Towards an *Ab Initio* Description of Magnetism in Ionic Solids

F. Illas,[1] J. Casanovas,[1] M. A. García-Bach,[2] R. Caballol,[3] and O. Castell[3]

[1]*Departament Química Física, Universitat de Barcelona, C/Martí i Franquès 1, 08028 Barcelona, Spain*
[2]*Departament Física Fonamental, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*
[3]*Departament Química, Universitat Rovira i Virgili, Pça. Imperial Tarraco 1, 43005 Tarragona, Spain*
(Received 14 June 1993)

The physical contributions to the $KNiF_3$ magnetic exchange coupling integral have been obtained from specially designed *ab initio* cluster model calculations. Three important mechanisms have been identified. These are the delocalization of the magnetic orbitals into the anion "p" band, the variational contribution of the second-order interactions, and the many-body terms "hidden" in the two-body operator of the Heisenberg Hamiltonian.

Magnetic properties of ionic solids have experienced a renewed interest due to the discovery of high-T_c superconductors [1,2]. A relationship between magnetism and superconductivity arises from the new superconductor mother compounds, such as La_2CuO_4, which are antiferromagnetic insulators close to the Mott transition [3]. From the point of view of theory, two approaches have been used. The first one is based on local spin-density calculations [4] whereas the second one uses simplified model Hamiltonians [5–7]. While highly desirable, a fully *ab initio* description has not been reported yet. The reason for this lack is that, in spite of the high degree of accuracy that can be achieved by the modern quantum chemistry, the problem of magnetism in solids is very difficult since it involves very small energy differences.

For molecular complexes, de Loth *et al.* [8] suggested a second-order nonempirical treatment based on the theory of effective Hamiltonians. A variational version of this procedure has been reported recently and generalized to different physical situations [9,10]. In principle, there is no reason why such theoretical approaches could not be applied to solids as well if a suitable model is used. This is the aim of the present work.

In a series of papers Malrieu and co-workers have used a magnetic model to study alkali metals, conjugated hydrocarbons, and related systems [11–14]. In this model the exchange coupling integral (J) is extracted from accurate calculations in simple models. The idea behind this approach is very attractive because it implies that the magnetic behavior of extended systems can be obtained from nonempirical model Hamiltonians with parameters extracted from accurate quantum chemical calculations on small models, usually dimers.

The aim of this work is to explore the magnetic structure of a simple ionic solid such as $KNiF_3$ using a parameter-free approach (see also Refs. [15,16]). We will use different cluster models for $KNiF_3$ and different *ab initio* wave functions to show that there are three main factors governing magnetism in $KNiF_3$. For the first time, we will quantify the importance of these contributions to the final coupling exchange constant.

The $KNiF_3$ cubic perovskite is known to be an excellent example of a simple nearest-neighbor exchange Heisenberg system. The spin Hamiltonian can be written simply as

$$\hat{H} = -\sum_{\langle ij\rangle} J\hat{S}_i\hat{S}_j , \tag{1}$$

where $\langle ij\rangle$ means that the summation in (1) is over all nearest-neighbor pairs i and j Ni^{2+} cations on $KNiF_3$ structure. Moreover, the ground state of Ni^{2+} in $KNiF_3$ is ^3F so each cation can be simply seen as a particle with a total spin angular momentum $S=1$.

If we consider only two Ni^{2+} cations the different spin rearrangements give rise to one singlet ($|S\rangle$), one triplet ($|T\rangle$), and one quintuplet ($|Q\rangle$) state. Since the three states do not mix, it is easy to show that $|S\rangle$, $|T\rangle$, and $|Q\rangle$ are eigenfunctions of the spin Hamiltonian (1) holding

$$\hat{H}|S\rangle = E_S|S\rangle = 2J|S\rangle ,$$

$$\hat{H}|T\rangle = E_T|T\rangle = J|T\rangle , \tag{2}$$

$$\hat{H}|Q\rangle = E_Q|Q\rangle = -J|Q\rangle .$$

Hence, the ground state is the antiferromagnetic coupling of the two spin cations and $E_S - E_T$ provides a way to estimate the value of the exchange coupling integral J, whereas $E_T - E_Q$ will be always $2J$. In this work we will use this Heisenberg picture to obtain J from *ab initio* calculations. In the above discussion it has been assumed that H contains only two-body operators or that any collective effect is also contained in J provided it is obtained from experiment. In order to explore in more detail the origin of J we suggest to use a model containing four Ni^{2+} cations in a square geometrical arrangement. The number of spin states involved in the coupling of four Ni^{2+} cations (each with $S=1$) is large: one state with $S=4$, three with $S=3$, six with $S=2$ and $S=1$, and three with $S=0$. Of these states, we are only interested in the ferromagnetic ($S=4, |F\rangle$) and the lowest singlet $|A\rangle$. While $|F\rangle$ is already an eigenvector of H, to obtain the spin eigenfunction $|A\rangle$ one can make use of the Clebsch-Gordan coefficients and diagonalize the matrix

representation of H. The final result is

$$\hat{H}|F\rangle = E_F|F\rangle = -4J|F\rangle ,$$

$$\hat{H}|A\rangle = E_A|A\rangle = +4.680188J|A\rangle ,$$

(3)

which tells us that $E_A - E_F = +8.680188J$ and permits a different way to obtain J from finite models.

We suggest using finite cluster models to obtain the different contributions to J. The first model contains explicitly two Ni^{2+} cations and their bridge F^- anion and will be denoted as Ni_2F (see Fig. 1). In the second model, we explicitly include the F^- anions surrounding each one of the Ni^{2+} cations, leading to the Ni_2F_{11} model. Finally, we use a cluster model containing explicitly four Ni^{2+} cations arranged in a square plus their four bridge anions. This Ni_4F_4 model is shown in Fig. 2. These models are embedded in an array of optimized point charges to explicitly include the Madelung potential [17].

Once the physical model is chosen, all we have to do is compute the electronic wave function for each one of the electronic states involved in the spin coupling in which we are interested. In this work, we use nonempirical pseudo-potentials to describe the inner cores of Ni and F atoms and a basis set of contracted Gaussian-type orbitals (CGTOs) to describe the $3d^8$ electrons of each Ni^{2+} cation and the $2s^2 2p^6$ of each F^- anion. The CGTO basis sets we use are rather large $(3s\,3p\,5d/2s\,2p\,3d)$ for each Ni^{2+} cation and $(5s\,5p\,1d/3s\,3p\,1d)$ for the bridge F^- anions. The embedding F^- anions have been described with a minimal basis set contraction of the preceding primitive GTO basis. We must point out that the quantities of interest $(E_S - E_T$ and $E_A - E_F)$ have been found to be rather insensitive to improvements in the GTO basis sets. For instance, results do not change upon inclusion of f functions on the Ni^{2+} cations or of a second polarization function on F^-.

Once the basis set of CGTOs is given, one must obtain the set of one-electron functions [i.e., molecular orbitals (MOs)] which will be used to construct the N-electron (or Slater determinants) basis in which the total wave function is expanded. There are several possible choices for the one-electron MO basis set. One can simply take orthogonal atomic orbitals (OAO) which correspond to the ab initio valence bond model recently reported [18], use MOs from a Hartree-Fock self-consistent field (SCF) calculation in the highest multiplet or those from a multiconfigurational self-consistent field (MCSCF) cal-

culation in the lowest state. It is also possible to analyze the effects introduced when going from the purely ab initio ionic model to the SCF functions by using the constrained space orbital variation (CSOV) method [19,20]. We have used all these possibilities but here will only report the most illustrative calculations.

When the MO basis set has been decided there is still a choice for the final form of the cluster wave function. In this work we use two kinds of wave functions. The first one is a full configuration interaction in a small limited orbital space; this is a complete active space configuration interaction (CASCI) wave function and is univocally defined once the orbital space (the CAS) has been defined. Our CAS contains only the open-shell magnetic orbitals. For the Ni_2F and Ni_2F_{11} cluster models there are four electrons in four orbitals (those arising from the e_g^2 electron configuration on each Ni^{2+} cation) giving rise to a final CASCI wave function containing 36 Slater determinants (if no symmetry is used). For the larger Ni_4F_4 model, the CAS contains 8 electrons in 8 orbitals leading to 1252 determinants. The CASCI wave function contains all physical effects in the CAS, such as kinetic exchange, but lacks many important situations involving simultaneous processes in magnetic centers and neighbor ions, as double spin polarization, charge transfer, or kinetic exchange polarization [8,21,22] which are only considered when correlation is included. The most significant of these missing interactions can be introduced by performing a specific configuration interaction (SCI) using the CAS as reference space but including only those configurations which contribute to the energy difference between the different spin states. If the CAS is taken as a model space one can use the framework of the quasidegenerate perturbation theory (QDPT) to construct an effective Hamiltonian which up to second order is

$$\langle \Phi_i | \hat{H}^{\text{eff}} | \Phi_j \rangle = \langle \Phi_i | \hat{H} | \Phi_j \rangle$$
$$+ \sum_{k \notin \text{CAS}} \frac{\langle \Phi_i | \hat{H} | k \rangle \langle k | \hat{H} | \Phi_j \rangle}{E_0 - E_k} , \quad i,j \in \text{CAS} .$$

(4)

Then, one can use diagrammatic many-body perturbation theory to demonstrate that only certain $|k\rangle$ determinants outside the CAS contribute to the energy difference between states belonging to the CAS [8,23,24]. In this
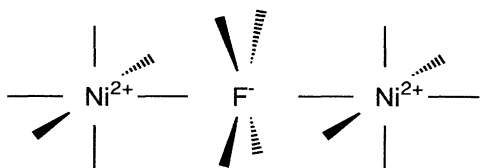

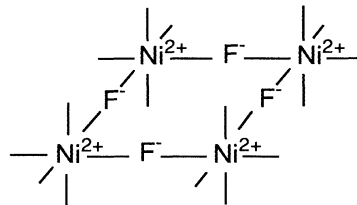FIG. 1. Schematic representation of the Ni_2F cluster model of $KNiF_3$.

FIG. 2. Schematic representation of the Ni_4F_4 cluster model of $KNiF_3$.

work we have generated all the determinants which contribute up to second order to the energy difference between the different states; the resulting list of determinants is variationally included in the final CI wave function (see [9,10]). In the Ni_2F cluster where no symmetry has been considered there are 57676 determinants in the differential space, in Ni_2F_{11} when the D_{2h} point group is specified there are 73664 or 73432 depending on the symmetry of the wave function of the considered space and for the Ni_4F_4 the number is so large that it cannot be handled with the present computer facilities. Results from this computational approach will be denoted as SCI(CAS).

Finally, we would like to point out that the beauty of *ab initio* calculations is that results are uniquely defined once the cluster geometry, basis sets, and pseudopotential parameters are specified. This information is available upon request to the authors.

Here we report results for the *ab initio* calculated exchange coupling integral J appearing in Eq. (1) and compare it with the experimental value reported by Lines [25]. From a set of complementary experimental techniques a value of $J = 89 \pm 4$ K was reported.

For the smallest Ni_2F model, if the starting orbitals are simply the OAO the CASCI result leads to the wrong conclusion that the ferromagnetic state is the lowest one although the energy difference between the three states is very small (see Table I). However, introduction of the second-order interactions correctly predicts the compound to be antiferromagnetic. Moreover, $E_T - E_Q$ is always twice $E_S - E_T$ as predicted by the Heisenberg picture. Indeed, this feature holds for all the forthcoming series of calculations reported here. Another interesting result appears if the CASCI wave functions are obtained using the SCF (for the $|Q\rangle$ state) or CASSCF (for the $|S\rangle$ state) MOs. In both cases $KNiF_3$ is predicted to be antiferromagnetic at the CASCI level with a considerable contribution to J from the SCI(CAS). The calculated value for J is, however, 4 times smaller than experiment. We must point out that within this cluster model we have

TABLE I. *Ab initio* CASCI and SCI(CAS) energy differences (in K) between the different spin states corresponding to two interacting Ni^{2+} cations. Notice that according to the Heisenberg picture $E_S - E_T = J$ whereas $E_T - E_Q = 2J$.

Cluster model	MO	Wave function	$E_S - E_T$	$E_T - E_Q$
Ni_2F	OAO	CASCI	1.3	2.2
		SCI(CAS)	−13.9	−26.5
	SCF	CASCI	−10.6	−21.3
		SCI(CAS)	−22.4	−44.8
	CASSCF	CASCI	−13.3	−26.5
		SCI(CAS)	−23.0	−46.4
Ni_2F_{11}	SCF	CASCI	−21.0	−42.2
		SCI(CAS)	−44.2	−89.0
	CASSCF	CASCI	−25.6	−50.8
		SCI(CAS)	−45.1	−92.2

been unable to improve the result by systematic improvement of the basis set. We have also considered the possibility of the superexchange interaction with the K^+ cations but without any improvement on J.

Now let us consider the more extended Ni_2F_{11} cluster model. In this case we find a dramatic effect already at the CASCI level, the calculated value being twice that of the smaller Ni_2F cluster. We have investigated the origin of this effect by performing the CASCI calculation with different sets of orbitals obtained at each step of the CSOV procedure. The result is also surprising: The J value is only affected when the magnetic orbitals are allowed to mix with the "p" band of the F_{11} unit. This physical effect is the delocalization of the magnetic orbitals. The correlation effects accounting for the second-order interactions are also enhanced due to the larger orbital space in which the SCI(CAS) is carried out. The final result for J is still too low by a factor of almost 2. It is difficult to see which are the lacking effects if only two interacting cations are considered. The contributions of the determinants appearing at higher orders might be important but we think this is unlikely to be the case.

In order to investigate the collective effects that may be "hidden" in the two-body J operator we have carried out CASCI calculations for the Ni_4F_4 cluster model, J being extracted from Eq. (3). The resulting value for J is 17.7 K which has to be compared with 10.6 K when the Ni_2F cluster model is considered at the same level of calculation. The fact that now each Ni^{2+} interacts directly with two other cations produces a 67% increase on the *ab initio* calculated J. This result shows the importance of collective effects in the magnetic behavior of $KNiF_3$ and precludes using two interacting atoms to derive the *ab initio* Heisenberg Hamiltonian.

Results for the Ni_2F and Ni_2F_{11} permit us to understand two basic contributions to the magnetic interaction. These are the differential correlation effects [see Eq. (4)] and the delocalization of the magnetic orbitals. Correlation effects are larger for the Ni_2F_{11} because the orbital space relevant to Eq. (4) is larger than for Ni_2F. Likewise, the effect of delocalization will be larger if a larger cluster is used. However, it is difficult to see how to improve the description obtained through the Ni_2F_{11} model without introducing more magnetic centers. It is important to see that these two factors already account for 50% of the total magnetic interaction. We have proven that the difference from the experimental J has its origin in the collective effects. The Ni_4F_4 cluster is probably too small and quantitative results will need a Ni_6F_6 cluster with a central cation having the proper magnetic coordination. However, it is unlikely that the physical mechanism arising from the present study will be changed.

In conclusion, for the first time *ab initio* techniques have been applied to understand the different physical contributions to the exchange coupling integral (J) involved in the Heisenberg Hamiltonian in ionic solids. By using a set of different cluster models we have been able

to identify three leading mechanisms contributing to J. These are the magnetic orbital delocalization into the anion "p" band, the correlation effects accounting for kinetic exchange and simultaneous processes involving both metal and neighbor ions, as charge transfer, double spin polarization, or kinetic exchange polarization, and the collective effects "hidden" in the two-body operator. The three contributions are important and can be reasonably estimated from well designed *ab initio* cluster model calculations.

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] A. Schilling, M. Cantoni, J. D. Guo, and H. R. Ott (to be published).

[3] N. F. Mott, Proc. Phys. Soc. **62**, 416 (1949).

[4] W. A. Pickett, Rev. Mod. Phys. **61**, 433 (1989).

[5] P. W. Anderson, Science **235**, 1196 (1987).

[6] T. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).

[7] J. Zaanen and G. A. Sawatzky, Can. J. Phys. **65**, 1262 (1987).

[8] Ph. de Loth, P. Cassoux, J. P. Daudey, and J. P. Malrieu, J. Am. Chem. Soc. **103**, 4007 (1981).

[9] J. Miralles, J. P. Daudey, and R. Caballol, Chem. Phys. Lett. **198**, 555 (1992).

[10] J. Miralles, O. Castell, R. Caballol, and J. P. Malrieu, Chem. Phys. (to be published).

[11] J. P. Malrieu and D. Maynau, J. Am. Chem. Soc. **104**, 3021 (1982).

[12] D. Maynau and J. P. Malrieu, J. Am. Chem. Soc. **104**, 3029 (1982).

[13] J. P. Malrieu, D. Maynau, and J. P. Daudey, Phys. Rev. B **30**, 1817 (1984).

[14] M. Said, D. Maynau, J. P. Malrieu, and M. A. García-Bach, J. Am. Chem. Soc. **106**, 571 (1984).

[15] A. J. W. Wachters and W. C. Nieuwpoort, in *Selected Topics in Molecular Physics*, edited by E. Clementy (Verlag-Chemie, Weinheim, 1972), pp. 135–142.

[16] R. L. Martin, J. Chem. Phys. **98**, 8691 (1993).

[17] C. Sousa, J. Casanovas, J. Rubio, and F. Illas, J. Comp. Chem. **14**, 680 (1993).

[18] A. Lorda, F. Illas, J. Fubio, and J. B. Torrance, Phys. Rev. B **47**, 6207 (1993).

[19] P. S. Bagus, K. Hermann, and C. W. Bauschlicher, J. Chem. Phys. **80**, 4378 (1984); **81**, 1966 (1984).

[20] P. S. Bagus and F. Illas, J. Chem. Phys. **96**, 8162 (1992).

[21] J. P. Daudey, Ph. de Loth, and J. P. Malrieu, in *Magneto-Structural Correlation in Exchange Coupled Systems*, edited by R. D. Willett et al. (D. Reidel, Dordrecht, 1985), pp. 87–104.

[22] M. F. Charlot, M. Verdaguer, Y. Journaux, Ph. de Loth, and J. P. Daudey, Inorg. Chem. **23**, 3802 (1984).

[23] J. P. Malrieu, J. Chem. Phys. **47**, 4555 (1967).

[24] O. Castell, R. Caballol, and J. P. Malrieu (to be published).

[25] M. E. Lines, Phys. Rev. **164**, 736 (1967).