

Absence of collective effects in Heisenberg systems with localized magnetic moments

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Existence of collective effects in magnetic coupling in ionic solids is studied by mapping spin eigenstates of the Heisenberg and exact nonrelativistic Hamiltonians on cluster models representing KNiF_3 , K_2NiF_4 , NiO , and La_2CuO_4 . *Ab initio* techniques are used to estimate the Heisenberg constant J . For clusters with two magnetic centers, the values obtained are about the same for models having more magnetic centers. The absence of collective effects in J strongly suggests that magnetic interactions in this kind of ionic solids are genuinely local and entangle only the two magnetic centers involved. [S0163-1829(97)04634-1]

The proper and accurate description of magnetic interactions in systems with localized magnetic moments, i.e., ionic solids, is of importance not only from the point of view of basic knowledge but also to understand the electronic structure and magnetic behavior of superconductor parent compounds.¹ The experimental and theoretical study of the magnetic coupling in ionic solids is often based on the use of the Heisenberg Hamiltonian which may be written as

$$\hat{\mathcal{H}} = - \sum_{\langle i,j \rangle} J \hat{S}_i \hat{S}_j, \quad (1)$$

where the $\langle i,j \rangle$ symbol means that the summation is restricted to nearest-neighbor i and j magnetic centers with total spin moment S . The question addressed in this work concerns whether J contains two-body interactions only or if it is better regarded as an effective two-body parameter containing collective effects from the whole solid. We must point out that existence of collective effects in J is claimed mainly from intuition and has not been theoretically or experimentally proven.

Because ionic solids are extended systems, it is customary to investigate their electronic structure by using a solid-state approach, usually exploiting translational symmetry. Notice, that this approach cannot provide an answer to the above question because there is no way to separate the collective effects from the two-body interactions. From a purely *ab initio*, or first-principles, point of view of the theory of the electronic structure, these solid-state approaches are often based on modifications²⁻⁶ of the local-density approach (LDA). Without these modifications the LDA fails to describe the antiferromagnetic order of many compounds such as NiO or La_2CuO_4 .⁷ More recently, the periodic Hartree-Fock, in its unrestricted or spin-polarized version, has been applied to a variety of antiferromagnetic systems with, on first sight, a rather good agreement with experiment.^{8,9} An alternative approach, different albeit complimentary, is one based on the use of cluster models.¹⁰⁻¹⁸ By construction, the

cluster model permits one to investigate the importance of the collective effects. From a technical point of view, the main difference between periodic and local approaches lies in the way to estimate the instantaneous electron-electron interactions. Hence, while the former are constrained to the use of more or less approximate correlation (or exchange-correlation) functionals, the latter permits the use of more accurate computational algorithms, usually based on configuration interaction expansions, that can be systematically improved with only the limitation of the computer resources. This local approach has permitted one to understand the basic mechanisms involved in magnetic coupling although a fully quantitative answer has not yet been possible.^{11,12,16-18}

For three-dimensional (3D) magnetic systems such as KNiF_3 and NiO , the *ab initio* cluster model approach has been applied to the computation of the magnetic coupling constant, J , and been able to explain roughly 50% of the experimental value even after explicit inclusion of electronic correlation effects.^{11-14,17,18} However, for a two-dimensional (2D) magnetic system such as La_2CuO_4 the same approach permits one to obtain a much larger fraction ($\approx 80\%$) of the experimental value.¹⁶ In all cases, part of the remaining difference with respect to the experimental value has been attributed to the collective effects that might be included in J [Eq. (1)]. Notice that for these systems the restriction on the summation in Eq. (1) to nearest neighbors only is well supported from experiments.¹⁹⁻²⁶ In previous work, existence of collective effects was proposed from a cluster model containing more than two magnetic centers, but with a crude representation of the surroundings.¹¹ Later, *ab initio* UHF periodic calculations on KNiF_3 and K_2NiF_4 reported values of about 66% of experiment, considerably larger than those obtained by the cluster model approach, and what is more surprising, without explicit consideration of electronic correlation effects.^{8,9} These values appeared to provide further support for the existence of collective effects. However, in a very recent study Moreira and Illas have shown that, for KNiF_3 and K_2NiF_4 , the agreement between periodic and cluster

UHF calculations was almost complete¹⁸ because the J values calculated within the periodic approach reported in Refs. 8 and 9 used two different definitions of the Heisenberg Hamiltonian for theory and experiment, a constant factor of 2 being missing. The fact that, within the same *ab initio* computational approach, cluster and periodic calculations conducts to the same calculated J value for these two different Ni compounds is against the proposal that collective effects are responsible for a large fraction of the experimental magnetic coupling constant. Moreover, *ab initio* cluster model calculations on K_2NiF_4 similar to those previously reported for KNiF_3 yielded a similar description of J , only about 50% of the experimental J was recovered. This result is quite surprising since K_2NiF_4 is best described as a 2D magnetic system and, if the collective effect were to play an important role, one would expect a result closer to experiment as for La_2CuO_4 .^{10,15,16}

In order to have conclusive answers on the role of collective effects we present here state-of-the-art *ab initio* calculations for different cluster models representing KNiF_3 , K_2NiF_4 , NiO (all with formal Ni^{2+} cations in a d^8 configuration) and La_2CuO_4 (with Cu^{2+} cations in a d^9 configuration). First, we will present results for models with two magnetic centers only. These results have been obtained at a very high level of theory, not available for larger cluster models. Next, we compare the J values for two and many magnetic center cluster models. In this case special care has been taken that the *ab initio* methods applied permit an equivalent description for all cluster models. Now, J contains either interactions from two magnetic centers only or explicitly includes effects arising from many magnetic center interactions. Comparison between the two sets of results will provide a direct answer about the role of collective effects.

For all systems, we define a local region which contains the nuclei and electrons that are explicitly treated and an outer, or embedding, region defined by an array of total ion potentials (TIP's) and point charges (PC's) placed at the bulk ion sites. TIP's account for the finite size of the cations closer to the local region and prevent artificial polarization of the ligand anions and PC's are added to have a good representation of the long-range Madelung potential. For KNiF_3 and K_2NiF_4 , the local regions are Ni_2F_{11} , Ni_3F_{16} , and Ni_4F_{20} cluster models where each magnetic center has its proper bulk coordination (Fig. 1). For La_2CuO_4 , we use Cu_2O_{11} and Cu_2O_7 for the two magnetic center models and Cu_3O_{10} and Cu_5O_{16} models for the many magnetic center models. Notice that Cu_2O_7 , Cu_3O_{10} , and Cu_5O_{16} contain in-plane oxygen atoms only; as shown recently apical oxygen makes only a tiny contribution to J .¹⁶ Finally, the NiO , the local regions are simply Ni_2O_{11} and Ni_3O_{16} .

Once the cluster models are defined, we obtain J by a suitable mapping of the eigenstates of exact nonrelativistic and Heisenberg Hamiltonians.^{11–18} For the exact nonrelativistic Hamiltonian we obtain reasonable estimates of the proper eigenstates and eigenvalues using a multireference zeroth-order wave function and by explicitly accounting for external correlation effects with difference dedicated CI (Ref. 27) (DDCI), and/or multireference second-order perturbation theory²⁸ for the pertinent spin states. In these calculations, the reference space is defined by the eigenfunctions of a complete active space configuration interaction (CASCI)

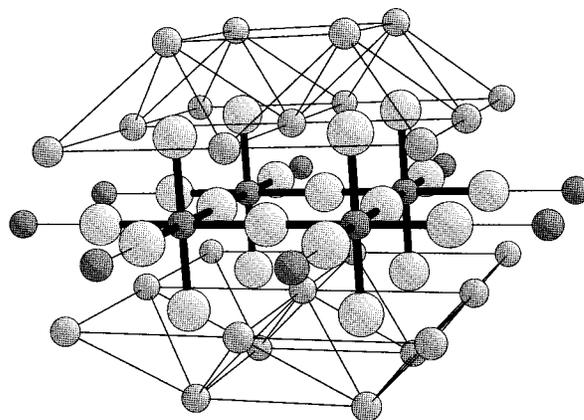


FIG. 1. Schematic representation of the Ni_4F_{20} cluster model used to represent K_2NiF_4 . Also shown are the total ion potentials for the nearest K^+ and Ni^{2+} cations surrounding the Ni_4F_{20} cluster. Thick lines link cluster atoms while thin lines link cluster atoms to TIP's; small dark spheres represent Ni^{2+} , small light spheres K^+ , and large spheres F^- anions.

expansion. The active space consists of the cation open shells, or magnetic orbitals, with their corresponding electrons. Hence, for Ni compounds, the magnetic orbitals are d_{z^2} and $d_{x^2-y^2}$ and, for both Ni_4F_{20} clusters, the CAS contains 8 electrons in 8 orbitals whereas for both Ni_3F_{16} and Ni_3O_{16} it contains 6 electrons in 6 orbitals. Likewise, in the case of La_2CuO_4 there is one $d_{x^2-y^2}$ magnetic orbital per center and, for Cu_5O_{16} , the CAS has 5 electrons in 5 orbitals. The CASCI eigenfunctions are expansions of Slater determinants built up of molecular orbitals (MO's) which in turn are expressed as a linear combination of Gaussian-type atomic basis functions. The MO's are obtained from a spin-restricted open-shell Hartree-Fock calculation on the highest spin state. The external correlation, out of the CAS, is accounted for by exploiting the ideas of quasidgenerate perturbation theory (QDPT) and taking the CAS as model space. In this case the off-diagonal elements of the second-order effective Hamiltonian, $\hat{\mathcal{H}}_{I,J}^{\text{eff}(2)}$, take the following form:

$$\hat{\mathcal{H}}_{I,J}^{\text{eff}(2)} = \sum_{I,J \in \text{CAS}} \sum_{K \notin \text{CAS}} \frac{\langle I | \hat{\mathcal{H}} | K \rangle \langle K | \hat{\mathcal{H}} | J \rangle}{E_K^0 - E_J^0} \quad (2)$$

and the $|K\rangle$ determinants are single and double excitations from the CAS determinants. Depending on the number of differences in holes and particles with respect to those in the CAS, the $|K\rangle$ determinants may have two, three, or four degrees of freedom.²⁷ In the DDCI, the $|K\rangle$ determinants with two degrees of freedom are treated up to infinite order. This is because these determinants are the ones with the largest contribution to the energy difference between the eigenvalues of the second-order effective Hamiltonian.²⁷ In the present work, for the clusters with two magnetic centers, the external correlation is included in two parts. The determinants with two degrees of freedom are treated up to infinite order through DDCI and the rest of the terms in Eq. (2) by second-order perturbation theory. These calculations are carried out at the all-electron level using large basis sets (series A). For the larger clusters, the external correlation is always included up to second order. Moreover, the core electrons are

TABLE I. Calculated and experimental J values for different compounds extracted from different cluster models. Series A refers to the all electron calculations on the two magnetic center models whereas series B corresponds to the pseudopotential description of two and many magnetic center models.

Compound	Model	J (meV)	
		Series A	Series B
KNiF ₃	Ni ₂ F ₁₁	-6.1	-3.8
	Ni ₃ F ₁₆		-3.9
	Ni ₄ F ₂₀		-4.0
Expt (Refs. 19–21)			-7.7
K ₂ NiF ₄	Ni ₂ F ₁₁	-6.6	-4.1
	Ni ₃ F ₁₆		-4.4
	Ni ₄ F ₂₀		-4.3
Expt (Refs. 19–21)			-8.6
La ₂ CuO ₄	Cu ₂ O ₁₁	-100.1	-88.4
	Cu ₂ O ₇		-92.4
	Cu ₃ O ₁₅		-96.6
	Cu ₅ O ₂₀		-95.1
Expt (Refs. 22–25)			-120.0
NiO	Ni ₂ O ₁₁	-10.6	-7.8
	Ni ₃ O ₁₆		-8.1
Expt. (Ref. 26)			-19.8

replaced by a suitable pseudopotential (series B). Results for the two magnetic center model have also been carried out at this level for comparison purposes. Further technical details on basis set, pseudopotentials, and embedding can be found in Refs. 12, 14, and 16–18.

In Table I we present a brief summary of results for the different systems described above. First, we discuss the *ab initio* all-electron calculations for the cluster models with two magnetic centers (series A). In all cases, agreement with experiment is quite impressive. This is an important point given the very small energy differences involved and show the level of accuracy of the *ab initio* methods used in the present approach. Now, we come to the key point of this work. This concerns the origin of the difference between calculated and experimental results. It may be due to limitations of the computational approach: the requirement to include higher orders in the treatment of external correlation and the need to enlarge the active space, or to the limitations on the cluster model approach: the necessity to include more magnetic centers. At present it is hardly possible to go beyond the level of accuracy given by series A but we may investigate the limitations of this cluster model approach by considering the results for many magnetic center models. For the four materials and the different clusters, the general trend is the same; namely, that the calculated value of J (series B) is found to be almost independent of the number of magnetic centers explicitly included in the *ab initio* computational model. Given the fact that the systems chosen to carry

out this study are very different, this is a highly surprising result. In fact, it holds for the KNiF₃ and K₂NiF₄ perovskites, 3D and 2D magnetic systems, but where the proper coordination of each cation is essential to describe the magnetic interaction. This is because the magnetic orbitals d_{z^2} and $d_{x^2-y^2}$ are both directed straight towards the anions. Thus, the presence of the ligands influences the spatial extent of the magnetic orbitals and hence the magnetic moment and the magnetic coupling constant. This strong influence of the ligands permits one to understand why a simpler Ni₄F₄ cluster model, where the cations did not have the proper environment, led to a J value larger than that for a Ni₂F model and seemed to provide an argument for the existence of collective effects. Clearly this was an arbitrary, unexpected, cluster artifact. We must point out that, although not given in the table, the results corresponding to the CASCI wave function (which include essentially the terms arising from Anderson superexchange mechanism) exhibit the same trend. The calculated J values are, of course, smaller but they do not evidence any dependence with respect to the number of magnetic centers.

The conclusion of this work can be summarized in a very concise way. Upon consideration of the correct mapping between spin eigenstates of the Heisenberg and using a reliable *ab initio* representation of those of the exact nonrelativistic Hamiltonian, for cluster models with two or more magnetic centers it is possible to obtain a reasonable estimate of the magnetic coupling constant J and to investigate the possible existence of collective effects. Surprisingly enough, the J value obtained from clusters with two magnetic centers is about the same as obtained when more magnetic centers are explicitly included in the model. This is found to be the case for four different materials with fairly different physical and chemical properties. Previous attempts to proclaim the existence of collective effects have been found to arise from cluster artifacts or from an improper comparison between calculated and experimental results (see Ref. 18). The absence of collective effects in the magnetic coupling constant found for KNiF₃, K₂NiF₄, NiO, and La₂CuO₄ strongly suggests that the magnetic interactions in this kind of narrow band systems are genuine local and entangle only the two magnetic centers involved.

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