Magnetic interactions in molecules and highly correlated materials: Physical content, analytical derivation and rigorous extraction of magnetic Hamiltonians

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1 Introduction

Magnetism is a phenomenon that has always captured the imagination of humans. Its discovery in the western world is attributed to the ancient Greek civilization. More than 2500 years ago, the pre-Socratic philosopher Thales of Miletus already described that magnetite (Fe_3O_4) attracts iron. Older evidences of knowledge on magnetism have been found in China. One may quote for instance the orientation of houses according to the magnetic north (1350-1050 BC, Shang dynasty), the appearance of magnetic fortune tellers (221-206 BC, Qin dynasty) and the manufacturing of compasses for navigation (1088 AD). This period corresponds to the *ancient age* of magnetism according to Coey's classification of the history of magnetism in seven ages.[1] After the magnetostatics and the theory of magnetic fields, the contributions to the theory of magnetism in the 19th and 20th centuries were prodigious. The 19th century is essentially marked by the revolution of electromagnetism and is called *electromagnetic age* in Coey's classification while the first half of the 20th century, which saw the birth of the quantum theory and relativity, allowed magnetism entering the *understanding age*. In particular, this period established the existence of the spin angular momentum of the electron and other elementary particles. Since this time, a constant effort has been devoted to the study of the magnetic properties of matter, for which the underlying physics is sometimes difficult to assess as evidenced by the landmark textbook of Abragham and Bleaney.[2] As an illustration of such difficulties, one may quote the long progression towards the complete understanding of the magnetic properties of the paradigmatic copper acetate molecule, which have raised a series of fundamental questions. At first, copper acetate was assumed mononuclear in the meaning that is should contain just one Cu atom per molecule. However, the magnetic susceptibility, first measured by Guha in 1951,[3] showed a decrease at low temperature and this unexpected behavior attracted the attention of Bleaney and Bowers[4] who performed an electron paramagnetic resonance (EPR) study in 1952. They observed a small zero-field splitting in the first excited triplet state and proposed the existence of interacting pairs of cupric ions to rationalize the magnetic susceptibility behavior. These studies opened several debates, one concerned the nature of the magnetic interactions (either metal-metal or through ligand) while another one was about the nature of the zero-field splitting. This last question was finally solved in 2008 when a new EPR study[5] showed that the axial anisotropy parameter is negative, for which a theoretical rationalization was proposed in 2011.[6] Such topics which aim at understanding and determining the nature and magnitude of the microscopic interactions and their dependence to electronic and structural factors have permitted considerable advances in the fields of experimental characterization and modeling.[7]

In the mean time, applications of magnetism have crossed the ages and their scope continue to expand. After the compass and the horseshoe magnet, motors and magnetic recording devices were massively manufactured. Nowadays magnetic properties are exploited everywhere, and Coey speaks of *Applications age*. Magnetism is present in both basic and leading edge technological applications, from everyday life electrical and electronic appliances to superconducting devices. The discovery of giant magnetoresistive effects opened a new research field and triggered the exploration of the enormous potential of spintronics for applications.[8–19]

Despite the advances in the understanding of magnetic phenomena reached over the last century and the large number of applications based on magnetism, the effort for further understanding is neither obsolete nor trivial. New challenges arise for researchers constantly. Important examples include the understanding of the high-T_c superconductivity and of some fundamental issues of quantum mechanics, such as coherence-decoherence, tunneling, and interferences, which are presently studied in various magnetic objects. A less ambitious but not less important issue is the detailed understanding of the physics that induces the magnetic properties of matter in order to contribute to the certainly crucial task of designing new suitable magnetic systems that exhibit new and/or improved properties. This review addresses questions relative to the theoretical determination of the physical mechanisms that govern the interactions between spin angular momenta (or spins, for short) in pure magnetic systems, and between spin and charges in doped systems.

Most of the chemical systems do not exhibit magnetism (excluding diamagnetism) under standard conditions, i.e. the populated lowest states in which all electrons are paired do not have any spin angular momentum. Nevertheless magnetic phenomena occur in a wide variety of systems from small molecules such as O_2 to extended systems like molecular materials or strongly correlated materials. The microscopic origin of magnetism lies in relativistic quantum mechanics. However, except for some peculiar properties such as the single molecular magnet behavior, most of the magnetic properties can be determined in a nonrelativistic framework through the *ad hoc* treatment of the electron spin. Magnetic behavior appears when the system has one or more unpaired electrons. The wave functions of the states resulting from the coupling of these electrons are intrinsically multi-determinantal, i.e. their description requires the use of strongly-correlated methods. Unfortunately the size of most of the interesting magnetic systems often prohibits the use of such methods within an all-electron description. For this reason, simpler model Hamiltonians that only consider the magnetic electrons are used both to experimentally characterize their macroscopic properties and to theoretically model them. In general, these models are physically based and usually reproduce with satisfying accuracy the energy spacings between the lowest energy states.

In this context, the use of theoretical chemistry, which deals with the all-electron exact electronic Hamiltonian, may have several purposes. Depending on the size of the magnetic object, theoretical chemistry studies may concern the whole system for relatively small molecules, or fragments of it when dealing with large molecules, clusters or solids. The determination of the electronic structure of the lowest states and their energetic ordering usually gives access to the chemical features that are responsible for the magnetism such as weak/strong interactions, geometrical characteristics, among others. A second important application of theoretical chemistry consists of extracting and eventually deriving model Hamiltonians rigorously from the energies and wave functions computed using the exact electronic Hamiltonian. Indeed, as it will be shown in several sections of this review, (semi-)empirical model Hamiltonians are sometimes too simple to describe accurately complex systems. The refinement of these model Hamiltonians is not always easy to anticipate from phenomenological arguments and sophisticated calculations combined with rigorous techniques of extraction are required to determine appropriate models. From a more quantitative point of view, quantum chemistry tools may be employed to determine the magnitude of the leading interactions, such as hopping integrals and magnetic coupling parameters between local magnetic units.

This review describes how theoretical chemistry can provide insight in the magnetic structure of systems with unpaired electrons. These can be either delocalized over several atoms as generally found in organic radicals, or strongly localized on metallic sites in inorganic systems. The next section provides a framework for the theoretical description of magnetic systems by defining some fundamental concepts as the magnetic orbitals and the theoretical foundations of model Hamiltonians. Thereafter, the extraction from quantum chemistry calculations will be explained within the effective Hamiltonian theory framework and we will show how to use the Hubbard Hamiltonian as a guideline for the derivation of simpler model Hamiltonians.

Section 3 reviews the physics of the simplest magnetic system, namely the two-electrons in two-orbitals problem. Minimal valence space models are discussed and the extensions of these to analyze the most important contributions to the coupling of the spin moments. After these two introductory sections, we will review the most extensively used computational schemes in the field of magnetic systems in section 4. Although both wave function (WF) methods and schemes based on density functional theory (DFT) are reviewed, the emphasis lies on the first ones, since many excellent reviews have been published recently on the application of DFT in magnetic systems.[20–25]

The two last sections are dedicated to the physics of more complex magnetic systems in which we go beyond the two-electrons in two-orbitals system. Section 5 reviews the possibilities of theoretical chemistry to extract information about many-body operators in multi-center systems, and discusses the validity of the simple Heisenberg Hamiltonian for systems that have magnetic units with spin angular moments larger than 1/2, i.e. more than one unpaired electron per center. The last part of the review (section 6) is dedicated to doping and describes systems in which the number of electrons and orbitals in the valence space is not strictly equal. This comprises also a discussion of the physics of the mixed valence complexes.

We want to emphasize that this review does not pretend to give a complete overview of all the applications of theoretical chemistry that have been published in the field of magnetic systems, but rather give an overview of the theoretical foundations of model Hamiltonians and the procedure to condense the information of *ab initio* calculations in simpler models providing understanding and rationalizations of magnetic behavior in relatively simple analytical expressions.

2 Theoretical background

2.1 Magnetic sites and magnetic orbitals

Magnetic systems are characterized by the presence of unpaired electrons. The number of unpaired electrons (n) and their spatial localization (magnetic orbitals) could in principle be determined from the diagonalization of the exact density matrix of the N-electron ground state wave function. The occupation numbers of the so-obtained natural orbitals are close to two or zero for most orbitals, while n of them are close to one. The corresponding orbitals are the hypothetical magnetic orbitals. Since the obtention of the exact wave function is impossible for any nontrivial system, the magnetic orbitals are determined by approximate treatments of different complexity. In this section, magnetic orbitals will only be introduced from the most elementary approaches while sophisticated determinations will be discussed in section 4. The following presentation may appear as being trivial for many readers. However, the *a priori* identification of the magnetic orbitals is crucial for starting a theoretical calculation, in particular for calculations performed using symmetry criteria in which one assigns the unpaired electrons to orbitals belonging to a particular irreducible representation. This recall may also be useful to people entering the field of the magnetism in coordination chemistry that are less familiar with ligand field arguments. Similarly, some basic features regarding organic free radicals are outlined.

2.1.1 Transition metal paramagnetic units

This section briefly recalls the physical factors that govern the main features (spatial and spin configurations of low energy, energy spacings between the lowest states, *etc.*) of a mononuclear complex constituted of a transition metal (TM) ion and its surrounding ligands. The ligands are assumed to have a closed-shell electronic configuration, so that the magnetic electrons are located in the orbitals which are essentially of metal-d character with delocalization tails on the ligand orbitals. The energetic order of the spatial configurations arising from the d^n manifold depends on the energy spacings of the metallic orbitals which are usually governed by the crystal field. The crystal field theory was originally developed to rationalize the properties of ionic crystals[26,27] and later generalized to molecular complexes. Since the theory has been discussed in many textbooks,[28–31] it will not be detailed here. The only information that will be used in this review concerns the energetic ordering of the d orbitals of a transition metal ion surrounded by its ligands. In crystal field theory, the surrounding ligands are condensed to point charges and the energetic ordering of the TM-d orbitals is governed by the electrostatic repulsion between the metallic orbitals and the point charges. Since only the position of these points charges counts, the energetic order of the orbitals is determined by the geometry of the complex. In practice this theory consists of diagonalizing the electrostatic operator in the basis of the orbitals. In the simple case of an octahedral symmetry point group, one easily sees that the orbitals of the e_g irreducible representation, which are directly pointing towards the ligands, will be more destabilized than the three other orbitals of the t_{2g} irreducible representation. For other symmetry point groups (D_3, for instance), the orbitals that diagonalize the electrostatic operator are linear combinations of these orbitals. This electrostatic model gives also access to the energy differences between the various orbitals, which are usually expressed as functions of the so-called crystal field parameters.

When the delocalization between the metal and the ligand orbitals is very strong, the final energetic order may be different from the one predicted from crystal field theory. In such cases, the ligand field theory[32,33] must be used to explicitly introduce the delocalization between the metal and ligand orbitals. The energy of the spatial configurations (i.e. distribution of the electrons over the orbitals) does not only depend on the orbital energies but also on the electron-electron repulsions which are accounted for through the two-electron integrals. This electron repulsion tends to minimize the number of doubly occupied orbitals and the number of electrons in the same region of space. As a consequence, the number of unpaired electrons may vary depending on the magnitude of the electronic repulsion and the orbital energy splittings. Taking the d^6 configuration in an octahedral environment as an example (Figure 1), it is well-known that the so-called weak-field ligands cause such a small splitting of the d orbitals that the electronic configuration with the lowest energy has one doubly occupied d-orbital and the other d orbitals are filled by a single electron.

On the contrary, strong-field ligands lead to double occupancy of the three lowest d-orbitals, while the other two remain empty. In case of intermediate-field, spin crossover between the low-spin and the high-spin states may appear.[34] To facilitate the determination of the lowest spatial configuration, the most common ligands are classified depending on the strength of the field they exert on the TM. One may however note that for some ligands, the lowest spatial configuration may change according to the nature of the metal and its oxidation number, in particular for intermediate ligand fields.

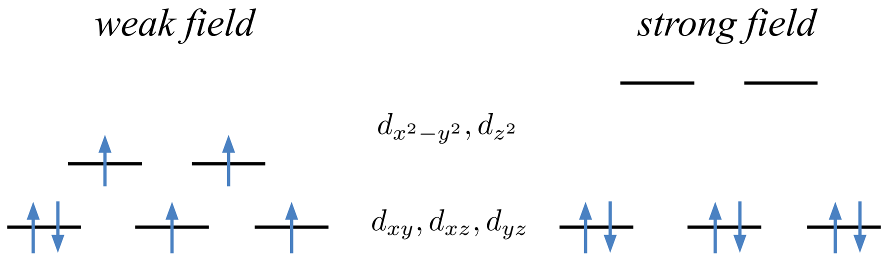

Figure 1: Most stable electron distributions for the TM-d^6 configuration of an octahedral complex at weak (left) and strong (right) ligand field strengths.

For a given spatial configuration with several open shells, the energetic order of the spin states obeys the Hund's rule, i.e. the ground state has the highest spin angular momentum, the high-spin state. The unpaired electrons are coupled through the local exchange integrals, which always stabilize the highest spin states. Due to the delocalization tails onto the ligand, the energetic ordering between the various spin states of the same spatial configuration does not strictly obey the Landé interval (see eq 2). However, since these exchange integrals are large (between 0.6 eV and 1 eV for first-row TMs), the first excited spin state is usually relatively high in energy in comparison to the high-spin ground state. This feature is rather important when dealing with polynuclear species, because the common models to describe magnetic properties only consider the ground state of each magnetic center and neglect the role of all local excited spin states.

In general, the metallic ions are inherently responsible for the magnetism in inorganic systems. However, the magnetic orbitals have tails extending onto the ligands and *vice-versa* (Figure 2), implying that the ligands play a crucial role in the interactions between the spin angular momenta of the different metal centers. For TM complexes involving σ- and/or π-donor ligands, the magnetic orbitals have antibonding tails on the ligands (i.e. they present a node between the metal and the ligand). On the contrary, for a π-acceptor ligand the tails are bonding. The delocalization is caused by ligand-to-metal charge transfer excitations (LMCT) in the first case and metal-to-ligand charge transfer excitations (MLCT) in the second one. Sticking to a strongly localized orbital description requires models with two different types of basis functions, namely atomic orbitals on the metal and pure ligand orbitals. Such models are usually referred to as two-band (or multi-band) models due to the fact that at least two different electron hopping processes (metal-metal and metal-ligand) are active, leading to two (or more) bands.[35–37] Starting from a picture with partially delocalized orbitals that incorporate the metal-ligand electron hopping result in a single-band model.[37–39] In the following we will essentially work within the second paradigm.

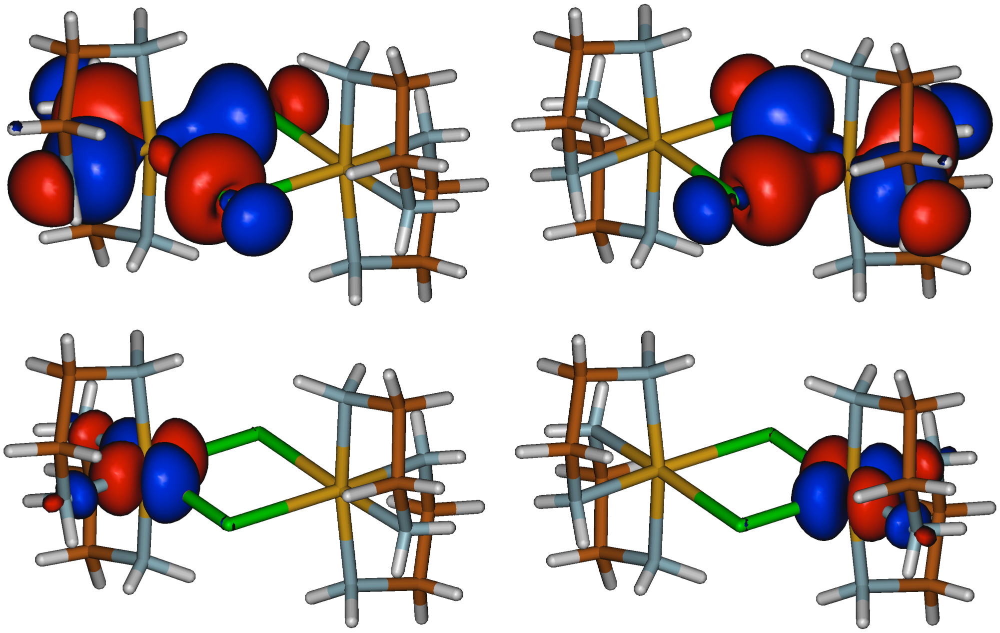

Figure 2: Localized ligand (above) and magnetic (below) orbitals in a binuclear Cu^{II} complex showing the tails of ligand orbitals on the metal and of metal orbitals on the ligands.

Of course magnetism is also present in lanthanides and actinides where f orbitals carry the unpaired electrons.[40–64] However, this field in which the relativistic effects are important is out of the scope of the present review.

2.1.2 Organic magnetic units

Many different units are used in the design of organic magnetic architectures. Among the most common ones, we mention nitroxides, thiazyl radicals, verdazyl radicals, carbenes, nitrenes, phenoxides, ketyl radicals, triphenylmethyl radicals and derivated molecules. Free radicals in organic chemistry are usually more unstable (reactive) than the magnetic metal ions in coordination chemistry. As counterexamples, one should however quote the thiazyl[65] and verdazyl[66] radicals, and the nitroxides.[67] The latter are specially versatile units in the conception of magnetic organic molecules.[68–70] The magnetic MO of these units is essentially localized, for instance on the N and O atoms of the nitroxide group, and can show delocalization tails on the conjugated system to which it is attached (Figure 3).

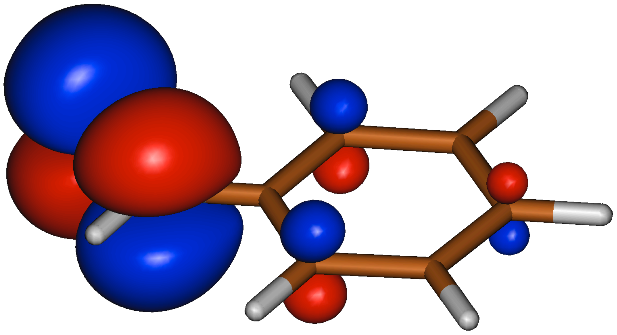

Figure 3: Magnetic orbital localized on the nitroxide group with tails on the conjugated system.

A second type of radicals concerns conjugated hydrocarbons[71] with an odd number of conjugated carbons. The spin distribution can be either essentially localized on extracyclic groups such as methylene in a benzyl radical or have a much more delocalized character as occurs in phenalenyl. This molecule has three fused benzene rings and the magnetic MO shows important amplitudes on six peripheral carbon atoms as illustrated in Figure 4, in strong contrast with the localized character of the magnetic orbitals of transition metal ions. EPR gives an indirect access to the spin distribution on the carbon atoms through McConnell's relation.[72] The resulting distributions coincide reasonably well with the spatial distribution of the unpaired electron provided by the simple topological Hückel Hamiltonian[73] and other more elaborate descriptions proposed by

Borden and collaborators.[74,75] If the hydrocarbon is alternant, i.e. free from odd-membered rings, the carbon atoms can be divided in two groups in such a way that a carbon atom of one group is always linked to carbon atoms of the other group. The Hückel method predicts that the magnetic orbital has zero amplitude on the carbons in the group with less atoms, whereas more accurate treatments predict small negative spin density on these atoms. This feature has been confirmed by EPR spectroscopy.[72,76]

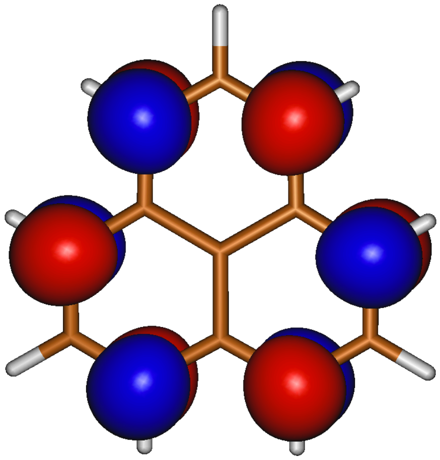

Figure 4: Delocalized magnetic orbital of the phenalenyl radical.

In many cases, simple rules can be used to assess the magnetic character of the ground state of a conjugated system. If there exists a Kékulé form in which all electrons are paired, usually the ground state is a spin singlet. This rule has some exceptions, in particular for non-alternant hydrocarbons.[77] The existence of a Kékulé form does not tell whether the system is a closed-shell system or a biradical with a low-lying excited singlet state. The Chichibabin molecule and the system with two phenalenyl radicals bridged by an acetylenic bond are well-known examples of such a problematic situation.[78–83] These molecules apparently possess a biradicalar character despite the fact that they present a Kékulé bond pairing. An intense debate is running concerning the biradical character of long polyacenes. DFT calculations[84–86] suggest a biradical nature and density matrix renormalization group (DMRG) calculations in the complete π valence space[87] support this interpretation. On the contrary, calculations that include electron correlation beyond the small complete active space self-consistent field (CASSCF) reference wave functions plead for a closed-shell character.[88–90] Obviously, the question remains open for discussion.

When the molecular graph does not accept a Kékulé pairing of adjacent carbons, the Ovchinnikov rule[91] can be used to anticipate the spin multiplicity of the ground state of alternant organic units. The rule states that the spin S of the ground state is given by the M_S value of the most alternant spin distribution, i.e. the spin distribution that minimizes the number of parallel alignments of the spin moments (spin frustrations) on adjacent atoms. This rule is equivalent to Lieb's theorem[92] for bipartite lattices. For nonalternant systems, the Kékulé and Ovchinnikov rules may be in conflict,[77,93] giving potentially rise to spin-crossover phenomena. Regarding alternant hydrocarbons, the Ovchinnikov rule apparently does not suffer exceptions when it predicts a high-spin ground state. When a singlet ground state is predicted, there is a low-lying, nearly degenerate triplet state if the system can be divided into two disjoint radical units,[94,95] as for example in tetramethyleneethane, where the two non-bonding orbitals are connected by atoms where the Hückel orbitals have zero amplitudes.

The delocalized character of the magnetic orbitals makes that the energy difference between the ground state and the first excited state in organic magnetic units with $S > 1/2$ is much smaller than in analogous inorganic units. Therefore, the calculation of reliable spin state energy differences requires an accurate treatment of the electron correlation for this kind of materials.[96–102]

2.1.3 Nature of the bridges

The chemical nature of the ligands that form the bridge between the magnetic units also has a large influence on the magnetic coupling. The first effect is the mixing of the magnetic orbitals and the ligand orbitals, which facilitates the delocalization of the unpaired electrons and enhances the coupling between the magnetic units. The second effect is a more complex electron correlation process involving the magnetic electrons and the ligand electrons. This effect is responsible for the charge and spin polarizations, which will be analyzed in section 3.3 and proceed through low energy excitations such as π to π^* excitations in long conjugated bridges. Because of their small size, diamagnetic atomic ions such as Cl^-, O^{2-} or closed-shell metal ions are usually good spin linkers causing in principle a significant delocalization between the magnetic centers. However, the degree of delocalization depends strongly on the overlap between the magnetic orbitals on the metal and the valence orbitals of the ligands. The absence of low-lying valence excitations results in rather small spin and charge polarization contributions. At variance, molecular ions such as oxalate, acetate, azide, etc. and conjugated bridges do show low-lying excited valence states and generate larger spin and charge polarization effects. Closed-shell metal ions can also act as ligands in M'–M–M' architectures, where the spin carriers M' are either paramagnetic TM ions or organic magnetic units. Such situations are rather frequent in new generations of strings of transition metal ions.[103–105]

Many efforts are nowadays devoted to the research of long conjugated ligands that are both spin and charge polarizable, ensuring a non-negligible coupling between remote spin carriers. Among them one may quote polyenes,[106] polyphenylene,[107,108] alternance of double or triple bonds with 6-membered rings,[109,110] polyacenes.[111–114] Other dienes with long-range interactions have also been discussed.[115]

2.1.4 Typology of magnetic assemblies

With the three basic ingredients discussed in the previous sections (TM ions, organic radicals and linking bridges), magnetic materials can be assembled in a rational way[116] by properly choosing the magnetic units and connecting them either directly (through space) or mediated by bridges (through bond) in such a way that the material shows a new magnetic moment. The classification of the different magnetic materials can be made based on the nature of the magnetic units. Three classes can be distinguished, either containing organic or inorganic magnetic units only, or assembled from mixtures of the two types. Here, we shortly review the main features of the three types of assemblies.

An important effort has been devoted to the design of molecules containing paramagnetic TM ions with a non-zero net magnetic moment.[117,118] Such electronic states can result from the ferromagnetic coupling between the local spins, from the antiferromagnetic coupling between magnetic units with different spins, and even from double exchange mechanisms in mixed valence systems.[119–122] Within this group of discrete moieties, the molecules with a uniaxial magnetic anisotropy are of particular interest both from technological[123] and fundamental[124,125] points of view, especially when they present a slow relaxation of the magnetization. As prototypes of these single molecule magnets (SMM) we mention the Mn_{12},[119] Mn_6[126] and Fe_4[127] molecular complexes. This phenomenon also exists in mononuclear species, for instance in complexes containing a single lanthanide ion.[128,129] Despite the complexity due to the high nuclearity and/or importance of relativistic effects, such systems have been inspected theoretically by means of DFT.[130]

To go beyond this molecular level, an important advance was made by extending the interactions in several directions leading to 1D,[131–135] 2D[136] and 3D[137–139] (molecule-based) magnetic materials. Again, magnetic anisotropy can lead to slow relaxation of the magnetization giving rise to the single chain magnets (SCM).[140,141] Two-dimensional antiferromagnetic materials have been shown to exhibit remarkable transport properties upon doping, and the most famous examples are the high-T_c superconductivity in cuprates[142] and the colossal magnetoresistive effects in manganites.[143,144] The photomagnetic properties of Prussian blue analogs[145,146] provide an example of the special magnetic properties of 3D materials.

Magnetic architectures can be built as well from coupled organic units. As shown in references 147–150, it has been possible to conceive finite high-spin organic magnetic units using the Ovchinnikov rule as a guide. The synthesis of high-spin architectures has also been achieved from assembling carbenes with a local $S = 1$ spin.[151,152] Ferro-, antiferro- and ferrimagnetic 2D architectures have been synthesized with pure conjugated hydrocarbons as building-blocks. The field of the "carbon based magnetism" is under rapid development.[114,147–150,153–161] The design of these lattices may follow a bottom-up strategy, but a seducing alternative consists of starting from a graphene sheet and introducing local spin carriers by appropriate exclusions of some sites from the conjugated system. These subtractions are realized by carving holes or by locally saturating some carbon atoms. If the tailoring of the graphene lattice is periodic, ferro- or antiferromagnetic lattices emerge.[162–166]

A special domain concerns the Bechgaard salts[167–169] for which electron transfer between organic donor and acceptor molecules generates unpaired electrons on both partners. In addition to magnetic properties, these architectures may even exhibit quasi-one-dimensional superconductivity.

Molecular radicals such as nitroxides can also be used to build magnetic structures, either molecular systems or extended materials of various magnetic dimensionality. Actually, the first molecular ferromagnetic lattice was a crystal of nitroxides,[170] although its Curie temperature was very low, only 1.48 K. When nitroxides are packed in a crystal, often bridged through intermolecular hydrogen bonds, the mechanisms and balance of the intermolecular spin couplings are more complicated than for the 2D architectures of conjugated hydrocarbon radicals. The correct interpretation of the temperature dependence of the magnetic susceptibility depends critically on a proper selection of the most important through-space couplings and their ratios.[171–178] On the contrary, when the nitroxide radicals are chemically bonded, the coupling proceeds through bonds and/or space.[174,179–184]

Among the different strategies that have been developed for designing magnetic systems, the "metal-radical" approach has led to promising results. This approach was proposed by Gatteschi and co-workers[185] and aims at strong direct metal-ligand magnetic exchange interactions from the coordination of paramagnetic transition-metal ions with stable free radicals. The strategy has been used to synthesize molecules with very strong magnetic couplings. In some cases, the interactions can be extended in one, two, or three spatial directions, giving rise to molecule-based systems with cooperative magnetic behavior.[186–192]

At this stage, we also remark the interesting behavior of the so-called non-innocent ligands in transition metal complexes. The concept was introduced to rationalize the spectroscopic and magnetic properties of complexes in which redox reactions take place on the ligands.[193] These non-innocent ligands exist with several oxidation states and possess a net spin moment in some cases. In several hybrid magnetic complexes, organic ligands behave as magnetic units coupled to the paramagnetic TM ions. The experimental and theoretical characteristics of such complexes have intensively been investigated by the groups of Wieghardt and Neese.[194–197] Important prototypes of the non-innocent ligands are the well-known (pyridinecarboxamido)benzene derivatives,[198–200] the aminophenolates and aminothiophenolates, and the glyoxal-bis(2-mercaptoanil) anion for which both experimental and theoretical studies have evidenced the non-innocent character.[194–196,201–203] The study of metal-radical interactions (sometimes involving non-innocent ligands) extends into biochemistry since such magnetic interactions have been evidenced to exist in the active sites of metalloproteins.[202,204,205]

Other interesting properties of potential technological interest can be coupled to magnetism. Highly interesting layered bifunctional materials have been obtained by combining magnetic lattices of TM anionic compounds such as bimetallic oxalates or polyoxometalates with cationic organic layers as tetrathiafulvene and derivates.[206–211] The combination of magnetic layers with photoactive or proton conductive layers has also been reported.[212,213] On the other hand, materials with interesting optical properties such as magneto-chiral dichroism can be obtained by mixing chirality with magnetism.[214]

2.1.5 The role of theory

From this brief overview of the domain of molecular magnetism, quantum chemical theory and the related computational tools can make important contributions in different areas:

i) The characterization of the spin carriers, i.e. the number of unpaired electrons, their spatial localization and the energy separation between the local high-spin ground state and the excited states. Taking a biradical unit as example, it is not always clear whether such system has to be treated as an $S = 1$ spin unit or should be considered as two ferromagnetically coupled $S = 1/2$ spins. The former modelization is simpler, but it neglects the local singlet state. When these singlet states are low in energy, they contribute to the interactions between the magnetic units as will be illustrated in sections 5.3 and 6.3. As an extreme projection of an electronic problem onto a spin model, we mention that the derivation of the Ovchnnikov rule was based on a magnetic description of the π-electrons of a conjugated molecule as a system of antiferromagnetically coupled $S = 1/2$

spins. Actually, the π-system of conjugated hydrocarbons can be seen as a spin system[215–218] and treated through a Heisenberg Hamiltonian. The efficiency of this simple magnetic model in the treatment of conjugated hydrocarbons, usually considered as highly delocalized, is rather astonishing. Both ground and excited states can be described in an accurate way within this magnetic description.[219,220]

ii) Insight in the coupling between magnetic sites is crucial to understand the properties of magnetic materials. Theory can provide a validation for simple models or empirical rules that anticipate the relative magnitude of the coupling. The rational use of these conceptual tools has played a crucial role in the design of beautiful architectures by Kahn and co-workers[136,221,222] and are still applied to design new and complex multifunctional materials. Quantitative quantum chemical approaches can confirm or revise simple models, evidence new effects, and establish the importance of presumably negligible interactions. In some cases, the experimental magnetic susceptibility is perfectly reproduced by fitting the parameters of an inappropriate model. In other cases, such as in molecular crystals of nitroxides or analogous radicals, computation is the unique route to assess the relative amplitudes of competing intersite interactions. More generally, the nature and mechanism of the magnetic coupling (through space / through ligand, direct exchange / kinetic exchange, spin polarization / spin delocalization etc.) can be clarified from the analysis of high-level calculations.

iii) Finally the accuracy and the domain of applicability of quantum chemistry is now sufficient to be used as an exploratory tool for the design of new interesting materials.

An important part of this review focuses on transition metal based magnetic systems. Nevertheless, quantum chemical calculations have also been performed on the other types of magnetic systems previously described. For instance, magnetic hydrocarbons were investigated by Borden and co-workers,[96–99,101,102] nitroxides and metal-nitroxides have been the subject of many theoretical works[100,111,175,184,223–240] while metal-verdazyl radicals complexes were inspected by Robert and collaborators.[241–243] Finally, metal-radical complexes have been intensively studied by Neese and co-workers.[244–248] The list of references in this paragraph is of course far from being exhaustive.

2.2 Model Hamiltonians as effective Hamiltonians

Due to the complexity of magnetic systems, simple Hamiltonians called model Hamiltonians are commonly applied to model the macroscopic properties of magnetic systems. These Hamiltonians have often been proposed on the basis of the chemical/physical intuition, as phenomenological Hamiltonians. One of the roles of theoretical chemistry in the domain of magnetism consists of providing evidences of the validity (or invalidity) of these models. When the model is appropriate (which is very often the case), values of its constitutive interactions can be extracted from first principles calculations. In case of invalidity, one may expect that the tools of theoretical chemists should also enable the determination of new accurate models. The studies presented hereafter use the effective Hamiltonian theory to establish the validity and the physical content of different model Hamiltonians from the all-electron non-relativistic Born Oppenheimer Hamiltonian $\hat{H}$. In this section, we will first present the simplest model spin Heisenberg Dirac van Vleck (HDVV) Hamiltonian and then recall briefly the main equations of the effective Hamiltonian theory and use it to extract the HDVV Hamiltonian in a simple system of two centers each bearing a spin $S = 1/2$.

2.2.1 The Heisenberg Dirac van Vleck Hamiltonian

The relevance of most model Hamiltonians is based on the assumption that a large gap exists between the electronic ground state of the magnetic centers and their locally excited or ionized states. This should also hold when dealing with a multi-center magnetic system. As a consequence, the space that spans the model Hamiltonian can be restricted to products of local ground states. The determinants that describe these states are usually referred to as *neutral* determinants, where *neutral* does not mean that the metal ions are uncharged, but maintain their oxidation state as in the ground state. Hence, for a purely magnetic system, the only degrees of freedom are the M_S components of the spins of the units. For instance, in the two-center case of spins $S = 1/2$, the model space in the total $M_S = 0$ subspace is constituted of two functions $|\downarrow\uparrow\rangle$ and $|\uparrow\downarrow\rangle$, or more commonly $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$. In all pure spin Hamiltonians, the spatial configuration can be omitted since it is common to all the states and the basis is constituted of pure spin functions. The spin Hamiltonian that works within the basis of pure spin functions is called the Heisenberg Dirac van Vleck (HDVV) Hamiltonian[249–251] and has the following expression for a multi-center system of spins S_i:

$$\hat{H}_{HDVV} = -\sum_{i<j} J_{ij}\left(\hat{S}_i \cdot \hat{S}_j - \frac{n_i n_j}{4}\hat{I}\right) \tag{1}$$

where n_i and n_j are the number of unpaired electrons on centers i and j, $\hat{I}$ is the identity operator, $\hat{S}$ is the spin operator with the vector components $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ and J_{ij} is the magnetic coupling between centers i and j. This definition fixes the zero of energy at the energy of the highest spin multiplicity state. The low-lying states of a two-sites system that obeys the HDVV Hamiltonian respect the Landé interval rule:

$$E(S-1) - E(S) = JS \tag{2}$$

When holes (or extra electrons) are introduced in a multi-center system, the model space also considers all possible distributions of these holes on the magnetic centers, but the spatial part of the wave function cannot be neglected any longer. For instance, in the above mentioned two-center case, the model space of the ionized system in the total $M_S = 1/2$ subspace is constituted by the two functions $|core\ \uparrow \cdot\rangle$ = $|core\ a\rangle$ and $|core \cdot \uparrow\rangle$ = $|core\ b\rangle$, where the dot represents an electron vacancy and *core* represent all the doubly occupied orbitals.

2.2.2 The effective Hamiltonian theory

The effective Hamiltonian theory has been formalized by Bloch[252] in 1958. Two years later, des Cloizeaux proposed a hermitian version of this formalism,[253] which is the most useful for our purpose. Since both theories have been explained in many papers,[254–263] they will not be detailed here. For the sake of clarity, we only recall their philosophy and their main equations.

From a theoretical point of view, model Hamiltonians must reproduce as accurately as possible the low energy solutions (energies and wave functions) of the exact electronic Hamiltonian while working on the basis of a small number of determinants or functions. The effective Hamiltonian theory makes possible to determine an effective Hamiltonian which insures the maximum satisfaction of these requirements and can then be compared to the model Hamiltonian. The N lowest solutions of the exact electronic Hamiltonian $\hat{H}$ spanned by a large space S constitute a subspace of S called the target space S'. These target solutions are defined as:

$$\hat{H}|\Psi_i\rangle = E_i|\Psi_i\rangle. \tag{3}$$

For instance, if one wants to extract the HDVV interaction (i.e. the magnetic exchange integral J) for a two $S = 1/2$ system, the two target states are the lowest singlet and triplet states. The main idea of the effective Hamiltonian theory is to establish a one-to-one correspondence between the target space S' and an iso-dimensional model space S_0 that spans the effective Hamiltonian. The projector $\hat{P}_0$ onto this model space is defined as:

$$\hat{P}_0 = \sum_{I \in S_0} |I\rangle\langle I|. \tag{4}$$

where $\{|I\rangle\}$ is an orthonormal basis of this space. In the considered example, the model space is constituted of the two determinants $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$. The effective Hamiltonian is defined such that its N eigenvalues are equal to N eigenvalues of $\hat{H}$ and that its eigenvectors are the projections of the corresponding eigenvectors of $\hat{H}$ on S_0:

$$\hat{H}^{eff}|\widetilde{\Psi}_i\rangle = E_i|\widetilde{\Psi}_i\rangle \tag{5}$$

where

$$|\widetilde{\Psi}_i\rangle = \hat{P}_0|\Psi_i\rangle \tag{6}$$

The quality of the so-defined Hamiltonian depends of course strongly on the norms of the projections, since they univocally determine the relevance of the model space. The main difference between the Bloch and des Cloizeaux formalism resides in the definition of the spectral decomposition of the effective Hamiltonian. Indeed, since the projections have no reason to be orthogonal, the Bloch's formulation may lead to nonhermitian effective Hamiltonians. In order to overcome this drawback, des Cloizeaux proposed to use the orthonormalized (ON) projections defined by:

$$|\widetilde{\Psi}_i^{ON}\rangle = S^{-1/2}|\widetilde{\Psi}_i\rangle \tag{7}$$

in the spectral decomposition of the effective Hamiltonian given by:

$$\hat{H}^{eff} = \sum_i |\widetilde{\Psi}_i^{ON}\rangle E_i \langle\widetilde{\Psi}_i^{ON}| \tag{8}$$

In eq 7, S is the overlap matrix of the projected eigenfunctions $\{|\widetilde{\Psi}_i\rangle\}$. From eq 8 all the matrix elements of the effective Hamiltonian can be numerically calculated and compared to the analytical elements of the model Hamiltonian. This comparison permits both to calculate the interactions of the model Hamiltonian and to check its validity. In the considered example, the off-diagonal numerical matrix elements of the effective Hamiltonian is half the coupling constant and the value of the exchange integral J can be calculated. One should note that this definition may introduce nonzero effective interactions between all the functions of the model space, even when there are more than two differences in the orbital occupations of the determinants considered. The above described procedure is illustrated in Figure 5.

Two different uses of the effective Hamiltonian theory can be found in the literature. The most common one only uses the energies to calculate the effective interactions. If the number of unknown quantities (parameters of the model Hamiltonian) is lower than or equal to the number of calculated energy differences, it is possible to calculate all the necessary interactions by solving the system of equations given by the analytical expressions of the eigenvalues of the model Hamiltonian. To extract the parameters, symmetry can advantageously be used to obtain parametric expressions of the energy of different states.[264] Except in particular cases of strong inconsistency between the model Hamiltonian and $\hat{H}^{eff}$, this procedure usually provides enough information to determine all the interactions. If the system of equations is overdetermined, it is possible to extract

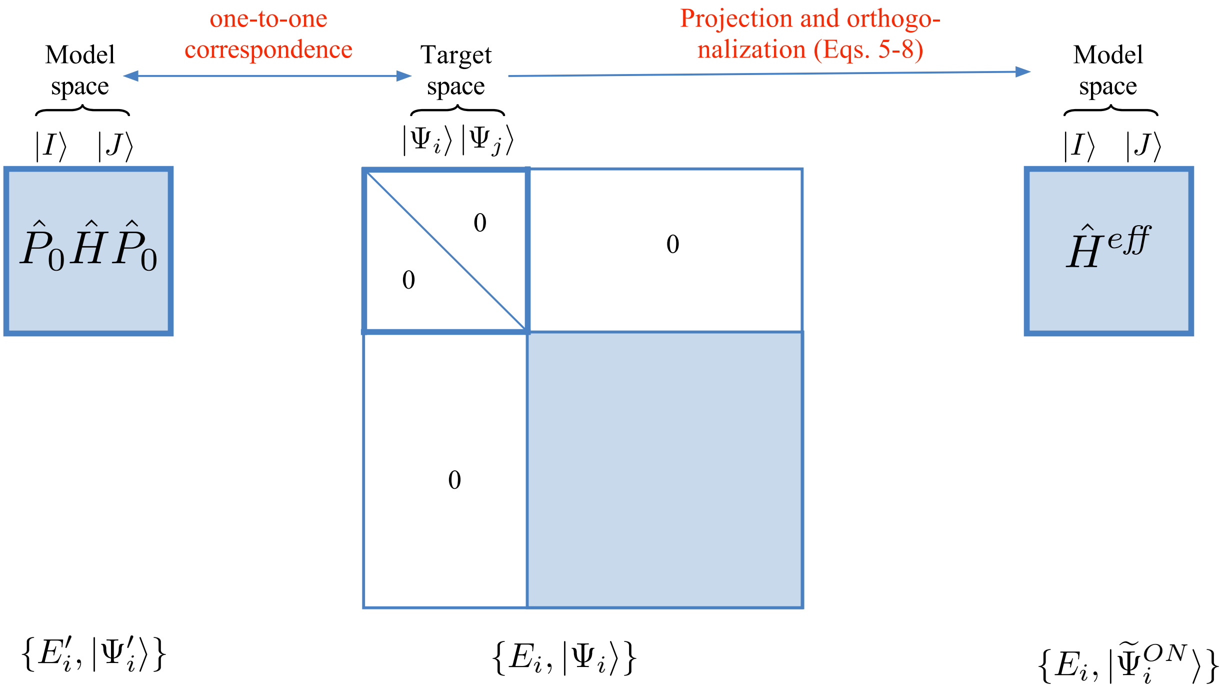

Figure 5: Graphical illustration of the relation between the model space (left and right) and the target space (center) and of the representative matrices of the exact n-electron Hamiltonian (left and center) and the effective Hamiltonian (right).

the same interactions from different equations and assess the accuracy of the model Hamiltonian. It should however be pointed out that this procedure does not ensure that all relevant physical interactions have been taken into account, which is a general problem of fitting procedures.

The second, more rigorous, procedure consists of determining all matrix elements of the model Hamiltonian using both the energies and wave functions of the all-electron Hamiltonian. Such a procedure obviously provides much more information. As shown in previous studies (some of them discussed below in section 5.2 and 6.3), this procedure extracts a large number of interactions, but also leads to question the validity of the model Hamiltonian. Basically, there are two different reasons for invalidating model Hamiltonians upon comparison with $\hat{H}^{eff}$. The first one is that the model space does not contain the essential physics. This occurs when the norms of (some of) the projections are too small and indicates that other functions should be added to the model space. The analysis of the all-electron Hamiltonian wave functions provides the information to decide which functions should be included in the model space.

The second reason for questioning the phenomenological model Hamiltonian is that some essential interactions are missing. While the exact electronic Hamiltonian only involves two-body interactions, the effective Hamiltonian may also introduce three, four or more body-interactions. These interactions are not easily anticipated phenomenologically from the chemical or the physical intuition and are rarely included in the model Hamiltonians. Different situations may arise depending on the type of material. For example, some particular two-body terms are neglected in the model Hamiltonian according to the topology of the constituting units (typically, non-nearest-neighbor interactions) in a case where the extraction of the interactions based on rigorous calculations of energies and wave functions evidence their role. This does not change the nature of the model Hamiltonian, but shows that a number of interactions cannot be disregarded. In other situations, many-body interactions arising from complex couplings in the model space or with determinants in the outer space can also appear. In this case, new terms of a different nature than the standard two-body interactions have to be added to the model Hamiltonian to correctly describe the physics of such systems. Some examples are discussed in section 5.

An illustration of the difficulties to extract all physically based effective interactions is given in the study of the magnetic interactions of a binuclear Ni^{II} complex.[265,266] In this case, the number of interactions of the accepted model is equal to the number of energy differences, i.e. the reproduction of the calculated spectrum from the interactions extracted from the energies is perfect and the projections of the exact wave functions onto the model space are good. Yet the numerical effective Hamiltonian exhibits interactions that are assumed to be zero in the accepted analytical model Hamiltonian of the same order of magnitude as the standard interactions. One can legitimately wonder whether there is interest to extract a more complicated Hamiltonian while it provides the same spectrum as the simpler one. Two answers can be given to that question. First of all the *understanding* of the factors governing the properties requires to evidence all important interactions. Secondly, if the Hamiltonian is extracted for a fragment of the system (as it is often the case for large systems) it will only be transferable to study the full system (or a larger fragment) if it contains all required interactions.

To end this general discussion of the properties and applicability of the effective Hamiltonians, we note that the use of model Hamiltonians makes possible the treatment of larger systems than those accessible by *ab initio* calculations. However, it should not be forgotten that spin Hamiltonians are used to model systems with strongly correlated electrons, and hence, often intrinsically multi-determinantal. This restricts the applicability of the model Hamiltonians to a limited number of magnetic sites. For instance, the HDVV Hamiltonian can be exactly diagonalized for a restricted number of eigensolutions of $S = 1/2$ systems with up to 40 sites.[267] If larger models are needed, one necessarily has to drive back on approximate schemes to determine the eigenvalues of the model Hamiltonian. When the model space should be enlarged, the applicability domain of the new Hamiltonian is restricted in comparison to the first simplest model Hamiltonian. On the contrary, when the model space is relevant but interactions are missing, only the complexity of the Hamiltonian is increased while the applicability domain is not reduced.

2.3 Derivation of model Hamiltonians from the generalized Hubbard Hamiltonian with quasidegenerate perturbation theory

While we have seen in the previous subsection that model Hamiltonians can be extracted from the exact all-electron Hamiltonian by effective Hamiltonian theory, the understanding of the physical mechanisms that are responsible for the physical origin of the interactions cannot be provided by this numerical procedure of extraction. Rationalizations can however be made by analytical derivations of these models from the Hubbard Hamiltonian using quasidegenerate perturbation theory (QDPT).

The Hubbard Hamiltonian model space is not restricted to the neutral determinants only, but contains all the determinants obtained by distributing the magnetic electrons in the magnetic orbitals in all possible ways. The two main interactions of this Hamiltonian are (i) the hopping integral $t_{ij} = t_{ji}$ between orbitals i and j, which is the Fock operator matrix element F_{ij} (analogous to the β integral of the Hückel Hamiltonian) and (ii) and the on-site repulsion U_i of two electrons in the same magnetic orbital, which in case of a two-electron in two-orbital problem is equal to $J^C_{ii} - J^C_{ij}$, the difference between on-site and inter-site electron repulsion Coulomb integrals. To distinguish the Coulomb integral from the Heisenberg exchange parameter, we use J^C for the Coulomb integral. The expression of the Hubbard Hamiltonian is

$$\hat{H}_{Hubbard} = \sum_{i \neq j} t_{ij} \left(\hat{a}^\dagger_i \hat{a}_j + \hat{a}^\dagger_{\bar{i}} \hat{a}_{\bar{j}} \right) + \sum_i U_i \hat{a}^\dagger_i \hat{a}^\dagger_{\bar{i}} \hat{a}_{\bar{i}} \hat{a}_i - \sum_{i<j} K_{ij} \hat{S}_i \hat{S}_j \tag{9}$$

where $\bar{i}$ and $\bar{j}$ indicate orbitals with spin down electrons and K_{ij} is the two-center exchange integral. The basis spanning this model Hamiltonian is constituted of neutral determinants, singly-ionic, doubly-ionic, tri-ionic and so on, the energies of which are respectively 0, U, $2U$, $3U$ etc. Here, ionic is used with respect to the charge of the metal ions in their ground state. In the singly-ionic determinants, one electron is transferred from center 1 to center 2 (or *vice-versa*) generating a state in which the charge of the metal is formally changed by ± 1. Doubly-ionic, tri-ionic, etc. make reference to double, triple, etc. electron transfer from one center to another one. In case of magnetic centers bearing more than one unpaired electron the on-site Coulomb and exchange integrals should be introduced (cf. section 5.3) in order to reproduce the preference for local high spin ground state, *i.e.* the Hund's rule. This generalized Hubbard Hamiltonian covers all the essential physics in terms of rather intuitive parameters and is therefore a good starting point for rationalizations of simpler models working in a model space of lower dimensions.

In general, the U integral is the largest interaction, ranging from less than 1 eV in systems with strongly delocalized magnetic orbitals to more than 5 eV for localized TM-3d magnetic orbitals. Hence, the lowest eigenvectors of the Hubbard Hamiltonian are usually dominated by the neutral determinants. Actually, when dealing with magnetic states in TM compounds, the weight of the neutral determinants is so large that it becomes relevant to consider only these determinants in the model space and to work with a simpler Hamiltonian. The full neutral space is actually the model space of the HDVV Hamiltonian for systems with one unpaired electron per center, i.e. systems of spin $S = 1/2$. For magnetic centers with more than one unpaired electron per center, the dimension of the model space of the HDVV Hamiltonian is smaller than the number of neutral determinants.

It is constituted of the products of local ground state wave functions, i.e. the products of the local highest-spin states. The full space of neutral determinants also contains local excited states, called non-Hund states, which in some cases may play a non-negligible role in the physics of the lowest states and therefore explain some non-Heisenberg behaviour (section 5.3).

Based on these considerations, we start by dividing the complete Hubbard space S in a model space $S_0 = \{|\Phi_I\rangle\}$ that spans a simpler model Hamiltonian (e.g. the HDVV Hamiltonian) and the complementary, or outer space $S' = \{|\Phi_r\rangle\} = S - S_0$. The zeroth-order Hamiltonian is diagonal in the basis of S:

$$\begin{aligned} \hat{H}^{(0)}|\Phi_I\rangle &= E_I|\Phi_I\rangle \\ \hat{H}^{(0)}|\Phi_r\rangle &= E_r|\Phi_r\rangle \end{aligned} \tag{10}$$

where the zeroth-order energies are the mean values of $\hat{H}_{Hubbard}$ according to the Epstein-Nesbet choice of the zeroth-order Hamiltonian. The perturbation operator $\hat{V} = \hat{H}_{Hubbard} - \hat{H}^{(0)}$ couples Φ_I and Φ_r by the interactions of the Hubbard Hamiltonian, for instance by the hopping integral t. The objective of QDPT is to take into account the effect of these couplings between model and outer space by introducing effective interactions between the functions of the model space through analytical expressions rather than a numerical evaluation as described before. Applying second-order QDPT introduces the effect of the outer space functions that are directly coupled to the model space through the following expression of the effective Hamiltonian matrix elements

$$\langle\Phi_I|\hat{H}^{eff}|\Phi_J\rangle = \langle\Phi_I|\hat{H}|\Phi_J\rangle - \sum_r \frac{\langle\Phi_I|\hat{V}|\Phi_r\rangle\langle\Phi_r|\hat{V}|\Phi_J\rangle}{E_r - E_J} \tag{11}$$

where the first term represents the bare coupling of the functions in the model space S_0 and the second term is the second-order correction involving the coupling between inner and outer space. In many cases this relatively simple expression permits to rationalize the model Hamiltonian and analyze the physics it contains, but sometimes second-order perturbation theory is not enough and higher order corrections need to be invoked. As mentioned, this will introduce the effect of the outer space determinants that are not directly coupled with the model space, but may be essential to explain the physics of the system. These terms appear at the fourth-order of perturbation and the expression for the matrix elements of the effective Hamiltonian reads[254,268]

$$\begin{aligned}
\langle\Phi_I|\hat{H}^{eff}|\Phi_J\rangle = \langle\Phi_I|\hat{H}|\Phi_J\rangle &- \sum_{r}\frac{\langle\Phi_I|\hat{V}|\Phi_r\rangle\langle\Phi_r|\hat{V}|\Phi_J\rangle}{E_r-E_J}\\
+\sum_{r,s}\frac{\langle\Phi_I|\hat{V}|\Phi_r\rangle\langle\Phi_r|\hat{V}|\Phi_s\rangle\langle\Phi_s|\hat{V}|\Phi_J\rangle}{(E_r-E_J)(E_s-E_J)} &- \sum_{r,K}\frac{\langle\Phi_I|\hat{V}|\Phi_r\rangle\langle\Phi_r|\hat{V}|\Phi_K\rangle\langle\Phi_K|\hat{V}|\Phi_J\rangle}{(E_r-E_J)(E_r-E_K)}\\
-\sum_{r,s,t}\frac{\langle\Phi_I|\hat{V}|\Phi_r\rangle\langle\Phi_r|\hat{V}|\Phi_s\rangle\langle\Phi_s|\hat{V}|\Phi_t\rangle\langle\Phi_t|\hat{V}|\Phi_J\rangle}{(E_r-E_J)(E_s-E_J)(E_t-E_J)}&\\
+\sum_{r,s,K}\frac{\langle\Phi_I|\hat{V}|\Phi_r\rangle\langle\Phi_r|\hat{V}|\Phi_s\rangle\langle\Phi_s|\hat{V}|\Phi_K\rangle\langle\Phi_K|\hat{V}|\Phi_J\rangle}{(E_r-E_J)(E_s-E_J)(E_s-E_K)}&\\
+\sum_{r,s,K}\frac{\langle\Phi_I|\hat{V}|\Phi_r\rangle\langle\Phi_r|\hat{V}|\Phi_K\rangle\langle\Phi_K|\hat{V}|\Phi_s\rangle\langle\Phi_s|\hat{V}|\phi_J\rangle}{(E_r-E_J)(E_r-E_K)(E_s-E_J)}&\\
-\sum_{r,K,L}\frac{\langle\Phi_I|\hat{V}|\Phi_r\rangle\langle\Phi_r|\hat{V}|\Phi_K\rangle\langle\Phi_K|\hat{V}|\Phi_L\rangle\langle\Phi_L|\hat{V}|\Phi_J\rangle}{(E_r-E_J)(E_r-E_K)(E_r-E_L)}&
\end{aligned} \tag{12}$$

where $|\Phi_{I,J,K}\rangle$ belong to the model space and $|\Phi_{r,s,t}\rangle$ are determinants of the outer space. In addition to being rather elaborate, this equation also shows that the effective Hamiltonian constructed with QDPT is not necessarily hermitian. Only if the model space is degenerate and the derivation is restricted to second-order, the hermitian character of the effective Hamiltonian is guaranteed. In some cases, it is better to use spin-adapted combinations of the determinants inside both the model and the outer spaces in order to account for interactions inside each subspace and cancel some higher order contributions. For example, the transformation of a basis of determinants (eigenfunctions of $\hat{S}_z$) to spin eigenfunctions of $\hat{S}^2$ by taking the appropriate linear combination of determinants significantly reduces both the size of the spaces and the number of nonzero off-diagonal elements.

The fourth-order expression of eq 12 looks rather complex and so is the analytical derivation at the fourth-order of perturbation. Nevertheless, they provide an opportunity to analyze the physics of the problem and identify the elementary mechanisms responsible for the appearance of interactions between functions of the model space which are not directly coupled through $\hat{H}$. One may notice that when expanding the perturbation until infinite order the results of the effective

Hamiltonian theory of Bloch are recovered, provided that the power expansion converges.

2.4 Experimental determination of the magnetic coupling parameters

Before analyzing the mechanisms of the magnetic coupling from theory, we will first spend a few words on the experimental determination of exchange parameters. We will only highlight the basic ingredients of the most common techniques to put the theoretical approaches in perspective. An excellent overview of the different experimental techniques can be found in the book by Gatteschi, Sessoli and Villain.[269]

The most frequently used procedure for obtaining exchange coupling parameters is based on magnetic susceptibility measurements in a temperature range, which typically runs from 4 to 300 K, although the limits depend on the system and the available equipment. The statistical mechanics expression of the magnetic susceptibility can be related to the thermal population of the energy levels under the effect of the external magnetic field through the van Vleck expression,[251] simplified by Bleaney and Bowers[4]

$$\chi = \frac{Ng^2\beta^2}{3kT}\frac{\sum_S S(S+1)(2S+1)exp(-E(S)/kT)}{\sum_S (2S+1)exp(-E(S)/kT)} \tag{13}$$

N, g, β, k and T are Avogadro's number, the gyromagnetic factor, the Bohr magneton, the Boltzmann constant, and the temperature, respectively. S is the total spin of the system. An operative expression to calculate χ needs the knowledge of the energy spectrum. In systems with two or more magnetic sites, $\hat{H}_{HDVV}$ (with or without correction terms) usually provides this spectrum. In finite systems, a magnetic topology of the system is proposed from the structural data and the corresponding spin Hamiltonian is built by including the supposedly relevant interactions. The energies can then be expressed as function of the magnetic interaction parameters in an analytical way and introduced in the above equation to calculate $\chi(T)$.[7] The fitting of this curve to the experimental one enables experimentalists to extract the coupling parameters within the chosen magnetic topology. This fitting procedure works very well for molecular systems with well defined magnetic structure and a reduced number of different interactions. No analytical expressions can be derived for infinite systems, although approaches have been developed to extend this treatment to 1D chains and 2D square or hexagonal lattices.[270–272] For cases where analytical expressions cannot be derived, one usually relies on a simple model description of the system. The Hamiltonian is diagonalized to obtain the energy levels as function of the relevant parameters, which are then fitted to reproduce the experimental measured data.

A second important technique for determining magnetic coupling parameters is based on inelastic neutron scattering (INS).[273,274] Incoming neutrons are scattered by the interactions with the unpaired electrons of the sample causing transitions between states that differ at most by one in the spin moment ($\Delta S = \pm 1$). Hence, the energy difference between the peaks in the spectrum are directly related to the energy difference between two spin states of the system under study. The extraction of the magnetic interaction parameters is immediate and only requires an adequate choice of the Heisenberg Hamiltonian.

Other experimental techniques that can provide useful information include magnetization measurements as function of an external magnetic field. This is especially useful for antiferromagnetically coupled systems. Ideally a stepwise increase of the magnetization can be observed and the change in the applied external magnetic field to induce an increase in the magnetization can be related with the energy difference between two subsequent spin states, and hence, to the magnetic coupling parameters. EPR and nuclear magnetic resonance can also provide information, although these techniques are mostly used to determine properties related to the magnetic anisotropy of the system.

3 The physics of the magnetic interaction between two S = 1/2 spins

3.1 The physics of the minimal valence space

The essential physics of the magnetic coupling can be understood by analyzing the elementary problem of the interaction between two unpaired electrons occupying two remote orbitals, *a* and *b*, in a centro-symmetric system. These orbitals are frequently obtained from a variational calculation on the triplet state $|T_u\rangle$ with

$$|T_+\rangle = |core\ h\bar{h}gu| \quad ; \quad |T_-\rangle = |core\ h\bar{h}\bar{g}\bar{u}| \tag{14}$$

for the $M_S = \pm 1$ components and

$$|T_0\rangle = \frac{1}{\sqrt{2}}\left(|core\ h\bar{h}g\bar{u}| - |core\ h\bar{h}u\bar{g}|\right) \tag{15}$$

for the $M_S = 0$ component. Here *g* and *u* are singly occupied symmetry adapted MOs of *gerade* and *ungerade* symmetry, respectively. The label *h* is used as a generic label for the doubly occupied orbitals, either valence or inner-shell orbitals and *core* will be dropped from now on for simplicity. The optimization of the energy with respect to the atomic orbital coefficients used to expand the MOs gives optimal doubly occupied MOs and optimal magnetic orbitals *g* and *u*, which can be transformed by a simple rotation into localized magnetic orbitals *a* and *b*:

$$a = \frac{g+u}{\sqrt{2}} \qquad b = \frac{g-u}{\sqrt{2}} \tag{16}$$

or

$$g = \frac{a+b}{\sqrt{2}} \qquad u = \frac{a-b}{\sqrt{2}} \tag{17}$$

Despite the local nature, a and b are orthogonal orbitals contrary to the local atomic-like orbitals used in qualitative models. For this reason, the magnetic orbitals can have significant delocalization tails on the atoms surrounding the magnetic site as illustrated in Figure 6.

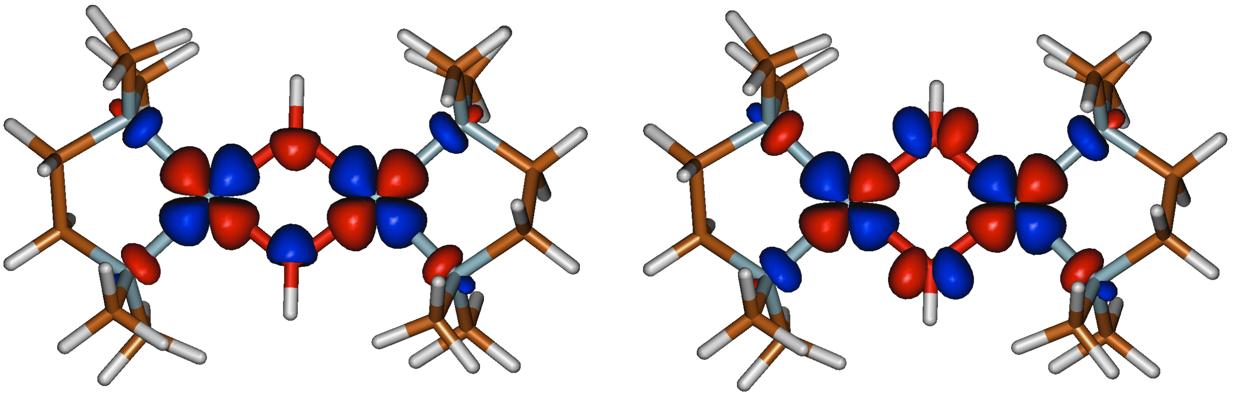

Figure 6: Symmetry adapted magnetic orbitals u (left) and g (right) for a binuclear Cu$^{\mathrm{II}}$ compound.[275]

With the two electrons and two orbitals, a valence subspace can be defined containing two neutral determinants

$$N = \{|h\bar{h}a\bar{b}|, |h\bar{h}b\bar{a}|\} \tag{18}$$

and two ionic determinants

$$I = \{|h\bar{h}a\bar{a}|, |h\bar{h}b\bar{b}|\} \tag{19}$$

The orbital occupations of these determinants are shown in Figure 7.

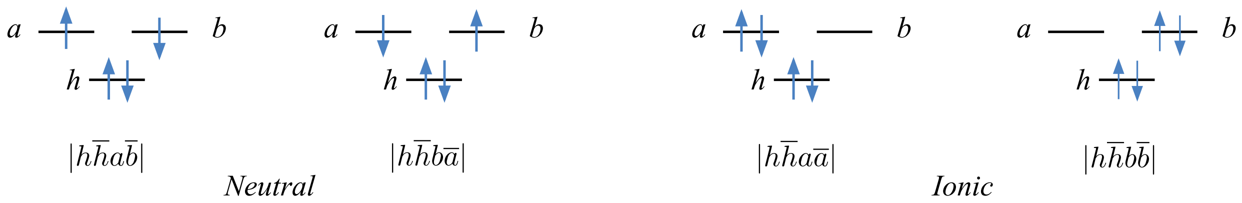

Figure 7: Orbital occupations of the neutral and ionic determinants. a and b are the localized orthogonal magnetic orbitals, h is a doubly occupied orbital outside the minimal valence space.

The four determinants define the 2 electrons in 2 orbitals complete active space (CAS), for which the corresponding CI matrix expressed in localized orbitals can be written as

$$\begin{array}{c} |h\bar{h}a\bar{b}| \\ |h\bar{h}b\bar{a}| \\ |h\bar{h}a\bar{a}| \\ |h\bar{h}b\bar{b}| \end{array} \left[\begin{array}{cccc} 0 & K_{ab} & t_{ab} & t_{ab} \\ K_{ab} & 0 & t_{ab} & t_{ab} \\ t_{ab} & t_{ab} & U & K_{ab} \\ t_{ab} & t_{ab} & K_{ab} & U \end{array}\right] \tag{20}$$

where the energy of the neutral determinants is taken as the energy origin. The exchange integral $K_{ab} = \langle a\bar{b}|\frac{1}{r_{12}}|b\bar{a}\rangle$ is the self-repulsion of the *ab* overlap electronic distribution and thus necessarily positive. The on-site repulsion U is equal to $J^C_{aa} - J^C_{ab}$, the difference between the Coulomb repulsion in the ionic and neutral determinants. Since $J^C_{aa} = \langle a\bar{a}|\frac{1}{r_{12}}|a\bar{a}\rangle$ is larger than $J^C_{ab} = \langle a\bar{b}|\frac{1}{r_{12}}|a\bar{b}\rangle$, U is also positive. The third parameter appearing in the CI matrix is the hopping integral $t_{ab} = \langle a\bar{b}|\hat{H}|a\bar{a}\rangle = \langle a|\hat{F}|b\rangle$, where $\hat{F}$ is the Fock operator. The hopping integral is a measure of the coupling between the neutral and the ionic determinants. As shown by Hay *et al.*,[276] the hopping integral and the on-site repulsion can be expressed in terms of the symmetry adapted orbitals g and u. t_{ab} is given by the difference of the diagonal elements of the Fock matrix, $t_{ab} = (F_{gg} - F_{uu})/2 = (\varepsilon_g - \varepsilon_u)/2$, and $U = 2K_{gu}$, where $K_{gu} = \langle g\bar{g}|\hat{H}|u\bar{u}\rangle$.

The form of the CASCI matrix is analogous to what is obtained from the Hubbard Hamiltonian given in eq 9. The difference lies in the values of the matrix elements and how they are obtained. For CASCI, these elements are exactly defined by the integrals as specified in the previous paragraph, while they are parameters in the Hubbard model, which can be chosen in such a way that they reproduce the physics of the system. In the general case, the CASCI matrix elements are not optimal for a quantitative description and should not be used right away to define model Hamiltonians. A better description is obtained when the CASCI matrix elements are dressed with the effects that go beyond the valence-only description as will be explained in section 3.3. The dressing process converts K, t and U in effective or screened parameters.

The diagonalization of the CI matrix (eq 20) gives four eigenstates, namely the triplet state of ungerade symmetry ($|T_u\rangle$), two singlet states of gerade symmetry ($|S_g\rangle$, $|S'_g\rangle$), and one singlet state of ungerade symmetry ($|S_u\rangle$). The $M_S = 0$ component of the triplet state can be written as

$$|T_0\rangle = \frac{1}{\sqrt{2}}\left(|h\bar{h}a\bar{b}| - |h\bar{h}b\bar{a}|\right) \quad ; \qquad E(T) = -K_{ab} \tag{21}$$

showing its purely neutral character. Before further analysis of the other eigenstates, we introduce the neutral and ionic singlet configurations S_N and S_I to obtain more compact expressions. The configurations are fixed linear combinations of the neutral or ionic determinants defined above:

$$S_N = \frac{1}{\sqrt{2}}\left(|h\bar{h}a\bar{b}| + |h\bar{h}b\bar{a}|\right) \quad ; \qquad S_I = \frac{1}{\sqrt{2}}\left(|h\bar{h}a\bar{a}| + |h\bar{h}b\bar{b}|\right) \tag{22}$$

Taking into account that the energy of S_N is K_{ab}, that the energy of S_I is equal to $K_{ab} + U$, and that $\langle S_N|\hat{H}|S_I\rangle = 2t_{ab}$, the *gerade* singlet matrix can be written as:

$$\begin{array}{c} S_N \\ S_I \end{array} \begin{bmatrix} K_{ab} & 2t_{ab} \\ 2t_{ab} & U + K_{ab} \end{bmatrix} \tag{23}$$

The energy of the lowest $|S_g\rangle$ state is obtained from the diagonalization of this matrix and reads:

$$E(S_g) = K_{ab} + \frac{U - \sqrt{U^2 + 16t_{ab}^2}}{2} \tag{24}$$

and the corresponding eigenvector is dominated by the neutral singlet configuration

$$|S_g\rangle = \lambda S_N + \mu S_I \qquad (\lambda > \mu > 0) \tag{25}$$

The singlet-triplet energy difference is obtained from eqs 21 and 24:

$$J = \Delta E_{ST} = E(S_g) - E(T) = 2K_{ab} + \frac{U - \sqrt{U^2 + 16t_{ab}^2}}{2} \tag{26}$$

When $U \gg |t_{ab}|$, the second term can be written as a Taylor expansion to obtain a simpler expression, which in fact is equivalent to the one obtained in a perturbative approach treating the ionic contribution as a perturbation to the purely neutral singlet.[277–279]

$$J = 2K_{ab} - \frac{4t_{ab}^2}{U} \tag{27}$$

This expression clearly shows the opposite sign of the two contributions to $J = J_F + J_{AF}$. The first one is the "direct exchange" and is ferromagnetic (tending to a parallel alignment of the spin moments), while the second contribution is known as the "kinetic exchange" and favors the antiparallel alignment (antiferromagnetic). It reflects the ability of the magnetic electrons to move from one site to the other in the singlet state as illustrated in Figure 8.

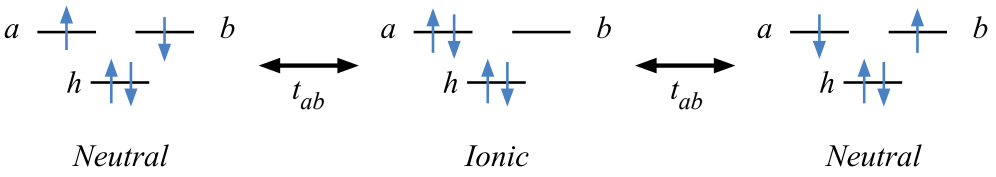

Figure 8: Schematic representation of the kinetic exchange mechanism introducing the interaction of the two neutral determinants via an ionic determinant. A similar mechanism exists for the $|h\bar{h}b\bar{b}|$ intermediate.

This development based on centro-symmetric systems remains essentially valid when the magnetic sites are not equivalent. A rotation of the triplet singly occupied orbitals is always possible without changing the determinant, and any localization criterion such as the Boys, Ruedenberg, Pipek-Mezey procedures,[280–283] or atomic orbitals projection, etc.[284] will give localized magnetic orbitals a and b. The CASCI matrix expressed in the basis of neutral and ionic VB components takes the same structure as for the centro-symmetric system, with the exception of energies of the ionic determinants, which will become U_a and U_b, respectively. This is without further consequences on the reported analysis.

Numerical estimates at this valence-only description of the magnetic coupling are rather discouraging since they give rarely more than 25% of the values derived from experiment, as illustrated in Table 1 for a series of binuclear Cu$^{\text{II}}$ and Ni$^{\text{II}}$ compounds (CASCI entry). This behavior is independent of the set of MOs used to construct the Slater determinants in the CI expansion. Table 2 shows that the calculated J value remains small when singlet optimized orbitals are used or when each state is expressed in its own optimal set of orbitals (state-specific SS entry in Table 2). This indicates that descriptions limited to the magnetic orbitals,[285–287] orthogonal or not, can only give qualitative trends but no numerical accuracy.

Table 1: Magnetic couplings (in cm^{-1}) calculated with different CI wave functions (Figure 10) using a minimal CAS as reference. The MOs of the highest spin state are used to express the Slater determinants of the CI expansion.

	CASCI	CAS+S	DDCI2	DDCI	Exp.
La_2CuO_4[a]	-255	-706	-744	-1077	[-1030,-1096][g]
$Sr_2CuO_2Cl_2$[a]	-160	-464	-482	-952	-1008[h]
$[Cu(tmeen)(OH)]_2Br_2$[b]	-35	-159	-184	-500	-507[i]
$[Cu(bipy)(OH)]_2(NO_3)_2$[c]	33	73	63	157	172[j]
$[Cu(L1)(C_2O_4)]_2$[d]	-7.3	-21.9	-23.2	-78.3	-75[k]
$[Ni(L2L3)(C_2O_4)]_2$[e]	-1.0	-8.5	-8.9	-16.0	-28.8[l]
$[Ni(L4)(C_2O_4)]_2$[f]	-2.8	-7.1	-7.7	-11.4	-22.8[l]

(a) from embedded cluster calculations (see section 4.6)
(b) tmeen=N,N,N',N'-tetramethylethylenediamine, (c) bipy=2,2'-bipyridine
(d) L1= 1,1,4,7,7-pentaethyldiethylene-triamine,(e) L2= diethylenetriamine, L3= H_2O, (f) L4=(C_2O_4)
(g) refs 288–290, (h) ref 291, (i) ref 275, (j) ref 292, (k) ref 293, (l) ref 294

3.2 Qualitative minimal valence space models

The first interpretations of the magnetic coupling in coordination chemistry of TM complexes by Kahn and Briat[285] adopted the traditional Heitler-London Valence Bond (VB) approach. The magnetic orbitals are defined from a ligand field picture as the singly occupied atomic-like orbitals centered on the magnetic sites with delocalization tails on the ligands in the surroundings. Except for symmetry reasons, these orbitals show finite mutual overlaps, and therefore, the CI matrix has to be expressed in terms of nonorthogonal VB determinants. In principle, the neutral determinants dominate in nonorthogonal VB approaches, although the ionic structures cannot be

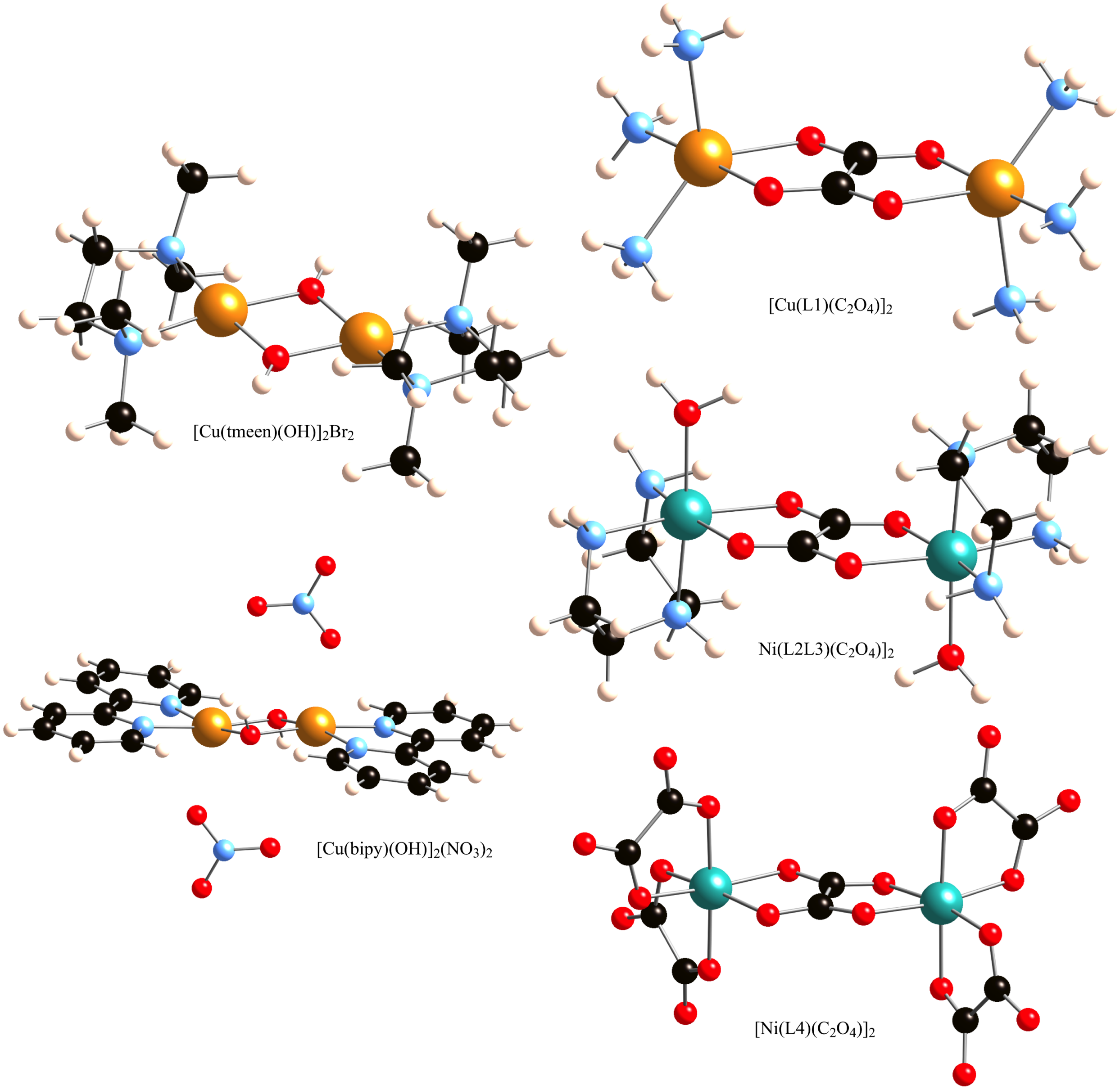

Figure 9: Ball and stick representation of the five complexes listed in Table 1. Larger spheres represent Cu (gold-like) and Ni (green), medium-sized spheres are C (black), N(blue) and O(red), the small spheres correspond to H.

Table 2: CASCI and DDCI magnetic coupling constants (in cm^{-1}) as function of the applied MO set (T: SCF triplet MOs; S: CASSCF singlet MOs; SS: state-specific MOs). A CAS(2,2) is used as reference wave function.

	CASCI			DDCI			Exp
MO set	T	S	SS	T	S	SS	
La_2CuO_4[a]	-255	-387	-315	-1077	-1149	-1174	[-1030,-1096][d]
$Sr_2CuO_2Cl_2$[a]	-160	-237	-195	-952	-1002	-1026	-1008[e]
$[Cu(tmeen)OH]_2Br_2$[b]	-35	-72	-52	-500	-523	-526	-509[f]
$[Cu(bipy)OH]_2(NO_3)_2$[c]	33	31	32	157	156	178	172[g]

(a) from embedded cluster calculations (see section 4.6)
(b) tmeen=N,N,N',N'-tetramethylethylenediamine, (c) bipy=2,2'-bipyridine
(d) refs 288–290, (e) ref 291, (f) ref 275, (g) ref 292

dismissed completely.

After approximating some of the two-electron integrals in terms of overlap of the magnetic orbitals S_{ab}, Kahn and Briat derived a simple working equation that relates J with the direct exchange (ferromagnetic) and the overlap of the magnetic orbitals (antiferromagnetic).

$$J = 2K_{ab} + 4\beta S_{ab}, \tag{28}$$

where $\beta = \langle a|\hat{h}(1)|b\rangle$ and $\hat{h}(1)$ is an effective one-electron operator. β can be understood as the hopping integral t in a semi-empirical context. This model has been extremely useful since it gives a simple guide to interpret the structural factors governing the sign and the amplitude of the magnetic coupling.[134,295–300] In any case, the model suffers from two limitations: (i) The orbitals are not optimized in the field generated by the complete molecule and (ii) the physics is reduced to two electrons in two orbitals, independently of the nonorthogonality of the magnetic orbitals applied in the model.

The alternative qualitative model proposed by Hay, Thibeault and Hoffmann[276] starts from a mean-field description of the whole complex, and hence, the singly occupied orbitals appear in an optimized form as in the analysis of the minimal valence space in the previous section.

After simplifying the expression of the singlet-triplet energy difference, the following equation was proposed for J:

$$J = 2K_{ab} - \frac{(\varepsilon_g - \varepsilon_u)^2}{J^C_{aa} - J^C_{ab}}, \tag{29}$$

where ε_g and ε_u are the orbital energies of the symmetry adapted magnetic orbitals defined in eq 17. In practice, this model has basically been applied in the scope of semi-empirical schemes such as the extended Hückel approach. Although the one-electron character of the Hückel Hamiltonian prevents the evaluation of K_{ab} and $J^C_{aa} - J^C_{ab}$ in eq 29, the method offers important insights on the dependence of J to structural factors through the variations of $\varepsilon_g - \varepsilon_u$,[301–310] which can be calculated with extended Hückel theory or more sophisticated treatments. The hopping integral t of the kinetic exchange contribution $4t^2/U$ can be estimated by scaling the overlap between the localized magnetic orbitals (eq 28),[311] calculated for instance by the extended Hückel method.[312,313]

3.3 Beyond the minimal valence space

Electron correlation is an essential ingredient for the accurate description of the magnetic coupling. It is frequently divided into nondynamic and dynamic correlation effects. The former takes place in the space spanned by the valence molecular orbitals, both occupied and virtual. It is provided by the full-valence CAS. The dynamic correlation involves non-valence virtual MOs, *i.e.* determinants outside of the full-valence CAS and is sometimes divided in radial and angular correlation.[281,314–318]

The effect of the determinants external to the CAS on the magnetic coupling has been analyzed by some of us in a series of three articles.[260,319,320] Here we present the main ideas of this analysis, the reader is referred to the original papers for a more detailed description. To start the discussion, we first classify the determinants external to the CAS according to the number of holes (h) created in the core and the number of electrons (particles, p) sent to previously unoccupied orbitals. The ligand-to-metal and metal-to-ligand charge transfer configurations (LMCT and MLCT, respectively) moving one electron from the ligand occupied orbitals to the magnetic ones or from the magnetic orbitals to the ligand virtual ones belong to the $1h$ and $1p$ classes, respectively. Single excitations $\left(\hat{a}_p^\dagger \hat{a}_h + \hat{a}_{\bar{p}}^\dagger \hat{a}_{\bar{h}}\right)$ not involving active orbitals generate determinants belonging to the $1h$-$1p$ class and similar for the remaining classes. As an example, the double substitution operator $\hat{a}_p^\dagger \hat{a}_a^\dagger \hat{a}_{h'} \hat{a}_h$ sends two electrons from inactive orbitals to the magnetic orbital a and to a virtual one, and generates a determinant belonging to the $2h$-$1p$ class. Because of the two-electron nature of the Hamiltonian, the subset of determinants interacting with the CAS determinants is limited to nh-mp classes with n, m $\leqslant$2. Figure 10 illustrates schematically the nature of the different excitations and groups them by the computational methods explained in section 4.3.

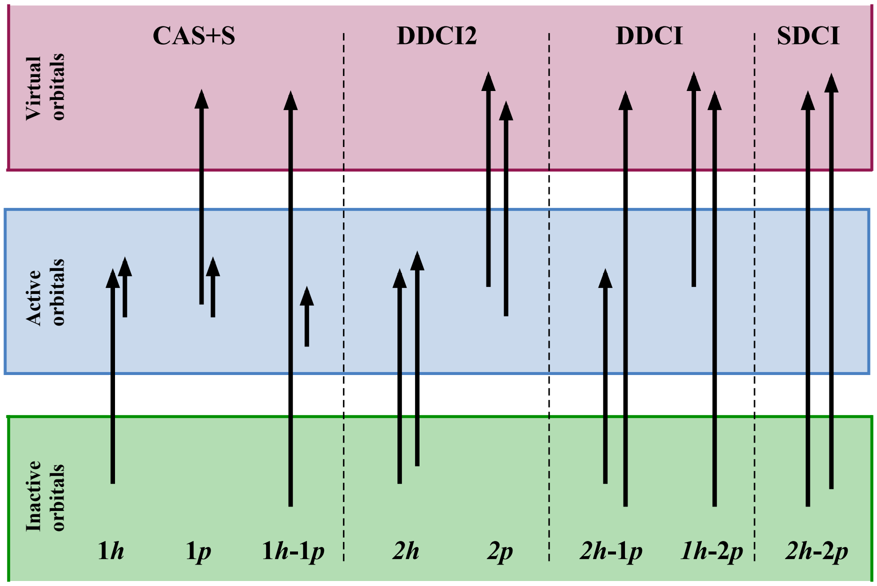

Figure 10: Classification of the different excitations considered in a multiconfigurational reference singles-doubles CI (MR-SDCI) following the number of holes (h) and particles (p) created in the inactive and virtual orbitals, respectively. CAS+S is also referred to as DDCI1 in the literature and DDCI3 is often used as synonym for DDCI.

To numerically estimate the role of the different excitation classes on the magnetic coupling, different CI calculations can be performed by including successively different sets of determinants. The CAS+singles (CAS+S) level of calculation includes $1h$, $1p$ and $1h$-$1p$ determinants; adding the $2h$ and $2p$ classes to the CAS+S includes all singlet-triplet differential effects up to second-order in a description based on a VB neutral determinant model space, while adding also $2h$-$1p$ and $1h$-$2p$ determinants includes all differential second-order effects when the model space includes also the ionic VB forms, *i.e.* the model space is the CAS. As will be described in section 4.3, these two last CI levels are known as DDCI2 and DDCI, respectively. The progression of the magnetic coupling constants calculated with these CI spaces is illustrated in Table 1.

3.3.1 The 1*h* and 1*p* excitations

When the Slater determinants of the minimal valence space shown in Figure 7 are expressed in the orbitals optimized for the triplet state, the interaction between the configurations obtained from single excitations and $|T_0\rangle$ is zero as reflected by the generalized Brillouin theorem.[321,322] Specifically, for the $1h$ excitations:

$$\langle T_0|\hat{H}|\left(\hat{a}^{\dagger}_{a}\hat{a}_{h}+\hat{a}^{\dagger}_{\bar{a}}\hat{a}_{\bar{h}}\right)T_0\rangle = 0 \tag{30}$$

The same excitation applied on $|S_g\rangle$ gives a nonzero contribution since Brillouin's theorem no longer applies.

$$\langle S_g|\hat{H}|\left(\hat{a}^{\dagger}_{a}\hat{a}_{h}+\hat{a}^{\dagger}_{\bar{a}}\hat{a}_{\bar{h}}\right)S_g\rangle = t_{ah} \tag{31}$$

In general, the interaction is rather small due to the fact that singlet and triplet optimized orbitals are nearly identical. When h belongs to a bridging ligand, these $1h$ excitations can be classified as LMCT configurations. Hence, the use of self-consistently optimized orbitals largely cancels the direct effect of the LMCT configurations or so-called superexchange mechanism shown in Figure 11.

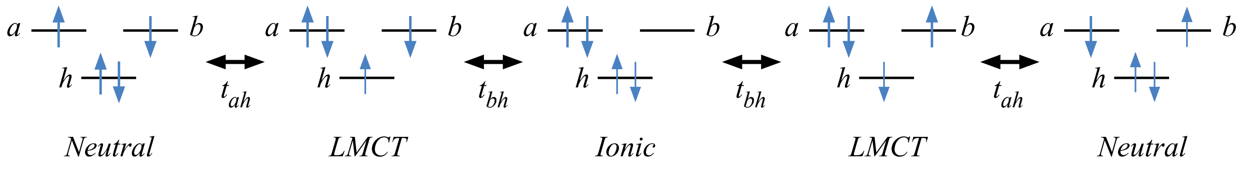

Figure 11: Fourth-order interaction between the neutral determinants involving LMCT and ionic intermediates.

The same remarks are valid for the determinants arising from single excitations from the active orbitals to the unoccupied orbitals p, corresponding to MLCT configurations if p belongs to the ligand. The interaction is zero with $|T_0\rangle$ and small with $|S_g\rangle$

$$\langle T_0|\hat{H}|\left(\hat{a}_p^\dagger \hat{a}_a + \hat{a}_{\bar{p}}^\dagger \hat{a}_{\bar{a}}\right) T_0\rangle = 0 \quad , \qquad \langle S_g|\hat{H}|\left(\hat{a}_p^\dagger \hat{a}_a + \hat{a}_{\bar{p}}^\dagger \hat{a}_{\bar{a}}\right) S_g\rangle = t_{pa} \tag{32}$$

Table 3 presents the numerical confirmation of the negligible contributions of the $1h$ and $1p$ classes for four binuclear Cu$^{\text{II}}$ compounds (entries CAS+$1h$ and CAS+$1p$). In the present situation of two electrons in two magnetic orbitals, the determinants of the $1h$ and $1p$ classes can only be generated by single excitations. This is no longer strictly the case in systems with more unpaired electrons. Nevertheless, the contributions of the $1h$ and $1p$ determinants are also rather small in these cases.

Table 3: Impact of the different excitations of the DDCI space on the magnetic coupling constants (in cm^{-1}). The triplet CASSCF MOs set and a CAS(2,2) is used as reference wave function. See Figure 10 for CI partitioning.

	La_2CuO_4[a]	$Sr_2CuO_2Cl_2$[a]	$[(Cu(tmeen)OH)_2]^{2+}$ [b]	$[(Cu(bipy)OH)_2]^{2+}$ [c]
CAS	-255	-160	-35	33
CAS+$1h$	-276	-169	-37	33
CAS+$1p$	-285	-180	-49	34
CAS+($1h$-$1p$)	-523	-336	-102	61
CAS+($2h$-$1p$)	-274	-167	-38	40
CAS+($1h$-$2p$)	-189	-123	-10	36
CAS+S	-706	-464	-159	73
DDCI2	-744	-482	-184	63
DDCI2+($2h$-$1p$)	-1462	-1256	-750	195
DDCI2+($1h$-$2p$)	-569	-386	-117	57
DDCI	-1077	-952	-500	157
Exp.	[-1030,-1096][d]	-1008[e]	-509[f]	172[g]

(a) from embedded cluster calculations (see section 4.6)

(b) tmeen=N,N,N',N'-tetramethylethylenediamine, (c) bipy=2,2'-bipyridine

(d) refs 288–290, (e) ref 291, (f) ref 275, (g) ref 292

Other orbitals may be used instead of the triplet ones. If strongly localized orbitals are used both on the metal and on the ligands, the antiferromagnetic mechanism represented in Figure 11 becomes relevant for the magnetic coupling and the LMCT (as well as the MLCT) configurations must be included in the model. This is the mechanism proposed by Anderson[277] under the name of *superexchange*. This two-band VB model has been analyzed in depth by some authors,[286,287] reducing the ligand to a single occupied MO. The four-step mechanism of Figure 11 is automatically incorporated in the kinetic exchange when optimized magnetic MOs are used.

3.3.2 The 1*h*-1*p* excitations: Dynamic charge polarization

The determinants created by moving one electron from the inactive orbitals to the virtuals without changing the spin part are single excitations with respect to $|T_0\rangle$, and hence, the interaction is again strictly zero if triplet optimized orbitals are used:

$$\langle T_0|\hat{H}|\left(\hat{a}_p^{\dagger}\hat{a}_h + \hat{a}_{\bar{p}}^{\dagger}\hat{a}_{\bar{h}}\right) T_0\rangle = 0, \tag{33}$$

The interaction between these determinants and the $|S_g\rangle$ state is much larger than for the 1h and 1p excitations. In the first place, we recall that the interaction of the S_N configuration with the spin conserving 1h-1p excitations is strictly zero.[319] On the contrary, the $|h\bar{p}a\bar{a}|$ and $|p\bar{h}a\bar{a}|$ determinants (and those with two electrons on b), which are formally doubly excited with respect to the leading neutral determinants of $|S_g\rangle$ as illustrated in Figure 12, have a strong interaction with the ionic S_I configuration of this state.

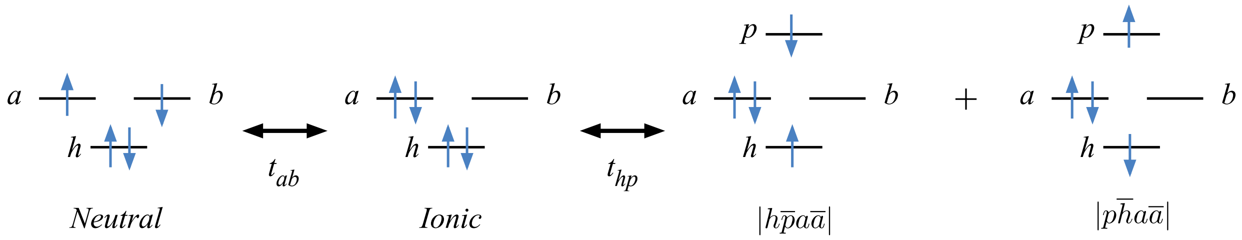

Figure 12: Interaction of the spin conserving 1h-1p determinants with the ionic determinants belonging to the minimal valence space.

The field created by the two magnetic electrons in the same orbital is represented by $2\hat{J}_a^C$ (or

$2\hat{J}_b^C$) instead of the sum of the two Coulomb operators $\left(\hat{J}_a^C + \hat{J}_b^C\right)$, for which the orbitals have been optimized. The interaction between the ionic determinant $|h\bar{h}a\bar{a}|$ and the $1h$-$1p$ generated from it can be written as[319]

$$\langle h\bar{h}a\bar{a}|\hat{H}|\frac{\left(h\bar{p}a\bar{a} + p\bar{h}a\bar{a}\right)}{\sqrt{2}}\rangle = \sqrt{2}\langle h|\left(\hat{J}_a^C - \hat{J}_b^C - \frac{\hat{K}_a - \hat{K}_b}{2}\right)|p\rangle \tag{34}$$

Since these spin conserving $1h$-$1p$ excitations only affect the ionic determinants, they can be considered as lowering the energy of these determinants from U to U_{eff}. The size of this correction has been estimated from second-order perturbation theory and reads:[323]

$$U_{eff} = U - \sum_{h,p} \frac{|\langle h|\left(\hat{J}_a^C - \hat{J}_b^C\right)|p\rangle|^2}{U + \varepsilon_p - \varepsilon_h} \tag{35}$$

where the small intersite exchange term of eq 34 has been neglected. The lowering represents the dynamic response of the inactive electrons to the fluctuation of the field created by the active electrons in the singlet state or, in other words, the dynamic charge polarization. In fact, the importance of including dynamic correlation to relax the ionic VB forms has already been pointed out in the field of organic biradicals in the 1980s.[324,325] CASSCF(2,2) gives poor results in many of these systems both for the optimized geometries and vertical and adiabatic singlet-triplet energy differences of these systems, as noticed and extensively discussed by Borden and collaborators. These authors attribute the defects to the excessive energy difference between neutral and ionic VB components of the singlet state, which results in an underestimation of kinetic exchange.[324,325] Numerical calculations for TM complexes have shown that this effect is extremely important, since U_{eff} can be reduced to just 30% of its original value U.[260] It turns out that the AF contribution to J in eq 27 changes to $-4t_{ab}^2/U_{eff}$. Consequently, the coefficient of the ionic VB component in the singlet wave function increases, since it is proportional to t_{ab}/U_{eff}. This effect is clearly visible in Table 4. For the systems with AF coupling, the ratio of the coefficients of neutral and ionic determinants (C_I/C_N) becomes twice as large when the $1h$-$1p$ determinants are added to the wave function (CAS+S entry). The underestimation of the kinetic exchange when neglecting the charge polarization effect is a well-known problem.[326–329] In first-row transition metal compounds, the effect has been estimated to increase the AF contribution by roughly a factor two[330] as confirmed by comparing the CAS and CAS+(1h-1p) entries of Table 3.

Table 4: Relation between the magnetic coupling J (in cm^{-1}), the ratio of the coefficients of the neutral and ionic determinants (C_I/C_N), and the coefficient of the LMCT determinants.

	La$_2$CuO$_4$ [a]			[(Cu(tmeen)OH)$_2$]$^{2+}$ [b]			[(Cu(bipy)OH)$_2$]$^{2+}$ [c]		
	J	C_I/C_N	LMCT	J	C_I/C_N	LMCT	J	C_I/C_N	LMCT
CASCI	-255	0.0406	–	-35	0.0218	–	33	0.0009	–
CAS+S	-706	0.0910	0.0292	-159	0.0544	0.0197	73	0.0005	0.0098
DDCI2	-744	0.0955	0.0300	-184	0.0571	0.0208	63	0.0004	0.0104
DDCI	-1077	0.1180	0.1250	-500	0.0966	0.1218	157	0.0132	0.1031

(a) from embedded cluster calculations (see section 4.6)

(b) tmeen=N,N,N',N'-tetramethylethylenediamine, (c) bipy=2,2'-bipyridine

3.3.3 The 1*h*-1*p* excitations: Spin polarization

A different class of 1h-1p determinants is obtained by the subsequent application of $\hat{a}^\dagger_b\hat{a}_h$ and $\hat{a}^\dagger_{\bar{p}}\hat{a}_{\bar{b}}$ on the neutral determinant $|h\bar{h}a\bar{b}|$, and the combined action of $\hat{a}^\dagger_{\bar{b}}\hat{a}_{\bar{h}}$ and $\hat{a}^\dagger_p\hat{a}_b$ on $|h\bar{h}b\bar{a}|$. The resulting formally doubly excited $|hp\bar{a}\bar{b}|$ and $|\bar{h}\bar{p}ab|$ determinants with M_S=1 in the active space and M_S=-1 in the inactive orbitals or *vice-versa* are schematically represented in Figure 13. The spin polarization mechanism also involves $M_S = 0$ triplet excitations in the inactive orbitals, but they do not contribute to the energy difference.

The differential effect of these determinants on J has been derived in ref 319 and can be considered as a correction to the direct exchange integral taking into account the so-called spin polarization effects:

$$K_{ab,\mathit{eff}} = K_{ab} + 2\sum_{h,p} \frac{\langle h|\hat{K}_a|p\rangle\langle p|\hat{K}_b|h\rangle}{\varepsilon_p - \varepsilon_h} \tag{36}$$

Note that $K_{ab,\mathit{eff}}$ can become negative for large AF contributions of the spin polarization. The

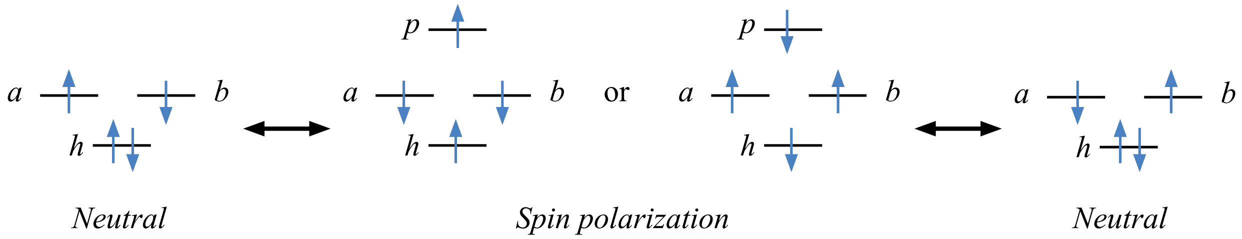

Figure 13: Interaction of the spin polarization $1h$-$1p$ determinants with the neutral determinants belonging to the minimal valence space.

correction to J due to the spin polarization equals two times the second term of eq 36 and its sign depends on the molecular architecture. It is in general only important when the bridging ligand orbitals (h and p) have significant amplitudes close to both magnetic sites and when the triplet excitation of the ligand is low in energy. Consequently, this is in general a very important effect when conjugated bridging ligands are present in the molecule.

In some cases the spin polarization may be so large that the open-shell configuration of the ligand becomes lower in energy than the closed-shell configuration as in non-innocent ligands.[194–196,201–203] If this happens, four open-shell orbitals (a, ligand HOMO and LUMO, and b) must enter in the zeroth-order description of the system, i.e. the molecule has to be considered as a four-electrons in four-orbitals system. A similar phenomenon may also appear in systems where the magnetic sites are bonded through spin polarizable covalent bonds.[239]

As a final comment on the $1h$-$1p$ excitations, we mention that comparing the CAS+S values with those of the individual classes ($1h$, $1p$ and $1h$-$1p$) in Table 3 shows the synergistic (or nonadditive) effects between the three classes, which results in a large enhancement of J.

3.3.4 The 2*h* and 2*p* excitations

The double excitations from active to virtual orbitals give rise to the $2p$ excitation class. The inclusion of these determinants tends to stabilize the singlet slightly more than the triplet state. The most relevant determinants of this class are the ones generated from the S_I configuration of the singlet function, since they introduce angular and radial correlation of the monocentric electron pair in the ionic determinants. The relevant virtual orbitals are nonvalence atom-centered orbitals such as the 4(p,d,f) orbitals for systems with 3d-type magnetic orbitals. The 2h class contributes in the same AF direction through excitations sending two electrons from the doubly occupied inner-shell orbitals of the magnetic sites to the empty magnetic orbital of the ionic determinants. The numerical confirmation of the weak AF contribution of the 2h and 2p excitations can be found in Table 3 by comparing the CAS+S and DDCI2 results.

3.3.5 The 2*h*-1*p* and 1*h*-2*p* excitations

The 2h-1p and 1h-2p classes of excitations have been demonstrated to play a crucial role in the quantitative evaluation of magnetic coupling.[260,319,320] This is particularly true for the variational calculation of the coupling parameter, which only reaches a good agreement with experimental values when these classes are included, as can be seen by comparing the DDCI2 and DDCI entries in Tables 1 and 3. For instance, for the $[(\mathrm{Cu(tmeen)OH})_2]^{2+}$ system with $J_{exp} = -509$ cm^{-1}, the J-value changes by more than 300 cm^{-1} when these excitations are added to the CI space. This large effect does not find its origin in the direct interaction of the 2h-1p and 1h-2p excitations with the determinants of the CAS. The isolated effect of these classes is only -3 cm^{-1} (AF) and $+25$ cm^{-1} (F), respectively, as evidenced in the CAS+(2h-1p) and CAS+(1h-2p) entries of Table 3. A second-order perturbative evaluation with CASPT2 or NEVPT2 (sections 4.1 and 4.2) also leads to relatively small contributions of the (2h-1p) and (1h-2p) excitations. In the before mentioned copper complex, CASPT2 leads to contributions of -94 cm^{-1} and $+43$ cm^{-1}, respectively. The variational evaluation of the full list of determinants in the DDCI space gives a J-value of -500 cm^{-1}, while the same space treated perturbatively gives a value of only -249 cm^{-1}.

These results suggest that the effect of these excitations comes from perturbative orders higher than two and proceeds through more complicated coupling schemes in which LMCT and (1h-1p) determinants play an important role.[320] Analytical and numerical analysis show that the 2h-1p and 1h-2p excitations increase the delocalization of the magnetic orbitals onto the ligands.[319,331] This effect is not only visible when the shape of the CASSCF magnetic orbitals is compared to the natural orbitals resulting from the CI calculation, but also in the large increase of the weight of the

LMCT configurations in the wave function when the $2h$-$1p$ and $1h$-$2p$ excitations are accounted for. Analogous to the previous dressing (or screening) effect of the $1h$-$1p$ excitations on K and U, the $2h$-$1p$ and $1h$-$2p$ excitations change t_{ah} and t_{pa} (defined in eqs 31 and 32) in effective parameters $t_{ah,eff}$ and $t_{pa,eff}$ between the magnetic orbitals and the occupied and virtual orbitals of the ligands. In general, the absolute value of the effective hopping integrals is larger than the bare value.

The consequences of this magnetic / ligand orbital delocalization are multiple: the effective direct exchange is increased and the superexchange mechanism (Figure 11) now becomes effective, increasing the AF contribution. This results in an increase of the coefficients of the ionic VB forms upon the inclusion of the $2h$-$1p$ and $1h$-$2p$ excitations as shown in Table 4 (compare entries DDCI2 and DDCI). The spin polarization mechanism may also be enhanced by processes involving successive single excitations, starting from LMCT or MLCT configurations. In systems where the spin polarization prevails (as in many ferromagnetic systems), the latter effect results in an increase of the ferromagnetic coupling. Therefore, although the $2h$-$1p$ and $1h$-$2p$ excitations introduce contributions of different sign, the overall effect is an amplification of the magnetic coupling whatever its sign.

The precedent discussion has shown the importance of the inactive electrons treated in DDCI in the magnetic coupling process. The bare valence-only description gives a rather poor, incomplete description of the coupling. Nevertheless, it is always possible to project the effect of the inactive electrons into an effective valence-only CI matrix by replacing the matrix elements K_{ab}, t_{ab} and U by the effective values $K_{ab,eff}$, U_{eff} and $t_{ab,eff}$ following the procedure described in section 2.2.2 and discussed in ref 260. It is in principle not possible to fix these three parameters from the mere knowledge of the singlet-triplet energy difference and the neutral/ionic coefficient C_I/C_N ratio in the correlated singlet function. A third equation is needed to determine all parameters. The energy of the upper ionic singlet $|S'_g\rangle$ state can give this equation but this state has often a very high energy and can be strongly mixed with MLCT and LMCT states. An alternative solution consists of identifying the value of $K_{ab,eff}$, from a CI calculation excluding the ionic configuration from the CI space and including all the excitation classes previously discussed. The remaining two parameters are then fixed by the knowledge of J and C_I/C_N . This leads to effective integrals that can be counterintuitive, as for instance the effective direct exchange that can become negative.[260,332]

4 Computational Methods

This section describes the methods most frequently used in the study of magnetic interactions. We start with commonly used wave function (WF) methods for these systems, namely multi-configurational reference (MR) approaches including dynamic correlation either up to second-order of perturbation or at a variational level. For any magnetic system, the minimal reference space is defined by the distributions of magnetic electrons in magnetic orbitals (namely a Complete Active Space) which incorporates the non-dynamic correlation effects. In the Full Configuration Interaction (FCI), this subspace is only coupled with singly and doubly excited configurations generating a CAS(SD)CI space which incorporates the main dynamic correlation effects. As all truncated schemes, MR(SD)CI suffers from size-consistency errors, and higher excitations are needed to approach the FCI limit.

A short overview of other WF methods that have been applied to standard biradical problems will follow. Since excellent reviews have recently been published on DFT applications in this area of research,[20–25] here we will limit the discussion to some essential aspects of the application of this methodology to magnetic systems. Finally, a brief comment on the methods suitable for extended systems is given.

4.1 CASPT2

One of the most successful implementations of many body perturbation theory for a MR wave function is the complete active space second-order perturbation theory (CASPT2) approach of Andersson, Roos and co-workers. After a first intent in the early 1980s,[333] a more complete implementation was reported ten years later.[334,335] CASPT2 is nowadays applied to many different areas of chemistry and has also been used to calculate magnetic coupling strengths.[336–346] CASPT2 is implemented in the Molcas[347] and Molpro[348] quantum chemistry packages. The latter implementation also provides the third-order correction to the energy.[349] Here, we will not enter in the details of the formulation of the perturbation theory but only review the computational ingredients that are essential for the calculation of accurate/reliable estimates of the magnetic coupling and other related electronic structure parameters. Attention is focused on the adequate choice of the active space, the zeroth-order Hamiltonian, and the intruder state problem.

4.1.1 Choice of active space

The central problem to all MR methods is the proper choice of the reference wave function. Whereas this issue does not exist for problems in which the electronic structure is clearly dominated by a single configuration (the Hartree-Fock determinant), the quality of the wave function in multi-configurational situations is often critically dependent on the choice of the proper reference wave function. This wave function necessarily includes the essential physics of the problem. It should not only include the important electronic configurations, but the reference wave function should also give a more or less appropriate ratio between them. This is of utmost importance for most of the computational schemes in which the dynamic correlation effects are estimated with perturbation theory, since these methods normally do not allow for a revision of the ratio of the basic configurations. In variational treatments, such as the difference dedicated CI discussed below, the inclusion of the remaining electron correlation can modify the ratio to get more accurate results. Hence, the choice of the active space is less critical and can often be restricted to a minimal active space.

Recalling the analysis of the previous sections, we know that a zeroth-order description should at least include the neutral and ionic configurations, and due to the fact that the ratio between these configurations remains unchanged in the standard implementations of perturbation theory, the active space should probably also contain ligand-to-metal charge transfer configurations. Starting with the simplest case of the interaction between two localized $S = 1/2$ spin angular moments, the minimal active space includes two magnetic orbitals and the two corresponding unpaired electrons. The relative importance of the ionic determinants is generally largely underestimated due to the very limited treatment of the electron correlation in this CAS(2,2) calculation. This leads to a systematic underestimation of the magnetic coupling when the minimal CAS wave function is used as reference for CASPT2. This underestimation is larger for systems with large kinetic exchange contributions to the coupling such as the mentioned binuclear $\mathrm{Cu^{II}}$ complexes and smaller for system with less important contributions from the ionic determinants as in binuclear TM complexes with less electronegative metals, *e.g.* $\mathrm{Mn^{II}}$ instead of $\mathrm{Cu^{II}}$.[338]

The straightforward extension of the minimal active space with ligand orbitals to account for the ligand-to-metal charge transfer suffers from the same defects as described for the ionic determinants. The weight of the LMCT configurations is strongly underestimated in the reference wave function. Therefore, a more elaborate recipe has to be followed to improve the description of the magnetic coupling with CASPT2. A generally accepted strategy to get better reference wave functions is to extend the minimal active space with a set of formally virtual d-orbitals.[350–352] These orbitals are often referred to as TM-$3d'$ orbitals but are also sometimes referred to as TM-$4d$ orbitals in the case of the first-row TM ions. These extra orbitals play an important role to describe correctly the radial electron correlation of the crowded TM-$3d$ shells in the late transition metal ions of the first-row (Mn–Zn) and are less important for earlier TM ions or second- and third-row TMs. The results in Table 5 for two binuclear complexes (one with Cu and the other with Ni, Figure 14) show that the extension of the active space with a second d-shell only slightly increases the antiferromagnetic coupling. Therefore, more orbitals need to be included in the active space to obtain a more quantitative description.

The second extension of the active space that can be considered is the inclusion of occupied ligand orbitals. Adding these orbitals to the minimal active space does not improve the reference wave function because of the limited flexibility of the wave function. It is better to combine the extension with ligand orbitals with the addition of the second d-shell and even better also of a correlating orbital for each occupied ligand orbital that is added to the active space. This offers

Table 5: CASSCF and CASPT2 magnetic coupling parameters (in cm^{-1}) for [N,N',N"-trimethyl-1,4,7-triazacyclononane$_2$Cu$_2$(μ-1,3-N$_3$)$_2$]$^{2+}$ (Cu-azido) and [((1,3-diaminopropane)$_2$Ni)$_2$(μ-1,3-N$_3$)$_2$]$^{2+}$ (Ni-azido) as function of the size of the active space.

	Cu-azido [a]		Ni-azido [b]	
Active space	CASSCF	CASPT2	CASSCF	CASPT2
minimal CAS	-134	-693	-14	-83
+ second *d*-shell	-147	-698	-15	-87
+ ligand orbitals	-192	-761	-17	-104

(a) $J_{exp} = -800$ cm^{-1}, ref 353, (b) $J_{exp} = -114$ cm^{-1}, ref 305

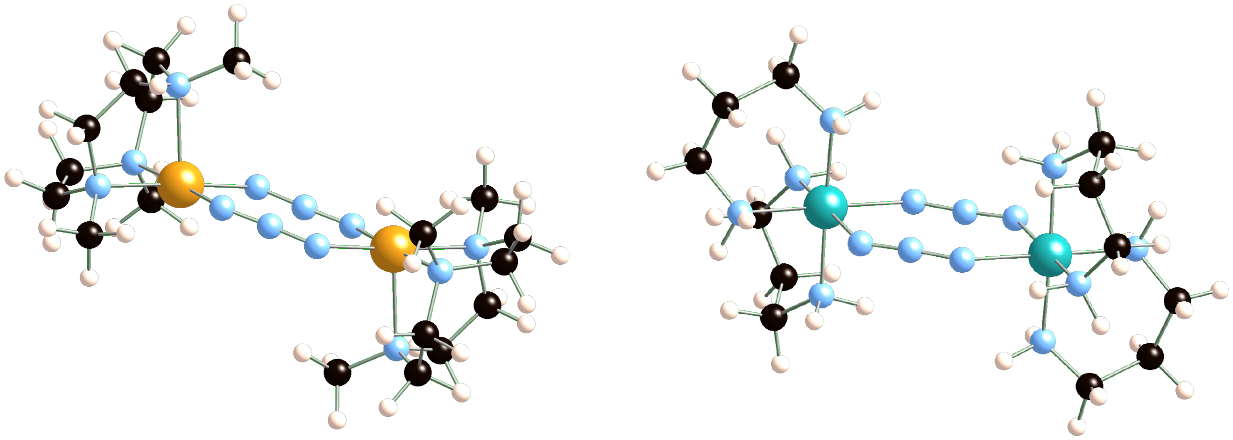

Figure 14: Ball and stick representation of N,N',N"-trimethyl-1,4,7-triazacyclononane$_2$Cu$_2$(μ-1,3-N$_3$)$_2$]$^{2+}$ (Cu-azido) and [((1,3-diaminopropane)$_2$Ni)$_2$(μ-1,3-N$_3$)$_2$]$^{2+}$ (Ni-azido). Larger spheres represent Cu (gold-like) and Ni (green), medium-sized spheres are C (black) and N (blue), the small spheres correspond to H

enough flexibility and the extended CAS wave function does show some important LMCT effects. This is again accompanied by a modest increase for CASSCF and a slightly stronger increase in the coupling for CASPT2, as illustrated in Table 5. In summary, to obtain qualitative estimates of J, it is often enough to consider a minimal active space with just the magnetic orbitals and the unpaired electrons. However, to obtain a more quantitative number, one should add some occupied ligand orbitals to the CAS and then add a virtual orbital for each orbital. Such an extended CAS represents a real bottleneck for the CASSCF step and severely hinders the application of CASPT2 to systems containing several magnetic centers.

In principle, the multi-state implementation of CASPT2[354] can be used to revise the relative importance of the different electronic configurations in the reference wave function under the influence of dynamic correlation. It has been successfully applied to get rid of the artificial mixing of Rydberg and valence state character in excited states of organic molecules.[355–357] However, the strategy does not work to improve the description of magnetic coupling. The multi-state CASPT2 relies on a state average description of the electronic states in the model space. This is perfectly suitable in the case of a collection of low-lying states as in organic molecules with valence and Rydberg states in the same energy interval, but highly problematic for the energy difference between low-spin and high-spin states in magnetic coupling calculations. As mentioned before, the model space of a $\mathrm{Cu}^{\mathrm{II}}$ binuclear system contains four states. In order to revise the neutral/ionic ratio with MS-CASPT2, the three singlets should be treated in a state average calculation and the remaining triplet receives necessarily a single state treatment. The CASSCF relative energies of the ionic states are very high (typically larger than 20 eV in $\mathrm{Cu}^{\mathrm{II}}$ systems), and a state average treatment gives a rather poor description of these singlet states. Hence, an extremely unbalanced description arises, in which the triplet is always much lower in energy than the singlet. Moreover, the CASPT2 treatment of the ionic states suffers from severe intruder state problems, which cannot be repaired with the level shift technique.

Finally, we mention the convergence problems with $\mathrm{Cu}^{\mathrm{II}}$ binuclear complexes following the above-outlined recipe for doubling the CAS. It turns out that there is no way to converge the extended CAS wave function with the desired character of the active orbitals.[338] The Cu-3d' orbitals usually turn into polarization functions on Cu or some atom located on the bridging ligand. A practical solution consist of adding the two doubly occupied Cu-3d orbitals (one on each center) with the highest orbital energy to the active space before doubling the CAS. The resulting CAS wave function easily converges to the expected active orbitals, but it is clearly not a strategy that can be applied to systems with more than two magnetic centers. The *gerade* active orbitals of the CAS(10,12) Cu-azido are drawn in Figure 15.

The extension of the formalism to restricted active space SCF reference wave functions (RASPT2)[358–360] extends the range of applicability of the perturbative approach. Multi-center TM systems may be treated with RASPT2 by putting restrictions on the occupations of the ligand and TM-3d' orbitals in the active space. For large organic molecules, the π-orbitals can be divided in groups to avoid the bottleneck of a full valence CAS calculation. RASPT2 has been applied to calculate the singlet-triplet splitting in binuclear Cu-oxo and Cu dioxygen complexes,[358,361] and in isobenzo(hepta)fulvenes.[362]

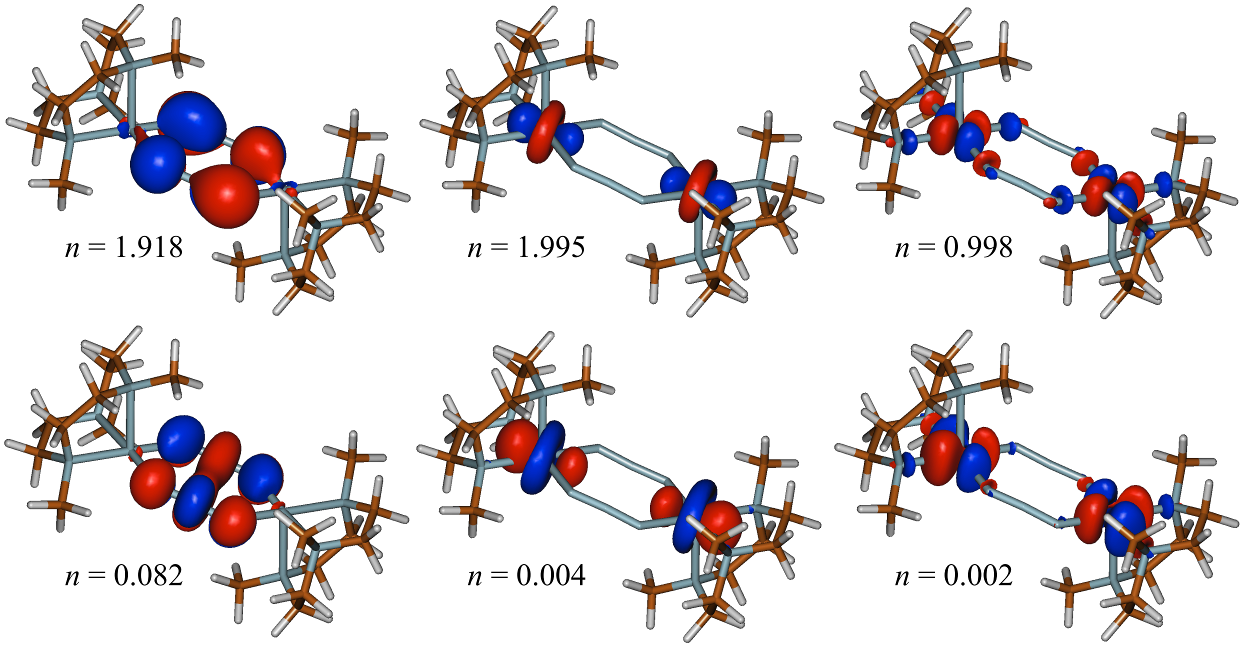

Figure 15: CASSCF(10,12) active orbitals of *gerade* symmetry and natural occupation numbers of the Cu-azido complex. The *ungerade* orbitals are similar.

4.1.2 Zeroth-order Hamiltonian and first-order wave function

A common degree of freedom in the formulation of perturbation theory treatments of complicated systems is the choice of the zeroth-order Hamiltonian $\hat{H}^{(0)}$. In the original formulation of CASPT2, a Fock type operator was chosen that converges to the well-known Møller-Plesset Hamiltonian in the limit of zero active orbitals. It was readily found that this operator systematically underestimates dissociation energies by approximately 0.2 eV due to an unbalanced treatment of systems dominated by closed-shell configurations (typically molecules near their equilibrium geometry) versus systems with open-shell configurations (such as dissociated fragments). Several modifications of $\hat{H}^{(0)}$have been published to improve this aspect,[363,364] among which the so-called IPEA Hamiltonian is the most successful and has become the standard $\hat{H}^{(0)}$for CASPT2.[364] This Hamiltonian introduces a shift of 0.25 au. to the orbital energies of the active orbitals to make them better resemble the ionization energy or electron affinity.

In principle the calculation of the magnetic interaction should not be affected by the choice of $\hat{H}^{(0)}$, since all states involved in the process are dominated by open-shell configurations. However, several tests have shown that the IPEA Hamiltonian introduces important numerical noise to the energy differences of the electronic states with different spin coupling leading to unphysical J values and strong deviations to the regular spectrum of the Heisenberg Hamiltonian.[365] Table 6 illustrates this behavior and it is obvious from the data that the original $\hat{H}^{(0)}$is the best choice for the calculation of J. However, it should be noted that this Hamiltonian also leads to non-negligible deviations of the Heisenberg spectrum that do not show up in more precise, variational calculations.[365,366]

MR second-order perturbation theory can follow different schemes to construct the first-order interaction space.[367] CASPT2 uses the internally contracted expansion proposed by Knowles and Werner.[368,369] In this formulation the configurations external to the CAS are generated by applying excitation operators on the reference wave function as a whole:

$$\Psi^{(1)} = \sum_{pqrs} c_{pqrs}\hat{E}_{pq}\hat{E}_{rs}\Psi^{(0)} \tag{37}$$

Table 6: Magnetic coupling (in cm^{-1}) of Ni-azido calculated with CASPT2 using the original (IPEA=0.0) and new definition (IPEA=0.25) of $\hat{H}^{(0)}$. $J_{ST} = E(S) - E(T)$ and $J_{TQ} = (E(T) - E(Q))/2$. J_{exp} = -114 cm^{-1}(ref 305)

CAS	J	IPEA = 0.0	IPEA = 0.25
minimal CAS	J_{ST}	-94	-219
	J_{TQ}	-72	-84
+ second *d*-shell	J_{ST}	-100	-179
	J_{TQ}	-74	-51
+ ligand orbitals	J_{ST}	-127	-184
	J_{TQ}	-81	-71

where $\hat{E}_{pq}$ are defined as the spin averaged excitation operators and $\Psi^{(0)}$ is the CASSCF wave function.

4.1.3 Intruder state problems

The one-electron nature of the zeroth-order Hamiltonian can lead to the appearance of intruder states characterized by small interaction matrix elements with the reference wave function but nearly equal expectation values of $\hat{H}^{(0)}$. In this case the denominator in the expression of the second-order correction to the energy becomes close to zero and an artificially large contribution appears that leads to unreliable estimates of the total energy. A pragmatic solution involves the application of a level shift to the $\hat{H}^{(0)}$expectation values of the external configurations to avoid the near degeneracies and correct *a posteriori* for this shift.[370,371] Experience shows that the intruder state problems are not frequent in magnetic coupling problems. Moreover, they can be resolved with modest level shift in most cases. However, it should be kept in mind that the application of a level shift introduces a degree of uncertainty in the CASPT2 estimate of J. For too small shifts, the value may still be affected by the intruder state and for larger shifts the correlation effects are damped and tend to the CASSCF value. Therefore, it is preferable to report J values with an error estimate when a level shift has been applied to remove the effect of intruder states.

4.2 *N*-electron valence perturbation theory

Beside CASPT2, the *n*-electron valence state perturbation theory (NEVPT2) approach has also been used to evaluate the magnetic coupling constants. This is an alternative implementation of the MR second-order perturbation theory,[372–375] which has shown to give very reliable results in different MR problems, such as the study of excited states in organic systems,[375–379] reaction profiles,[380,381] metal-metal multiple bonds,[382–384] and magnetic systems.[320,365,385–388]

Different formulations of NEVPT2 are possible depending on the degree of contraction of the perturbers.[375] The applications on magnetic systems make use of two different partitions of the Hamiltonian, the externally partially contracted (PC) and strongly contracted (SC) versions. Both partitions use the Dyall Hamiltonian[389] to define the zeroth-order energies, while the level of contraction in the first-order interacting space is lower in the PC than in the SC version. Compared to CASPT2, the Dyall Hamiltonian contains all two-electron interactions between the active electrons, while the CASPT2 zeroth-order Hamiltonian is based on an effective one-electron Fock-type operator. The perturbing vectors are linear combinations of determinants, but in contrast with CASPT2, they are directly orthogonal. The level of contraction of the PC version of NEVPT2 is similar to that of CASPT2. The absence of intruder states in NEVPT2 is one of the main advantages of this method. Other interesting properties are the size-consistency, the invariance under a unitary transformation of the orbitals inside each class (doubly occupied, active and empty), and the correct spin properties of the first-order correction to the wave function. The reader is referred to the original papers[372–375] for more details.

Although a slight numerical improvement in the calculation of J is observed when comparing with CASPT2 results and the deviation from the expected Heisenberg splitting is much smaller,[365] the NEVPT2 approach on the basis of a minimal CAS presents the same difficulty as CASPT2, *i.e.*, a marked underestimation of the coupling constant when only the magnetic orbitals are introduced in the active space (Table 7, Singlet MOs entry). The origin of this underestimation is the same as for CASPT2 since the two methods use a contracted reference wave function. The ratio between the ionic and neutral forms is the same as in the CASSCF reference wave function and is not modified by the perturbation approach. As discussed before, CASSCF predicts the ionic forms too high in energy (U is too large), and consequently, J is too small. To circumvent this problem, a decontraction procedure has been proposed,[390] which produces a significant increase of the ionic/neutral ratio with respect to the reference wave function, but the J values, although improved, are still underestimated. Recently, this problem has been attacked from a different point of view.[385] It was shown that the overestimation of U and the underestimation of t at the CASSCF(2,2) level in systems with two $S = 1/2$ magnetic sites can efficiently be overcome by using MOs resulting from the diagonalization of an average density matrix constructed from the two lowest singlet states, mainly neutral and ionic in nature. Table 7 compares the J values obtained for a set of binuclear Cu^{II} systems using this strategy (Average MOs entry) and illustrates its potentiality for NEVPT2 and CASPT2 evaluations of J.

In addition to the original NEVPT2 code,[391] the NEVPT2 approach has also been implemented in the quantum chemistry software packages Molpro, Dalton and Orca and is interfaced to Molcas.[347,348,392–394]

Table 7: Magnetic coupling constant J (cm^{-1}) computed with MR second-order perturbation theory starting from the CAS (2,2) space and using the singlet or neutral/ionic average MOs.

	Singlet MOs		Neutral/ionic average MOs		Exp.
	PC-NEVPT2	CASPT2	PC-NEVPT2	CASPT2	
La_2CuO_4 [a]	-605	-711	-1084	-1041	[-1030, -1096][g]
$Sr_2CuO_2Cl_2$ [a]	-380	-480	-984	-1065	-1008 [h]
$[Cu(tmeen)(OH)]_2Br_2$ [b]	-138	-200	-398	-549	-507 [i]
$[Cu(L1)(C_2O_4)]_2$ [c]	-20	-35	-86	-158	-75 [j]
$[Cu(L5)(N_3)]_2$ [d]	-198	-336	-1114	-1954	< -800 [k]
$[Cu(bipy)(C_2O_4)]_2$ [e]	-71	-106	-226	-329	-382 [l]
$[Cu(oxpn)]_2$ [f]	-77	-117	-274	-364	-440 [m]

(a) from embedded cluster calculations (see section 4.6)

(b) tmeen=N,N,N',N'-tetramethylethylenediamine, (c) L1= 1,1,4,7,7-pentaethyldiethylene-triamine

(d) L5 = L=N,N',N"-trimethyl-1,4,7-triazacyclononane, (e) bipy=2,2'-bipyridine

(f) oxpn=N,N'-bis(3-aminopropyl)oxamido

(g) refs 288–290, (h) ref 291, (i) ref 275, (j) ref 293, (k) ref 353, (l) ref 395, (m) ref 396

4.3 Difference Dedicated Configuration Interaction

An alternative WF method that is widely applied in the calculation of magnetic coupling parameters and related electronic structure parameters is the difference dedicated configuration interaction (DDCI). Whereas CASPT2 and NEVPT2 give a perturbational estimate of the electron correlation effect beyond the minimal active space description, DDCI accounts for electron correlation in a variational, and hence, in principle more precise manner.

4.3.1 DDCI method

The standard variant of DDCI starts from a MR wave function spanned by the determinants that can be constructed by distributing the unpaired electrons of the systems over the magnetic orbitals in all possible ways, *i.e.* a minimal CAS reference wave function. Subsequently a CI matrix is built by adding all singly and doubly excited determinants involving at least one of the orbitals in the active space. This restriction of the full singles and doubles CI space can be justified with quasidegenerate perturbation theory (QDPT) arguments. Contrary to the more usual approach of first diagonalizing a small model space S and secondly include perturbatively the effect of the determinants external to S for each state separately, QDPT first accounts for the effect of the external determinants and then diagonalizes the resulting effective Hamiltonian of the model space. Following the definition given in eq 11 of the matrix elements of the effective Hamiltonian that includes all second-order contributions, the effect of the doubly excited determinants not involving any active orbital (the so-called $2h$-$2p$ determinants, $|\hat{a}^\dagger_p\hat{a}^\dagger_{p'}\hat{a}_h\hat{a}_{h'}\Phi_I\rangle$=$|\hat{D}_{pp',hh'}\Phi_I\rangle$) on the energy difference between the determinants Φ_I and Φ_J of the model space is easily evaluated. The off-diagonal matrix elements of $\hat{V}$ become zero

$$\langle\hat{D}_{pp',hh'}\Phi_I|\hat{V}|\Phi_J\rangle = 0 \qquad (I \neq J) \tag{38}$$

because the number of different columns in the two Slater determinants is larger than two. On the other hand, the contribution to the diagonal elements of the effective Hamiltonian is nonzero. In a

Møller Plesset division of the exact Hamiltonian, the following is obtained

$$\sum_{\hat{D}_{pp',hh'}\Phi_I} \frac{\langle\Phi_I|\hat{V}|\hat{D}_{pp',hh'}\Phi_I\rangle\langle\hat{D}_{pp',hh'}\Phi_I|\hat{V}|\Phi_I\rangle}{E_I^{(0)} - E^{(0)}_{\hat{D}_{pp',hh'}\Phi_I}} = \sum_{p,p',h,h'} \frac{|\langle pq||hh'\rangle|^2}{\varepsilon_h + \varepsilon'_h - \varepsilon_p - \varepsilon'_p} \tag{39}$$

However, this contribution only involves quantities that depend on the inactive (h,h') or virtual $p,p')$ orbitals, and hence, it is identical for all the diagonal elements.

The different variants of DDCI will be reviewed from a historical perspective, intimately related to the increasing precision in the *ab initio* calculation of the magnetic coupling constant. The foundation of the direct calculation of the energy difference between two states was laid in the late 1960s by the observation that many terms in the n^{th}-order correction to the wave function and energy are the same for ground and excited state.[397] One of the first practical applications of this idea to the field of molecular magnetism was given in the paper by de Loth and co-workers on the singlet-triplet energy difference in the copper acetate dimer.[323] In that study, all second-order perturbation contributions to the energy difference were calculated assuming the zeroth-order description of the singlet and triplet wave functions with neutral determinants only ($|h\bar{h}a\bar{b}|$ and $|h\bar{h}b\bar{a}|$). The same list of determinants was used by Broer and Maaskant to analyze the magneto-structural correlations in the $[\mathrm{Cu_2Cl_6}]^{2-}$ complex.[398] Instead of the perturbational estimate of de Loth *et al.*, the list of second-order contributions was treated in a configuration interaction approach, thus obtaining a variational singlet-triplet energy difference.

This variational treatment of the second-order contributions was placed on a firm basis in the two papers of Miralles and co-workers published in the early 1990s.[399,400] The first paper addresses the exactly degenerate reference space containing only the neutral determinants $|h\bar{h}a\bar{b}|$ and $|h\bar{h}b\bar{a}|$ and shows that for such a reference space only the determinants with at most two changes in the occupancies of the inactive or virtual orbitals with respect to Φ_I or Φ_J contribute to the energy difference of the eigenfunctions of the effective Hamiltonian defined in eq 11. The off-diagonal elements are not affected by the determinants with more than two changes in the occupancies. For instance, the $1h$-$2p$ determinant $|h\bar{b}p\bar{p}|$ has a nonzero matrix element with $|h\bar{h}a\bar{b}|$, but the application of the Slater rules shows that the second integral in the numerator is zero since $|h\bar{b}p\bar{p}|$ has three different columns with respect to $|h\bar{h}b\bar{a}|$. Although the contribution to the diagonal matrix elements of these excited determinants is nonzero, they do not affect the relative energies of the eigenstates. This is most easily illustrated with an example using two different $1h$-$2p$ determinants. The $|h\bar{b}p\bar{p}|$ determinant with energy E_α gives rise to the following contributions to the diagonal matrix elements

$$\frac{|\langle h\bar{h}a\bar{b}|\hat{V}|h\bar{b}p\bar{p}\rangle|^2}{E_\alpha - E_I} \neq 0 \qquad \text{and} \qquad \frac{|\langle h\bar{h}b\bar{a}|\hat{V}|h\bar{b}p\bar{p}\rangle|^2}{E_\alpha - E_J} = 0 \tag{40}$$

On the other hand, the $|h\bar{a}p\bar{p}|$ determinant with energy $E_{\alpha'}$ gives

$$\frac{|\langle h\bar{h}a\bar{b}|\hat{V}|h\bar{a}p\bar{p}\rangle|^2}{E_{\alpha'} - E_I} = 0 \qquad \text{and} \qquad \frac{|\langle h\bar{h}b\bar{a}|\hat{V}|h\bar{a}p\bar{p}\rangle|^2}{E_{\alpha'} - E_J} \neq 0 \tag{41}$$

However, the two nonzero contributions are of course strictly equal for the degenerate reference space and the net effect of the two determinants is a uniform shift of the diagonal matrix elements of the effective Hamiltonian. This can be generalized to all determinants external to the reference space, and hence, the second-order perturbation reasoning shows that only the determinants with not more than two changes in the occupancies of the inactive or virtual orbitals are relevant to the energy difference when a strictly degenerate reference space is considered. The extension to magnetic systems with more than two unpaired electrons was made in 1994[401] and this CI level is nowadays known as the DDCI2 variant of DDCI. In parallel, the generalization to a CAS model space was also developed[400] giving rise to a specific CI able to accurately estimate a wide variety of energy differences. This CI is presently known as DDCI or DDCI3. Similarly, CAS+S is often referred to as DDCI1.

The DDCI2 method was applied in several transition metal dimers and organic biradicals with rather satisfactorily results, experimental couplings were reproduced with reasonable accuracy.[223,234–236,401–405] However, the calculation of the magnetic coupling parameter in La_2CuO_4 gave values that were strongly underestimated with respect to the experimental ones.[406,407] The magnetic interaction path is constituted by a linear Cu^{2+} — O^{2-} — Cu^{2+} arrangement, similar to the ones considered by Anderson in the original papers on the superexchange mechanism. The singlet-triplet energy difference associated to this topology is about one order of magnitude larger than those considered hitherto with the DDCI2 methodology. A careful analysis of the wave function showed that the ratio between neutral and ionic determinants is no longer small enough to consider the reference space as a strictly degenerate space. Therefore, the list of second-order contributions based on the neutral determinants only is no longer enough and should be extended with those generated from the complete active space reference, adding $|a\bar{a}|$ and $|b\bar{b}|$. The resulting list is exactly the one of the standard DDCI approach outlined above. The calculated magnetic coupling for the linear Cu^{2+} — O^{2-} — Cu^{2+} pathway is much stronger than for DDCI2 and in excellent agreement with experiment.[408] The results also confirm the virtually irrelevant role of the $2h$-$2p$ excitations.

The fundamental role of the $2h$-$1p$ excitations in the correct description of the antiferromagnetic coupling of two localized spin moments triggered the development of a DDCI variant that is computationally less expensive than the full DDCI scheme but includes the important part of the $2h$-$1p$ excitations. The largest effect on the magnetic coupling was observed when the $2h$-$1p$ excitations consist of a ligand-to-metal charge transfer excitation ($1h$) coupled with a $1h$-$1p$ excitation that accounts for the instantaneous polarization of the charge density in response to the CT excitation.[407,409] By including the LMCT excitations in the reference wave function through an extension of the active space with properly chosen orbitals on the bridge, the coupling with the $1h$-$1p$ excitations can in principle be accounted for by single excitations on the extended CAS wave function, CAS_{ext}+S.[410] This enlargement of the CAS cannot be achieved through a CASSCF treatment, since it would provide the orbitals giving the lowest total energy rather than those contributing to the magnetic coupling. Instead, one should start from the minimal CAS and identify or define the most suitable inactive orbitals to mediate the spin coupling. Different techniques have been proposed, either based on the recognition of the best canonical orbitals[410,411] or on appropriate rotations of the inactive MOs.[331,412] It was observed that the combination of an extended

CAS with DDCI2 introduces a part of the $1h$-$2p$ excitations, giving rise to slightly more accurate results.[412] However, there is no definite recipe that ensures the stability of the results with respect to the size and content of this enlargement.[413]

The DDCI wave function is not complete, it misses the effect of the $2h$-$2p$ excitations. However these excitations do not contribute to the lower orders of perturbation neither to the vertical energy differences (as explained above) nor to the observables involving monoelectronic operators, such as the transition moments between states dominated by determinants of the reference space. Under the assumption that the spin-orbit operator can be represented as an effective one-electron operator,[414] the use of the DDCI wave functions to calculate the effect of the spin-orbit couplings is relevant. The $2h$-$2p$ excitations must be considered when one considers adiabatic energy differences, or nuclear geometry changes. It is sometimes sufficient to evaluate this contribution in a simple Møller-Plesset type 2nd-order perturbative treatment.[366,415–418]

4.3.2 Applications of DDCI

Two main packages are of common use to perform the calculations: CASDI, coded by Maynau and collaborators,[419,420] and ORCA, developed by Neese.[394] A modified version of the CIPSI code,[421–423] interfaced to Gaussian or Gamess packages through QUIOLA, developed by Barone and collaborators,[424] is also used. A completely renewed version of the latter code (Baloo) has recently been released.[425]

Although the DDCI approach is in principle applicable to any kind of vertical excitation energy, most applications concerned the evaluation of the coupling parameter J in a wide range of magnetic materials. In general, a remarkably good agreement with experiment is obtained. A large number of studies has been reported on organic biradicals,[223,235,236,242,404,418,426–431] as well as on magnetic TM compounds, covering a large number of different aspects. The structural dependence of the magnetic coupling constant has been analyzed in a variety of binuclear TM complexes[365,366,398,402,403,432–441] and the role of water and hydrogen bonding as a mediator in magnetic coupling in $\mathrm{Cu^{II}}$ compounds has been evidenced.[442–444] Furthermore, the magnetic topology of several extended systems with different TM-TM' pairs and total local spin moment have been investigted.[445,446] The magnetic interactions in Cu cubane-like clusters has been studied[447–449] and DDCI studies on Ni and Pt dimers as precursors of conducting molecular wires have also been reported.[263] The magnetic behaviour of TM complexes with non-innocent ligands has been analyzed.[241,243,244,248,450] Finally, the DDCI approach has been applied to study Heisenberg Hamiltonian deviations in $S = 1$ systems[451,452] and new insights on the double exchange mechanism derived from DDCI wave functions have been reported.[453,454] Magnetic interactions in larger molecules as polyoxometallates have also been reported. By using fragmented models, electron delocalization in mixed-valence polyoxometallates has been discussed[455–458] and the antiferromagnetic coupling in the complex structure $[Cu_{20}Cl(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$(ref 459).

Anisotropic magnetic interactions can also be treated within the DDCI framework within a two-step procedure. Accurate excitation energies are derived with DDCI and subsequently spin-orbit coupling is included through QDPT or state interaction treatments. In this setting zero field splitting parameters,[6,460–462] EPR spectra and molecular g-tensors[344,463–466] or circular dichroism spectra[467] have been successfully determined. Magnetic anisotropy in Ni^{II} dimers,[266] in cupric oxide[468] and $LiCu_2O_2$ chains[469] has recently been analysed.

An important number of applications has addressed magnetic interactions in solid state materials by using the embedded cluster model (section 4.6). A variety of problems has been analyzed showing that quantum chemistry methods are also applicable to local phenomena in extended systems. From the early calculation of the coupling parameter in nickel perovskites,[470] effective values of electronic structure parameters as magnetic coupling parameter, hopping integral, on-site repulsion, etc., have been determined in different phases and dimensionalities of undoped or doped materials. Perovskites,[408,471,472] cuprates,[406,409,410,473–479] vanadates,[480–482] among others have been the object of many studies where different model Hamiltonian as Heisenberg and $t-J$ model Hamiltonians, Heisenberg deviations, the role of next-nearest-neighbor terms, etc have been discussed. The spectroscopy of materials containing impurities in actinide compounds has also been studied by combining DDCI with spin-orbit treatments.[483,484]

4.3.3 Limits and prospects

Despite the restriction of double excitations to semi-active ones, the computational cost of the DDCI method is still large. Its application is limited by the number of inactive and virtual orbitals, with a dependence on the third power of their total number N, and by the exponential increase of the CAS when the number of magnetic electrons increases. The size of the DDCI space is therefore proportional to $N_{CAS}N^3$. The size of the DDCI2 matrix only scales as $N_{CAS}N^2$ and was used by Barone and co-workers in the study of bisnitronyl nitroxide biradicals and the role of polyenic and aromatic spacers.[235,236,404,405]

Another way to reduce the computational cost of the DDCI procedure consists of limiting the length of the loops over the inactive and virtual MOs. This can be accomplished by using different strategies. One way consists of calculating the density matrices of two states at a low level of theory (for instance CAS+S) and to diagonalize the difference of both matrices to identify the inactive and virtual MOs playing the largest role in the energy difference. These orbitals have been called Difference Dedicated MOs.[485,486] By eliminating the less involved MOs, the size of the CI matrix is conveniently reduced.[241,243,402,410,457,477,487] Another strategy consists of using projection techniques to localize the occupied MOs, as well as the virtual valence and nonvalence MOs in the CASSCF wave function.[488,489] By using topological criteria such as the distance to the magnetic centers, the summations on the inactive and virtual MOs can be limited in the generation of the DDCI space.[490–492]

An alternative strategy, called Excitation Selected CI (EXSCI), has recently been developed by Maynau and co-workers[448,489,493] to reduce the size of the CI matrix and make possible the calculation of medium-sized systems. The method is based on the use of localized orbitals and acts at three levels: orbitals, integrals and determinants. The orbitals are eliminated depending on their topology. For many molecules, sigma C-H or C-C bond orbitals, core orbitals, etc. play a minor role in the magnetic phenomena and can safely be discarded. Regarding the determinants, only excitations involving *interacting* local orbitals are retained. Two orbitals m and n are considered as interacting when the exchange integral K_{mn} is larger than a certain threshold. A double excitation is retained when the corresponding exchange integrals are larger than the threshold (more details can be found in ref 447). Supplementary savings can be obtained by eliminating small molecular integrals, following a procedure similar to that used to shorten the list of determinants. A further refinement of the method consists of describing different zones of the molecule with different thresholds.[448] The truncation of the integrals, orbitals and determinants produce a significant reduction of the computational cost and allows for the study of large, polynuclear systems by means of CI approaches.[241,447–449]

Finally, one can design a mixed strategy by estimating from perturbation theory the effect of the determinants that interact weakly with the targeted eigenvectors of the CAS. This solution is implemented in the SORCI program[494] of the ORCA code.[394] Barone and collaborators also have proposed a mixed variational-perturbative computational strategy for large organic biradicals where localization and fragmentation schemes are combined with DDCI. The variational calculation is performed on a subset of the MOs and the remaining contributions are estimated at second-order.[234,429,430]

The dependence of the computational cost on the number of active electrons (n_a) is more problematic. For polyradicalar $S = 1/2$ systems, the calculations remains feasible in almost all practical cases as long as the system can be described with a bilinear Heisenberg Hamiltonian considering only nearest-neighbor interactions. The values of the different magnetic couplings among the n_a $S = 1/2$ sites are given by considering the high-spin solution ($M_S^{HS} = n_a/2$) and the n_a solutions for $M_S^{HS-1} = n_a/2 - 1$. The size of the CAS for the M_S^{HS} state is of course one, while the active space for the M_S^{HS-1} solution becomes equal to n_a^2, which remains moderate in practically all cases. However, this procedure does not give enough equations to estimate the amplitudes of biquadratic operators or non-neighor interactions in the effective Hamiltonian as previously indicated in section 2.2.2. To overcome these limitations, constrained variational CI techniques have recently been proposed to estimate the diagonal energies of the spin effective Hamiltonian.[495] The procedure is best illustrated by considering a system with three $S = 1/2$ sites. The quartet state defines 3 localized magnetic MOs, a, b and c and three $M_S = 1/2$ reference determinants, $|\bar{a}bc|$, $|a\bar{b}c|$ and $|ab\bar{c}|$.

Taking the $|\bar{a}bc|$ determinant as reference, a DDCI or SDCI calculation is performed, in which $|a\bar{b}c|$ and $|ab\bar{c}|$ are eliminated. Subsequently the same is done for the other two reference determinants and the resulting energies are mapped on the diagonal matrix elements of the model space spanned by the three reference determinants. Each of the three CI vectors has zero component on the other two references in this so-called Projected Single Reference CI. Since the differences between the diagonal energies define entirely the off-diagonal matrix elements of the Heisenberg Hamiltonian, as will be discussed in section 5.1, the effective spin Hamiltonian may be obtained from a series of single reference CI calculations avoiding the bottleneck of a large active space for systems with a large number of unpaired electrons. The method may be extended to systems of spins larger than 1/2. A disadvantage of the method is the fact that the independently calculated CI vectors are not necessarily orthogonal. Furthermore, it faces the same spin contamination problem as the broken symmetry DFT calculations, discussed in section 4.5.2.

4.4 Other wave function methods

Although most of the wave function based computations of magnetic couplings have been performed either through the DDCI variational approach or from second-order perturbative expansions from CAS zeroth-order descriptions, it is worth to mention some alternative approaches. One enters here a domain of intense methodological efforts. The main motivations for these strategic developments are the problem of covalent bond breaking, the treatment of transition states in chemical reactions, and the description of excited states. All these problems present the same methodological difficulty as the treatment of magnetic systems, since the wave functions are intrinsically multideterminantal and since the requested precision requires accurate treatments of dynamic correlation. Progress in this area will therefore be beneficial for improved treatments of the magnetic systems. This is the reason why we present a short overview of the current efforts in this field, focusing on the treatments that have been applied on benchmark biradicalar organic systems, as methylene, trimethylenemethane (TMM), tetramethyleneethane (TME), xylylene and dehydrobenzene isomers.

4.4.1 Multi-configurational reference perturbation theory methods

The previously discussed perturbative methods (CASPT2 and NEVPT2) are contracted schemes. The perturbation vectors are linear combinations of single determinants, whose ratio is imposed by the variational solution of the reference wave function. On the contrary, the first implementations of MR perturbative methods were uncontracted and considered the individual outer space single determinants as perturbers. Among them we quote the CIPSI method[421–423] and the MR Møller-Plesset method of Hirao.[496,497] A closely related method was introduced by Nakano[498] and makes use of effective Hamiltonian theory to dress CAS matrix up to second-order. The first correlated *ab initio* calculation of the magnetic coupling of copper acetate dimer was made in this uncontracted formalism.[323] Most of the determinant-based MR-PT methods are not strictly size-consistent or separable in the sense that the inclusion of a noninteracting system B should not affect the relative energies of the system A. More details can be found in refs 367 and 499. Strictly separable versions can be formulated by introducing some degree of self-consistency in the determination of the coefficients of the outer space determinants. Such solutions were proposed by Heully *et al.*,[500] or derived from Mukherjee's formulation of MR coupled cluster theory.[501,502] The latter treatment has been applied successfully to the organic biradicals TMM and 1,2,3-tridehydrobenzene by Chattopadhyay *et al.*[503] The Nakano procedure has been applied to different biradicals as the family of bis-verdazyl biradicals,[504] TME and bis-allyl benzene.[505]

4.4.2 Multi-configurational reference CI methods

The numerous purely inactive double excitations ($2h$-$2p$) are the main origin of the serious size-consistency problem of MR-SDCI calculations. The absence of these excitations in the DDCI treatment makes this error negligible or at least much less important in this approach. There are other more or less approximated procedures to correct the size inconsistency of an MR-CI treatment, which we only overview here. An exhaustive, excellent presentation can be found in the recent review by Szalay and co-workers.[506]

The simplest procedure to restore the size-consistency is the generalization of the Davidson correction to MR wave functions.[507] Unfortunately, this procedure is rather approximate and more sophisticated methods are required to obtain accurate results. Most of these schemes aim to introduce corrections consisting of an approximate cancellation of the so called unlinked terms that are responsible of the size-consistency error. The averaged coupled-pair functional, MR-ACPF[508,509] and the MR coupled electron pair approximation (MR-CEPA)[510–514] methods belong to this class. A procedure for a rigorous cancellation of all unlinked terms has been proposed under the name of MR-$(SC)^2$CI (multi-configurational reference size-consistent self-consistent CI)[515] but has not been tested extensively enough to draw conclusions for its applicability in magnetic systems. The method known as MC-CEPA was used by Staemmler and co-workers in the study of magnetic coupling in inorganic systems as oxo-bridged dinuclear complexes of Ti, V, Cr, Co and Ni.[326–328,516,517] The MC-CEPA treatment of the electron correlation increases the magnetic coupling by a factor of 3-4 in comparison to the valence-only CI reference, providing a nearly quantitative agreement with experiment and accurate magnetostructural correlations. The related MR average quadratic coupled cluster, MR-AQCC[511,518,519] approximation has been used in para-benzyne.[520]

In the context of MR-CI methods one must also quote the internally contracted MR-SDCI of Werner and co-workers.[369,521] As in the previously discussed contracted MR perturbative methods, the number of vectors spanning the outer space is drastically reduced by considering only those generated by the action of the excitation operators on the eigenvector of the reference CAS. The same logics has been recently applied in a variational transcription of the NEVPT3 method.[522] An explicit short-range Slater-type geminal function (or F_{12}) has been recently introduced by Werner in the contracted MR-SDCI method.[523,524] Despite the contracted nature of the CI, this code allows the projections of the eigenvectors in the CAS space to be revised under the effect of the interaction with the outer space, i.e. under the effect of the dynamic correlation. Although the MR-SDCI are in general rather efficient, they all have to deal with the size-consistency problem.

For transition metal magnetic systems, Staemmler and co-workers[330,516] have developed an inexpensive technique based on a valence CI (VCI) treatment of the $3d$ electrons in terms of localized magnetic orbitals and have applied it to first row transition metal systems. The kinetic exchange contribution is isolated by truncating the CI to the covalent (neutral) VB components, giving the direct exchange contribution. The superexchange is then estimated from the energy difference of the full CASCI calculation and the truncated CI. As previously mentioned this treatment greatly underestimates the antiferromagnetic contribution due to the lack of the dynamic polarization effect. In the first papers, the authors correct the so-evaluated kinetic exchange by an empirical factor, usually taken as 2.0. The transferability of this factor is of course problematic. In a more recent work on Ni, Co and Mn systems, Fink[525] introduces the modified VCI technique, in which the energies of the VB ionic forms are shifted by correcting the ionization potential and the electron affinity of each ion by its relaxed CASSCF energy. This correction introduces the leading charge polarization effects, discussed in section 3.3.2, arising from the $1h$-$1p$ excitations in the DDCI method. These determinants are obtained as single excitations on the top of the ionic VB components, resulting in an effective energy lowering of these components and an increase of the kinetic exchange. Other applications have also been reported.[526–529] These procedures do not take into account the spin polarization contribution discussed in Section 3.3.3.

In biradicalar hydrocarbons with a well-identified π-electron subsystem, which includes the magnetic MOs, the minimal (2,2) CASSF has been replaced by a full valence π CASSCF,[100] or CI calculations beyond singles and doubles up to quadruply excited determinants in this orbital space.[530–532] These treatments incorporate the dynamic charge and spin polarization effects brought by the π electrons, but miss the dynamic response of the σ electrons. The latter effect may be non-negligible, in particular in systems that can be interpreted as a pair of disjoint radicals, as for instance the tetramethyleneethane[98] and 1,2,4,5-tetramethylenebenzene.[531] The shortcomings of such limited CI calculations have been outlined.[533]

The nonorthogonal CI (NOCI) approach of Broer and co-workers[329,534,535] takes a slightly different route to calculate the magnetic exchange parameters. The observation that the optimal orbitals for the neutral determinants and the ligand-to-metal charge transfer determinants are significantly different led to the idea to express both type of determinants in their own optimal orbitals and perform the configuration interaction between them in a nonorthogonal setting. The resulting wave function has only a limited number of determinants, and hence, is very interesting for analysis purposes. Dynamic electron correlation is difficult to include in the NOCI wave function. Nevertheless, quite reasonable estimates of the magnetic coupling were obtained for some copper oxide systems.[329,536]

4.4.3 Coupled Cluster methods

Linear response (LR) theory provides an accurate computational scheme to describe excited states and transition energies for molecules whose ground state is essentially of closed-shell character. Electron correlation may be added to the Hartree-Fock single determinant through a Coupled Cluster (CC) treatment, whatever the level of sophistication of the wave operator, including single, double, and eventually triple excitations. On top of this description, it is possible to apply LR or Equation of Motion (EOM) methods[537,538] to obtain transition energies. The method is frequently presented in the Random Phase Approximation (RPA) which expresses the excitation operator that generates the excited state from the ground state as a linear combination of single excitations and single de-excitation operators. Notice that these methods assume that the amplitudes of the double excitations are transferable to some extent from one state to another. These frequently used techniques are not directly applicable to the magnetic systems for two reasons: (i) They only provide excited states of the same spin multiplicity as that of the ground state, while we are interested in energy differences between states of different multiplicities, and (ii) they rely on an expansion from a single closed-shell reference determinant, while the low-spin state has a multi-determinantal nature in magnetic problems.

Several techniques have been developed to circumvent these difficulties. One consists of the introduction of an artificial closed-shell reference. Starting for instance from the optimized MOs of the triplet state, and hence the two magnetic MOs, one may take as reference the determinant obtained by putting 4 electrons in these magnetic orbitals. From this doubly anionized state, the states of interest are given by a double ionization and may be described using the EOM-CC method.[539,540] This method is strongly advocated by Bartlett and co-workers and gives rather good results as illustrated in the work of Demel *et al.* on the singlet-triplet gap of TMM.[541] However, the extension to systems with several singly occupied MOs is problematic.

Another possibility consists of an adaptation of the EOM to make possible spin changes. This is the Spin-Flip EOM or time-dependent treatment, first conceived by Krylov.[542–547] The reference is again a single determinant, namely the determinant describing the upper multiplet with maximum M_S value. Then the excitation operators include a change of the M_S value to produce the lower multiplicity states. The method has been essentially applied to the calculation of singlet to triplet, or doublet to quartet energy differences. The first version of the method resulted in rather strong spin contamination, which has been reduced by further improvements of the method and even eliminated in the CI of singles version of the spin-flip algorithm.[548] At present, the method is essentially employed in the DFT context, as will be evoked later-on. The examples of biradicals that have been more frequently studied are TMM, benzyne and xylylene isomers. Geometry optimizations and adiabatic singlet-triplet gaps of these biradicals have also been reported.[549,550] Within this scheme, a double spin-flip procedure has been introduced to extent the method to tetraradicals.[551]

The generalization of the coupled cluster method to MR wave functions has been and remains the subject of intense theoretical efforts which has been excellently reviewed in a recent work by Bartlett and co-workers.[552] In principle, these methods can be considered as the optimal tool for the treatment of magnetic systems, since they combine one of the most accurate treatments of dynamic electron correlation with a rigorous treatment of the intrinsic multi-determinantal nature of the wave function. The Jeziorski-Monkhorst expansion[553] is able in principle to provide several states simultaneously but in practice faces major difficulties due to the presence of intruder states in the targeted spectrum, and therefore most of the proposals for MR-CC are essentially state-specific and make use of the intermediate effective Hamiltonian concept.[554] Some developments working in the Fock space[555,556] have been successfully applied to atomic spectroscopy.[557,558]

Two main families may be distinguished in state-specific methods. The first one is actually a generalized single reference expansion[559–561] applied to a CAS. The wave operator introduces both the internal excitations that generate the CAS from an arbitrary single determinant, and the semi-active or purely inactive double excitations. Although asymmetrical in the case of degenerate reference determinants, and therefore in some sense not aesthetical –taking $|a\bar{b}|$ as reference determinant to describe an open-shell singlet state, $|\bar{a}b|$ is not equally treated–, the method is rather convenient, at least for small CAS. Another alternative to avoid a true MR expansion consists of considering the eigenvector of the CASCI space as a reference in an internally contracted MR-CC formalism.[562–564] Shen *et al.* have applied this idea in a block-correlated treatment to benzyne and TMM.[565,566] The Reduced MR-CC method of Li and Paldus[567] also follows this strategy.

On the other hand, the *true* state-specific MR-CC techniques face the basic difficulty of the multiple-parentage. The determinants of the outer space may be obtained from different reference determinants by different double excitations, hence the number of excitation operators is larger than the number of outer space determinants interacting with the references, which prevents the direct determination of their amplitudes. Some additional and rather arbitrary conditions have to be imposed to define these amplitudes. Three different solutions have been proposed, by Mukherjee *et al.*[568,569] in the so-called equal parentage solution, by Malrieu *et al.*[570] by scaling the parentage on the interactions between the reference determinants and the outer space ones through the Hamiltonian matrix elements, and by Hubac *et al.*[571] in the Brillouin-Wigner MR-CC. The first method has been efficiently implemented[572] and has been tested essentially on model systems,[573,574] where it exhibits some formal and accuracy problems and possible improvements are still under investigation. The method has been applied to the study of the triplet-singlet gap in TMM.[575] The Brillouin-Wigner solution proposed by Hubac *et al.*[571] has also been applied to the TMM singlet-triplet gap by Brabec and Pittner[576] and has recently been improved by introducing explicit F_{12} correlation factors.[577] To obtain a reliable and general state-specific (SS) MR-CC method is definitely the goal which should be reached for a firm, unbiased study of magnetic systems.

Many of these MR methods have been applied to singlet-triplet energy differences in closed-shell systems, in open-shell atoms or small molecules like carbene. The real biradicalar systems that have received systematic studies are the three benzyne isomers, for which experimental estimates of the singlet to triplet excitation energies are available. Among the three isomers, only the para isomer presents a small energy gap (between 2 and 4 kcal/mol). One may quote the results of the spin-flip CCSD method[578] and those of Mukherjee's MR-CCSD formalism[579] which are in satisfactory agreement with experiment. Recent calculations on TMM and oxyallyl biradicals[580] and on several copper dimers[581] have also been reported. The internally contracted MR-CCSD formalism of Hanauer and Köhn[582] seems somewhat less accurate.

4.5 Density functional theory

There are several theoretical approaches using DFT to calculate magnetic couplings and related electronic structure parameters. All of them stand within the Kohn-Sham version of this theory, and thus rely on single-determinant based evaluations of the density. The most popular technique exploits the broken symmetry (BS) solutions, but alternatives have been proposed. In the following, we shortly review the different implementations and discuss the main points relevant to the magnetic coupling.

4.5.1 Analysis of the coupling in a spin-unrestricted setting

Before discussing the computational *ins and outs* of the BS solution, we will first extend the analysis made in section 3 of the mechanisms that govern the magnetic coupling to the spin-unrestricted case. This analysis can contribute to a more detailed understanding of the magnetic interactions given the large number of studies that have been published on magnetic coupling problems treated within the the BS approximation.

In the general unrestricted context (either unrestricted Hartree-Fock (UHF) or DFT), the triplet is written as the $M_S = 1$ determinant

$$\Phi_{M_S=1} = \Phi_{HS} = |h_\alpha \bar{h}_\beta ab| \tag{42}$$

where the different spatial part of the α and β spinorbitals (h_α and h_β) introduce the spin polarization of the inactive orbitals. Due to this spin polarization, Φ_{HS} is not an eigenfunction of $\hat{S}^2$, although the spin contamination is usually weak and $\langle\Phi_{HS}|\hat{S}^2|\Phi_{HS}\rangle \approx 2$. The $M_S = 0$ determinant is a BS determinant and is defined as

$$\Phi_{M_S=0} = \Phi_{BS} = |h'_\alpha \bar{h}'_\beta a' \bar{b}'| \tag{43}$$

The spin polarization introduced by the inactive orbitals h'_α and h'_β is different from the previous one, as will be shown below. Φ_{BS} is not an eigenfunction of $\hat{S}^2$ and in this case the spin contamination is large, in general $\langle\Phi_{BS}|\hat{S}^2|\Phi_{BS}\rangle \approx 1$. The nonorthogonal magnetic orbitals of the BS solution a' and b' may be expressed in terms of the orthogonal orbitals a and b making use of perturbation theory.[583] Taking the neutral determinant $|a\bar{b}|$ (h_α and h_β are left out for clarity) as zeroth-order description $\Psi^{(0)}$, the valence CI matrix given in eq 20 shows that interaction with the ionic component $|a\bar{a}+b\bar{b}|$ gives $\Psi^{(1)} = -\frac{t_{ab}}{U}|a\bar{a}+b\bar{b}|$ as first-order correction to the wave function. The corresponding second-order correction to the energy is $E^{(2)} = -2\frac{t_{ab}^2}{U}$. By writing a' and b' in terms of the orthogonal magnetic orbitals a and b

$$a' = a - \frac{t_{ab}}{U}b \qquad b' = b - \frac{t_{ab}}{U}a \tag{44}$$

the overlap between a' and b' is equal to $\frac{2t_{ab}}{U}$. If we compare the first-order expression of Φ_{BS} with what is obtained from the substitution of eq 44 in eq 43

$$\Phi_{BS} = |a\bar{b}| - \frac{t_{ab}}{U}(|a\bar{a}| + |b\bar{b}|) + (\frac{t_{ab}}{U})^2|b\bar{a}| \tag{45}$$

it is readily observed that the two only differ by a second-order term proportional to $(S_{a'b'})^2 \propto (t_{ab}/U)^2$. Since t_{ab} is in general much smaller than U, the last term can be neglected for the analysis purpose and the expression of the BS determinant in terms of the orthogonal magnetic orbitals a and b can be truncated at first-order. By limiting the analysis at this point to the magnetic orbitals and neglecting the spin polarization in the core orbitals, the second-order corrected energy difference between the BS and HS determinants reads

$$E_{BS} - E_{HS} = K_{ab} - 2\frac{t_{ab}^2}{U} \tag{46}$$

The comparison with eq 27 shows that this approach gives exactly half of the total contribution of both the direct and the kinetic exchange. Therefore, the magnetic coupling parameter J can be estimated as

$$J = 2\left(E_{BS} - E_{HS}\right) \tag{47}$$

when the condition of a small $S_{a'b'}$ is fulfilled, *i.e.* when $\langle \Phi_{BS} | \hat{S}^2 | \Phi_{BS} \rangle$ is close to 1.

The analysis can be extended to the spin polarization effects due to the inactive occupied orbitals. Expressing the nonorthogonal orbitals h_α, h_β, h'_α, h'_β in terms of a perturbative mixture of the orthogonal orbitals h and p obtained in a spin-restricted calculation, the spin polarization contribution to the energy of the HS determinant is

$$E_{HS}^{SP} = 2\sum_{h,p} \frac{|\langle h | \frac{1}{2}\left(\hat{K}_a + \hat{K}_b\right) | p \rangle|^2}{\varepsilon_h - \varepsilon_p} \tag{48}$$

and to the energy of the BS determinant

$$E_{BS}^{SP} = 2\sum_{h,p} \frac{|\langle h | \frac{1}{2}\left(\hat{K}_a - \hat{K}_b\right) | p \rangle|^2}{\varepsilon_h - \varepsilon_p} \tag{49}$$

The total contribution to J of this spin polarization effect in the inactive occupied orbitals is

$$\Delta E_{BS}^{SP} = 2\sum_{h,p} \frac{\langle h | \hat{K}_a | p \rangle \langle p | \hat{K}_b | h \rangle}{\varepsilon_p - \varepsilon_h} \tag{50}$$

which is exactly half the contribution of the spin polarization of the $1h$-$1p$ excitations in the spin restricted formalism as given by eqs 27 and 36. Although underestimated, the spin polarization is correctly included using eq 47 in a spin unrestricted treatment of the magnetic coupling.

The precedent analysis is valid in the unrestricted Hartree-Fock as well as in the DFT context, where the only difference lies in the use of an exchange-correlation potential to obtain the spin orbitals.

4.5.2 Exploiting the broken symmetry solutions

The general ideas of the BS approaches were introduced by Ginsberg[584] and Noodleman[585] and have been reviewed in several recent articles.[20–24] They all rest on a mapping between the energies of single determinants and the diagonal elements of the Heisenberg Hamiltonian, which correspond to the energies of the Ising Hamiltonian. In the above discussed two $S = 1/2$ sites systems, the two energies are those of the triplet and the $M_S = 0$ BS determinants. The coupling parameter is extracted from their energy difference according to eq 47. For systems with a larger number of sites and therefore a larger number of parameters to be extracted, the energies of the $M_{S_{max}}$, $M_{S_{max}-1}$, etc. determinants have to be used. Section 5.1 includes a detailed discussion on the extraction procedure in this more general case. The method can also be applied to systems with higher spin angular momentum per site as will be discussed in section 5.3.

Although these mapping procedures seem rather straightforward at first sight, there is an interesting issue concerning the spin contamination of the unrestricted determinants. The single bond breaking problem, intensively studied for the H_2 bond, illustrates that the symmetry breaking of the $M_S = 0$ solution starts only beyond a critical interatomic distance r_c and that the evolution of $\langle \hat{S}^2 \rangle$ smoothly changes from 0 for the pure singlet at distance shorter than r_c to $\langle \hat{S}^2 \rangle = 1$ for fully localized electrons at long distances. Depending on the strength of the coupling of the spin moments, the BS determinant describes a situation somewhere in between these two extremes. This has opened an intense debate about the spin-contamination problem. A first aspect concerns the meaning of $\langle \hat{S}^2 \rangle$ of the Kohn-Sham determinant.[586–589] A second one concerns the necessity of spin-decontaminating the BS solution to obtain a relevant energy for the low-spin state. Some authors have used the energy of the BS solution as the real singlet[308,444,590–594] in what has been called the strong delocalization limit. This faces one difficulty, namely the existence of two equivalent and nonorthogonal BS solutions of the same spin-free density does not obey the assumed one-to-one correspondence between the N-electron function of the ground state and its density. Other authors assume the strong localization limit.[226,595–598] The analysis of the overlap between the α and β spinorbitals and $\langle \hat{S}^2 \rangle$, which are related,[583] shows that most magnetic systems are closer to the second limit, even if the magnetic Kohn-Sham orbitals are significantly more delocalized than the HF ones. The debate around this question has continued[590,599,600] but the strong dependence of the calculated magnetic coupling on the choice of the exchange-correlation potential, as evidenced by several authors, has downplayed the importance of this controversy.

More rigorous attempts, some of which will be discussed below, have tried to deal with the spin contamination problem, which affects both the HS and the BS solutions. Although this is normally neglected, the function of maximum M_S is not an eigenfunction of $\hat{S}^2$. In the case of two $S = 1/2$ magnetic sites, the HS determinant contains contributions of quintet configurations with four open-shells and thus $\langle \Phi_{HS} | \hat{S}^2 | \Phi_{HS} \rangle \geq 2$. The deviation gives a measure of the spin contamination, although part of it should be ascribed to the spin polarization of the closed-shell MOs, which is a real physical factor. The spin polarization is not entirely taken into account at this level of treatment, since it also involves double excitation processes, as shown in section 3.3.3.

Similarly, $\langle \Phi_{BS} | \hat{S}^2 | \Phi_{BS} \rangle$ also deviates from 1, which is the expectation value of $\hat{S}^2$ for the BS determinant when expressed in the MOs obtained in a spin restricted approach. The spin polarization of the core MOs introduces some components of triplet configurations with four open-shells, and therefore enhances $\langle \hat{S}^2 \rangle$. On the contrary, the mixing between the singly occupied MOs a and b to produce the relaxed magnetic MOs a' and b' introduces some ionic components in the wave function. The ionic contributions have singlet character in the two-electron two-orbitals system under consideration, and therefore always decrease $\langle \hat{S}^2 \rangle$. Usually, the spin polarization is less important than the intersite delocalization of the magnetic electrons (the kinetic exchange). Hence, the second factor prevails and $\langle \Phi_{BS} | \hat{S}^2 | \Phi_{BS} \rangle < 1$. However, systems with large spin polarization may show expectation values larger than one. An interesting example is the family of long polyacenes. The ground state singlet of decacene presents a spin-symmetry breaking and the BS determinant gives $\langle \hat{S}^2 \rangle = 1.39$.[83]

Assuming that the spin polarization does not introduce any spin quintet component, the BS solution can be written as a linear combination of pure singlet (S) and triplet (T) configurations

$$\Phi_{BS} = \lambda S + \mu T \tag{51}$$

with $\lambda^2 + \mu^2 = 1$. Then, the energy of the BS determinant can be written as

$$E_{BS} = \lambda^2 E(S) + \mu^2 E(T) \tag{52}$$

and the expectation value of $\hat{S}^2$ is equal to

$$\langle \Phi_{BS} | \hat{S}^2 | \Phi_{BS} \rangle = \langle \lambda S + \mu T | \hat{S}^2 | \lambda S + \mu T \rangle = 2\mu^2 \tag{53}$$

From the normalization condition it is derived that $\lambda^2 = 1 - \langle \hat{S}^2 \rangle_{BS}/2$. The substitution of λ and μ in eq 52 gives

$$E_{BS} = \left(1 - \frac{\langle \hat{S}^2 \rangle_{BS}}{2}\right) E(S) + \frac{\langle \hat{S}^2 \rangle_{BS}}{2} E(T) \tag{54}$$

Assuming that T is equal to Φ_{HS} and consequently, $E(T) = E_{HS}$, one obtains:

$$E_{BS} - E_{HS} = E(S) - \frac{\langle \hat{S}^2 \rangle_{BS}}{2} E(S) + \frac{\langle \hat{S}^2 \rangle_{BS}}{2} E(T) - E(T) \tag{55a}$$

$$E(S) - E(T) = \frac{2\,(E_{BS} - E_{HS})}{2 - \langle \hat{S}^2 \rangle_{BS}} \tag{55b}$$

Similarly, the expectation value of $\hat{S}^2$ for T can be taken as $\langle \hat{S}^2 \rangle_{HS}$, which gives: $\langle \hat{S}^2 \rangle_{BS} = \mu^2 \langle \hat{S}^2 \rangle_{HS}$ and an alternative expression for the singlet-triplet energy difference

$$E(S) - E(T) = \frac{\langle \hat{S}^2 \rangle_{HS}\,(E_{BS} - E_{HS})}{\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{BS}} \tag{56}$$

Yamaguchi[601–603] proposed an expression closely related to eq 56:

$$E(S)-E(T)=\frac{2\,(E_{BS}-E_{HS})}{\langle\hat{S}^2\rangle_{HS}-\langle\hat{S}^2\rangle_{BS}} \tag{57}$$

If the spin moments of the magnetic sites are not restricted to $S=1/2$ a more general expression emerges and J can be expressed as

$$J=\frac{2\,(E_{BS}-E_{HS})}{\langle\hat{S}^2\rangle_{HS}-\langle\hat{S}^2\rangle_{BS}}, \tag{58}$$

which transforms to Noodleman's equation[585] for the magnetic coupling in case of nonoverlapping orbitals

$$J=\frac{2\,(E_{BS}-E_{HS})}{S^2_{max}} \tag{59}$$

A generalization of this formula to polyradicals with higher spin angular momenta has been proposed.[604] However, the BS solution is in this case contaminated by components of various spin multiplicities. For instance, in systems with two $S=1$ sites, $\Phi_{BS}=|a'_1a'_2\bar{b}'_1\bar{b}'_2|$ can be expressed as

$$\Phi_{BS}=\lambda S+\mu T+\nu Q \tag{60}$$

where Q represents a quintet configuration. $\langle\hat{S}^2\rangle_{BS}$ depends on the weights of the relative importance of the different spin functions in Φ_{BS}

$$\langle\Phi_{BS}|\hat{S}^2|\Phi_{BS}\rangle=\langle\hat{S}^2\rangle_{BS}=2\mu^2+6\nu^2 \tag{61}$$

These weights cannot be obtained from this single equation only, and therefore, a spin decontaminated singlet energy cannot be obtained in this case.

As mentioned before, one of the main drawbacks of the J evaluations based on DFT calculations is the dependence of the calculated J value on the exchange-correlation functional. Comparisons between the results of various functionals have been performed by different authors. Copper dimers have frequently been used for these comparisons. Adamo *et al.*[595] have shown the dispersion of the results of different functionals in dicopper azido complexes. Bencini and collaborators[226] compared the local density approximation (LDA), X_α and Becke-Perdew (BP) gradient corrected exchange-correlation functionals by using both the BS approach and the single determinant formalism,[605,606] which is in fact a valence CI method, to estimate the singlet-triplet energy difference of different model systems. Unfortunately the results are not conclusive. Ruiz *et al.* have compared the results of standard functionals with and without the Perdew-Zunger correction[607] of the self-interaction error[590] and conclude that the self-interaction correction in general reduces the singlet-triplet separation. More comparisons were made by Valero and co-workers,[596] who tested the PBE0, B3LYP, and different functionals of the M06 family[608,609] and conclude that the M06-2X version reduces the coupling compared to gradient corrected or the traditional hybrid functionals as B3LYP. The M0X-family was also tested by Ruiz for $\mathrm{Cu^{II}}$, $\mathrm{Fe^{III}}$ and $\mathrm{V^{IV}}$ complexes. He observed that M05 and M06 give similar accuracy as B3LYP.[610] On the other hand, the comparison by Rivero *et al.*[611] on the performances of HSE and LC-PBE range-separated hybrid functionals on several organic biradicals and dicopper complexes leads to the conclusion that, at least for dicopper complexes, these functionals reduce the overestimation of the coupling parameter given by B3LYP. The performance of the longe-range corrected functionals have also been investigated by Ruiz.[591] It was concluded that the improved asymptotic behavior of these functionals reduces the self-interaction error leading to a higher degree of localization of the spin density, and hence, smaller magnetic coupling. Ess and Cook[612] have recently compared a series of functionals and conclude that only the B97X-D, the M06-2X, and a specifically modified mPW1PW91 functionals give reasonable accuracy for singlet-triplet gap in small molecules when using spin-projection. Similar comparisons have been performed on Fe dimers by Sorkin *et al.*[613] The comparison of 63 different functionals by Zein *et al.*[614] ranks the Becke00-x-only functional[615] as the most reliable one and confirms the tendency to overestimate the magnetic coupling by most functionals.

Special attention has been paid to the impact of the percentage of Fock exchange in the hybrid functionals. Martin and Illas have shown in copper oxides and nickel perovskites that increasing the percentage of Fock exchange reduces the overestimation of the coupling.[597,598] Their embedded cluster study showed that mixing 50% of exact exchange to different exchange potentials significantly improved the antiferromagnetic coupling constant in these systems. Later they tested the behavior of these ionic insulators in periodic calculations and concluded that increasing the percentage of Fock exchange in B3LYP to 35% provides rather accurate coupling parameters.[616] Similar conclusions have been reached in systems with a Cu_2O_2 magnetic core[617] and on iron dimers.[526,618] As noticed by Corà et al.[619,620] the optimal percentage for the magnetic coupling parameter is not system-independent and can result in incorrect estimations of other properties. The overestimation of the antiferromagnetic coupling by numerous functionals can be related to the spatial extent of the magnetic orbitals shown in Figure 16. They are in general more diffuse than the Hartree-Fock ones and often even more diffuse than the natural orbitals obtained from highly correlated treatments.[331] The resulting overestimation of the magnetic coupling is easily rationalized. The three main components of the magnetic coupling, the direct exchange, the kinetic exchange and the spin polarization of the ligand, increase with the overlap between the magnetic orbitals. Since the kinetic exchange is in general the dominant contribution, a larger differential overlap leads to larger antiferromagnetic coupling.

The effective on-site repulsion parameter U was first introduced in DFT[621–623] to correct the spurious gapless character of some insulating materials largely due to the self-interaction error. This U correction indeed turns out to improve the results of magnetic coupling. Rivero *et al.* have calculated the coupling parameter by using LDA+U and GGA+U procedures in a series of copper complexes and organic biradicals,[624] as well as on a series of cuprates,[625] and conclude that the choice of U is far from trivial. Although these procedures can be useful in large systems, especially when using plane waves, they also conclude that hybrid functionals give more accurate results. A self-consistent linear-response GGA+U corrected approach[626] was applied to the multiplet splittings of Fe_2 and Fe_2^-.[627] The method was also applied successfully to extract the magnetic coupling of $FeSbO_4$[620] and iron-sulfur proteins[529,628] in combination with spin-projection. The success of the LDA+U of GGA+U functionals can certainly be attributed to the energetic penalty of the ionic

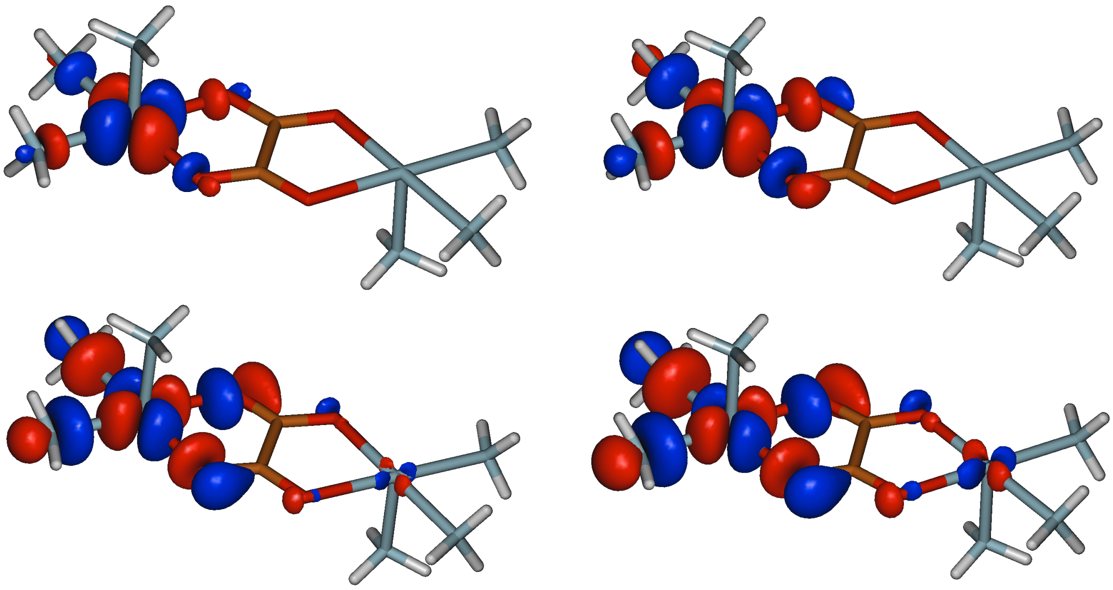

Figure 16: Localized magnetic orbitals of the model systems [$Cu_2\mu$-oxalato$(NH_3)_6]^{2+}$ for different computational methods. Above CAS(2,2) and DDCI, below B3LYP and LDA.

valence bond structure imposed by this parameter which results in a stronger localization of the magnetic orbitals.

In any case, although the values of the magnetic coupling are very sensitive to both the spin decontamination procedure and to a larger extent to the choice of the density functional, the magneto-structural trends are certainly reliable in most of the system families, which allows rationalizations. In systems where different magnetic couplings are potentially present, BS approach is likely to provide reasonable ratios between these various couplings. Novoa and co-workers have applied this strategy in their "bottom-up" procedure[175] to fit the magnetic susceptibility in organic crystals and hybrid organic-inorganic crystals,[237,238,629–631] where each radicalar unit interacts with different neighbors. To fine-tune the agreement with the experimental temperature dependence of the magnetic susceptibility uniform scaling factors may be applied to the calculated coupling constants.

An advantage of wave function methods is the possibility to analyze the various physical factors contributing to the magnetic coupling, in particular the decomposition in terms of direct exchange, spin polarization, and kinetic exchange. The BS DFT calculations basically only deliver a number, and the interpretation of this final result in terms of mechanisms is still lacking, although recently a strategy was proposed to split the global energy difference into various contributions.[632] The difference between the energy of the restricted open-shell HF $M_S = 1$ determinant $|h\bar{h}ab|$ and the energy of the determinant $|h\bar{h}a\bar{b}|$ expressed in the same orbitals gives the direct exchange K_{ab}. Freezing the magnetic MOs and relaxing the core orbitals for both determinants without imposing the spin restrictions gives $|h'_{\alpha}\bar{h}'_{\beta}ab|$ and $|h''_{\alpha}\bar{h}''_{\beta}a\bar{b}|$ and introduces the spin polarization of the core under the exchange field of ab or $a\bar{b}$. The corresponding energy difference gives access to the spin polarization correction to the magnetic coupling. On the contrary, freezing the core MOs and relaxing the magnetic orbitals in the $M_S = 0$ determinant $|h\bar{h}a'\bar{b}'|$ introduces ionic components and the energy stabilization quantifies the kinetic exchange. The effects are nearly additive, since the sum of the three terms practically coincides with the value obtained in the standard BS DFT calculation.

A final remark on the role of spin contamination concerns geometry optimization and more generally the calculation of potential energy surfaces of magnetic systems, especially of the low-spin state based on the BS solution. Since the contamination is strongly dependent on the distance of the magnetic sites, the decontamination correction should be performed along all the optimization process. Analytical procedures have been derived by Kitagawa *et al.*[633] and Toru and Thiel.[634] A simple recipe has been recently proposed by Malrieu and Trinquier.[635] Some packages as QUILD implement decontamination corrections along the iterative optimization procedure.[636]

4.5.3 Beyond the single KS determinant

The Kohn-Sham (KS) implementation of DFT deals very well with situations that can be described with a single determinant reference within the wave function approaches. However, Schipper, Gritsenko and Baerends demonstrated the impossibility to represent the total density with a single KS determinant in multi-configurational cases by the comparison of a nearly exact density of C_2 calculated with MR-CI and the one resulting from KS-DFT.[637] Only by using a three-determinant ensemble an accurate description could be obtained. This obviously leads to fractional orbital occupation as in the FON-DFT concepts described by Wang and Schwarz,[638] based on earlier works[639,640] in which DFT calculations were performed allowing for fractional occupation numbers.

An early multi-determinant scheme to handle the atomic multiplet structure is due to Daul.[606] The energy of the N-electron states is expressed as a weighted average of the energies of several KS determinants, where the ratio between the determinants is fixed by symmetry. The recipe was first applied to calculate the ligand-field states of transition metal complexes[641–643] and later also to magnetic coupling problems.[644,645]

Gräfenstein *et al.* developed a KS energy expression for restricted open-shell singlets for the two-electrons in two-orbitals case: ROSS-DFT.[646,647] Basically, the method adds $2K$ to the energy of the open-shell singlet state and treats the Coulomb correlation separately for up and down spin electrons. It was mentioned by the authors that the spin restricted formalism does not allow for spin polarization effects. Since the Coulomb correlations are weak in the treated examples, the triplet state is always lower and antiferromagnetic situations cannot be described.

In analogy to this approach, an extension was made by Filatov and Shaik.[648] Their restricted open-shell KS (ROKS) scheme can be considered as the DFT equivalent of restricted open-shell Hartree-Fock (ROHF). Energy expressions are derived using the Roothaan spin coupling coefficients. A more general scheme was presented in a second paper;[649] the restricted ensemble KS (REKS) approach. The energy expression is optimized as a function of the KS orbitals and the weighting factors of the determinants. These weighting factors are the (fractional) occupation numbers of the nearly degenerate orbitals. To some extent, this approach can be considered as the equivalent of an multi-configurational SCF approach within the DFT setting. Weighting factors are no longer imposed by symmetry, and therefore, situations can be treated that go beyond the symmetry-imposed degeneracy of the orbitals, as in atomic multiplets. The applicability was demonstrated by calculating the PES of ethene and later applied to magnetic coupling parameters by Illas and co-workers.[650,651] The lack of spin polarization is one of the reasons for the systematic underestimation of J. The optimization of an ensemble energy in the KS framework was already outlined by Gross, Oliveira and Kohn in 1988.[652]

The idea of treating the nondynamic or static electron correlation with a multi-configurational wave function approach and add the remaining dynamic correlation with DFT has been worked out by several groups.[653–660] The main problem is how to avoid the double counting of the electron correlation treated in the multi-configurational step of the calculation. Various attempts have been made to resolve this question by designing new functionals or relying on a spatial separation of nondynamic (long-range) and dynamic (short-range) correlation.[661–665] The method of Pérez-Jiménez and co-workers[658] has been applied to calculate the magnetic coupling of some model systems.[666] When appropriate corrections for double counting are applied, the method reduces the overestimation of the coupling that is usually observed for GGA functionals. A semi-quantitative agreement with reference data was obtained.

4.5.4 Spin-Flip DFT

Shao, Head-Gordon and Krylov formulated a spin-flip implementation for DFT[667] based on the method developed by Krylov for *ab initio* schemes.[542,543] The formulation was based on the Tamm-Dancoff approximation (TDA) to time-dependent DFT (TD-DFT). While ordinary TD-DFT only considers the spin conserving blocks of the response matrix, the spin-flip implementation of Shao and co-workers puts these blocks to zero and only the $\alpha\beta$ block is considered, resulting in a net change of one of the number of α versus β electrons. Using a pure functional there is no coupling in the $\alpha\beta$ block, but by using hybrid functionals, this so-called collinear implementation of spin flip (SF) TD-DFT leads to nonzero contributions. Larger amounts of exact Fock exchange were required to obtain reasonable agreement than usually applied for ground state properties. The reference state is the $M_S = 1$ triplet determinant with two unpaired electrons in two orbitals. The target states of the SF TD-DFT are the four $M_S = 0$ determinants with closed-shell or open-shell occupations. An interesting feature of this method is that the open-shell singlet has practically no spin contamination: $\langle \hat{S}^2 \rangle < 0.1$ for the singlet state in twisted ethylene.

An implementation using full TD-DFT was presented by Wang and Ziegler,[668] albeit for non-hybrid functionals only. The use of a noncollinear spin formulation activates the α-β coupling for pure functionals as well. This noncollinear variant of TD-DFT was originally developed in a relativistic setting, where α and β orbitals can mix. A TDA variant of noncollinear SF-DFT was presented by Rinkevicius[669] and a full implementation for hybrids was published shortly thereafter.[670] The methods have recently been reviewed and their performance compared by Bernard and co-workers.[671] It was reported that the TDA implementation has some advantages over the full implementation, since the latter may experience problems with 'negative' excitation energies, *e. g.* when the open-shell singlet is lower in energy than the reference high-spin determinant.

Another problem with SF-DFT concerns the spin contamination in states that go beyond the strict target space of the four $M_S = 0$ determinants that can be constructed with the two electrons in the two singly occupied orbitals of the reference. This issue is discussed in depth by Li and Liu[672]and a spin adaptation scheme was presented to solve this problem.

The SF-DFT scheme has recently been adapted to the calculation of magnetic coupling parameters in transition metal systems[673] and tested for eight binuclear copper complexes. Using a functional with 50% Fock exchange, the method provides reasonable results for all complexes.[674] Similar conclusions were obtained for triply bridged binuclear copper complexes.[675] From the systematic study of Valero, Illas and Truhlar on a set of twelve transition metal complexes, it was concluded that the spin-flip variant reduces the systematic error of DFT. The MPW1K functional was found to give the most precise couplings.[676]

4.5.5 Constrained DFT

To close this section on the DFT methodology in the scope of the magnetic coupling problems, we briefly mention the constrained-DFT (CDFT) formulation due to van Voorhis and collaborators.[677] The foundations of CDFT were laid in the 1980s when LDA was used to investigate the electronic structure of Ce impurities in Pd and Ag. To obtain information about charge fluctuations an additional potential was added to the Kohn-Sham equations to force that integrating over a certain volume yields exactly N electrons.[678] In the formulation of CDFT for systems with two magnetic sites n_a α electrons are constrained to volume A and n_b β electrons to B. The nonoverlapping volumes A and B cover the whole molecule and are chosen such that they both contain one of the magnetic sites. Comparison with standard BS approaches show that the overestimation of the AF contribution is significantly reduced. This is ascribed to a reduction of the self-interaction error due to more localized character of the magnetic orbitals. Moreover, the optimization of the Kohn-Sham orbitals of the low-spin determinant is in general easier due to the constraints imposed on the solution. The method has also been used to calculate hopping integrals[679] and a review was published recently.[680]

4.6 Extended systems

The calculation of electronic structure parameters with the above outlined computational strategies is straightforward in molecular systems. The discrete units present in the molecular crystals can be treated without further complications. Given the dependency of the magnetic coupling on the geometry, usually the experimental structure is adopted when available. Otherwise, geometry optimizations have to be performed. In the earliest application of the WF methods, the real external ligands were replaced by model ligands[326,328,398] to reduce the computational time needed to calculate the relevant wave functions and energies. This issue is nearly irrelevant when DFT approaches are used, and nowadays, the modeling of the external ligands is also less costly for CI or PT2 calculations, both because of the increase of computing power and the development of time-reducing computational techniques such as the Cholesky decomposition of the integrals,[681,682] resolution of the identity approaches,[683–685] or CI scheme based on localized orbitals.[489,493,686,687] The effect of the counter-ions on the magnetic coupling has been studied[688] and in general only play a minor role, except in some special cases where the counter-ion influences the geometry of the exchange interaction path.[689]

The situation becomes more complicated when the materials contain extended structures. Molecule-based magnetic materials can contain one-dimensional chains,[136,690,691] spin ladders,[692] two-dimensional sheets[207,693,694] or extend in all three dimensions. These type of extended structures are also found in atom-based magnetic materials such as the ionic transition metal oxides and related compounds.

There are two ways to model the extended materials for the extraction of the electronic structure parameters. In the first place, one can opt for the so-called periodic approach. To a very good approximation a crystal can be considered as constructed from a small building block (the unit cell) that is repeated nearly infinitely in the three spatial directions. Hence, all symmetry equivalent atoms in the bulk of the crystal experience the same influence of their surroundings and a natural simplification is the introduction of translational symmetry by imposing periodic boundary conditions, thus leading to the band theory of electrons moving in a periodic potential. The second option is to model the crystal by a small number of atoms at positions as they occur in the real crystal and to embed this collection of atoms in a potential that accounts for the part of the crystal not explicitly treated. This way of representing the crystal is generally known as the embedded cluster approach.

The periodic approach provides an accurate representation of the extended system and is the method of choice in the large majority of cases to obtain information about the properties of the system. The calculation of the electronic structure heavily leans on one-electron models such as the Hartree-Fock theory and the Kohn-Sham implementation of density functional theory. In the latter case, electron correlation can be taken into account by making the proper choice of exchange-correlation functional as explained in the previous section. The parameters are then determined from the energies of a set of BS determinants with different spin alignments in the unit cell.This strategy is based on a mapping of the BS solutions on the energies of an Ising Hamiltonian (*i.e.* the diagonal matrix elements of the Heisenberg Hamiltonian) and will be further worked out in section 5.1. Excellent descriptions of the extraction procedure for obtaining magnetic coupling constants can be found in the work of Moreira, Illas and co-workers[20,650,695] and other groups.[696,697] On the other hand, the use of correlated wave function approaches within the periodic modeling of the extended systems is more complicated. Nowadays, the calculation of the second-order correction to the energy through Møller-Plesset perturbation theory is becoming a well-established strategy for nonmagnetic systems.[698] However, the extension to materials with (localized) nonzero spin-angular momenta has not been reported yet in the literature, and hence, this approach is less interesting in the scope of this review.

Although the periodic approach certainly provides valuable information, the extraction of the electronic structure parameters is solely based on energy differences. Therefore, it is impossible to simultaneously estimate all the parameters when the number of parameters is larger than the number of independent spin arrangements, and assumptions have to be made *a priori* to equal the number of energy equations and the number of unknown parameters. A second disadvantage of the periodic DFT approach is the fact that results depend on the choice of the exchange-correlation functional. The experience gained over the last two decades makes the correct choice of functional easier but also established that the optimal choice is both material and property dependent.[699,700] As far as the magnetic coupling is concerned, LDA and GGA functionals tend to severely overestimate the antiferromagnetic component of the coupling and predict too strong couplings. In line with the observations for molecular entities, the admixture of Fock exchange improves the description and good results have been obtained with B3LYP[616,701–709] and functionals with slightly larger amounts of Fock exchange.[710–714]

The second way to approach the modeling of extended structures takes a completely different –although in many aspects complementary– viewpoint. Instead of considering the whole structure, the embedded cluster method adopts a quasimolecular approach. A limited number of atoms is cut from the crystal structure and treated as accurately as possible, while the effect of the remainder of the crystal is taken into account via an embedding potential. In the case of ionic insulators, the embedding consists of two distinct parts and is illustrated in Figure 17. The first accounts for the Madelung potential in the cluster region due to the other ions and is usually represented by a set of (optimized) point charges at the lattice positions. The second part accounts for the short-range interactions, basically Coulomb and exchange interactions between the electron density due to the cluster atoms and those in the immediate surrounding. The quantum mechanical nature of the exchange interactions prevents a simple exact representation as for the Madelung potential. However, accurate approximations have been developed as an extension of the effective potentials that represent core electrons. Two strategies should be mentioned. In the first place, the atom based embedding such as the Total Ion Potentials (TIPs) introduced by Winter, Temple and Pitzer[715] and the more rigorous *ab initio* Embedding Model Potential (AIEMP) scheme of Barandiarán and Seijo.[716,717] Both embedding schemes absorb the interaction of the cluster electrons with other electrons into an effective 1-electron Hamiltonian acting on the electrons of the atoms in the local region only. Secondly, frozen density embedding[718] schemes have been developed by different groups.[719–728] The electron density obtained in a HF or DFT periodic treatment of the material is translated into an effective one-electron operator that is absorbed in the cluster Hamiltonian. Closely related is the strategy developed by Lepetit and collaborators in which the energies of some core orbitals of the cluster wave function are aligned with the corresponding core levels of the band structure calculation.[729]

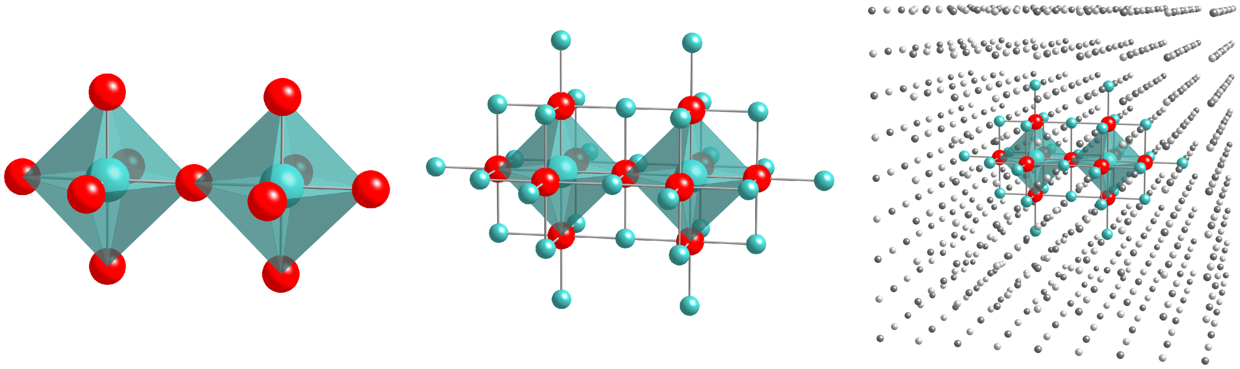

Figure 17: Embedded cluster representation of NiO. The Ni_2O_{11} cluster (left) embedded in an effective potential representing 30 Ni^{2+} ions (middle) and point charges (right).

The comparison of embedded cluster results with those obtained within the periodic approach have been of fundamental importance to establish the reliability of the modeling of extended structures by means of embedded clusters. In order to make a meaningful comparison, the one-electron basis set and treatment of the electron correlation should be as equal as possible in both calculations. This limits the comparison to spin-unrestricted Hartree-Fock or DFT based calculations, since spin restricted representations of the low-spin solutions cannot be obtained in a periodic approach. Furthermore, a Gaussian type one-electron basis is more practical than the use of plain waves. This basis is rather convenient for periodic calculations and can also be used for isolated molecules by placing the molecule in a large empty box that is repeated in all three directions.

However, the presence of the embedding of the cluster complicates the treatment with plane waves.

After the pioneering work of Towler *et al.* on the ferromagnetic and antiferromagnetic spin arrangements of NiO and MnO,[730] the first calculation of the magnetic coupling parameter in a periodic approach was published by Ricart, Dovesi and co-workers in 1995 for the ionic perovskites $KNiF_3$ and K_2NiF_4.[731–733] Approximately at the same time, the magnetic coupling of these compounds was studied within the embedded cluster approach.[470,471] It was observed that the Hartree-Fock results were similar in both approaches and a few years later a rigorous comparison of embedded cluster and periodic calculations was published showing that both approaches lead to basically identical numbers.[472] This finding has later been confirmed in other studies on different materials[468,476,616,711,734–742] providing a firm basis for modeling extended structures with embedded clusters. Table 8 lists the magnetic coupling for different materials calculated within a periodic setting to those obtained with an embedded cluster. The comparison is made for UHF and/or DFT(B3LYP) calculations. In some studies, minimal CASCI cluster calculations were contrasted against periodic UHF results. This is a reasonable approximation, since UHF and CASCI wave functions include the same physics to a certain extent and the calculated J values are usually very similar. Nevertheless, we have not included these comparisons in the Table to minimize the differences between the two ways of modeling the material.

The results of embedded cluster calculations can also be used to construct a periodic model of the material. Magnetic coupling parameters, hopping integrals and other local interactions are extracted in small units (spin dimers or slightly larger clusters) and then used to parametrize the model Hamiltonian in the periodic set-up. This strategy is extensively used by Whangbo and co-workers to study the magnetic properties of extended materials.[697,743–748] Applying extended Hückel tight-binding calculations in small fragments, they have studied spin-ordering, magnetic anisotropy, spin frustration, and incommensurate magnetic structures, among other long-range properties.

Table 8: Comparison of the magnetic coupling constants (in meV) for a series of magnetic materials obtained with periodic and embedded cluster calculations.

		Method	Periodic	Cluster	Ref.
CuO	J_1 [a]	UHF	-12.8	-10.4	468
	J_3	UHF	7.7	7.5	
La_2CuO_4		UHF	-36.1	37.8	597,734
Sr_2CuO_3		UHF	-36.7	-43.7	476
		B3LYP	-239.8	-257.2	
Li_2CuO_2	J_1 [b]	UHF	11.0	10.9	739
	J_2	UHF	-0.47	-0.57	
$KNiF_3$		UHF	-2.57	-2.71	472
K_2NiF_4		UHF	-2.70	-2.90	472
NiO		UHF	-5.4	-4.8 (c)	616
		B3LYP	-29.2	-23.4 (c)	
$LaMnO_3$		UHF	0.88	1.05(c)	741
		B3LYP	2.09	2.77(c)	

(a) J_1 and J_3 are the in-plane and inter-plane interactions, respectively

(b) J_1 and J_2 are the nearest- and next-nearest-neighbor interactions, respectively

(c) newly calculated data

4.7 Computational cost versus accuracy

To conclude this section we summarize the advantages, limits and possible improvements of the most frequently used techniques.

In the context of the DFT methods, the BS approach gives a computationally cheap and useful tool to determine magnetic couplings since it is rather simple and applicable to very large systems, involving several magnetic ions and large ligands, as exemplified by the studies of the single molecule magnets as Mn_{12} and related polynuclear systems.[749–753] Additionally, the technique also allows geometry optimization (at least of the determinant of uppermost multiplicity), and opens the possibility to study magnetic coupling in periodic systems. The weaknesses concern the spin contamination problem, which is not easily cured for high-spin sites and multi-site systems, and the dependence of the computed magnetic couplings on the choice of the density functional. As mentioned before, provided that the exchange correlation functional has been properly calibrated on a series of complexes involving the same metal ions and similar ligands, magneto-structural relations can be certainly considered as reliable. In particular, a DFT calculation is a good exploratory tool for the study of the magnetic couplings in complex systems. Although the absolute values of the magnetic couplings can be affected by the mentioned drawbacks, their ratios can be employed as guidelines for the fitting of thermodynamic properties.

The use of a preliminary calculation of magnetic MOs from DFT, followed by a calculation of correlation effects, as performed in EOM (or TD) SF DFT calculations, is computationally more demanding, and has been employed only occasionally in coordination chemistry. Actually this type of calculation is more or less similar to a CI computation (CI of singles at the RPA level). One should compare and analyze the results of the same method using either CASSCF (or ROHF) MOs and DFT MOs. As recalled above the CAS+S results are rather poor and higher excitations or 4th-order corrections are necessary to recover satisfactory values of the couplings. The comparative success of EOM SF DFT suggest the alternative of checking the use of DFT orbitals in low level CI calculations as CAS+S or DDCI2. Although excessively delocalized in general, DFT orbitals are closer to the DDCI natural MOs than the CASSCF ones and can therefore provide a good starting point for these two CI techniques, which are obviously less demanding than DDCI.

The MR second-order treatments, at least those that consider a minimal CAS reference, miss a significant part of the coupling. Enlarging the CAS is not a general recipe to improve the results, and the choice of the MOs to be added is not always clear. On the other hand, the MR-CI calculations from the minimal CASSCF give accurate results for most of the transition metal complexes provided that rather complex and numerous double excitations (all the semi-active doubles) are included, as done in the DDCI method. One conceptual advantage of the method is that it allows one to decompose the contributions and to identify mechanisms contributing to the value of J.[320,332] It should be noted that in some special cases, the definition of the active space is not completely straightforward,[377,433] although in the large majority of the systems the minimal active space is sufficient. The attempts to enlarge the CAS with some ligand MOs that are supposed to play an important role in the coupling and limit the CI space are not sufficiently convincing to propose it as a generally applicable strategy that provides accurate estimates of J at a reduced computational cost. The bottleneck of the applicability of DDCI is the size of the reference CAS. However, in many applications the coupling constant can be determined from the energy difference between the two states of highest spin multiplicity and this problem is less severe, since the CAS wave function is small anyway for these states. By using efficient truncations of the inactive and virtual orbitals subsets, the limits of DDCI can be enlarged as discussed in section 4.3.3. Nevertheless, DDCI remains a highly demanding method from the computational point of view.

Based on (i) the important fourth-order role of the $2h$-$1p$ and $1h$-$2p$ excitations, (ii) the difficulty to obtain quantitative estimates of J with second-order perturbation theory based on a minimal active space, (iii) the significantly more delocalized character of the DDCI natural orbitals in comparison to the CASSCF orbitals, and (iv) the success of EOM spin-flip method starting from DFT MOs, the following question arises: *"Are the CASSCF orbitals good enough to construct the zeroth-order MR wave function for the variational or perturbational treatment of the electron correlation in magnetic coupling problems?"* This question was already raised a long time ago by Borden and collaborators for biradicalar conjugated hydrocarbons, and the answer was negative.[324] Regarding coordination chemistry compounds the answer is yes in most cases as long as one considers the full DDCI subset of excited configurations, but experience has shown that these orbitals are probably not the best choice for other, computationally less demanding techniques as CASPT2, NEVPT2, CAS+S, or DDCI2. As mentioned in section 4.2, improved starting orbitals for a MR-PT2 treatment of the electron correlation can be obtained by properly averaging the lowest neutral and ionic singlets in the preceding CASSCF calculation.[385] This produces orbitals that much better resemble the natural DDCI orbitals and lead to a remarkable improvement of the MR-PT2 results. DDCI treatment of electron correlation from the minimal active space orbitals produces very poor results in conjugated biradicals, while CASPT2 with a full valence π CASSCF reference provides accurate values of the singlet-triplet energy difference. Recently, a method based on a minimal active space but using improved orbitals has been proposed by Suaud *et al.*[431] This scheme replaces the CASSCF orbitals by natural orbitals obtained from an iterative minimal CAS+DDCI calculation where the h and p orbitals are restricted to the valence π space. Since this space remains always rather small, the corresponding DDCI calculation is easily performed and the resulting natural magnetic orbitals become significantly more delocalized. A subsequent DDCI treatment of the electron correlation from the minimal active space spanned in these improved active orbitals leads to a perfect agreement with the computationally more demanding CASPT2 from a full valence π active space reference calculation

It seems therefore that a possible enlargement of the domain of applicability of wave function based methods will come from avoiding the bias introduced in the definition of the magnetic MOs by the CASSCF step, which leads to exceedingly localized magnetic MOs. The results of Angeli and Calzado, and of Suaud and co-workers show that entering the problem with more relevant MOs, makes possible to stay with a minimal active space, and treat the leading correlation effects from second-order perturbation or DDCI2 variational calculations. The remarks pointing the defects of the small-CASSCF MOs also concern all MR-CEPA or MR-CC methods yet under development.

5 Beyond the two-electrons in two-orbitals systems

Section 3 extensively discussed the mechanisms that govern the magnetic interaction of two electrons in two orbitals. Although this is of course a very illustrative exercise from which many basic insights can be derived, the analysis of the magnetic interaction in the large majority of the real-world systems requires to go one step beyond this two-electrons in two-orbitals problem. In general, the number of magnetic centers is larger than two and the number of unpaired electrons per center can be larger than one. For systems containing TM ions, these unpaired electrons are usually largely localized on the metallic centers and the magnetic coupling involves magnetic centers with $S > 1/2$. However, in some special cases, it is better to consider a group of atoms with several unpaired electrons as one effective magnetic site. The description of the magnetic properties in the odd-legged ladders of the $\mathrm{Sr}_{n-1}\mathrm{Cu}_n\mathrm{O}2n-1$ series are very effectively described by considering the magnetic centers on the same rung as one $S = 1/2$ magnetic unit arising from the antiferromagnetic alignment of the individual spin moments on the Cu atoms.[754,755] A similar multi-center magnetic unit was proposed for α-$\mathrm{NaV_2O_5}$.[482]

5.1 Systems with more than two $S = 1/2$ spin carriers

The main problem of the analysis of the magnetic behavior related to the existence of more than two magnetic sites is the correct identification of the most important interaction paths. While the largest interactions usually involve nearest-neighbor (NN) centers, it is sometimes necessary to consider next-nearest-neighbor (NNN) interactions, or even beyond this. This issue is particularly important for molecular crystals built from radicals, where the shortest contacts between different units not necessarily coincide with the dominant magnetic interactions.[232,756] Furthermore, the spin density in these systems is typically delocalized over several atoms and this dramatically increases the number of possible important interaction paths. Hence, the extraction of the magnetic coupling strengths from susceptibility measurements becomes a nontrivial task.[449] Generally, a form of the phenomenological Hamiltonian is postulated by defining a set of significant interactions, and subsequently, their values are fitted to the experimental results. Although this procedure leads to reliable estimates of the magnetic couplings in many cases, it should also be noted that different sets of values may produce equally good fittings. This problem can, of course, also appear in theoretical extractions of the interactions. When the exploration of the possible interaction paths is not complete enough, one may also miss important interactions. In order to avoid such a bias, the theoretical treatment should be applied to clusters of different sizes and shapes. Ideally, clusters with a sufficient number of magnetic units should be used to ensure a well-balanced consideration of all the possible interactions between pairs of magnetic centers. Otherwise, an exhaustive exploration of smaller fragments has to be performed in order not to miss any relevant interaction.

A second important consequence of dealing with more than two magnetic centers is the possible appearance of multi-spin interactions. In the larger part of the compounds, the magnetism arises from two-center interactions which can be considered to a good approximation as additive. However, in some cases the simultaneous interactions of more than two spins make essential contributions to the magnetic properties of the system and cannot be neglected anymore. The theoretical procedure to examine these interactions will be discussed in section 5.2.

As a first case in the increasing complexity, we illustrate the limits of energy fittings by considering a cluster with three $S = 1/2$ sites, ABC, in an asymmetrical topology. The three magnetic orbitals a, b and c can be determined by the calculation of the quartet $M_S = 3/2$ restricted open-shell SCF or CASSCF optimized solution. *A priori*, one may consider that the low energy spectrum is ruled by a HDVV Hamiltonian involving 3 non-equivalent inter-site magnetic couplings

$$\hat{H}_{HDVV} = -J_{ab}\hat{S}_a \cdot \hat{S}_b - J_{bc}\hat{S}_b \cdot \hat{S}_c - J_{ac}\hat{S}_a \cdot \hat{S}_c - \frac{3}{4}\hat{I} \tag{62}$$

The spectrum involves 3 states, one quartet and two doublet states. Since there are only two energy differences, it immediately follows that the amplitudes of the three magnetic coupling constants cannot be fixed from the spectrum only, the equations admit an infinity of solutions. The fitting of the coupling parameters to the energies has to assume that one of the couplings is negligible, for instance from topological arguments.

The construction of an effective Hamiltonian provides a more satisfactory way to proceed. The appropriate model space is spanned by three determinants $|\bar{a}bc|$, $|a\bar{b}c|$, $|ab\bar{c}|$. The basis set of the model space can be expressed in terms of the three spin eigenfunctions for the $M_S = 1/2$ subspace. There is one quartet state

$$Q = \frac{1}{\sqrt{3}} \left(|\bar{a}bc| + |a\bar{b}c| + |ab\bar{c}|\right) \tag{63}$$

of energy $E(Q)$. This expression also gives the projection of the exact quartet state onto the model space. Two doublet $\hat{S}^2$ eigenfunctions can be defined as

$$\begin{aligned} D_1 &= \frac{1}{\sqrt{6}} \left(2|\bar{a}bc| - |a\bar{b}c| - |ab\bar{c}|\right) \\ D_2 &= \frac{1}{\sqrt{2}} \left(|a\bar{b}c| - |ab\bar{c}|\right) \end{aligned} \tag{64}$$

The orthogonal projections of the exact doublet states of energies $E(D)$ and $E(D')$ onto the model space are linear combinations of these two orthogonal doublet vectors:

$$\begin{aligned} |\tilde{D}\rangle &= \cos\gamma D_1 + \sin\gamma D_2 = \lambda|\bar{a}bc| + \mu|a\bar{b}c| + \nu|ab\bar{c}| \\ |\tilde{D'}\rangle &= -\sin\gamma D_1 + \cos\gamma D_2 = \lambda'|\bar{a}bc| + \mu'|a\bar{b}c| + \nu'|ab\bar{c}| \end{aligned} \tag{65}$$

The angle γ determines the coefficients of $\tilde{D}$ and $\tilde{D'}$. As discussed in section 2.2.2, the effective Hamiltonian that maps the HDDV Hamiltonian can be obtained from the spectral decomposition (eq 8) and the three coupling parameters are univocally determined. For example, J_{ab} is given by

$$J_{ab} = \langle \bar{a}bc|\hat{H}^{eff}|a\bar{b}c\rangle = \frac{1}{3}E(Q) + \lambda\mu E(D) + \lambda'\mu' E(D') \tag{66}$$

This illustrates the superiority of the effective Hamiltonian theory over an energy fitting. As previously indicated, the generalization of this procedure to more sites can give rise to interactions involving more than two bodies. Section 5.2 provides an example of four-body terms in systems with four $S = 1/2$ sites.

In the DFT context, the determination of the three magnetic couplings requires four different solutions. Three on-site magnetic MOs can be defined by localizing the magnetic orbitals of the high-spin $M_S = 3/2$ solution

$$\Phi_{HS} = |h_\alpha \bar{h}_\beta abc| \tag{67}$$

of energy E_{HS}. With these orbitals three distinct $M_S = 1/2$ determinants can be defined

$$\begin{aligned} \Phi_a &= |h_\alpha \bar{h}_\beta \bar{a}bc| \\ \Phi_b &= |h_\alpha \bar{h}_\beta a\bar{b}c| \\ \Phi_c &= |h_\alpha \bar{h}_\beta ab\bar{c}| \end{aligned} \tag{68}$$

After optimizing the energies through the relaxation of the MOs, the mean energies of the corresponding optimized determinants

$$\Phi'_a = |h'_\alpha \bar{h}'_\beta \bar{a}' b' c'| \tag{69}$$

of energy E'_a (and similar for the other two) can be assimilated to the diagonal energies of the HDVV Hamiltonian, so that

$$\begin{aligned} E'_a - E_{HS} &= -\frac{(J_{ab} + J_{ac})}{2} \\ E'_b - E_{HS} &= -\frac{(J_{ab} + J_{bc})}{2} \\ E'_c - E_{HS} &= -\frac{(J_{ac} + J_{bc})}{2} \end{aligned} \tag{70}$$

From these three energy differences the three magnetic coupling constants can be determined. This mapping of the localized unrestricted DFT solutions on the energies of the Ising Hamiltonian may be generalized to any number of sites, and may eventually give an evaluation of four-body operators, as will be shown in the next subsection. However, the spin contamination problem is more difficult to overcome than in the case of two $S = 1/2$ sites.

The existence of more than one unpaired electron per magnetic center may also introduce new physics. So far we have always assumed that the magnetic phenomena are well described by considering only the local ground state of the magnetic centers. For multi-electron magnetic centers this assumption is still valid in the majority of the cases, but sometimes local low-lying excited states come into play and lead to deviations with respect to what is described by the standard Heisenberg Hamiltonian as will be discussed in section 5.3.

5.2 Many-body interactions in multi-center systems: 4-spin operators

In polynuclear systems the presence of several magnetic centers introduces additional two-body terms, not only between nearest-neighbor (NN) centers, but also between next-nearest-neighbor (NNN) and so on. Furthermore, many-body terms appear that produce the simultaneous permutation of several spins. The impact of these extra terms on the magnetic properties is not always negligible, and consequently the spin model Hamiltonian needs to be extended with the corresponding operators to obtain a correct description of the system. Some well-known examples of the necessity of introducing additional interactions in the model Heisenberg Hamiltonian belong to the solid state physics field. To fully understand the magnetic excitations and the infrared and neutron scattering spectra of 2D[757–766] and spin ladder cuprates,[767,768] parent compounds of the high-T_c superconductor cuprates, the spin Hamiltonian has to be extended with second-neighbor magnetic coupling J_{NNN} and four-spin cyclic exchange terms J_{ring}. The J_{ring} terms originates in the cyclic movement of the electrons around the Cu_4O_4 plaquettes. It has been proposed that the resulting current plays an important role in the mechanism of superconductivity.[765,769] Similar four-body terms are crucial to describe the ground state properties of ^{3}He[770] and they are also present in π conjugated systems.[215]

Over the years, several strategies have been developed to evaluate these extra parameters. The additional two-body terms are relatively easily calculated from straightforward extensions of the HDVV Hamiltonian but the mentioned four-body interactions requires some additional development that will be reviewed in this section.

We consider the interaction between four unpaired electrons occupying the orbitals *a*, *b*, *c* and *d*, which are located on centers A, B, C and D, respectively. These centers are at the corners of a rectangular plaquette. For the sake of simplicity, the four sites are considered to be equivalent. Six $M_S = 0$ determinants can be written on the basis of these four orbitals: $|a\bar{b}c\bar{d}|$, $|\bar{a}b\bar{c}d|$, $|ab\bar{c}\bar{d}|$, $|\bar{a}\bar{b}cd|$, $|a\bar{b}\bar{c}d|$ and $|\bar{a}bc\bar{d}|$. The interaction between these determinants gives rise to six different magnetic interactions as shown in Figure 18. There are three different two-body terms (the nearest-neighbors coupling $J_\perp$ and $J_{||}$ and the next-nearest-neighbors J_d interactions) and three different four-body terms J_r. The first one, J_{r1}, permutes the four spins through a cyclic movement of the electrons mediated by hopping between connected atoms. This term scales as $t_{ab}t_{bc}t_{cd}t_{da}/U^3$, where t_{ij} represents the hopping integral between centers i and j and U is the on-site Coulomb repulsion. One of the pathways contributing to this term is represented in Figure 19. The second four-body term, J_{r2}, also permutes the four spins, but involves hopping between unconnected atoms. It produces the simultaneous exchange of the spins along the long sides (legs) of the plaquette. This term scales as $t_{ad}t_{bd}t_{bc}t_{ca}/U^3$ as can be seen in Figure 20. The third interaction, J_{r3}, is similar to J_{r2}. It produces the simultaneous exchange of the spins across the short sides (rungs) of the plaquette, and is equal to J_{r2} in a square geometry. It scales as $t_{ac}t_{cd}t_{bd}t_{ab}/U^3$ (Figure 21).

Since the amplitude of the hopping integrals through the diagonals (t_{ac} and t_{bd}) is smaller than between connected centers (t_{ab}, t_{bc}, t_{cd} and t_{ad}), it is expected that $J_{r1} \gg J_{r2} \approx J_{r3}$. The model spin Hamiltonian $\hat{H}_M$ is extended with these extra terms and takes the form:

$$\begin{aligned}\hat{H}_M = &-J_{||}\left(\hat{S}_A\cdot\hat{S}_D+\hat{S}_B\cdot\hat{S}_C-\frac{1}{2}\hat{I}\right)-J_\perp\left(\hat{S}_A\cdot\hat{S}_B+\hat{S}_C\cdot\hat{S}_D-\frac{1}{2}\hat{I}\right)\\ &-J_d\left(\hat{S}_A\cdot\hat{S}_C+\hat{S}_B\cdot\hat{S}_D-\frac{1}{2}\hat{I}\right)-J_{r1}\left[(\hat{S}_A\cdot\hat{S}_B)(\hat{S}_C\cdot\hat{S}_D)-\frac{1}{16}\hat{I}\right]\\ &+J_{r2}\left[(\hat{S}_A\cdot\hat{S}_D)(\hat{S}_B\cdot\hat{S}_C)-\frac{1}{16}\hat{I}\right]-J_{r3}\left[(\hat{S}_A\cdot\hat{S}_C)(\hat{S}_B\cdot\hat{S}_D)-\frac{1}{16}\hat{I}\right]\end{aligned} \tag{71}$$

By considering the six $M_S = 0$ determinants as basis of the model space, the matrix representation

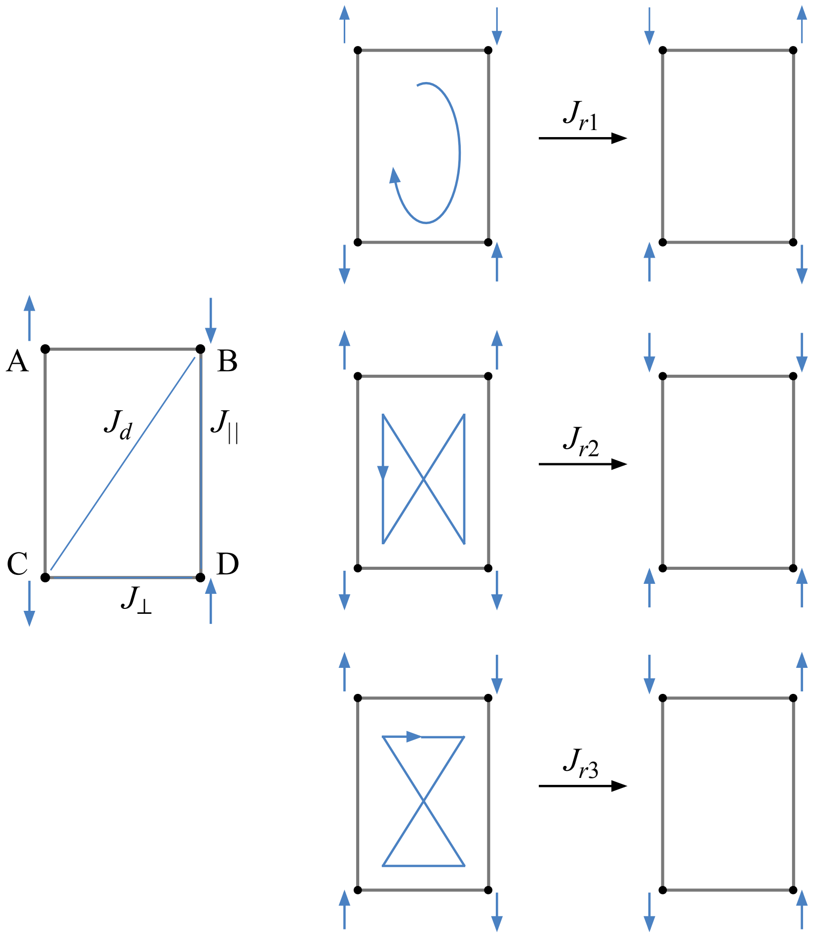

Figure 18: Magnetic terms present in a rectangular plaquette with $S = 1/2$ magnetic centers.

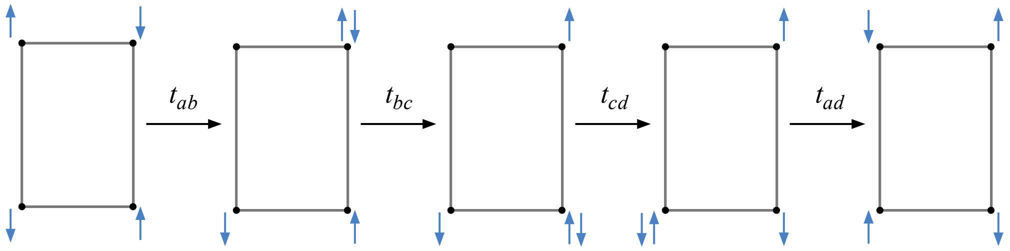

Figure 19: Contributions to J_{r1} due to the cyclic circulation of the four electrons of the plaquette.

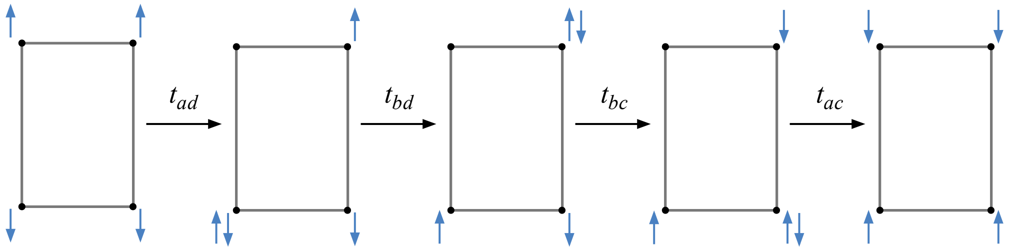

Figure 20: Contributions to J_{r2} due to the simultaneous exchange along the legs of the plaquette.

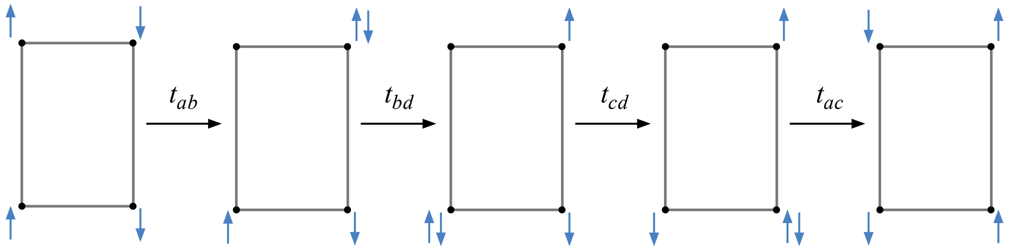

Figure 21: Contributions to J_{r3} due to the simultaneous exchange across the rungs.

of the spin Hamiltonian has the following form

$$\begin{array}{c|cccccc}
|a\bar{b}c\bar{d}| & J_{\parallel}+J_{\perp} & -J_{r1}/2 & -J_{\parallel}/2+A & -J_{\parallel}/2+A & -J_{\perp}/2+B & -J_{\perp}/2+B \\
|\bar{a}b\bar{c}d| & & J_{\parallel}+J_{\perp} & -J_{\parallel}/2+A & -J_{\parallel}/2+A & -J_{\perp}/2+B & -J_{\perp}/2+B \\
|ab\bar{c}\bar{d}| & & & J_{\parallel}+J_{d} & -J_{r2}/2 & -J_{d}/2+C & -J_{d}/2+C \\
|\bar{a}\bar{b}cd| & & & & J_{\parallel}+J_{d} & -J_{d}/2+C & -J_{d}/2+C \\
|a\bar{b}\bar{c}d| & & & & & J_{\perp}+J_{d} & -J_{r3}/2 \\
|\bar{a}bc\bar{d}| & & & & & & J_{\perp}+J_{d}
\end{array} \tag{72}$$

with A=(J_{r1}+J_{r2}-J_{r3})/8, B=(J_{r1}-J_{r2}+ J_{r3})/8 and C=(-J_{r1}+J_{r2}+J_{r3})/8. The diagonalization of this matrix gives six eigenstates: one quintet, three triplet and two singlet states. The energies can be written in terms of the parameters of the model Hamiltonian.[477] Since the five energy differences are obviously not sufficient to extract the six magnetic parameters, two alternatives are possible: (i) to neglect beforehand the presumably small four-spin interactions J_{r2} and J_{r3} and extract the rest of parameters from the energy differences, or (ii) to perform a simultaneous and unbiased evaluation of all the parameters by using the effective Hamiltonian theory. In this second scenario, we need the wave function and energy of the six eigenstates with the largest projections on the model space S_0 spanned by the six $M_S = 0$ determinants. The former is used to extract J from DFT calculations, while the latter can only be employed in WF approaches.

5.2.1 Numerical evaluation of 4-body terms from WF calculations

The procedure based on the use of an effective Hamiltonian has been employed to evaluate the exchange parameters for a set of spin ladder cuprates[477,771] ($SrCu_2O_3$, $Sr_2Cu_3O_5$ and $CaCu_2O_3$) as well as in the parent compound of the high-T_c superconductors, La_2CuO_4.[410,487,771] The results are presented in Table 9. All these materials contain CuO_2 layers and each Cu bears an unpaired electron in the in-plane $d_{x^2-y^2}$-type orbital. In all systems, a properly embedded Cu_4O_{12} plaquette was considered to extract the parameters and CI calculations were performed to determine the wave function and energy of the six eigenstates with the largest projection on the model space (details in ref 410). The CI contains all the single excitations on the top of an extended active space CAS(8,12) which includes the magnetic orbitals and four occupied orbitals centered on the bridging oxygen ligands, selected by means of the dedicated difference MO approach.[485,486] This type of calculations is less expensive than the corresponding CAS(4,4)DDCI, but provides results of similar quality. $SrCu_2O_3$ and $CaCu_2O_3$ are two-legged ladders, but the structure of $CaCu_2O_3$ presents Cu-O-Cu bond angles of 123° in the ladder rungs, and hence, the magnetic interaction along the rungs is much weaker than in $SrCu_2O_3$ for which all Cu-O-Cu bonds are linear. $Sr_2Cu_3O_5$ is a three-legged ladder, and it is possible to distinguish between the internal $J_{\parallel}^{int}$ and the external leg $J_{\parallel}^{ext}$. La_2CuO_4 is a two-dimensional system, represented by a square lattice with $J_{\perp} = J_{\parallel}$ and $J_{r2} = J_{r3}$.

In all systems, the two-body terms are antiferromagnetic, in good agreement with experimental data as well as with theoretical estimates based on binuclear fragments. For $SrCu_2O_3$ and $Sr_2Cu_3O_5$, the $J_{\perp}/J_{\parallel}$ ratio is close to 1, as expected from the geometrical features of the ladders. However, in $CaCu_2O_3$ this ratio considerably deviates from 1. The folding of the Cu-O-Cu rung bond is responsible for a low $J_{\perp}$ coupling due to an inefficient superexchange pathway through the bridging oxygen atoms, which $2p$ orbitals present an unfavorable overlap with the Cu $3d_{x^2-y^2}$ orbitals. Regarding the cyclic terms, J_{r2} and J_{r3} are small in all cases, never larger than 4 meV. The leading four-body term J_{r1} is significantly larger for ladder cuprates than for La_2CuO_4, representing about 10-20% of the first-neighbor coupling constants which agrees with the importance

Table 9: Magnetic exchange parameters (in meV) for several 2D and spin ladder cuprates from CI calculations on embedded clusters. Experimental values: $J_{\parallel} = J_{\perp} = -128 \pm 6$ meV (refs 288,289) and -134 ± 5 meV (refs 290,772) for La_2CuO_4 and $J_{\parallel} = -167 \pm 25$ meV for $CaCu_2O_3$ (ref 773).

	La_2CuO_4	$SrCu_2O_3$	$Sr_2Cu_3O_5$	$CaCu_2O_3$
$J_{\parallel}$	-124	-203	-195 (ext), -208 (int)	-147
$J_{\perp}$	-124	-157	-177	-15
J_d	-6.5	-13	-14	-0.2
J_{r1}	-14	-34	-39	-4
J_{r2}	-1	-4.1	-4.1	-1.3
J_{r3}	-1	-2.7	-3.3	$\sim$ -0.01

of these cyclic terms in the description of the magnetic data of these systems.[767,768]

5.2.2 Numerical evaluation of 4-body terms from DFT calculations

The procedure to extract the amplitude of the four-body terms from DFT calculations is based on the use of BS solutions and illustrates the possibility to determine the interactions by using only the calculated energies as outlined in section 2.2.2 and applied in section 5.1 for the three $S = 1/2$ site case.

For a rectangular plaquette, there are eleven solutions: one with $M_S = 2$, four degenerate solutions for $M_S = 1$ and six nondegenerate solutions for $M_S = 0$. The matrix elements for the $M_S = 0$ determinants are given in eq 72. For $M_S = 1$, the model space contains four determinants: $|abc\bar{d}|$, $|ab\bar{c}d|$, $|a\bar{b}cd|$ and $|\bar{a}bcd|$. The spin Hamiltonian on the basis of these determinants takes the following form:

$$\begin{array}{c} |abc\bar{d}| \\ |ab\bar{c}d| \\ |a\bar{b}cd| \\ |\bar{a}bcd| \end{array} \left[\begin{array}{cccc} \frac{J_{\parallel}+J_{\perp}+J_d}{2} + \frac{J_{r1}}{8} & \frac{-J_{\perp}}{2} - \frac{J_{r1}}{8} & \frac{-J_d}{2} + \frac{J_{r1}}{8} & \frac{-J_{\parallel}}{2} - \frac{J_{r1}}{8} \\ & \frac{J_{\parallel}+J_{\perp}+J_d}{2} + \frac{J_{r1}}{8} & \frac{-J_{\parallel}}{2} - \frac{J_{r1}}{8} & \frac{-J_d}{2} + \frac{J_{r1}}{8} \\ & & \frac{J_{\parallel}+J_{\perp}+J_d}{2} + \frac{J_{r1}}{8} & \frac{-J_{\perp}}{2} - \frac{J_{r1}}{8} \\ & & & \frac{J_{\parallel}+J_{\perp}+J_d}{2} + \frac{J_{r1}}{8} \end{array} \right] \tag{73}$$

The $M_S = 2$ determinant $|abcd|$ fixes the zero of energy.

Since standard DFT implementations only give access to the diagonal matrix elements, there are only four energy differences, while in principle six exchange parameters have to be determined (three two-body parameters, $J_{\|}$, $J_{\perp}$ and J_d, and three four-body terms). Hence, the exact extraction of all the parameters is not possible and it is necessary to neglect the J_{r2} and J_{r3} terms. The other parameters are fixed by identifying the energy of the BS solutions with the diagonal elements of the effective Hamiltonian matrix for $M_S = 0$,1 and 2.[771] This leads to the following system of equations:

$$E_{|abcd|} - E_{|abc\bar{d}|} = \frac{J_{\|} + J_{\perp} + J_d}{2} + \frac{J_{r1}}{8} \tag{74a}$$

$$E_{|abcd|} - E_{|a\bar{b}c\bar{d}|} = J_{\perp} + J_{\|} \tag{74b}$$

$$E_{|abcd|} - E_{|ab\bar{c}\bar{d}|} = J_{\|} + J_d \tag{74c}$$

$$E_{|abcd|} - E_{|a\bar{b}\bar{c}d|} = J_{\perp} + J_d \tag{74d}$$

Table 10 compares the parameters extracted from DFT calculations with two different functionals, namely the B3LYP functional and a variant of it with 33% Fock exchange. The results show that the amplitude of nearest-neighbor exchanges are overestimated in all systems when the B3LYP hybrid functional is employed. This can be ascribed to the excessive delocalization of the magnetic orbitals over the metal and ligands. When 33% Fock exchange is used a better agreement with experiment is obtained, in line with the findings for binuclear fragments.[260,331,597,598] Since four-spin cyclic terms scale as $5J^2/U$, the overestimation of the nearest-neighbor exchange give unlikely large four-spin cyclic terms. Again, a better agreement with CI results is obtained for the 33%-Fock exchange functional. The same procedure can be used to extract the many-body parameters using a periodic approach. Some examples concerning 2D and ladder cuprates can be found in refs 713 and 714.

Table 10: Magnetic exchange parameters (in meV) for several 2D and spin ladder cuprates from DFT calculations on embedded clusters using hybrid functionals: B3LYP mixing and 33% Fock exchange in the exchange functional. Experimental values: $J_{\|} = J_{\perp} = -128 \pm 6$ meV (refs 288, 289) and -134 ± 5 meV (refs 290,772) for La_2CuO_4 and $J_{\|} = -167 \pm 25$ meV for $CaCu_2O_3$ (ref 773).

		La_2CuO_4	$SrCu_2O_3$	$Sr_2Cu_3O_5$	$CaCu_2O_3$
$J_{\|}$	B3LYP	-195	-241	-240, -222 (ext,int)	-217
	33%Fock	-130	-164	-162, -153 (ext,int)	-138
$J_{\perp}$	B3LYP	-195	-225	-221	-19
	33%Fock	-130	-155	-152	-13
J_d	B3LYP	-12.5	-21	-21	-1
	33%Fock	-6	-10	-10	-0.6
J_{r1}	B3LYP	-64	-120	-120	-16
	33%Fock	-19	-39	-40	-5

5.3 Magnetic interactions for $S = 1$ spin systems

So far, the discussion of the magnetic interactions has focused on systems in which the magnetic units have an $S = 1/2$ spin angular momentum. In section 3 we have reviewed the magnetic interactions between two $S = 1/2$ units and section 5.2 discusses the possibility of multi-center interactions when one goes beyond the simple two-center case. In the following we will describe the theoretical treatment of spin systems with larger spin moments, concentrating on the $S = 1$ case, which is easily generalized to more unpaired electrons.

When a magnetic center has two unpaired electrons, these electrons are coupled through the local exchange integral K and the local ground state is the triplet, in agreement with Hund's rule. When the model space is restricted to products of the local triplet ground states, the only interactions that appear in the second-order derivation of the model Hamiltonian from the Hubbard Hamiltonian are the bilinear exchange interactions. The model Hamiltonian for polynuclear $S = 1$ species is then the HDVV Hamiltonian as expressed in eq 1.

The restriction of the model space to local ground states is well-founded for $S = 1/2$ systems, because the local excited states, usually arising from electron replacements in the TM-d orbitals

($d-d$ transitions), are higher in energy than the local ground state by several electron volts. Nevertheless, the first local excited singlet state of spin $S=1$ systems only lies at $2K$ (~ 1 eV) above the ground state for first row transition metals. The effect of this excited state, also called a non-Hund state, may generate non-Heisenberg behavior in the spectrum of the polynuclear system, implying that the energy differences between the spin states deviate from the Landé intervals predicted by the HDVV Hamiltonian. An accurate representation of the spectrum is obtained after the inclusion of two- and three-body biquadratic interactions in the model Hamiltonian. The analytical derivation of the associated operators requires to use the fourth-order perturbation theory (section 2.3) and consequently these interactions are always much smaller than the bilinear exchange interactions. Several theoretical and experimental works have investigated how higher order terms contribute to non-Heisenberg behavior[278,451,774–793]

Non-Heisenberg behavior can also be observed in systems with spin moments larger than $S=1$, where several non-Hund states may contribute to the deviations. Furthermore, it is expected that the deviations become more important for second- or third row transition metals, because the on-site exchange integral K tends to be smaller for these transition metals than for the first-row.[793] Due to the larger spin-orbit coupling, the magnetic anisotropy also becomes stronger and it may be difficult to separate both effects.

5.3.1 Analytical derivation of bilinear and biquadratic interactions from the Generalized Hubbard Hamiltonian

We first consider a magnetic system with two $S=1$ centers. The magnetic orbitals localized on centers A and B are labelled with a_1, a_2 and b_1, b_2, respectively. These orbitals could be, for instance, the $d_{2z^2-x^2-y^2}$ and $d_{x^2-y^2}$ orbitals of a transition metal ion with two unpaired electrons. For simplicity, we consider a centro-symmetric system and assume that the orbitals a_1 and b_1 belong to a different irreducible representation than a_2 and b_2.

The derivation of the HDVV Hamiltonian from the Hubbard Hamiltonian at the second-order of perturbations provides an expression of the bilinear exchange interaction which has the same physical content as the exchange interactions of systems of spin $S = 1/2$. To build the model space of the HDVV Hamiltonian for $S = 1$ species one needs to consider the three M_S components of the local triplets on both sites which are written : $T_+ = |a_1 a_2|$, $T_- = |\bar{a}_1 \bar{a}_2|$ and $T_0 = \frac{1}{\sqrt{2}} \left(|a_1 \bar{a}_2| - |a_2 \bar{a}_1| \right)$ on site A, for instance. In the $M_S = 0$ total subspace, the model space of the HDVV Hamiltonian is constituted of the following antisymmetrized products of local ground states:

$$\begin{aligned} T_+T_- &= |a_1 a_2 \bar{b}_1 \bar{b}_2| \\ T_-T_+ &= |\bar{a}_1 \bar{a}_2 b_1 b_2| \\ T_0T_0 &= \left(\left(|a_1 \bar{a}_2| - |a_2 \bar{a}_1| \right) / \sqrt{2} \right) \left(\left(|b_1 \bar{b}_2| - |b_2 \bar{b}_1| \right) / \sqrt{2} \right) \end{aligned} \tag{75}$$

These neutral functions are degenerate in a nonrelativistic setting and their energy is taken as the zero of energy. In the generalized Hubbard Hamiltonian, these functions are coupled through hopping integrals t_i with ionic functions. In the present case, the only nonzero hopping integrals of the Hubbard Hamiltonian are $t_1 = \langle a_1 a_2 \bar{b}_1 \bar{b}_2 | \hat{H} | b_1 a_2 \bar{b}_1 \bar{b}_2 \rangle = \langle a_1 | \hat{F} | b_1 \rangle$ and $t_2 = \langle a_1 a_2 \bar{b}_1 \bar{b}_2 | \hat{H} | a_1 b_2 \bar{b}_1 \bar{b}_2 \rangle = \langle a_2 | \hat{F} | b_2 \rangle$.

The second-order expression of the bilinear exchange interaction is a generalization of eq 27:

$$J = J^{(0)} + J^{(2)} = J^{(0)} - \sum_i t_i^2 U_i \tag{76}$$

where $t_i = t_{a_i b_i}$ is the hopping integral between orbitals of the same irreducible representation and U_i the corresponding relative energy of the ionic forms (on site Coulomb repulsion) with respect to the neutral ones. The zeroth-order description $J^{(0)}$ arises from the interaction of the neutral ground state determinants belonging to the model space. Both two-center direct exchange integrals ($K_{a_i b_i}$ and $K_{a_i b_j}$) contribute to this term. The previous expression is valid for an arbitrary number of unpaired electrons per center.

The bilinear exchange interaction of the Heisenberg Hamiltonian (eq 1) couples the products of local ground states, leading to the following quintet Q, triplet T and singlet S eigenstates with

$M_S = 0$:

$$\begin{array}{rcl} |Q\rangle &=& \sqrt{\frac{2}{3}}\left(T_0T_0 + \frac{1}{2}(T_-T_+ + T_+T_-)\right) \\ |T\rangle &=& \frac{1}{\sqrt{2}}\left(T_+T_- - T_-T_+\right) \\ |S\rangle &=& \frac{1}{\sqrt{3}}\left(T_0T_0 - T_-T_+ - T_+T_-\right) \end{array} \tag{77}$$

The corresponding eigenvalues are:

$$\begin{array}{rcl} E(Q) &=& 0 \\ E(T) &=& 2J \\ E(S) &=& 3J \end{array} \tag{78}$$

In case of non-Heisenberg behavior, the energy differences between the singlet, triplet and quintet states do not obey eq 78. In order to account for these isotropic deviations to the Heisenberg behavior, a biquadratic operator must be added to the Heisenberg Hamiltonian.[278,774,777] The expression of the resulting model Hamiltonian for a binuclear system is

$$\hat{H}_M = -J\left(\hat{S_A}\hat{S_B} - \hat{I}\right) + \lambda\left[\left(\hat{S}_A\hat{S}_B\right)^2 - \hat{I}\right] \tag{79}$$

The eigenvalues of this spin Hamiltonian are

$$\begin{array}{rcl} E(Q) &=& 0 \\ E(T) &=& 2J \\ E(S) &=& 3J + 3\lambda \end{array} \tag{80}$$

The analytical derivation of the Hamiltonian of eq 79 requires fourth-order QDPT and introduces the effect of the local non-Hund singlet states

$$S_0 = \frac{1}{\sqrt{2}}\left(|a_1\bar{a}_2| + |a_2\bar{a}_1|\right) \tag{81}$$

for site A and analogous for site B. The products of atomic spin states involving at least one non-Hund state are not directly coupled with the neutral functions of eq 77. Instead, they are coupled with the ionic configurations and hence come into play at the fourth-order of perturbation.

Among all the spin and spatial functions of the valence space (magnetic orbitals and unpaired TM-d electrons) that have been used for the derivation, the following linear combinations of products of local spin states play the most important role in the deviation to the standard Heisenberg behavior:

$$\begin{aligned}
|NH_1\rangle &= \frac{1}{\sqrt{2}}(S_0T_0+T_0S_0) \\
|NH_2\rangle &= \frac{1}{\sqrt{2}}(S_0T_0-T_0S_0) \\
|NH_3\rangle &= S_0S_0
\end{aligned} \tag{82}$$

The energies relative to the quintet ground state are $2K$, $2K$ and $4K$, respectively.

The analytical expressions for the two-body biquadratic interaction λ and the fourth-order correction to the bilinear exchange $J^{(4)}$ have been derived in ref 451 and read:

$$\begin{aligned}
\lambda &= \frac{B^2}{K} - \frac{(J^{(2)})^2}{4K} \\
J^{(4)} &= -\frac{B^2}{K}
\end{aligned} \tag{83}$$

where all terms proportional to $U_{1,2}^{-3}$ have been neglected, $J^{(2)}$ is the bilinear exchange interaction obtained at second-order of perturbation and the interaction B is:

$$B = \frac{t_1^2}{U_1} - \frac{t_2^2}{U_2} \tag{84}$$

The fourth-order correction affects the physical content and therefore the magnitude of the bilinear exchange for systems in which t_1^2/U_1 is different from t_2^2/U_2. This usually occurs when the overlap between the orbitals of symmetry 1 (a_1 and b_1) is different from the overlap between the orbitals of symmetry 2 (a_2 and b_2). It is possible to connect the difference of electron delocalization ($t_1^2/U_1 \neq t_2^2/U_2$) in the two symmetries and the appearance of local singlet contributions in the lowest state wave functions. Indeed, when the delocalization in symmetry 1 and 2 is different, the weights of the on-site determinants $|a_1\bar{a}_2|$ and $|a_2\bar{a}_1|$ are different and the local ground state is no longer a product of local triplets only but a mixing between the local singlet and triplet states.

Moreover, from eq 83 we easily see that the magnitude of the biquadratic interaction is small in comparison to that of the bilinear interaction. Figure 22 illustrates how the local singlet states S_0 contributes to the biquadratic exchange interactions.

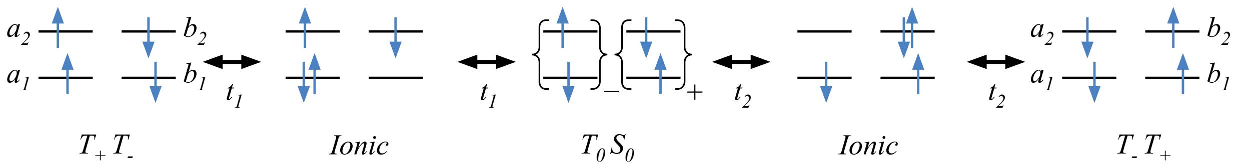

Figure 22: Electronic mechanism contributing to the biquadratic exchange interaction. The brackets in the T_0S_0 configuration indicate the triplet (- subscript) or singlet (+ subscript) linear combinations of the $M_S = 0$ determinants.

The biquadratic exchange is not the only source of deviations to Heisenberg behavior for multicenter systems. A non-negligible three-center biquadratic interaction has been invoked in the La_2NiO_4 perovskite to explain the magnetic behavior of three Ni^{2+} ions connected by two linear Ni–O–Ni bonds.[451] The following model Hamiltonian includes all interactions contributing to the deviation at the fourth-order of perturbation:

$$\begin{aligned}\hat{H} =& \sum_{i<j}\left[-J_{ij}\left(\hat{S}_i\hat{S}_j - \hat{I}\right) + \lambda_{i,j}\left(\left(\hat{S}_i\hat{S}_j\right)^2 - \hat{I}\right)\right] \\ &+ \sum_{i}\sum_{\substack{j<k \\ i\neq j\neq k}} \frac{B_{ij}B_{jk}}{2K}\left[\left(\hat{S}_i\hat{S}_j\right)\left(\hat{S}_i\hat{S}_k\right) + \left(\hat{S}_i\hat{S}_k\right)\left(\hat{S}_i\hat{S}_j\right) - \left(\hat{S}_i\hat{S}_i\right)\left(\hat{S}_j\hat{S}_k\right) - \hat{I}\right]\end{aligned} \tag{85}$$

As before, the three-center interaction is nonzero only when $B \neq 0$. Figure 23 illustrates one of the pathways involving S_0 that contributes to the three-center operator.

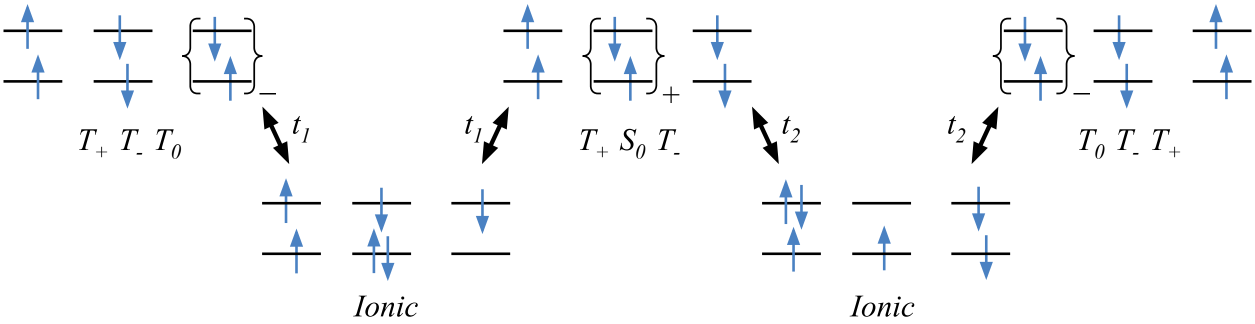

Figure 23: Electronic mechanism contributing to the three-center interaction. The brackets in the third and fifth configurations indicate the singlet (+ subscript) and triplet (- subscript) linear combinations of the $M_S = 0$ determinants, respectively.

5.3.2 Numerical evaluation of the bilinear and biquadratic interactions from WF calculations

The relative importance of the different operators to the non-Heisenberg behavior of the magnetic interactions can be assessed by fitting the Hamiltonian of eq 85 to the *ab initio* spectrum of a system with three $S = 1$ magnetic units. The subsequent (de-)activation of the operators gives a clear-cut analysis of the different contributions. As an example, we report the analysis of the magnetic coupling in La_2NiO_4 involving three Ni^{2+} ions.[451] Table 11 reports the values of the interactions extracted by fitting the model Hamiltonian to the DDCI2 spectrum containing one heptuplet, two quintets, three triplets and one singlet state. It also gives the contribution of the different models to the total deviation of the Heisenberg Hamiltonian. The deviation of each state can be quantified by the difference between the model energies reproduced using the extracted interactions and the computed energies. To get an average deviation per state, we have added all these energy differences and divided by the spectrum width and by the number of states. A percentage of deviation to the Heisenberg behavior (ε) is then defined such that the HDVV Hamiltonian (Model 1) reproduces 0% of the deviation while the computed spectrum reproduces 100%.

Model 1 only considers the isotropic bilinear exchange. It reasonably fits the DDCI2 spectrum, but necessarily neglects any deviation to the Heisenberg spectrum. The value of J_{NN} is slightly smaller than the experimental estimates of $\sim$ -30 meV,[794,795] in line with the usual underestimation of DDCI2. A much better agreement with experiment is obtained when the $2h$-$1p$ and $1h$-$2p$ determinants are considered in the *ab initio* calculations (DDCI entry of Table 12 in section 5.3.3). Model 2 and 3 add the biquadratic and *NNN* bilinear exchange, respectively. Somewhat surprising, the two-body biquadratic term (λ) only presents 8% of the deviation. The NNN interaction also gives a small contribution to the non-Heisenberg deviation. The combination of the two interactions in Model 4 does not improve the situation, the spectrum stays close to the one predicted by the Heisenberg Hamiltonian. Only after introducing the three-body interaction defined in eq 85 (Model 5), significant deviations to the Heisenberg behavior are reproduced. The strength of the three-body interaction is on the same order of magnitude as λ, but its differential effect on various spin states is much larger. Model 6 contains all *NN* and *NNN* interactions. It gives a perfect fit of the spectrum since the number of parameters is equal to the number of energy differences, but it shows that *NNN* interactions can safely be neglected in this system.

Table 11: Magnetic interaction parameters (in meV) extracted from an embedded three-center cluster representing La_2NiO_4 using different model Hamiltonians (*see text*). *NN* refers to nearest-neighbor ion interactions, and *NNN* concerns next-nearest-neighbor ions. Values are obtained by comparing to the *ab initio* spectrum determined through DDCI2 calculations.

	Model 1	Model 2	Model 3	Model 4	Model 5	Model 6
J_{NN}	-20.12	-20.24	-20.09	-20.09	-20.38	-20.38
J_{NNN}	-	-	$-7.7\cdot10^{-2}$	$-7.5\cdot10^{-2}$	-	$-5.7\cdot10^{-2}$
λ_{NN}	-	0.30	-	$7.3\cdot10^{-2}$	0.37	0.37
λ_{NNN}	-	-	-	-	-	$2\cdot10^{-3}$
$B_{NN}^2/2K$	-	-	-	-	0.26	0.27
$B_{NN}B_{NNN}/2K$	-	-	-	-	-	$5\cdot10^{-3}$
Contribution to deviation (%)	0	7.5	8.4	15.1	84.5	100

5.3.3 Numerical evaluation of the bilinear and biquadratic interactions from DFT calculations

The extraction of the bilinear exchange interaction of the spin $S = 1$ Hamiltonian from DFT calculations is analogous to the procedure outlined for $S = 1/2$ systems in section 4.5.2. It makes use of the BS determinant of minimum $M_S = 0$ value ($\Phi_1 = |a_1a_2\bar{b}_1\bar{b}_2|$) and the determinant of maximum $M_S = 2$ value ($\Phi_2 = |a_1a_2b_1b_2|$). The energies of these two determinants are mapped on the eigenvalues of the Ising model, or the diagonal elements of the Heisenberg Hamiltonian in the $\{\Phi_1, \Phi_2\}$ basis:

$$\begin{aligned} E_1 &= 2J \\ E_2 &= 0 \end{aligned} \tag{86}$$

The difference between the DFT energies of the two determinants directly provides the value of the bilinear exchange interaction, similar to the $S = 1/2$ systems. On the contrary, the determination of the two- and three-body biquadratic interactions is more laborious. The analytical expressions of the parameters that control the strength of these interactions, given in eqs 83 and 84, are functions of the standard parameters of the generalized Hubbard Hamiltonian discussed in section 2.3. Therefore, the extraction procedure of two- and three body biquadratic interactions consists of calculating the local exchange integral K and the ratios t_1^2/U and t_2^2/U assuming that $U_1 = U_2 = U$. In order to calculate these quantities, the energy of some additional determinants must be computed. These are $\Phi_3 = |a_1\bar{a}_2\bar{b}_1b_2|$, $\Phi_4 = |a_1a_2\bar{b}_1b_2|$ and $\Phi_5 = |a_1a_2b_1\bar{b}_2|$. The five determinants are schematically depicted in Figure 24 and the expressions of the energy at the second-order of perturbation are as follows:[796]

$$\begin{aligned}
E_1 &= -2\frac{t_1^2 - t_2^2}{U} \\
E_2 &= 0 \\
E_3 &= 2K \\
E_4 &= K - 2\frac{t_1^2}{U-K} \\
E_5 &= K - 2\frac{t_2^2}{U-K}
\end{aligned} \tag{87}$$

In these expressions, the intersite direct exchange integrals K_{ab} are neglected. In addition to these five determinants, other DFT solutions can be calculated, providing a way to check the internal consistency of the various equations. When some of the solutions cannot be converged, it is also possible to calculate K for a mononuclear complex.

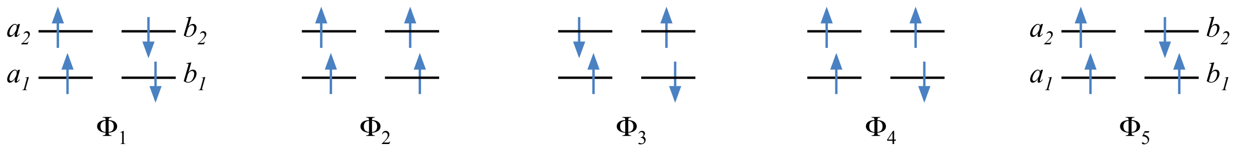

Figure 24: BS solutions that are required for the determination of the two-body and three-body biquadratic interactions.

To illustrate the extraction procedure, we report DFT calculations on La_2NiO_4, the same material as in the previous section, but now using a two-center cluster with two Ni^{2+} ions and their oxygen ligands. Although there are only two magnetic centers in this cluster, eqs 83 and 84 still allows us to directly calculate the $B = B_{NN}$ parameter from the values of K and t_i^2/U extracted from eq 87 as explained above. We use the standard B3LYP exchange-correlation functional and a variant of it in which the percentage of exact exchange has been increased to 28%. Table 12 compares the DFT results to DDCI calculations, which accurately reproduce the experimental estimate of the bilinear exchange interaction. As explained in the previous section, the determination of B from the energies computed with wave function based methodologies requires three-center clusters, the two energy differences available from two-center clusters are not enough to determine J, K and B.

Table 12: DFT and DDCI magnetic interaction parameters (in meV) extracted from an embedded two-center cluster representing La_2NiO_4. J_{exp}=-30 meV.[794,795]

	J	λ	B	t_1^2/U	t_2^2/U	K
DFT / B3LYP	-38.31	1.46	36.86	37.59	0.73	680
DFT / 28% Fock exch.	-29.81	0.83	28.91	29.36	0.45	735
DDCI	-26.00	0.70	-	-	-	-

As observed in many applications, the strength of the magnetic interactions is rather sensitive to the percentage of Fock exchange applied in the functional. Good agreement is obtained with DDCI results and the experimental data for 28% of Fock exchange, showing that DFT calculations can be used to gain insight in complex interactions provided that the adequate percentage of Fock exchange is used. Finally, the comparison of J and λ obtained with DDCI2 (Table 11) and DDCI indicates that the former method not only underestimates the bilinear exchange but also that the biquadratic interaction is strongly affected by electron correlation.

6 Interactions in doped systems

The preceding sections discussed the physics of magnetic systems where the number of orbitals in the model space is equal to the number of unpaired electrons. Hence, the orbitals are occupied by one electron on average and one generally speaks of half-filled models. The theoretical description of models with other fillings is, however, also important given the fact that many interesting phenomena are related to electron or hole doping. In the first place, all electric conduction properties are intrinsically related to the presence of holes and/or excess electrons. One of the most appealing consequences of doping is the superconductivity at high temperature in certain copper oxide perovskites,[37,797,798] iron pnictides[799] or related materials. Conductivity is of course not restricted to systems with (transition) metal atoms, but can also be observed in organic systems. Obvious examples of such materials are the conducting polymers,[800,801] but many other (super-)conducting organic and inorganic systems have been described in the literature.[168,802–807]

Secondly, a slightly different class of materials that also need to be described with models at non-half filling are the so-called mixed valence systems characterized by the existence of at least two metallic sites occupied by the same element, having a distinct or noninteger formal oxidation state.[808] The standard classification distinguishes three classes of mixed valence compounds depending on the nature of the extra electron in the system.[809,810] When this electron is strongly localized on one of the metal sites, the compound is classified as *class I*, while the opposite case of complete delocalization is usually labeled as a *class III* mixed valence system. In between, one can find the *class II* systems; the degree of delocalization results from the competition between the electronic coupling (the hopping integral t) and the vibronic coupling parameter λ, which is a measure of the difference in the ligand-metal bond lengths between the oxidized and reduced centers.[811–814] The hopping of the electrons through the material is only possible when some sites have empty valence orbitals, and hence, requires a model that goes beyond the simple half-filled case.

The interactions in doped systems are not easily evaluated from experiment. Estimations of parameters as the hopping integrals can be obtained from spectroscopic information, but the values are scarce and often subjected to large uncertainties, as discussed in section 6.1. This lack of quantitative data makes electronic structure calculations particularly valuable and theory can be used to provide accurate estimates that can be used in model Hamiltonians to interpret or predict properties of these doped materials.

Depending on the filling and the number of unpaired electrons per site, three different situations can be distinguished, described in detail in the next sections:

- Filled systems doped with an extra electron or a hole (Figure 25, top) correspond to the simplest mixed-valence systems and can be studied by means of the two-state model.
- Half-filled systems with one unpaired electron per site doped with an extra electron or a hole (Figure 25, middle), well-characterized by means of the $t-J$ model.
- Half-filled systems with more than one unpaired electron per site doped with an extra electron or a hole (Figure 25, bottom), modeled by means of the double-exchange Hamiltonian.

6.1 Mixed valence systems: the two state model

To start the discussion of the extraction of interactions in doped systems, we first consider the simplest mixed valence systems, i.e., filled systems doped with an electron or a hole. The model is composed of N distant sites A, B, C, ... N. For the electron-doped system, the extra electron can be delocalized among a set of empty orbitals $a, b, c, \ldots\ldots n$, each one localized on the corresponding active site (Figure 25, top row, central column). For the hole-doped system, this extra hole can move among different doubly occupied orbitals, again localized on each active site (Figure 25, top row, right column).The physics of compounds with more than one active orbital per site will be analyzed in section 6.3.

The delocalization of the extra electron (or hole) is controlled by the electron transfer or hopping integral t. This integral, usually called H_{ab} or V_{ab} in electron transfer theories,[815–819] is directly related to the rate of the hopping process.[815] V_{ab} can be estimated from the ultraviolet-visible-near-infrared absorption spectrum of the mixed valence state using the Hush formula,[810,820,821]

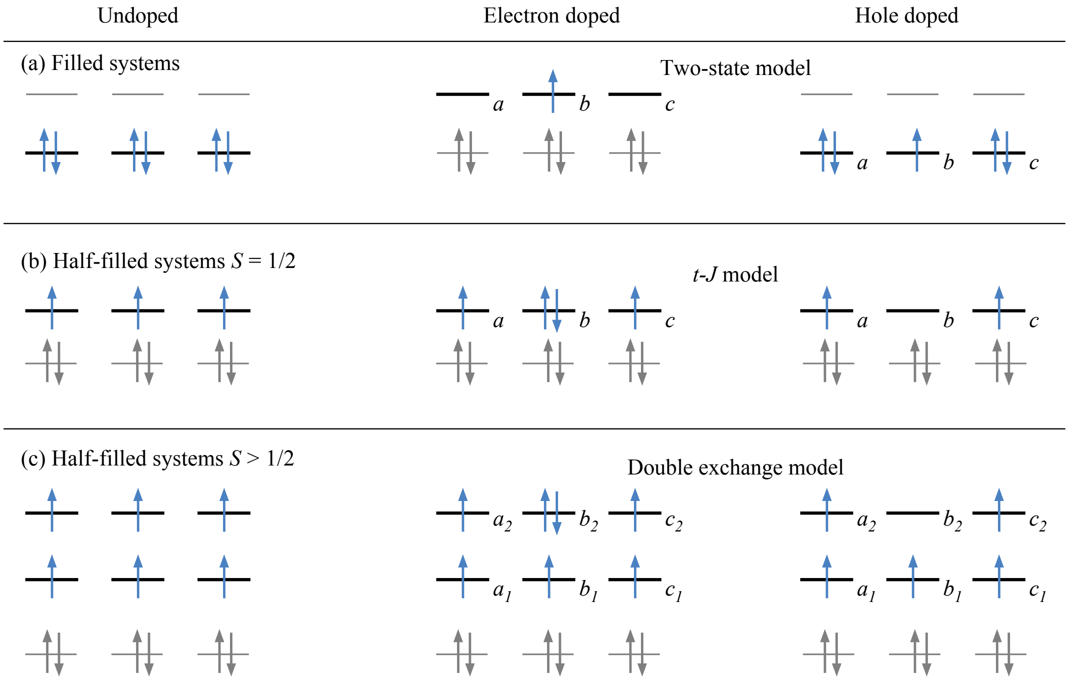

Figure 25: Interactions in filled and half-filled systems doped with electrons or holes. The thicker lines correspond to the active orbitals and the grey lines and arrows represent the orbitals and electrons of the core. Levels in the same column are localized on the same magnetic center.

which relates the hopping integral to characteristic spectroscopic features (band width, extinction coefficient, energy of maximum absorption) of the metal-to-metal charge transfer or intervalence transition (IT) bands. The application of the formula also requires knowledge about the distance R_{ab} between the donor and acceptor centers, which are modelled by a single point. This simple model has been employed to estimate hopping integrals in mixed valence organic and transition metal compounds, in particular to establish the distance dependence of charge transfer rates.[109,808,821–823] Despite its simplicity, the Hush approach is not free of arbitrariness. The detection of the IT bands can be difficult for different reasons, for example due to the low intensity in long mixed valence systems (the intensity is proportional to the hopping parameter). The band can also appear partially masked by LMCT transitions or as a shoulder of the main band. In these cases a deconvolution of the spectrum is required to obtain all the spectroscopic parameters needed to calculate V_{ab}. The dependence on R_{ab} adds another source of uncertainty in the evaluation of V_{ab}, especially in molecules with large conjugated π systems, where the extra electron (hole) is delocalized over several atoms. In such cases, R_{ab} is most effectively estimated on the basis of the transition dipole moment.[824] R_{ab} is also an elusive parameter in outer sphere electron transfer reactions (*i.e.* through space hopping between chemically unconnected units).

The hopping integral can also be evaluated from *ab initio* quantum chemistry calculations by means of the two state model.[825] It is important to keep in mind a subtle difference between the t parameters in Hubbard and two-state models. Both of them enable the delocalization of the unpaired electrons, but while the former corresponds to the coupling between the neutral and ionic forms, the t term in the two-state model represents the coupling between the two localized hole- or electron-doped forms. Without loss of generality, we can focus on a binuclear system, containing two sites A and B and one unpaired electron. In a simplified picture, the electron transfer can be seen as the hopping between two orbitals, a and b essentially localized on sites A and B, respectively. The hopping integral is equal to the coupling between the two localized states:

$$t = \langle \Phi_a | \hat{H} | \Phi_b \rangle \tag{88}$$

where $\Phi_a = |core\ a|$ and $\Phi_b = |core\ b|$ are the localized wave functions, representing the situations where the extra electron is placed on site A or B, respectively. In this notation, *core* corresponds to the inactive doubly occupied orbitals. There are two doublet states in competition, resulting from the in-phase and out-of-phase combinations of the two localized states:

$$\begin{aligned} |D_g\rangle &= \gamma|\Phi_a\rangle + \lambda|\Phi_b\rangle \\ |D_u\rangle &= \lambda|\Phi_a\rangle - \gamma|\Phi_b\rangle \end{aligned} \tag{89}$$

where $\gamma^2 + \lambda^2 = 1$ and the g and u labels are used even for cases when the system is not centrosymmetric. The energy of these two doublet states depend on the ratio of γ and λ:

$$\begin{aligned} E(D_g) &= \gamma^2 E_a + \lambda^2 E_b + 2\gamma\lambda t \\ E(D_u) &= \lambda^2 E_a + \gamma^2 E_b - 2\gamma\lambda t \end{aligned} \tag{90}$$

where E_a and E_b are the energy of the localized states. Solving for t gives:

$$t = \frac{(E(D_g) - E(D_u)) - (\gamma^2 - \lambda^2)(E_a - E_b)}{4\gamma\lambda} \tag{91}$$

For centro-symmetric binuclear systems, the two localized states have the same energy, $E_a = E_b$, and $\gamma = \lambda = 1/\sqrt{2}$, then

$$t = \frac{E(D_g) - E(D_u)}{2} \tag{92}$$

i.e., t is half the energy difference between the symmetric and antisymmetric doublet states. However, when the two sites are non-equivalent, the hopping integral cannot be evaluated from the energy difference alone. Now, both the energy of the localized states and the composition of the wave function of the involved states (i.e. the γ value) are necessary. In this case, the procedure requires the localization of the magnetic orbitals on the two active sites to obtain the $\gamma\,(\lambda)$ value and the use of the effective Hamiltonian theory to extract t from the off-diagonal element of the 2×2 effective Hamiltonian matrix, built in the basis of the two localized states:[826–830]

$$\begin{array}{c} \Phi_a \\ \Phi_b \end{array} \begin{bmatrix} H^{eff}_{aa} & H^{eff}_{ab} \\ H^{eff}_{ba} & H^{eff}_{bb} \end{bmatrix} \tag{93}$$

where $H^{eff}_{ab} = t$. It is worth noting that for asymmetrical situations, the two doublet states can belong to the same irreducible representation. In these cases the g and u notation continues to be used just for convenience. The factors influencing the amplitude of the electron transfer integral in mixed valence compounds have been analyzed by various authors[822,831–834] and will not be considered here.

Different methods based on quantum chemical calculations have been proposed to obtain estimates of t. In general, the evaluation of t involves the determination of the energy (and wave function) of the two lowest doublet states. The electronic wave functions can be obtained from different approaches ranging from semi-empirical to *ab initio* descriptions. Evaluations based on the extended Hückel Hamiltonian and semi-empirical methods are still frequent in the bibliography. Despite of being rather approximate, they frequently give correct orders of magnitude. Some recent applications of extended Hückel evaluations of t in the field of organic conductors can be found, for instance, in refs 835 and 836.

Regarding single determinant evaluations, for binuclear centro-symmetric systems the simplest approach consists of using Koopmans' theorem[837] and approximating t from the energy difference of the in-phase and out-of-phase orbitals ε_g and ε_u:

$$2t(2-n_a) = E(D_g) - E(D_u) \approx (\varepsilon_g - \varepsilon_u)(2-n_a) \tag{94}$$

where n_a is the number of active electrons. Depending on the overlap between the localized orbitals a and b, the hopping integral can be positive or negative. When the overlap is positive ($\varepsilon_g - \varepsilon_u < 0$), the ground state is D_g for $n_a = 1$ and D_u for $n_a = 3$, but in both cases t is negative. In case of a negative overlap ($\varepsilon_g - \varepsilon_u > 0$), the symmetry of the ground state is reversed (D_u for $n_a = 1$ and D_g for $n_a = 3$) and t is positive. The orbital energies can be obtained from the single determinant description of the neutral system (2 or 4 electrons in 2 orbitals). For the electron-doped system (1 electron in two orbitals), the orbital energies of the lowest neutral triplet determinant $|core\ gu| = |core\ ab|$ can be used to assure an equal treatment of the two localized states. For the hole-doped system (3 electrons in 2 orbitals) it is convenient to use the orbital energies of the four electron configuration: $|core\ g\bar{g}u\bar{u}|$. The estimates of the transfer integral from Koopmans' theorem in organic semiconductors are in good agreement with the results from electron-correlated CASPT2 and CAS-SI (CASSCF-State Interaction) calculations.[838–840]

An alternative consists of performing ROHF calculations for both states, and evaluate t just from the energy difference of these states.[840–842] In this case, both the core and active electrons are optimized in the electrostatic field of the considered state. It is also possible to extract t from UHF calculations. In this case, it is frequent that the localized solutions $\Phi_a^{UHF} = |core'a'|$ and $\Phi_b^{UHF} = |core''b''|$ are lower in energy than the symmetry-adapted ones. These localized solutions are degenerate in the case of symmetric systems and nonorthogonal. Therefore, the evaluation of t

requires the calculation of the overlap and interaction integrals between these two determinants[825]

$$t = \frac{H_{ab} - S_{ab}E_a}{1 - S_{ab}^2} \tag{95}$$

where $H_{ab} = \langle \Phi_a^{UHF} | \hat{H} | \Phi_b^{UHF} \rangle$ and $S_{ab} = \langle \Phi_a^{UHF} | \Phi_b^{UHF} \rangle$. These integrals can be evaluated with the corresponding orbital transformation.[843,844] The procedure has been employed both in organic and metal containing mixed valence systems.[845–848]

In line with this nonorthogonal scheme in a spin unrestricted setting, t can also be extracted from nonorthogonal spin restricted CASSCF wave functions for $|\Phi_a\rangle$ and $|\Phi_b\rangle$. Here, the two situations with the electron localized on either A or B are described with a CASSCF wave function using orbitals that are independently optimized for the electronic configuration in both cases, resulting in nonorthogonal N-electron states. In standard CASSCF calculations t-values are extracted from two states that are orthogonal either by symmetry (*gerade* versus *ungerade*) or due to the fact that they have been obtained in a state average CASSCF procedure when the two states belong to the same irreducible representation of the symmetry point group of the system. However, for the separately optimized states, the nonorthogonality is taken into account with the State Interaction[849] or the nonorthogonal CI procedure[534] and t is calculated using eq 95 in the case of degenerate states. The following equation can be used for non-equivalent centers:

$$t = \frac{1}{2}\sqrt{(\varepsilon_1 - \varepsilon_2)^2 - (H_{aa} - H_{bb})^2} \tag{96}$$

where ε_1 and ε_2 are the eigenvalues of the 2×2 secular problem. This approach has been applied to evaluate the hopping parameters in cuprates and some manganese oxides.[850–852] Depending on the size of the active space, this description accounts for some electron correlation.

Regarding descriptions with a more complete inclusion of the electron correlation, the energies of the two doublet states can also be obtained from CASPT2[839,840,853] and DFT calculations,[854] either in a spin-restricted or spin-unrestricted setting. Different functionals have been used including pure functionals and hybrids.[855–857] It is also viable to evaluate t from constrained DFT calculations.[679,858] Another possibility is to evaluate t from the energy spectrum obtained at the TD-DFT level, as in the organic mixed-valence systems analyzed by Brédas and co-workers[831] or the photoinduced electron transfer processes investigated by Ratner et al.[859]

Among the correlated descriptions, it is also possible to use strategies similar to those employed in the determination of J and evaluate t from the energy difference of the doublet states obtained from DDCI calculations, combined with the information contained in the wave function for asymmetric systems. Different applications can be found in the field of mixed-valence polyoxometalates,[457,458] high-T_c cuprates[410] and related copper oxide materials,[476] organic radical systems,[428] biomimetic systems,[860] among others. The comparison with FCI calculations performed on mixed valence model systems[409] indicates that a good agreement is achieved between DDCI and FCI results, while the t values obtained from DFT calculations are in general underestimated. This behavior contrasts with the overestimation usually found for the DFT magnetic coupling parameters.[260,331,597,598] A comparison of the t estimates resulting from embedded cluster DFT and DDCI calculations can be found in ref 476 for Sr_2CuO_3 and Ca_2CuO_3. These results confirm the underestimation found in model systems, and put in evidence the marked dependence of the t value on the functional employed in the DFT evaluations.

Finally, t evaluations from periodic calculations can be also found in literature. In such cases, the t values are extracted from LDA calculations by fitting the dispersion of the half-filled band using the linear combination of atomic orbitals scheme (LDA-LCAO)[861] or the linear muffin-tin orbital technique (LDA-LMTO).[862,863] Most of these evaluations are intended to parametrize the corresponding Hubbard Hamiltonian to explain the electronic and magnetic properties of extended systems, such as linear chain cuprates like Sr_2CuO_3 and Ca_2CuO_3,[864] pseudo-ladder compounds,[865] quasi-two-dimensional Mott insulator $SrCu_2(BO_3)_2$,[866] manganites,[867] or hole-doped cuprates.[868] By expressing the electron density obtained from a periodic calculations in localized Wannier orbitals, hopping parameters can be extracted from interaction matrix elements in a similar way as described above for wave function based calculations. This approach has been applied by Kováčik and Ederer to determine the Hubbard parameters and the Jahn-Teller (electron-phonon) coupling in $LaMnO_3$.[869,870]

6.2 Holes in $S = 1/2$ systems: the $t - J$ model

For finite doped molecular systems, the electron distribution is well defined, the holes or extra electrons being either localized or delocalized. In contrast, in doped extended systems, different electron distributions are possible which may lead to electronic disorder in the presence of inhomogeneities. The following discussion is restricted to homogeneous distributions of dopants. When the half-filled system is doped with holes or electrons two different processes are in competition: the coupling of the unpaired electrons on neighboring sites (J) and the delocalization of the hole or extra electron from one site to another. The latter process is controlled by the hopping integral t. The possibility of delocalizing the hole (or extra electron) on a neighboring site has a non-negligible impact on the magnetic properties of the system. The presence of holes (extra electrons) not only modifies the amplitude of the magnetic coupling between two active sites near the holes (extra electrons),[410,457] but can also affect collective properties such as the energy gap between diamagnetic and paramagnetic situations in polyoxometalates upon reduction.[458,871–876]

The usual model to deal with the physics of this type of systems is the $t - J$ Hamiltonian, proposed by Zhang and Rice[38] to rationalize the properties of the high-T_c Cu-oxide superconductors. This model contains both kinds of interactions:

$$\hat{H}_{tJ} = \hat{H}_J + \hat{H}_t \tag{97}$$

where $\hat{H}_J$ corresponds to the Heisenberg Hamiltonian, and $\hat{H}_t$ ensures the mobility of the hole or extra electron:

$$\hat{H}_t = \sum_{i \neq j} t_{ij} \left(\hat{a}_i^\dagger \hat{a}_j + \hat{a}_{\bar{i}}^\dagger \hat{a}_{\bar{j}} \right) \tag{98}$$

In its simplest version, the $t - J$ model contains only first-neighbor interactions, but it is also possible to include additional terms to account for the coupling between further sites (second- and third- neighbor terms).[877] The model can even be extended with other types of interactions such as the hole-hole repulsion, V, considered of key importance on hole-doped cuprates and the stripes formation,[878,879] or the exchange-transfer term,[813] also called singlet-displacement operator,[410,860,880] which moves a pair of electrons placed on two neighbor sites, coupled in a singlet, towards a hole placed on a nearby position. This operator produces the displacement of a singlet as a whole. The movement, represented in Figure 26 implies three active orbitals of the system $\{a,b,c\}$ in such a way that all of them change either the occupation (0 or 1) or the spin (up or down). It can be conceived as a two-step process in which first electron 1 moves to the orbital occupied by electron 2 (from a to b). The two electrons occupy the same site, increasing the energy of the system by $U' - J/2 \approx U'$, where U' corresponds to the on-site Coulomb repulsion corrected by the electrostatic interaction between the extra charges. Usually, $J/2$ is much smaller than U' and can be neglected. Then electron 2 is transferred to the site c. The local singlet $(|a\bar{b}| - |b\bar{a}|)/\sqrt{2}$ is displaced to $(|b\bar{c}| - |c\bar{b}|)/\sqrt{2}$, the hole moving from site c to site a. Hence, this term scales as t^2/U'. A similar reasoning holds for a two-band model with electron transfer processes between the magnetic centers and the bridging ligand orbitals. In such a case, the mechanism involves charge transfer intermediate states, and the operator scales as t_{ha}^4, with t_{ha} the hopping parameter between ligands and magnetic sites. A rationalization for the case of hole-doped high-T_c cuprates can be found in ref 410.

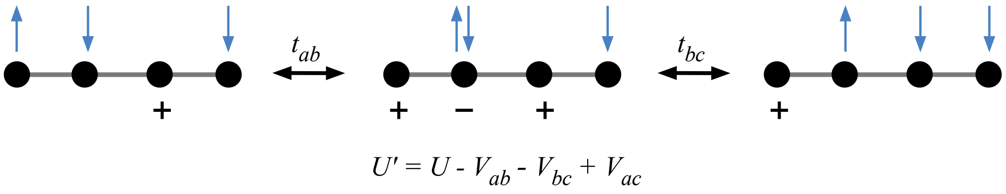

Figure 26: One-band model representation of the singlet displacement operator in a four site system carrying one hole. U' is the energy of the middle determinant and corresponds to the on-site repulsion corrected with the electrostatic interaction between the nearby holes.

The evaluation of the parameters included in the $t - J$ model Hamiltonian can be carried out by different approaches depending on the complexity of the system. In the best case, a similar procedure as those presented above can be employed, namely the evaluation of the energy and wave function of the low-lying states of the spectrum, the subsequent projection onto the $t - J$

model space, and the identification of the interaction parameters with the off-diagonal elements of the resulting effective Hamiltonian.

The calculations can be performed on the whole molecule or on a representative reduced fragment in the case of extended systems as the hole-doped high-T_c cuprates mentioned before. Several examples can be found in literature, including biomimetic molecules, high-T_c cuprates, polynuclear metal transition complexes and polyoxometalates.[410,456–458,875,881–883] To illustrate the procedure, we consider a simple model of three sites (A, B and C) placed on the corners of an isosceles triangle, where A and C are equivalent by symmetry. After doping the half-filled system with a hole, the model has two unpaired electrons and three magnetic orbitals a, b and c. The simplest $t-J$ model to describe the physics of this system only considers the magnetic coupling and electron transfer terms shown in the upper and middle part of Figure 27. Two magnetic coupling constants J_1 and J_2 and two-electron transfer terms, t_1 and t_2 can be distinguished.

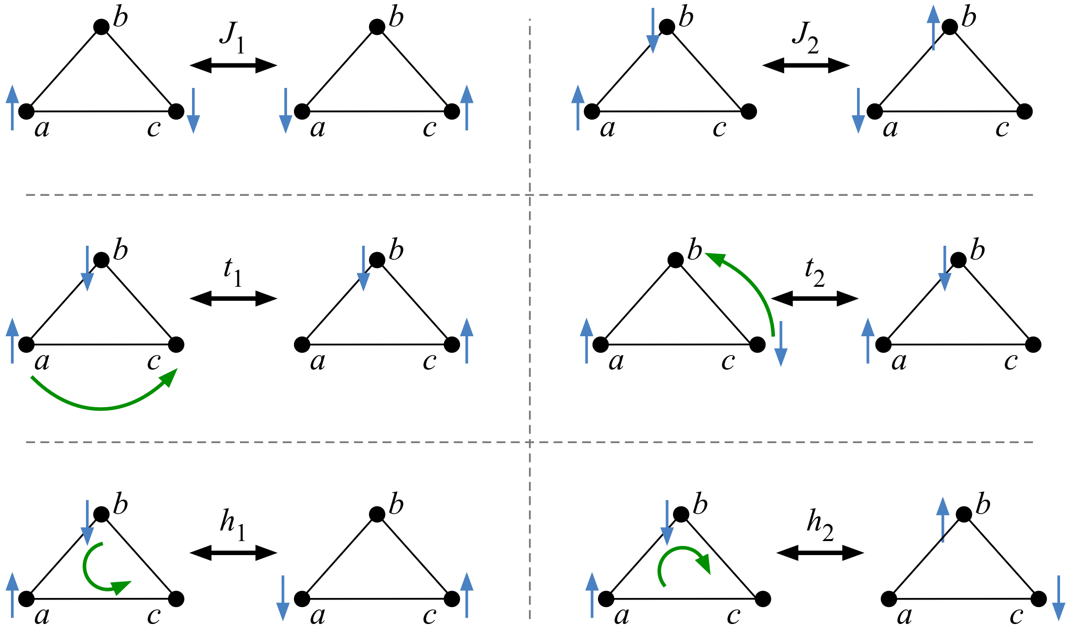

Figure 27: Magnetic coupling (J_1 and J_2), electron transfer (t_1 and t_2) and singlet displacement (h_1 and h_2) in a three-center / two-electron system.

The two electrons in three orbitals generate six neutral $M_S = 0$ determinants, which constitute the model space. The model Hamiltonian can be written as:

$$\begin{array}{c} |a\bar{b}| \\ |\bar{a}b| \\ |b\bar{c}| \\ |\bar{b}c| \\ |a\bar{c}| \\ |\bar{a}c| \end{array} \left[\begin{array}{cccccc} J_2 & -J_2 & 0 & -t_1 & t_2 & 0 \\ & J_2 & -t_1 & 0 & 0 & t_2 \\ & & J_2 & -J_2 & t_2 & 0 \\ & & & J_2 & 0 & t_2 \\ & & & & J_1+\varepsilon & -J_1 \\ & & & & & J_1+\varepsilon \end{array}\right] \tag{99}$$

The term ε represents the stabilization of the hole localized on site b with respect to the hole on a or c. The proper combinations of these six determinants generate three singlet and three triplet states. The diagonalization of this matrix gives enough analytical expressions to determine the four interaction parameters from the five energy differences between the singlet and triplet states. Alternatively, the interactions can be directly obtained from the value of the corresponding off-diagonal effective Hamiltonian matrix elements. One of the advantages of using the effective Hamiltonian approach resides in the fact that the presence of unexpected nonzero terms on the effective matrix can be considered as an indication of the necessity of adding extra terms with distinct physical contents to the model Hamiltonian. This is exactly what happens for the hole-doped cuprates[410] or the biomimetic $[L_3Cu_3O_2]^{3+}$[860] mixed valence compound. The effective Hamiltonian built with DDCI wave functions and energies shows important deviations from the model Hamiltonian of eq 99. The extra interactions not included in the $t-J$ model correspond to the singlet-displacement operator described in previous section and shown in the lower part of Figure 27. After including the operators h_1 and h_2, which scale as t_1t_2 and t_2^2, respectively, the new model Hamiltonian is:

$$\begin{array}{c} |a\bar{b}| \\ |\bar{a}b| \\ |b\bar{c}| \\ |\bar{b}c| \\ |a\bar{c}| \\ |\bar{a}c| \end{array} \left[\begin{array}{cccccc} J_2 & -J_2 & h_2 & -t_1-h_2 & t_2-h_1 & h_1 \\ & J_2 & -t_1-h_2 & h_2 & h_1 & t_2-h_1 \\ & & J_2 & -J_2 & t_2+h_1 & -h_1 \\ & & & J_2 & -h_1 & t_2+h_1 \\ & & & & J_1+\varepsilon & -J_1 \\ & & & & & J_1+\varepsilon \end{array} \right] \tag{100}$$

Table 13 shows the amplitudes of these parameters for the biomimetic mixed-valence $[L_3Cu_3O_2]^{3+}$ compound, shown in Figure 28 and described in detail in ref 860. These results show that the singlet-displacement terms are not negligible, with amplitudes similar to that found for the first-neighbor magnetic coupling constant. This puts in evidence the suitability of the evaluations based on the effective model Hamiltonian instead of on only energy differences.

Table 13: DDCI magnetic exchange, electron-transfer and singlet-displacement terms (in cm^{-1}) for one of the two $[L_3Cu_3O_2]^{3+}$ clusters in the unit cell. ε in eV.

	J_1	J_2	t_1	t_2	h_1	h_2	ε
DDCI	39.6	128.4	540.3	-1466.7	33.2	47.4	-3.62

6.3 Mixed-valence systems with several unpaired electrons per center: the double exchange mechanism

As a consequence of the possible coexistence of localized and delocalized unpaired electrons, the magnetic and electron transport properties are strongly coupled in mixed valence systems of class III with more than one unpaired electron per site.[814] The standard model to describe these compounds is based on the double exchange mechanism, which is usually invoked to rationalize the appearance of magnetoresistive effects,[884,885] the sudden drop of electric resistivity by several

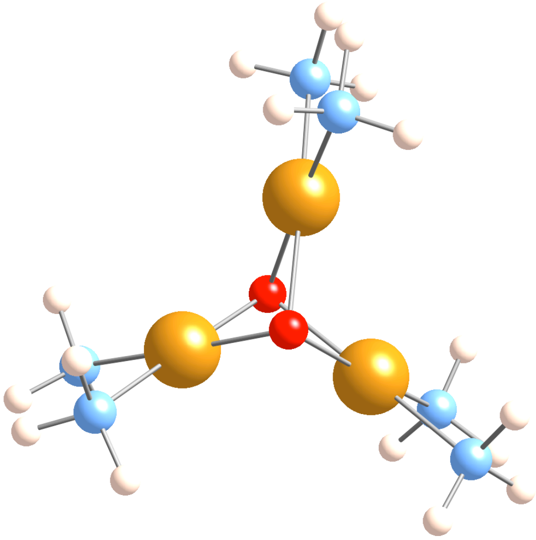

Figure 28: Model structure of $[L_3Cu_3O_2]^{+3}$ system employed in the calculations, where L ligands are replaced by NH_3 groups.

orders of magnitude under the influence of an external magnetic field. Among the various applications of this physical phenomenon, one may quote the use of colossal magnetoresistive effects for magnetic memories and spintronics. Another interesting group of systems where double exchange plays a key role is formed by the FeS proteins including mixed valence ferredoxins, which are the subject of intense research.[14,813,886–890] Double exchange may also be seen as another paradigm for the synthesis of high-spin molecules.[70] Although it is well-known from theoretical works[891–894] that the high spin state is stabilized by the double exchange mechanism, high-spin molecules exhibiting double exchange are relatively rare. The TM complex $[L_2Fe_2(\mu\text{-}OH)_3]^{2+}$ (L = N,N',N"-Trimethyl-1,4,7-triazacyclononane)[228,895–897] with ground spin state $S = 9/2$ and the purely organic mixed-valence bis(semiquinone) biradical anion[898] of spin $S = 1$ are examples of this phenomenon. Hybrid materials in which organic radicals are coordinated to diamagnetic transition metal ions have also been reported. Interesting examples are the Co^{III} complexes[899] containing mixed-valence nitronyl nitroxide-semiquinone and nitronyl nitroxide-catecholate ligands, for which the magnetic coupling is so strong that the high-spin $S = 3/2$ state is the only state with significant population up to 300 K.

While the double exchange phenomenon is an interesting mean to combine magnetism and conductivity in periodic systems and also an interesting mean to produce high-spin molecules, examples of double exchange systems are still relatively rare. Experimental information on molecular systems is consequently limited. Experiments mainly provide excitation energies from the high-spin ground state to the first excited states of same spin multiplicity. The relative energetic position of the states of lowest spin multiplicity are not accessible from absorption spectroscopy and the confrontation of theoretical results to experimental evidence is quite problematic in this nevertheless promising domain.

In two-center systems, the double exchange mechanism comes into play when a hole (or an electron) is delocalized over two centers while the other magnetic electrons of the centers remain essentially localized. The first microscopic model that describes the energies of the states resulting from the interactions between these local ground states was proposed by Zener to rationalize the magnetic and transport properties of manganites.[900,901] The only interaction of the Zener model is the hopping integral t of the additional electron (or hole) between the two magnetic ions A and B, coupling the two configurations $A^{n-1}B^{n}$ and $A^{n}B^{n-1}$ for $2n-1$ unpaired electrons.

In 1955, Anderson and Hasegawa described the double exchange model for binuclear complexes in a more general way.[902] They proposed two models in which the spins are treated either as classical vectors or within a quantum mechanical setting. Both models take into account the hopping integral t of the additional electron (or hole) and the intra-atomic exchange integral K. Contrarily to most of the model Hamiltonians, the Anderson Hasegawa (AH) models consider the local first excited spin states. The expressions of the quantum energies of the highest spin states in the AH model are:

$$E_{AH}(S_{max}, \pm) = \pm t \tag{101}$$

where ± refers to the in-phase and out-of-phase combinations of the $A^{n-1}B^{n}$ and $A^{n}B^{n-1}$ configurations. The energies of the other spin states are given by

$$E_{AH}(S \neq S_{max}, \pm) = \frac{1}{2}\left[\delta - \sqrt{\delta^2 + 4t\left(t \pm \frac{S+1/2}{S_{max}+1/2}\delta\right)}\ \right] \tag{102}$$

where S_{max} is the maximum spin moment that can be obtained by combining all the unpaired electron spins and δ is the energy difference between the ground and excited local states. This energy is proportional to K, as mentioned before in section 5.3. Since K is in general much larger than t, one usually takes the limit of $K \to \infty$ and an approximate expression can be derived in which the Zener (Z) hopping integral is the only interaction:

$$E_Z(t,S) = \pm t \frac{S+1/2}{S_{max}+1/2} \tag{103}$$

In this expression the highest spin state is always the ground state, which provides a rationalization of the proclivity of most double exchange systems to a ferromagnetic order.

The next step toward an accurate model of double exchange was made in the 1980s by Girerd and co-workers.[891,903,904] They introduced the effect of the delocalization of the other unpaired electrons using an interaction J (often antiferromagnetic) but neglecting the non-Hund states. The resulting expression of the energies of the different spin states is:

$$E_{ZGP}(t,S) = \pm t \frac{S+1/2}{S_{max}+1/2} - \frac{J}{2}\left[\left(S\left(S+1\right) - S_{max}\left(S_{max}+1\right)\right)\right] \tag{104}$$

where ZGP stands for Zener, Girerd and Papaefthimiou. Contrarily to the Zener model (eq 103), this new expression makes possible the existence of a low-spin ground state depending on the relative values of t and J.

Recently, it has been shown that a quantitive reproduction of the spectra of double exchange compounds requires the use of a model in which all interactions (t, δ, and J) are taken into account simultaneously.[453,905,906] The energies of the highest spin states in such combined model are still given by eq 101 while the expressions of the energies of the other states in this refined model are:

$$E_{AH-ZGP}(S \neq S_{max}, \pm) = \frac{1}{2}\left[\delta - \sqrt{\delta^2 + 4t\left(t \pm \frac{S+1/2}{S_{max}+1/2}\delta\right)}\right] - \frac{J}{2}\left[\left(S\left(S+1\right) - S_{max}\left(S_{max}+1\right)\right)\right] \tag{105}$$

As for any mixed valence system, the competition between the hopping mechanism, which leads to delocalization of the itinerant electron, and vibronic effects, which tend to trap the electron on a specific center, plays an important role in the properties of double exchange systems.[14,907,908]

6.3.1 Analytical derivation of a refined double exchange model from the generalized Hubbard Hamiltonian

In line with the derivation of the model Hamiltonian that accounts for bilinear and biquadratic magnetic interactions in section 5.3.1, we present here the derivation of the double exchange model accounting for the δ, K and t parameters from the generalized Hubbard Hamiltonian. A relatively simple centro-symmetric system is considered with three unpaired electrons distributed over two magnetic sites. The system has four magnetic orbitals, which are labeled as a_1 and a_2 for the orbitals localized on site A and b_1 and b_2 for site B. For convenience, a_1 and b_1 belong to the same irreducible representation, while a_2 and b_2 belong to another representation. This symmetry restriction is introduced to simplify the derivation, but the model is generalizable to complexes for which the local magnetic orbitals cannot be separated by symmetry. In the typical double exchange systems, one of the hopping integrals is significantly larger than the others, reflecting the difference of overlap between the underlying purely atomic orbitals. We will assume that there is a large overlap between the orbitals a_1 and b_1, a smaller overlap between the orbitals a_2 and b_2 and there is of course no overlap between the orbitals having a different symmetry, i.e. a different index 1 or 2. The zeroth-order model Hamiltonian can be separated in mono- and two-electron operators :

$$\hat{H}_M = \hat{H}_1 + \hat{H}_2 \tag{106}$$

The one-electron operator allows the extra electron (or hole) to delocalize over the two sites:

$$\hat{H}_1 = \sum_{i=1,2} \left[\varepsilon_{a_i} \hat{a}^{\dagger}_{a_i} \hat{a}_{a_i} + \varepsilon_{b_i} \hat{a}^{\dagger}_{b_i} \hat{a}_{b_i} + t_i |n_{a_i} - n_{b_i}| \left(\hat{a}^{\dagger}_{a_i} \hat{a}_{b_i} + \hat{a}^{\dagger}_{b_i} \hat{a}_{a_i} \right) \right] \tag{107}$$

where n_{a_i} is the occupation number of the orbital a_i, t_i the hopping integral between the orbitals a_i and b_i and $\varepsilon_i = \varepsilon_{a_i} = \varepsilon_{b_i}$ the one-electron energy of the electron occupying the orbital a_i or b_i. The two-electron operator accounts for the on site electron-electron repulsion and the spin-exchange.

Let us first consider the site bearing two electrons. The two-electron energy of the local triplet ground state (T) is taken as the zero of the one-site two-electron energies. The relative energy of the local open-shell excited singlet state is $2K$, where K is the exchange integral between the a_1 and a_2 orbitals, $K = K_{a_1a_2} = K_{b_1b_2}$. The ground state of the site with one unpaired electron is (of course) a simple doublet determinant. We label this determinant as $D^{(1)}_{1/2}$ when the hole occupies a_1 or b_1, otherwise $D^{(2)}_{1/2}$ is used. The high-spin coupling of the $D^{(1,2)}_{1/2}$ doublets with the $M_S = 1$ component of the local triplet ground state (T_+) on the other magnetic site leads to the following four different $M_S = 3/2$ determinants:

$$\Phi^{(1)}_1 = |D^{(1)}_{1/2}T_+|; \quad \Phi^{(1)}_2 = |T_+D^{(1)}_{1/2}|; \quad \Phi^{(2)}_3 = |D^{(2)}_{1/2}T_+|; \quad \Phi^{(2)}_4 = |T_+D^{(2)}_{1/2}| \tag{108}$$

$\Phi^{(1)}_2$ is schematically depicted in Figure 29. Depending on the way the three unpaired electrons of the complex are distributed over these orbitals, two families of quartet states can be defined. The first family has a delocalized electron in the orbitals of symmetry 1 and two localized unpaired electrons in the orbitals of symmetry 2. This is inverted in the second family of states. The two determinants of each symmetry are coupled through the one-electron part of the Hamiltonian. In the considered problem and taking as zero of energy the energy of the determinants $\Phi^{(1)}_1$ and $\Phi^{(1)}_2$, the energies of the quartet states (Q) are:

$$\begin{aligned} E(Q^{(1)}_\pm) &= \pm t_1 \\ E(Q^{(2)}_\pm) &= |\varepsilon_1 - \varepsilon_2| \pm t_2 \end{aligned} \tag{109}$$

The determinants that span the $M_S = 1/2$ model space can also be written as products of local states. At variance with the quartet states, we now also need to consider the $M_S = 0$ component of the local triplet state (T_0) and the $D_{-1/2}$ determinant of the local doublet. In order to derive the refined double exchange model, the local excited singlet state S_0 should also be considered. The resulting twelve determinants that span the model space are:

$$\begin{array}{lll}
\Phi_5^{(1)} = |D_{1/2}^{(1)} T_0|; & \Phi_6^{(1)} = |D_{-1/2}^{(1)} T_+|; & \Phi_7^{(1)} = |D_{1/2}^{(1)} S_0| \\
\Phi_8^{(1)} = |T_0 D_{1/2}^{(1)}|; & \Phi_9^{(1)} = |T_+ D_{-1/2}^{(1)}|; & \Phi_{10}^{(1)} = |S_0 D_{1/2}^{(1)}| \\
\Phi_{11}^{(2)} = |D_{1/2}^{(2)} T_0|; & \Phi_{12}^{(2)} = |D_{-1/2}^{(2)} T_+|; & \Phi_{13} = |D_{1/2}^{(2)} S_0| \\
\Phi_{14}^{(2)} = |T_0 D_{1/2}^{(2)}|; & \Phi_{15}^{(2)} = |T_+ D_{-1/2}^{(2)}|; & \Phi_{16}^{(2)} = |S_0 D_{1/2}^{(2)}|
\end{array} \tag{110}$$

The determinants Φ_8, Φ_9 and Φ_{10} are depicted in Figure 29. This space gives rise to four quartet and eight doublet states, i.e. two quartets and four doublets in each family of states. The energies of the lowest four doublet states (D), which are dominated by the determinants formed with local ground states, are given by

$$\begin{aligned}
E(D_{\pm}^{(1)}) &= K - \sqrt{K^2 + t_1(t_1 \pm K)} \\
E(D_{\pm}^{(2)}) &= |\varepsilon_1 - \varepsilon_2| + K - \sqrt{K^2 + t_2(t_2 \pm K)}
\end{aligned} \tag{111}$$

The remaining four doublets lie much higher in energy. The expressions for the energy differ from the others by a 'plus' sign in front of the square-rooted term. These states have large contributions from the determinants with S_0 (the local non-Hund singlets) and will not further be considered.

The electrons in the sixteen determinants and spin-adapted functions considered in the model space are unpaired. However, the ZGP model also considers the second-order effect of the determinants in which the two localized electrons are paired. The lower part of Figure 29 shows two examples of this kind of determinants. The determinant on the left has *neutral* character, while the one on the right is *ionic* with all three electrons on the same center. In the generalized Hubbard Hamiltonian the relative energy of the ionic determinant is U, while that of the neutral determinants is $3K$. These perturbers (determinants outside the model space) with an unpaired electron in symmetry 1 (or 2) will act solely on the lowest doublet states of family 1 (or 2). The perturbative treatment of these outer space determinants shows that it is possible to account for their effect using two effective magnetic couplings labelled J_1 and J_2 (one for each symmetry) as proposed by the ZGP model. However, to be rigorous one should in principle consider the bicentric direct

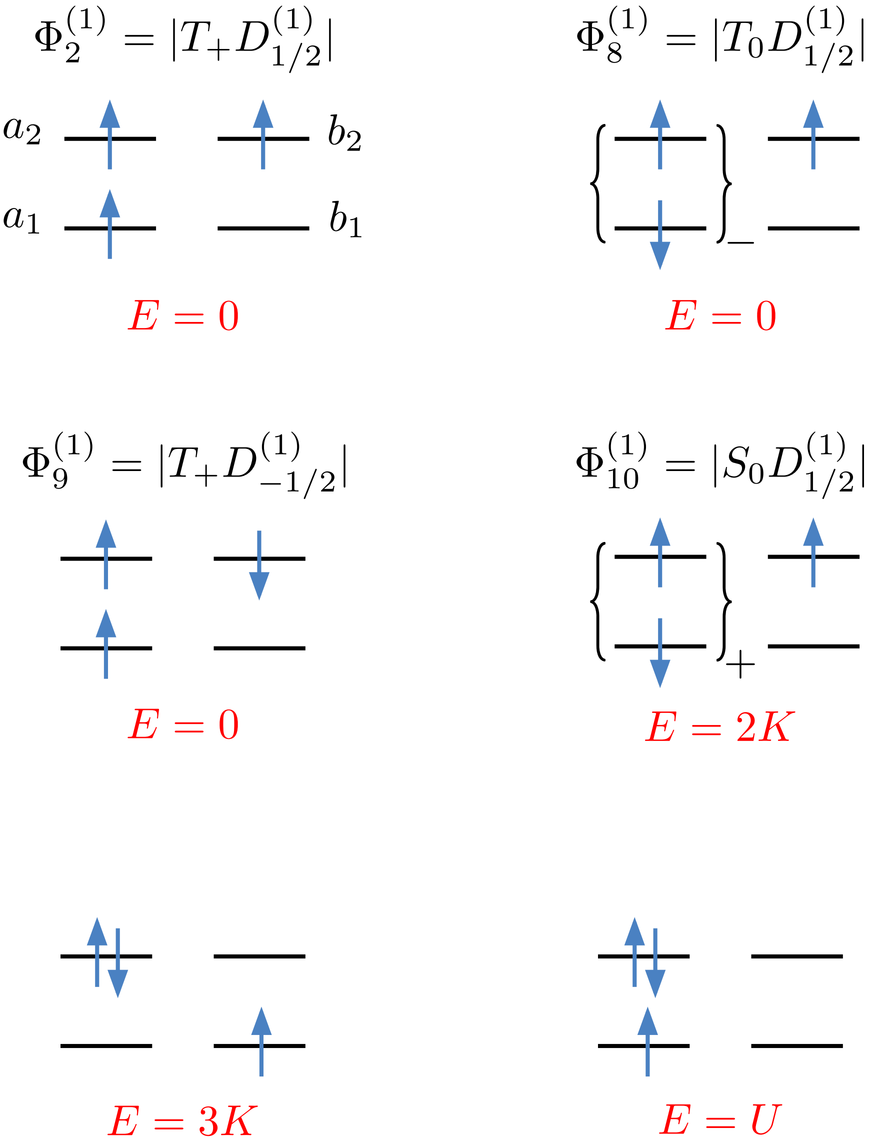

Figure 29: Representation of some determinants and spin-adapted functions of the double exchange model space (top and middle) and of some determinants (bottom) accounted for perturbatively in the ZGP and refined models. The 'plus' sign as subscript for the curly brackets indicates singlet coupling of the two electrons, while a 'minus' sign means triplet coupling. The energies in the generalized Hubbard model are also given.

exchange integrals which contribute ferromagnetically to the effective magnetic couplings J_1 and J_2. Defining F_i as the total ferromagnetic contribution, the expression of J_i as functions of the generalized Hubbard Hamiltonian interactions is:

$$J_{1,2} = F_{1,2} - \frac{1}{2}t_{2,1}^2\left(\frac{1}{3K} + \frac{1}{U}\right) \tag{112}$$

Both the neutral and the ionic perturbers can only contribute to the doublet energies.

$$\begin{aligned} E(D_\pm^{(1)}) &= K - \sqrt{K^2 + t_1(t_1 \pm K)} - \frac{3}{2}J_1 \\ E(D_\pm^{(2)}) &= |\varepsilon_1 - \varepsilon_2| + K - \sqrt{K^2 + t_2(t_2 \pm K)} - \frac{3}{2}J_2 \end{aligned} \tag{113}$$

As previously stated, the standard ZGP model space does not contain functions involving the local excited states S_0, which appear in the refined model through the presence of the term K. Their effect results in both a reduction of the energy difference between the two doublets of a same family and a stabilization of the mean value of these doublet states by a quantity equal to $-3t_i^2/8K$ at the second order of perturbation. In the ground state family $-3t_1^2/8K$ is much larger than $3J_1/2$ since J_1 is proportional to t_2^2 and the non-Hund states therefore bring the main antiferromagnetic contribution to the double exchange mechanism. On the contrary, in the second family of states, the antiferromagnetic contribution mainly comes from $3J_2/2$ which is of course large if t_1 is large. As a consequence, the lowest state of this second family may be a doublet. A schematic representation of the spectrum of the two families in case of strongly different values of t_1 and t_2 is given in Figure 30. This derivation is generalizable to systems with a larger number of unpaired electrons and leads to the expression given in eq 105.

As an example to illustrate the extraction procedure of the electronic structure parameters relevant to the double exchange mechanism, a model complex with three unpaired electrons distributed over two magnetic sites, namely the planar $(NH)_2^+$ cation will be discussed. The two NH molecules are separated by 5.0 Å and the H atoms are in trans positions. In this example, the hopping integrals are very small and as a consequence one of the magnetic exchange is ferromagnetic. This

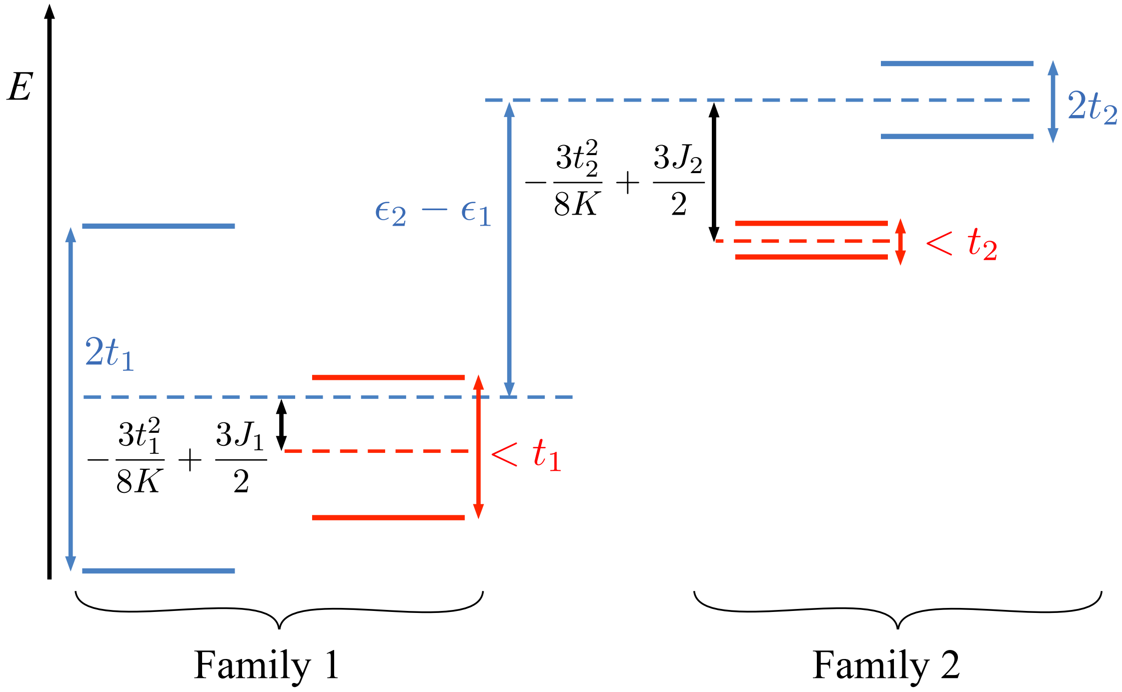

Figure 30: Schematic representation of the eight lowest-state energies of the two families. Second-order corrected energy differences between the states (plain lines) or their mean values (dashed lines) are indicated.

gives us the occasion to illustrate the below discussed difficulties met when extracting the double exchange interactions from DFT calculations. We first use the analytical expressions of the lowest quartet and doublet states to map the outcomes of DDCI calculations. Then we review how some of these parameters can be determined from DFT calculations.

6.3.2 Numerical evaluation of the double exchange interactions from WF calculations

The ground state of the NH molecule is a triplet state in which the two magnetic electrons occupy the two magnetic N-2p orbitals orthogonal to the NH axis. In the planar trans-geometry of the $(\mathrm{NH})_2^+$ ion that we consider here (illustrated in Figure 31), the in-plane magnetic N-2p orbitals have a larger overlap than the ones perpendicular to the plane. The interaction between the former orbitals leads to two σ-type MOs of gerade (g_1) and ungerade (u_1) symmetry. The localized orbitals obtained from linear combinations of these MOs are the a_1 and b_1 orbitals used in the previous section. The weaker interaction between the N-2p orbitals perpendicular to the plane give two π-type MOs labelled g_2 and u_2 from which we can define the localized orthogonal orbitals a_2 and b_2. Figure 31 gives a schematic representation of the four symmetry-adapted magnetic orbitals.

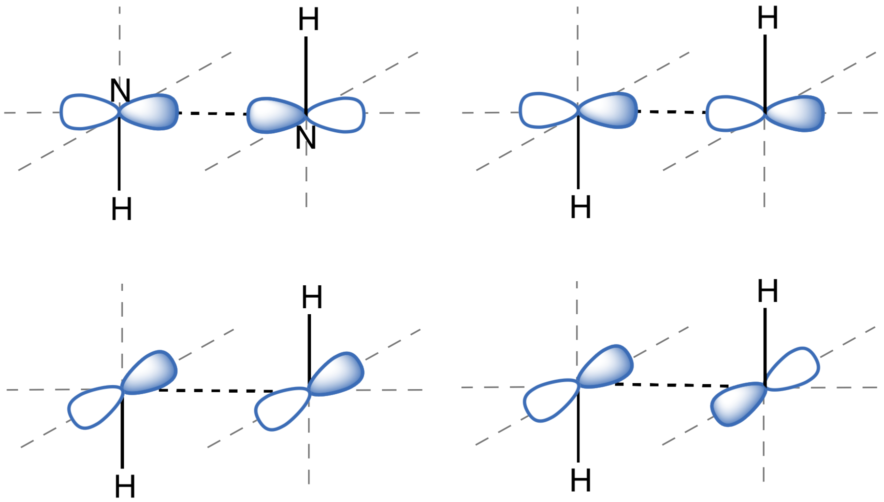

Figure 31: Schematic representation of the magnetic orbitals of the $(NH)_2^+$ cation. The upper part shows the σ orbitals g_1 and u_1. The lower part of the figure shows the π orbitals g_2 and u_2.

In the considered system, the two families of states do not mix for symmetry reasons. The first family has a delocalized electron in the σ orbitals and two localized unpaired electrons in the π orbitals. This is inverted in the second family of states. The quartet and doublet states of both families have been computed using DDCI calculations. Their energies are used to determine the interactions of the double exchange model. Half the energy difference between the quartet states gives the values of the hopping integrals:

$$|t_i| = \frac{|E(Q_+^{(i)}) - E(Q_-^{(i)})|}{2} \tag{114}$$

Subsequently, K can be determined from the energy difference between the doublet states $\Delta_{D_i} = |E(D_+^{(i)}) - E(D_-^{(i)})|$

$$K = \frac{\Delta_{D_i}}{4}\sqrt{\frac{\Delta_{D_i}^2 - 4t_i^2}{\Delta_{D_i}^2 - t_i^2}} \tag{115}$$

The value of K should preferably be extracted for the lowest family of states, since the highest family may be mixed with other excited states. Finally, the energy difference between the quartet states $\Delta_{Q_i} = |E(Q_+^{(i)}) - E(Q_-^{(i)})|$ and the values of K and t_i, fix the values of J_i by the equation:

$$J_i = \frac{1}{3}\left(\Delta_{Q_i} - \Delta_{D_i} + 2K + \sqrt{K^2 + t_i(t_i + K)} + \sqrt{K^2 + t_i(t_i - K)}\right) \tag{116}$$

The first entry of Table 14 shows the values of these interactions extracted from the DDCI calculations. The hopping integral t_1 is the dominant interaction and is responsible for the stability of the quartet state with the delocalized electron in the σ orbital (symmetry 1). The hopping integral t_2 is much smaller as expected from the weaker π overlap. The magnetic exchange J_1 is weakly ferromagnetic showing that the direct exchange dominates this interaction. As a consequence of the large value of t_1, the interaction J_2 (proportional to t_1^2) is strongly antiferromagnetic and is partly responsible for the appearance of a doublet ground state in symmetry 2.

The magnetic exchange is not the only factor that stabilizes the doublet states. The non-Hund determinants such as $|D_{1/2}S_0|$ also contributes to the doublet stability. As can be seen in Table 14, the local exchange interaction K, which is a measure for the relative energy of the non-Hund states, is rather small. Moreover, the non-Hund determinants interact directly with the $M_S = 1/2$ determinants of the model space, contrary to the case of undoped, pure spin systems discussed in section 5.3. The relative importance of the two antiferromagnetic contributions has been worked out in several publications.[453,454,905,906,909] It was shown that the contribution due to the non-Hund states of the AH model, which is usually neglected, is in general more important than the more commonly considered magnetic exchange contribution of the ZGP model.

Table 14: CAS(3,4)DDCI and DFT values (in cm^{-1}) of the interactions involved in the refined double exchange Hamiltonian for the two families of states of the $(NH)_2^+$ model system.

	t_1	J_1	t_2	J_2	$K = \delta/2$	U
CAS(3,4)DDCI	177	$3\cdot10^{-1}$	-19	-1.7	6090	-
UDFT-B3LYP	117	$-2\cdot10^{-2}$	-12	-1.6	4871	88720

6.3.3 Extraction of double exchange interactions from DFT calculations

A few works have been devoted to the study of double exchange systems from DFT calculations.[228,910] The main difficulty of the extraction is due to the multi-configurational character of the states. While the t values can be determined from the DFT energies of the two mono-determinantal spin states of highest spin multiplicity (provided that they are of different symmetry), the J values cannot be extracted directly from the energy of computed determinants. Indeed, the doublet states cannot be assimilated to the determinants having $M_S = \pm 1/2$. This statement is general: the J values cannot be extracted from the energies of the $M_S = M_S^{max} - 1$ single determinants, independently of the spin of the system. Nevertheless, as already shown for the extraction of biquadratic interactions, it is possible to extract the interactions of a Hubbard model and then determine the values of the exchange interactions from the analytical expressions as functions of the Hubbard interactions. The main assumption of this extraction is that the values of J_i can be determined under the neglect of the direct exchange contributions:

$$J_{1,2} = -\frac{1}{2}\left(\frac{t_{2,1}^2}{U} - \frac{t_{2,1}^2}{3K}\right) \tag{117}$$

Indeed, while K, t_i and U can easily be extracted from the different DFT solutions, F_i cannot be determined from standard calculations. When the effective exchange is antiferromagnetic and large the bicentric exchange can be neglected. However when the ferromagnetic contribution is important, the extraction will lead to incorrect values of the magnetic coupling. In the case under study and as we have seen in the previous section, the J_1 interaction is ferromagnetic. Hence, only the kinetic exchange contribution to the effective exchanges J_1 and J_2 will be extracted.

Due to self-interaction error, BS calculations did not converge and the interactions have been calculated from space-symmetry adapted spin-unrestricted DFT calculations using the B3LYP functional. Figure 32 gives a representative sample of all the determinants for which the DFT energy has been computed. The interactions of the Hubbard model are calculated from energy differences between these solutions. Hereafter we use $E_i = E(\Phi_i)$. The zero of energy is calculated as :

$$E_0 = -\frac{E_1 + E_2}{2} \tag{118}$$

The hopping integrals can be evaluated as :

$$\begin{aligned} t_1 &= \frac{E_2 - E_1}{2} \\ t_2 &= \frac{E_3 - E_4}{2} \end{aligned} \tag{119}$$

Using E_0 as zero of energy, K and U can be extracted from :

$$\begin{aligned} K &= E_5 - E_0 + t_1 \\ U &= 4\left[E_6 - E_0 - t_1 - 2t_2 - K\right] \end{aligned} \tag{120}$$

The values can also be determined from the energy differences between other, related determinants, and hence, the consistency of the extraction can be checked. The dispersion of the obtained values is less than 6% for the hopping integrals and less than 0.5% for K. The double exchange model interactions have then been calculated from those of the Hubbard model. Their mean values (between those extracted from the different solutions) are reported in Table 14 and compared to those extracted from the WF calculations.

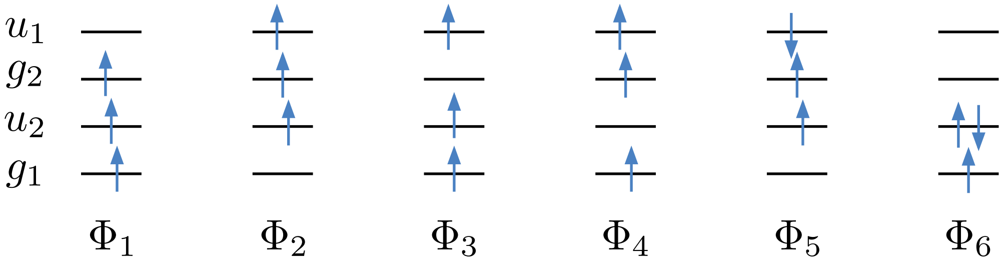

Figure 32: Sample of determinants, the energies of which can be used for the extraction of the Hubbard Hamiltonian interactions.

The DFT and WF values of J_2 are in good agreement. The DFT J_1 value has of course the wrong sign since only the kinetic exchange contribution could be extracted but it is very small as the WF one. Nevertheless, it should be stressed that while DFT accounts for spin polarization, the extraction of the effective exchanges from the t_i and U Hubbard interactions does not account for the spin polarization effect and would lead to unreliable values for strongly spin polarizable bridging ligands. It should also be noticed that there is a significant discrepancy between the DFT and WF values both for the hopping integrals and for the on-site exchange integral. Even if the DFT interactions have the correct order of magnitude, the extraction of the double exchange model interactions from DFT calculations is neither straightforward nor very precise.

7 Conclusions

The use of accurate model Hamiltonians is crucial to extract information on the magnetic interactions from the raw data obtained from (among others) magnetic susceptibility measurements, EPR or NMR spectroscopy. Combining information from different experimental techniques can be used to propose topologies and magnitudes of the magnetic couplings in the system under study, and from this, relevant phenomenological model Hamiltonians. Nevertheless, the magnetic interactions are not observable and theoretical input is crucial to validate the proposed Hamiltonians. Apart from giving numerical values for the magnetic interactions assumed to be dominant, standard fitting procedures do not provide insight on the mechanism of the couplings nor ensure that the underlying physics is contained in the proposed model Hamiltonian. Theory may eventually lead to the proposition of models with a more firm physical basis. As shown all along this review, the effective Hamiltonian theory plays a key role in both assessing the validity of the models and attributing values to the magnetic interactions. It provides a rigorous and rational way to study the magnetic interactions in molecular complexes and extended systems without the need of fitting a set of parameters of an *a priori* defined model Hamiltonian. Its power in the extraction of models is illustrated in section 5. Parallel and complementary to the extraction of numerical effective interactions from sophisticated calculations, the quasidegenerate perturbation theory constitutes an important conceptual tool for the derivation of new refined models, especially when handling the generalized Hubbard model. Such derivations are also useful to rationally exploit broken symmetry DFT solutions.

The qualitative description of magnetic molecules and solid materials rests on the assumption that a well-defined number of unpaired electrons occupy a set of magnetic orbitals, resulting from the *aufbau* principle which gives double occupancy to lower energy orbitals, imposed by the atomic electronic configuration, electrostatic interactions with the ligands, symmetry and delocalization features. This leads to a general description in terms of a core and the spin ordering of n unpaired electrons in n singly occupied orbitals associated with a unique spatial configuration. High level calculations including accurate treatments of electron correlation corroborate this qualitative picture, as definitively shown by the occupation numbers of the natural orbitals. The rational starting point of a computational strategy seems therefore to perform an optimization of these magnetic orbitals in a minimal CASSCF calculation with n electrons in n orbitals. Nevertheless, this minimal description gives poor values of the magnetic coupling, at most 20%-30% of the coupling in most cases. This failure can partially be attributed to the minimal CASSCF orbitals, which are excessively localized on the magnetic sites in comparison to the natural orbitals from nearly exact calculations. In contrast, Kohn-Sham DFT magnetic orbitals appear to be excessively delocalized in general. In both approaches, a crucial progress might consist of improving the quality of the magnetic orbitals.

The quantitative evaluation of the magnetic coupling represents a fascinating challenge for theoreticians, since the energy differences to be calculated are small compared to the total electronic energy of the states involved in the magnetic process. Calculation methods targeting energy differences such as Equation of Motion, used both in WF as in DFT procedures, or DDCI appear as especially suitable to address this problem. The problem is not only quantitative but also qualitative, since the states involved are of multi-determinantal character and cannot be obtained as excitations from a closed-shell state. This is therefore a key field for testing the performances of MR treatments, which remain the object of intense theoretical efforts as discussed in section 4.4. The yet unachieved goal is the development of methods which are both rigorous (size-consistent) and able to treat systems with a large number of unpaired electrons (high-spin momentum metal ions and systems with many magnetic sites) and with large ligands or spacers. Among them, hybrid methods such as CAS-DFT covering both dynamic and non dynamic correlation effects at a low computational cost could be of interest for the study of magnetic systems (section 4.5.3).

Despite the inherent complexity of strongly correlated systems, the calculation of the low energy states of purely magnetic compounds is a relatively easy task in comparison to the accurate description of the spin-crossover phenomenon, magnetic anisotropy, or photomagnetism, among others. Indeed, in purely magnetic systems, it is possible to define orbitals of comparable quality for the various target states, since they share the same leading spatial configuration. This is less evident in the treatment of magnetic anisotropy[261,460,469,911,912] where the excited states responsible for the main contributions to the zero-field splitting belong to different spatial configurations. The situation becomes even more complicated when treating (photo-)magnetism in spin crossover systems. There the complexity of dealing with states belonging to different spin and spatial configurations accumulates with that of treating different geometries.[913–917] As shown in various works, obtaining accurate relative energies requires the use of extremely large basis set,[913] improving the molecular orbitals[918] and also including the $2h$-$2p$ excitations which cannot be neglected anymore. In both problems, the spin-orbit coupling (and sometimes the spin-spin coupling) must be treated since it largely determines the transition rate between states of different multiplicity in spin-crossover systems and governs the magnetic anisotropy magnitude and nature. These two very important topics have not been addressed in the present review and deserve specific reviews.

Beyond the challenge of the problem for quantum chemistry methodologists, what are the potential contributions of computing magnetic interactions? Theoretical treatments, able to discriminate between different physical effects, permit to understand the various mechanisms involved in the magnetic couplings and to establish magneto-structural correlations. This often requires going beyond the application of black box tools, freezing in a selective way orbitals, configurations or interactions and eventually modifying the geometries and the nature of the chemical groups. It has enabled theoreticians to discriminate between through space and through ligand interactions and to establish the balance between direct exchange, kinetic exchange and spin polarization contributions to the magnetic coupling. The identification and understanding of the leading mechanisms may be useful in the dialog with experimentalists in charge of the synthesis for the design of new materials of potential technological interest.

Magnetism forces quantum chemistry to accomplish two important tasks. On the one hand, it must provide precise tools able to reproduce tiny energy differences, which requires highly technical and accurate methodologies. The conception of adequate methods is based on a deep understanding of the underlying physics. On the other hand, quantum chemistry must provide qualitative models and interpretations that are extracted from the analysis of reliable results, both energies and wave functions. In this quest for precision and qualitative interpretations, the partnership between theory and experiment is particularly necessary and fruitful. Magnetism is definitely a privileged field for such dialog.

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