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Accurate evaluation of magnetic coupling between atoms with numerous open-shells : an ab-initio method

Alain Gellé, Julien Varignon and Marie-Bernadette Lepetit

CRISMAT, ENSICAEN-CNRS UMR6508, 6 bd. Maréchal Juin, 14050 Caen, FRANCE

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Abstract. - We propose a new ab initio method designed for the accurate calculation of effective exchange integrals between atoms with numerous open-shells. This method applies to ferromagnetic as well as antiferromagnetic exchange, direct or ligand-mediated exchange. Test calculations on high spin transition metal oxides such as $KNiF_3$, Ba_2CoS_3 or $YMnO_3$ exhibit a very good accuracy compared either to the best ab initio calculations — when those are feasible — and with experimental evaluations.

In the last two decades transition metal oxides attracted a lot of attention due to the discovery of novel and intriguing properties. The interest of the physicists community was first triggered by the discovery of high-temperature superconductivity in copper oxide compounds. Since then, many transition metal oxides exhibiting properties of practical or theoretical interest were discovered. Presently the attention of the community is mainly focused on cobalt, manganese and iron oxides. Most of these systems present intriguing magnetic properties or ordering. It is thus of crucial importance for the understanding of these properties to be able to accurately evaluate the local effective interactions such as magnetic interactions between the Fermi-level, unpaired, electrons.

In these materials, the Fermi-level electrons are localized, essentially on the d orbitals of the metal ions. This localization is a consequence of the fact that the electron-electron repulsion is of larger magnitude than the kinetic energy. Such strongly correlated materials cannot be described by a simple band structure since such a description supposes the dominance of the delocalization effects over electron-electron repulsion ones. The importance of the electronic correlation results in charge, spin or orbitals occupation fluctuations arising from the competition between different configurations in the electronic structure. The nature of the ground and the low-lying excited-states is thus fundamentally multi-configurational. Therefore it is not surprising that ab-initio single-determinant based methods (such as density functional theory) encounter difficulties in properly describing strongly correlated systems. For this purpose physicists use model Hamiltonians. The knowledge of the pertinent degrees of freedom to be treated in such models and the amplitude of the interactions between them is thus of crucial importance.

In the case of copper, nickel or vanadium oxides, such microscopic models were accurately determined using exact diagonalization of selected configurations spaces (Configuration Interaction or CI methods) on embedded fragments [1,2]. The CAS+DDCI [3] (Complete Active Space + Difference Dedicated Configurations Interaction also found under the acronym of DDCI3) and LCAS+S [4] (Large CAS + single excitations) type of configurations selections proved their high reliability and efficiency. Indeed, they allowed the determination of magnetic couplings within experimental accuracy for the superconducting copper oxides [5,6]. In molecular systems, where the magnetic coupling can be experimentally evaluated with a great accuracy, the cited methods were able to reproduce them with an error smaller than 5 cm^{-1} [7]. Moreover the availability of the wave function offers the possibility to evaluate the pertinence of the chosen effective model. Let us recall the example of the famous $\alpha'NaV_2O_5$ where such ab initio study showed the incompleteness of the commonly used models that were neglecting the magnetic role of the oxygen ligands. The novel model, derived using CAS+DDCI ab initio calculations, allowed to explain the apparently contradictory experimental results of this compound [8].

Unfortunately the CAS+DDCI, LCAS+S and related methods cannot be used for systems involving more than

one or two unpaired electrons per magnetic center, and therefore not for high spin manganese, cobalt, iron oxides, etc. Indeed, for such systems the computational cost of the methods becomes prohibitive since the size of the space to diagonalize scales exponentially with the number of magnetic electrons. In this paper we propose an ab initio approach that overcomes this problem. We establish a simple physical criterion in order to select the important reference configurations, and derive from it a novel method with a strongly reduced computational cost. We will see that this method allows, for the first time, the determination within experimental accuracy, of effective magnetic interactions in high spin manganese or cobalt oxides, thus opening entire new classes of materials to ab initio studies.

Let us first recall the principle of the usual CAS+DDCI and LCAS+S methods. These variational methods are based on the expansion of the low lying states wave functions into a reference part and a screening part.

$$|\Psi_m\rangle = \overbrace{\sum_I C_{I,m}|\Phi_I\rangle}^{\text{reference}} + \overbrace{\sum_{J^*} C_{J^*,m}|\Phi_{J^*}\rangle}^{\text{screening}} = |\Psi_m^r\rangle + |\Psi_m^*\rangle \tag{1}$$

In the CAS+DDCI and LCAS+S approaches the reference configurations, $|\Phi_I\rangle$, span a Complete Active Space (CAS) and the screening configurations, $|\Psi_m^*\rangle$, are all single (or single and selected double) excitations on all the references $|\Phi_I\rangle$. The definition of the CAS is based on a mathematical formalization of the distinction between the core or ligands electrons — that are essentially paired — and the essentially unpaired magnetic electrons. Indeed, the orbital space is partitioned into three subsets : i) the *occupied orbitals* that are doubly occupied in all the CAS configurations, ii) the *active orbitals* that can take any occupation or spin values in the CAS configurations and iii) the *virtual orbitals* that are unoccupied in all CAS configurations. In the CAS+DDCI method the three orbitals sets strictly correspond to the orbitals supporting the essentially paired electrons, the magnetic electrons, and the rest. The screening configurations are then taken as all the single and double excitations on any of the CAS configurations, that contribute to the excitation energies at the second order of perturbation.

In the LCAS+S method one uses the fact that the screening effects are essentially supported by single excitations. The double excitations are thus eliminated from the calculations under the condition that the configurations associated with all important processes mediating the interactions between the magnetic atoms are incorporated within the references [4]. The LCAS+S method thus uses an active orbital set enlarged to the ligand orbitals mediating the interactions between the magnetic orbitals. The screening part is thus reduced to the single excitations on this large CAS. It was shown that the CAS+DDCI and LCAS+S methods yield results of equivalent accuracy [4], thus rooting the idea that the important effects to treat, in order to achieve accurate evaluation of local interactions, are the interactions between i) the magnetic configurations (referred to as zeroth-order) ii) the charge transfer configurations mediating the interactions (metal-to-metal and ligand-to-metal) and iii) the screening effects on the first two subsets as given by the single excitations on them.

$$\begin{aligned} |\Psi_m\rangle &= \overbrace{\underbrace{\sum_I C^0_{I,m}|\Phi^0_I\rangle}_{\text{zeroth-order}} + \underbrace{\sum_J C_{J,m}|\Phi_J\rangle}_{\text{charge transfer}}}^{\text{reference}} + \overbrace{\sum_{J^*} C_{J^*,m}|\Phi_{J^*}\rangle}^{\text{screening}} \\ &= |\Psi^0_m\rangle + |\Psi^{ct}_m\rangle + |\Psi^*_m\rangle \end{aligned} \tag{2}$$

The size of the configurations space to diagonalize in both the CAS+DDCI and LCAS+S methods is directly proportional to the size of the CAS that itself scales exponentially with the number of active orbitals. Thus, when the number of open shells per atom, or the number of magnetic atoms increases, it rapidly results in intractable calculations. For instance, the evaluation of the magnetic coupling between two Mn^{3+} atoms ($3d^4$) involves CI space to diagonalize of about 60 billions configurations using the CAS+DDCI method and of over 10 billions ones using the LCAS+S method. Among all those configurations, however, many of them are not really important for the physics. Indeed, the major difference between the case of metal atoms with a unique open shell and of metal atoms with multiple open shells lies in the number of multiple-charge-transfer configurations. In the former case, there are very few, while in the latter case there are the most numerous configurations in the reference space, while their pertinence for the low energy physics is far from obvious. For instance, the $Mn^{7+}Mn^{-}$ configurations exhibit a negligible contribution in the wave functions of states involving two high-spin Mn^{3+} ions, and contributes in a negligible way to the magnetic coupling between the two ions.

From this simple illustration one sees that the configurations involved in the usual methods are far too numerous compared to the really necessary ones for a proper description of the low-lying states physics. We shall thus find another criterion allowing to further select among the LCAS+S configurations the really pertinent ones. Let us make a perturbative analysis of equation 2. The so-called zeroth-order configurations are the configurations with large weight in the wave functions and the basis of any minimal model. As the Hamiltonian only contains one and two particle interactions, and using $|\Psi^0_m\rangle$ as zeroth-order wave functions, the quasi-degenerate perturbation theory tells us that only the singly-excited and doubly-excited configurations on $|\Psi^0_m\rangle$ are of real importance for the physics.

The method we propose in this work for the evaluation of local interactions takes advantage of the above analyses. The reference part in equation 2 shall be reduced to i) the zeroth-order part and ii) the *single* charge transfer configurations only. The screening part thus includes the single excitations on the zeroth-order part,

plus the double excitations built from a single excitation on top of a single charge transfer excitation. Compared to the LCAS+S we removed the multiple metal-to-metal and ligand-to-metal charge transfer configurations from the reference part, and the associated screening effects. Compared to the CAS+DDCI method (i) we removed the multiple metal-to-metal charge transfer configurations and associated screening configurations and (ii) we restricted the double excitations to the screening excitations on the ligand-to-metal charge transfers (as proved sufficient by the LCAS+S method [4]). Consequently the number of configurations is dramatically reduced. Going back to the two manganese example, the present method (referred to as Selected Active Space + Single-excitations or SAS+S) will involve only about 20×10^6 configurations to diagonalize instead of 10×10^9 for the LCAS+S and 60×10^9 for the CAS+DDCI method.

We tested the accuracy of the proposed method on the magnetic coupling of three compounds with respectively 2, 3 and 4 open shells per magnetic atoms and 3, 1 and 2 dimensionality of the magnetic interactions : $KNiF_3$, Ba_2CoS_3 and $YMnO_3$. Since for Ba_2CoS_3 and $YMnO_3$ the CAS+DDCI and LCAS+S methods are out of reach, we will present, for the sake of comparison between the different methods, calculations where the treatment of the screening effects are strongly pruned (only about 35% of the screening excitations are taken into account, see appendix for details). The evaluation of the exchange integrals will thus not be physically correct, however we will be able to compare the different methods. In a second time, we will use the method proposed in this work (SAS+S) using fully screened calculations in order to compare the computed values with experimental evaluations. Finally, for the sake of analysis of the relative importance of the multiple metal-to-metal and ligand-to-metal charge transfer configurations, we made an intermediate calculation where only the multiple ligand-to-metal charge transfer configurations were removed from the references. Since in each of the present examples the magnetic exchange are supposed to follow and Heisenberg Hamiltonian,

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

we can extract the exchange integrals from different spin excitations and, as a by product, verify the validity of the Heisenberg model.

Table 1 displays the evaluation of the magnetic exchange of the three compounds for the two reference methods, the SAS+S method and the intermediate calculation. One sees that for $KNiF_3$ the four methods yield very similar results with a relative difference of at most 3.5%. For Ba_2CoS_3 and $YMnO_3$ where the number of open shells is larger, the error of the present method compared to the reference ones is somewhat larger, of the order of 5 to 10% according to the reference method. Comparing now the LCAS+S and the intermediate calculations, one sees that the difference is negligible (less than 1%). The multiple ligand-to-metal charge-transfer configurations, present in the LCAS+S calculation and not in the intermediate one are thus of no influence on the exchange couplings, and more specifically on the super-exchange part of them. The role of the multiple metal-to-metal charge transfers can now be evaluated by the comparison between the intermediate and SAS+S calculations. This time their influence is somewhat larger for the Ba_2CoS_3 and $YMnO_3$ compounds, accounting for a relative decrease of the super-exchange term of about 5%.

$KNiF_3$ Calculations (meV)			
Calculation	$N_{CI}/10^6$	J_{01}	J_{12}
CAS+DDCI	28	6.89	7.06
LCAS+S	1.1	6.71	6.82
Intermediate	0.6	6.70	6.81
SAS+S	0.8	6.68	6.79

Ba_2CoS_3 Pruned calculations (meV)				
Calculation	$N_{CI}/10^6$	J_{01}	J_{12}	J_{23}
CAS+DDCI	34	1.86	1.85	1.84
LCAS+S	21	1.73	1.72	1.71
Intermediate	4.4	1.72	1.71	1.70
SAS+S	2.3	1.62	1.62	1.61

$YMnO_3$ Pruned calculations (meV)		
Calculation	$N_{CI}/10^6$	J_{34}
CAS+DDCI	35	1.51
LCAS+S	415	-
Intermediate	5.7	1.43
SAS+S	1.5	1.36

Table 1: Comparison of different methods using a pruned evaluation of the screening effects. SAS+S refers to the method proposed in the present work and intermediate refers to the calculation where only multiple ligand-to-metal charge transfer configurations were removed from the reference space. N_{CI} is the size of the CI space. J_{ij} correspond to the exchange integrals computed from the energy difference between the $S = i$ and $S = j$ spin states.

Table 2 displays the evaluation of the magnetic exchange for the three examples using the present SAS+S method with full calculation of the screening effects. Comparing ab initio results with the experimental data, on $KNiF_3$, Ba_2CoS_3 and $YMnO_3$, the magnetic exchange integrals are obtained within good accuracy to the experimental values. Indeed, the error to the nominal value is respectively of 9%, 4% and 7%, and within the error bar for Ba_2CoS_3, that is of the same order of magnitude of the best methods (CAS+DDCI and LCAS+S) for the single open-shell systems such as vanadium or copper oxides [9]. We also like to point out that the experimental incertitudes should be taken with caution since there is not a real proper way to extract the magnetic coupling from susceptibility measurements, specifically in 2D and 3D systems. In this respect

Material	B3LYP	CAS+DDCI	LCAS+S	SAS+S	Exp.
$KNiF_3$	14.86 [10]	6.98	6.77	6.74	7.7±0.4 [11]
Ba_2CoS_3	4.08	-	-	3.07	3.19±0.2 [12]
$YMnO_3$	0.59	-	-	2.8	3 [13]

Table 2: Exchange integrals evaluation. Comparison with experiments (in meV).

the experimental incertitudes are most likely larger than proposed on the 2D $YMNO_3$ and 3D $KNIF_3$ systems.

Let us sum up the main ideas supporting the present method. The CI space to diagonalize is built from three types of configurations. (i) The zeroth-order reference, that is the dominant configurations. These configurations are usually obvious from a simple analysis of the local physics. When the magnetic fragments are high-spin atoms they do correspond to the determinants for which the two magnetic atoms remain in a high-spin state. (ii) The configurations dominant in the mediation of the magnetic coupling. In most cases it does correspond to simple ligand-to-metal and metal-to-metal charge transfer configurations. However, in some complex cases, as for instance in cases where ligands present low-lying excited states involving bridging orbitals (occupied and virtual), the dominant configurations in the magnetic coupling mediation also involve metal-to-ligand charge transfers and the associated the low-lying ligand-to-ligand excitations. (iii) The screening effects on all the above cited reference configurations, that is all single excitations on all above reference configurations. Following these specifications our method is expected to be very general, applying to hetero-nuclear dimers of high-spin atoms, to complex ligands (extended, non-symmetric, conjugated, etc.), even to extended magnetic centers.

Let us also point out that the present method, that addresses the problem of numerous open-shells magnetic centers, can be profitably combined with complementary techniques developed for the reduction of the CI space as for instance : the treatment of large ligands using localized orbitals [14] or a more efficient treatment of the screening effects by the optimization of the virtual orbitals [15].

In conclusion, the SAS+S method presented in this work aim at the evaluation of magnetic couplings between atoms with multiple open shells. Indeed, on one hand, density functional theory encounters a lot of difficulties in the description of such strongly correlated systems. These difficulties are particularly dramatic for the evaluation of magnetic couplings since it often fails even to get the correct value by a factor two or more. On the other hand, embedded fragment quantum chemical ab initio methods succeeded in evaluating magnetic couplings when the magnetic atoms display only one or two open-shells. For larger numbers of open-shells, the size of the calculations were out of reach. We proposed in this paper a new CI method that condenses the pertinent information on magnetic excitations. This method allowed us to reach accurate ab initio evaluation of effective magnetic couplings in high spin cobalt or manganese compounds. It is the first time that such couplings become reachable. The SAS+S method thus opens new fields of research. For instance one can think to look at the local fluctuations of magnetic couplings in manganites, fluctuations known to be important for the colossal magneto-resistance effects but not experimentally directly accessible.

* * *

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Computational details The embedded fragments used for the magnetic couplings were built as follow. i) A quantum part containing the two magnetic atoms, the ligands mediating the interactions between them (S,F or O atoms) and their first shell of coordination (see figure 1). ii) The embedding part reproducing the main effects of the rest of the crystal on the quantum part : the exclusion effects and the Madelung potential. The exclusion effects are treated using two shells of total ions pseudo-potential [16] that forbid to the quantum part electrons to delocalize out of the fragment. The Madelung potential is computed using an appropriate renormalized set of charges [17] with an accuracy better than 10^{-2}meV.

The basis sets and pseudo-potentials used in this work are of valence 3ζ quality on the metal atoms and $3\zeta + P$ on the ligands. They can be found in reference [18].

The fragment orbitals were optimized using a Complete Active Space Self Consistent Field calculation on the highest spin state. The active orbitals were chosen as the magnetic opened $3d$ orbitals. This method is well known to yield a good separation between the occupied, active and virtual orbitals used in our reference spaces. The ligand orbitals mediating the interactions (used in the LCAS+S and SAS+S methods) were extracted from the occupied orbitals in a two-steps process. First, the ligand orbitals which occupation number fluctuates between different states (computed at a the minimal CAS+S level) were extracted from the Fermi sea using a multi-state natural orbitals method [19]. Second, among these orbitals the bridging ones were obtained by maximizing the hopping (kinetic integral) between them and the magnetic or-

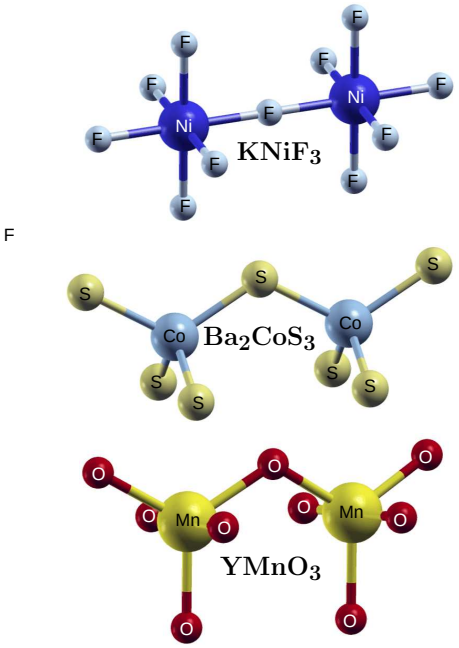

Fig. 1: Quantum part of the embedded fragments.

bitals. The bridging orbitals used in the present work are thus uniquely defined and qualitatively correspond to the bridging orbitals expected from simple physical considerations [12].

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The multi-state natural orbital method is an adaptation of the joint diagonalization method to the determination of natural orbitals diagonalizing simultaneously the density matrix of several states.