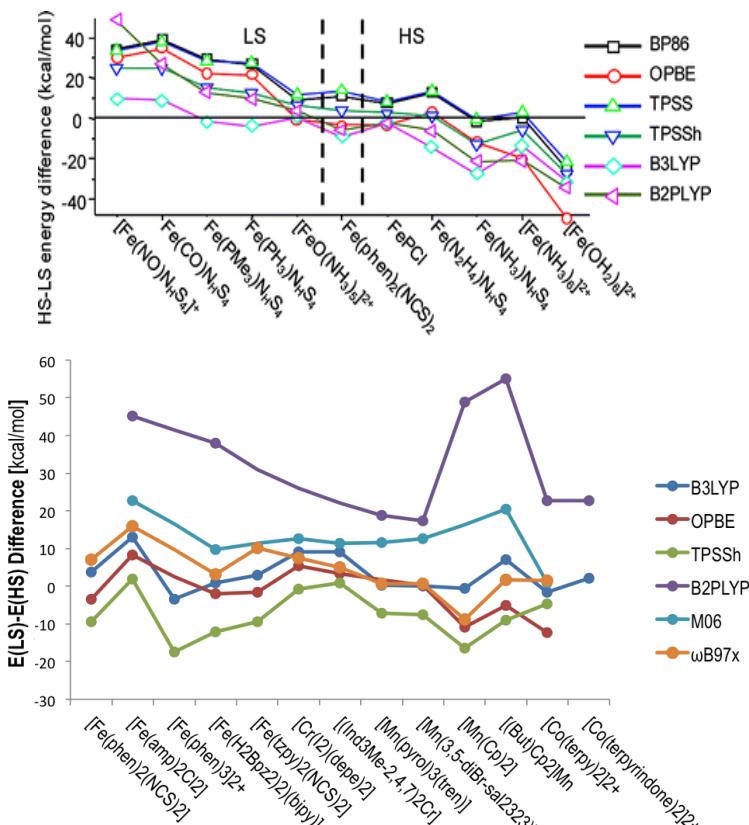


Figure 8. (Over) Results obtained by Neese and Sengfa (*Image taken Shengfa et al., ref. 33*) and (under) results obtained in this study.

The last functional to be commented and compared is ω B97x, a long ranged connected functional, which its tendency has resulted to be to favour HS states more than LS, as it was thought. This method has not been compared with others, as its methodology for obtaining molecular energies quite differs from the others, which are more conventional. The developers of this functional found that calculations in thermochemistry and kinetics are accurate. They also described that its performance for systems with small energy gaps like the ones studied here is not likely to be better than conventional functional, fact that has also been observed in this work.³¹

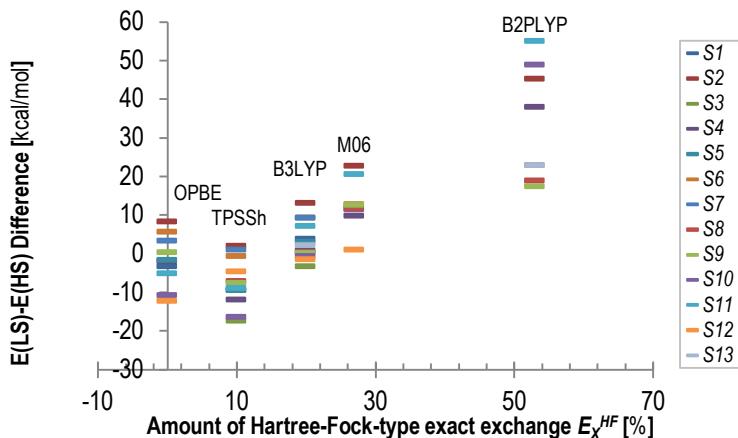


Figure 9. Correlation between the amount of the HF-type exact exchange with the differences of energy obtained for each compound studied.

Correlation between transition temperature and energy differences between both spin states has been found in Fe^{II} compounds, but not in d⁴ systems, and even not in compounds with the same metal centre. $E(LS) - E(HS)$ should increase as the $T_{1/2}$ becomes higher. The reason lies in that heat compensates the entropy contributions in the HS state at 0 K, therefore it compensates de differences of energy on the LS, which is more stable than the HS state. The more stable the energy of the LS state, the more energy is required in order to swap to the HS state, and hence the $T_{1/2}$ increases.

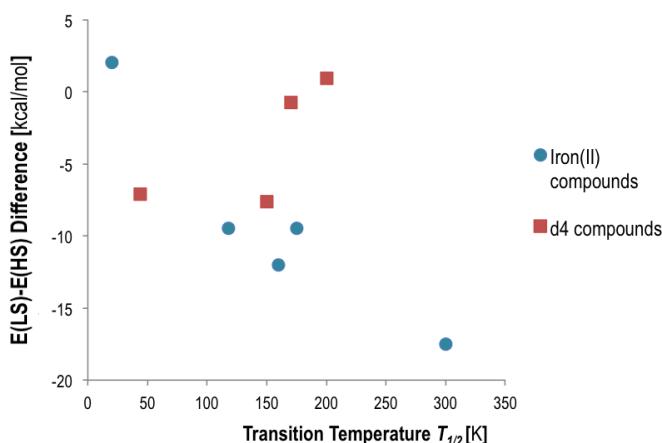


Figure 10. Representation of the differences of energy between high- and low-spin states with the transition temperature for Fe^{II} and d⁴ compounds. Correlation almost exists in Fe^{II} complexes studied, but it lacks in the rest of the compounds.

7. DISCUSSION OF ELECTRON TRANSPORT THROUGH SCO SYSTEMS

In this upcoming section, the ability of quantum transport when a difference of potential is applied is discussed for each metal centre studied. The prediction of the polarization of the current generated will also be debated. The energy of the molecular orbitals will be the main requirement to reach a conclusion about the conductance of each systems studied. In this project, the work function value of gold (-5.1 eV) is taken as the reference of its Fermi level and, when represented, is plotted as a yellow line in some figures where redox reactions could be expected in the molecules. In the other cases, despite that the full and empty frontier energy orbitals of the molecules are not exactly placed below and above the Fermi level of the electrodes, when molecule and electrodes enter in contact, an energy rearrangement of the molecular orbitals occurs to be placed around the Fermi level, if the energy differences are not too big (that would result in oxidation or reduction processes on the molecule, as stated).

The single-molecule device must be considered as a flow of electrons between electrodes that require having both empty and occupied molecular orbitals near the Fermi level. Orbitals that are further from the Fermi level will be involved current transport if the difference of potential applied between the electrodes is larger than its distance to the Fermi level. Hence, if a big gap of energy exists between HOMO and LUMO, conductivity will not be very effective, even negligible, unless an increase of difference of potential between the electrodes will be increased. As conductance depends of the interaction of the molecular orbitals and the levels of the electrodes, it is expected that systems with heteroatoms that strongly interact with metal surfaces and for instance, sandwich compounds will be good candidates to have high conductivity. Also systems which ligands have their π orbitals occupied (π -basic ligands) that do not generate a great splitting on the metallic degenerated d orbitals are excellent candidates to be good conductors, as these systems will present a small gap and, hence, electron jumps between HOMO and LUMO are easy to perform.

7.1. Fe^{II} SYSTEMS

The comparison between different iron nuclei complexes and the Fermi level of the gold electrodes provides a main conclusion: HS states always present a beta-polarized current of electron conduction (excepting S3), as the HOMO is filled with beta electrons and presents a small gap. In LS state, as both alpha and beta molecular orbitals present the same energy, the

current generated, if any, would be unpolarized. The biggest gaps of energy are shown by $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ (**S1**) and $[\text{Fe}(\text{H}_2\text{Bpz}_2)_2](\text{bipy})$ (H_2Bpz_2 = bis(pyrazolyl)borate) (**S4**), therefore their conducting ability will be poor. However, it is legitimate to claim that $[\text{Fe}(\text{amp})_2\text{Cl}_2]$ (amp = 2-pyridylmethylamine) (**S2**) will be the best LS candidate among iron(II) compounds to conduct electricity, as its gap between HOMO and LUMO is very low (approximately 2.6 eV). $[\text{Fe}(\text{tzpy})_2(\text{NCS})_2]$ (tzpy = 3-(2-pyridyl)[1,2,3]triazolo[1,5-a]pyridine) (**S5**) LS would be considered an acceptable conductor. Otherwise, $[\text{Fe}(\text{phen})_3]^{2+}$ (**S3**) has shown to be very different from the other iron(II) complexes. Its HOMO and LUMO for both high and low spin states are below the Fermi level. In other words, whilst **S3** has vacant orbitals in -5.1 eV, the electrode levels are filled. Hence, redox reactions are very likely to happen when **S3** is being in use. Therefore, this system would not be a potent candidate. In the HS state, **S4** presents the smallest gap of energy (1.2 eV), being the most appealing compound to generate a β -polarized current.

These gaps obtained are due the spectrochemical series of the ligands (as the metal remains the same for all the compounds in this subsection). Four of the five complexes studied for Fe^{II} are not pure FeN_6 compounds, that is to say, octahedral, excepting for **S3**, which is coordinated with three bidentate 1,10-phenanthrolines. Phenanthroline is a strong splitting ligand as a π -acid ligand (ligands that present empty orbitals before merging with a metal); therefore the consequent gap is big. The rest of the iron(II) systems studied are considered as pseudooctahedral, as their six-coordination geometries present almost the same spatial distribution. The gaps they present are narrower, as their ligands are less strong than *phen*, plus the effect of the mixing different kinds of ligands on the same compound is added. As said, **S2** would be the compound to generate more intensity due to its low gap. This little d splitting in gap is because of the strongly π -basic ligands chloride and 2-pyridylmethyl amine. The medium-conductor behaviour that **S4** and **S5** would present is due their neutral ligands (isothiocyanate and H_2Bpz_2). Even though 2,2'-Bipyridine and pyridine are strong splitting ligands, the global effect becomes a medium crystal-field splitting.

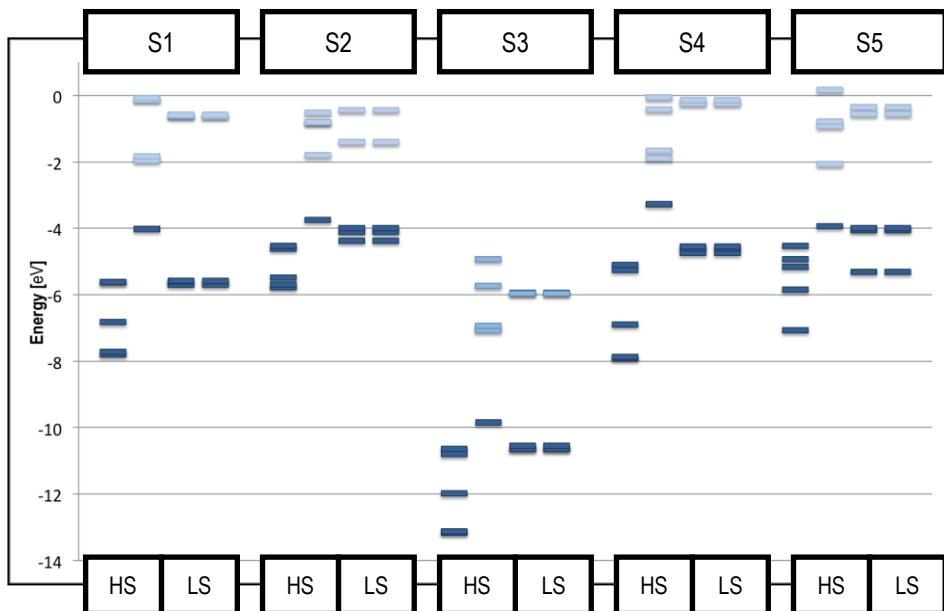


Figure 11. Molecular orbitals diagram for Fe^{II} systems studied. For every spin state, alpha MO are on the left and beta MO are on the right. More coloured lines represent occupied MO.

7.2. CR^{II} SYSTEMS

Both chromium(II) systems present a very similar MO distribution scheme. HS and LS may show similar conductivity as their LUMO MO present almost the same energies. However, HS molecules will generate an alpha polarized current (as there are no beta electrons), whereas an almost non-polarized current will be generated in LS complexes, as the LUMO orbitals can be reached easily by both alpha and beta electrons. Therefore, both systems would be chosen to provide electron transport. Both gaps obtained for $[(\text{Ind}^{3\text{Me}-2,4,7})_2\text{Cr}]$ ($\text{Ind}^{3\text{Me}-2,4,7}$ = (2,4,7-Me₃bis(indenyl)₂) (**S7**) and $[\text{Cr}(\text{I}_2)(\text{depe})_2]$ (depe = 1,2-bis(diethylphosphino)ethane) (**S6**), which almost present slightly π-acid ligands (excepting iodine, to most π-donor ligand of the series). Their splitting ability, then, generates not too big gaps, but neither negligible, and therefore the conducting ability for the HS state will not be exceptionable enough, but neither negligible.

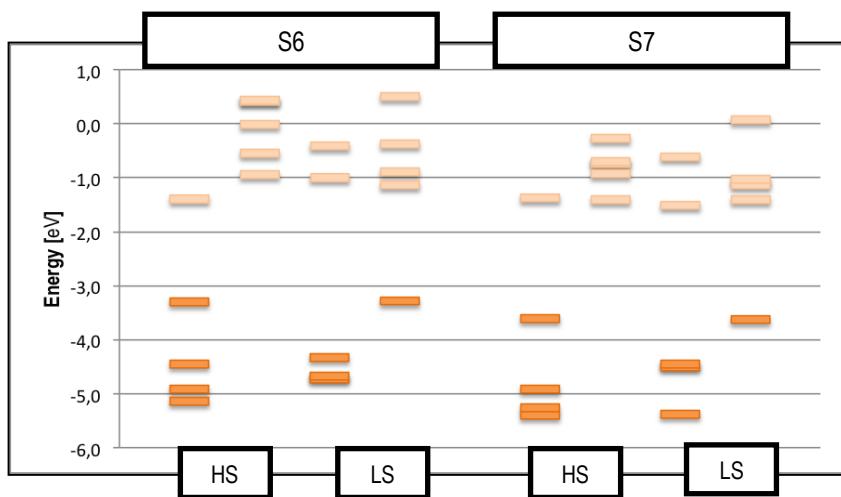


Figure 12. Molecular orbitals diagram for Cr^{II} systems studied. For every spin state, alpha MO are on the left and beta MO are on the right. More coloured lines represent occupied MO.

7.3. Mn^{III} SYSTEMS

Manganese(III) compounds share electronic configuration with chromium(II) compounds. Hence, it was expected that both systems would present almost a similar MO diagram. [Mn(pyrol)₃(tren)] (**S8**) almost presents this pattern but, on the contrary, [Mn(3,5-diBr-sal₂323)]⁺ (**S9**) has a quite different distribution. In this figure, the Fermi level has been plotted to remark the possibility of a redox reaction when **S9** would enter in contact with the electrode: unoccupied MO could be filled with electrons provided by the electrode and, therefore, become reduced. So, the best manganese(III) candidate is **S8**, which can generate alpha polarized current when it is in its HS state, and beta polarized current when in LS state as the LOMO level is lower.

The 3,5-diBr-Sal₂323 is a hexadentate ligand that coordinates by four amino groups and two oxygen atoms and contains two aromatic rings with bromines. As obtained in the molecular orbitals for the complex, this ligand has a neutral splitting pattern and generates not too big gaps. On the contrary, (pyrol)₃(tren), a monodentate trianionic Schiff base,⁶ presents a stronger splitting behaviour on the whole compound. Therefore, as the width of the gap is smaller for **S9**, this compound would generate more intense currents. Changing the electrode for one with a lower Fermi level so **S9** would not undergo a reduction reaction, this compound would be an interesting molecule for electron transport.

Returning to the gold electrode, if a comparison is made for both d⁴ systems, **S8** could become the best choice, as its LS form presents high conductivity. Both chromium(II) complexes present a mediocre conductivity in both spin states, that is, the intensity of the current generated does almost not change (even though polarization does). In order to design devices, changing the capacity of conduction can be an interesting parameter, along with swapping the polarity of the current generated, so the circuit in use can be working or not being operative according to the intensity or the polarity of the current provided by the single-molecule complex.

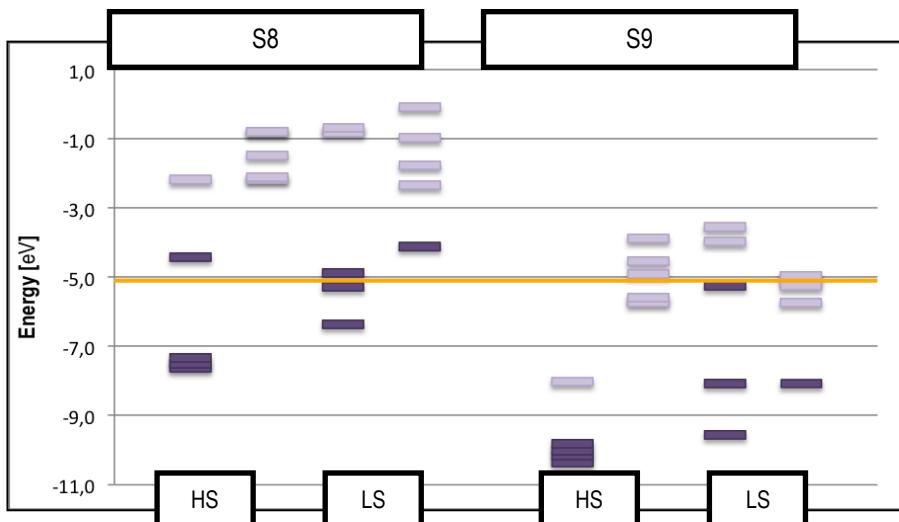


Figure 13. Molecular orbitals diagram for Mn^{III} systems studied. For every spin state, alpha MO are on the left and beta MO are on the right. More coloured lines represent occupied MO. The yellow line represents the Fermi level of the gold electrodes.

7.4. Mn^{II} SYSTEMS

Both complexes studied present practically the same MO diagram. This behaviour can be explained by taking into consideration that both systems have ligands that are very alike (Cp and Bu^t-Cp), which implies a very similar splitting pattern. These systems would show alpha-polarized current in HS state when a difference of potential is applied. LS would present a slightly beta-polarized current instead.

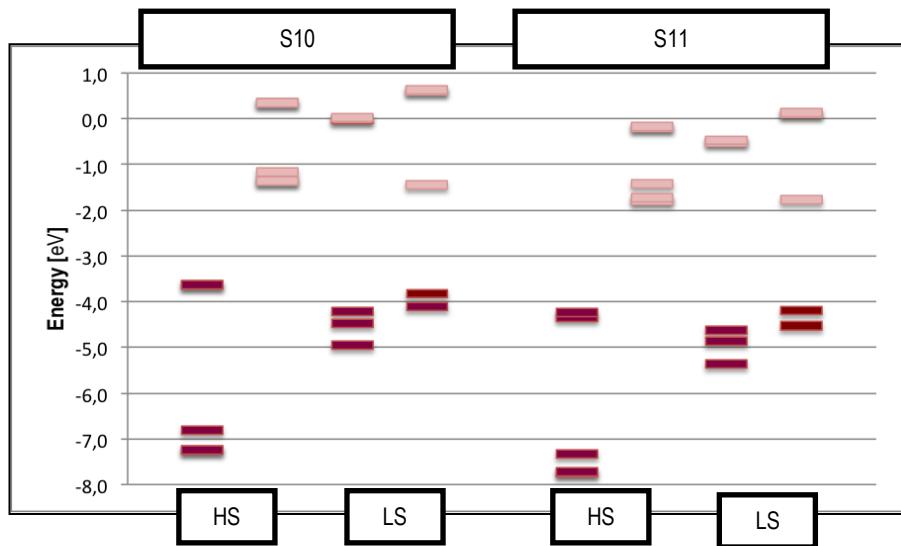


Figure 14. Molecular orbitals diagram for Mn^{II} systems studied. For every spin state, alpha MO are on the left and beta MO are on the right. More coloured lines represent occupied MO.

7.5. Co^{II} SYSTEMS

Optimization was just successful in $[\text{Co}(\text{terpy})_2]^{2+}$ (S12). This cobalt(II) system could share the same fate as S9 and S3 studied in the previous sections, as it could also be reduced when entered in contact with the gold electrode. Hence, it would not be a valid electronic transporter. Also, if another electrode with a lower Fermi level was used, this compound would not either be a valid conductor, as the width of its gap generated by the 2,2';6',2''-terpyridine splitting power is too huge (around 3.5 eV).

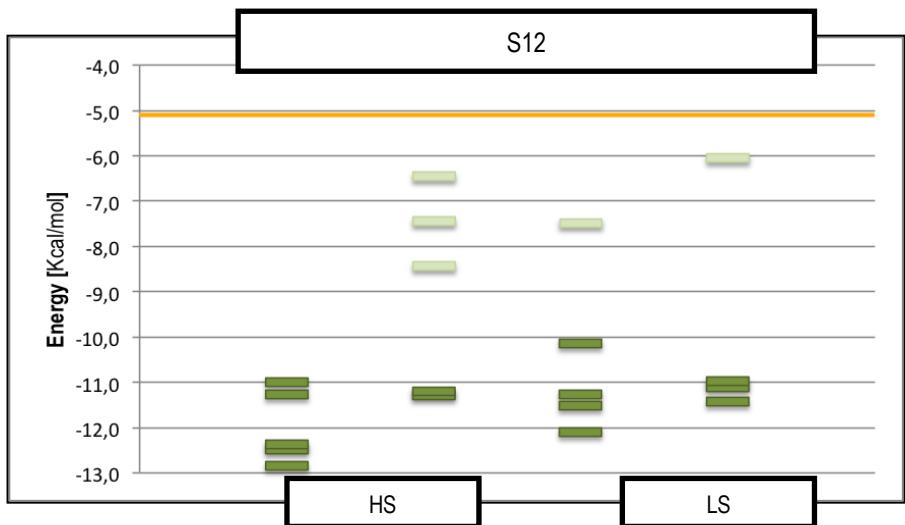


Figure 15. Molecular orbitals diagram for the only successful Co^{II} system studied. For every spin state, alpha MO are on the left and beta MO are on the right. More coloured lines represent occupied MO. The yellow line represents the Fermi level of the gold electrodes.

8. CONCLUSIONS

The differences of energy between high- and low-spin states of thirteen compounds that present spin-crossover have been studied. The hybrid functional with less HF-type exact exchange contribution, TPSSh, has been the best performing Exchange-Correlation functional for the energy determination of the ground states with the basis set used (TZV for ligands, QZVP for the transition metals) according to the criterion used (differences around 0 to 6 kcal/mol). The amount of HF-type contribution has been found to be extremely relevant in the energies determination between high- and low-spin states, as the more HF-type exchange a functional has, the more stable the high-spin state results: B2PLYP, the double hybrid functional with the highest amount of HF-type contribution (53%) has provided the worst results; the other hybrid functionals M06 (27% E_{X}^{HF}) and B3LYP (15% E_{X}^{HF}) have also provided a biased tendency in overstabilizing the high-spin state. ω B97x, a long-range corrected method, has also presented this tendency. OPBE, the only GGA method used, sometimes provided accurate results, but this tendency has shown not to be constant for all the systems studied even with no HF-type exact exchange contribution.

A couple of potential candidates for high-conducting single-molecule devices have been found. Fe^{II} complexes in the high-spin state present β -polarised current, in other words, a high transmission of β -spin electrons would be detected when entered in contact with gold electrodes. On the contrary, compounds in the low-spin state almost present a negligible current. The compounds [Fe(amp)₂Cl₂] and [Fe(H₂Bpz₂)₂(bipy)] would be the best candidates amongst the Fe^{II} systems studied to present the higher conductance in the LS state. Cr^{II} and Mn^{III} complexes with metallic centres that share the same electronic configuration would conduct in both high- and low-spin states. As the currents that would be generated would present different polarization (HS polarises in α and LS in β) further designs could take advantage of this property. Mn^{II} compounds could be acceptable electron transporters in the low-spin state, generating a slightly polarized β current. Their high-spin state does practically not present transportation properties, therefore these complexes could be of great interest, particularly [Mn((tBu)Cp)₂] for generating an almost unpolarized current.

Metallic Centre	System	Spin State	Electronic Transport	Polarization	Redox stability
Fe^{II}	S1	HS	Medium	β	✓
		LS	Negligible	Unpolarized	✓
	S2	HS	Medium/High	β	✓
		LS	Medium/High	Unpolarized	✓
	S3	HS	None	—	✗
		LS	None	—	✗
	S4	HS	High	β	✓
		LS	Negligible	Unpolarized	✓
	S5	HS	Medium	β	✓
		LS	Low	Unpolarized	✓
Cr^{II}	S6	HS	Medium/High	α	✓
		LS	Medium	β	✓
	S7	HS	Medium	α	✓
		LS	Medium	β	✓
Mn^{III}	S8	HS	Medium	α	✓
		LS	Medium/High	β	✓
	S9	HS	None	—	✗
		LS	None	—	✗
Mn^{II}	S10	HS	Poor	α	✓
		LS	Medium	Slightly β	✓
	S11	HS	Poor	α	✓
		LS	Medium/High	Slightly β	✓
Co^{II}	S12	HS	None	—	✗
		LS	None	—	✗
	S13	HS	—	—	—
		LS	—	—	—

Table 3. Table summarizing electronic transport characteristics of the systems studied.

All in all, $[\text{Fe}(\text{amp})_2\text{Cl}_2]$ has been found to be the best candidate to become a single-molecule device, followed by $[\text{Fe}(\text{H}_2\text{Bpzz})_2](\text{bipy})$], which has turned out to be a very appealing compound, as its high-spin state generates a high β -polarized current. $[\text{Cr}(\text{l}_2)(\text{depe})_2]$ could be the candidate system that generates the highest α -polarized current.

For further research it is interesting to considerate studying compounds with π -basic ligands that do not generate a great splitting of the d degenerate orbitals of the metal centre. Thus, the electronic jump in vacant molecular orbitals would become easier, therefore gaining an increase in electron transport.

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10. ACRONYMS

DFT: Density Functional Theory

SCO: Spin Crossover

LS: Low Spin

HS: High Spin

MO: Molecular Orbitals

T_{1/2}: Transition Temperature

amp: 2-pyridylmethylamine

H₂Bpz₂: = bis(pyrazolyl)borate

tzpy: 3-(2-pyridyl)[1,2,3]triazolo[1,5-a]pyridine

depe: 1,2-bis(diethylphosphino)ethane

Ind^{3Me-2,4,7}: (2,4,7-Me₃bis(indenyl)₂)

