***Ab initio* theoretical comparative study of magnetic coupling in KNiF_3 and K_2NiF_4**

Ibérico de P. R. Moreira and Francesc Illas

Departament de Química Física, Facultat de Química, Universitat de Barcelona, C/Martí i Franqués 1, 08028 Barcelona, Spain

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The origin of magnetic coupling in KNiF_3 and K_2NiF_4 is studied by means of an *ab initio* cluster model approach. By a detailed study of the mapping between eigenstates of the exact nonrelativistic and spin model Hamiltonians it is possible to obtain the magnetic coupling constant J and to compare *ab initio* cluster-model values with those resulting from *ab initio* periodic Hartree-Fock calculations. This comparison shows that J is strongly determined by two-body interactions; this is a surprising and unexpected result. The importance of the ligands surrounding the basic metal-ligand-metal interacting unit is reexamined by using two different partitions and the constrained space orbital variation method of analysis. This decomposition enables us to show that this effect is basically environmental. Finally, dynamical electronic correlation effects have found to be critical in determining the final value of the magnetic coupling constant. [S0163-1829(97)07707-2]

I. INTRODUCTION

The discovery of high- T_c superconductors has no doubt stimulated the research on the electronic structure, and related properties, of transition-metal ionic systems. Of particular interest are the magnetic properties because of the strong relationship between magnetic order and superconductivity.¹ Most of the high- T_c superconductor parent compounds exhibit antiferromagnetic order and the magnitude of the antiferromagnetic coupling constant J is much larger than that of isostructural related compounds. For instance, J is 120 meV in La_2CuO_4 ,²⁻⁵ while it is only ≈ 8 meV in the K_2NiF_4 isomorphous compound.⁶⁻⁸ On the other hand, K_2NiF_4 and KNiF_3 , which may be viewed as prototypes of two- and three-dimensional antiferromagnetic systems, respectively,⁶⁻⁸ exhibit J values that differ by ≈ 1 meV only. It seems logical to assume that these differences in antiferromagnetism arise from differences in the electronic structure. Hence theoretical studies should be able to provide answers to these scientifically provocative questions. Still, theoretical studies face difficulties because of the strong correlated nature and extended character of these compounds.

Since the magnetic coupling constant J is usually determined from experimental data with the help of a spin model Hamiltonian that involves two-body operators, several attempts have been made to compute J from a cluster-model representation of the extended system.⁹⁻¹⁸ A cluster model is also convenient because pure spin eigenstates can be easily handled. However, because of computational limitations, in both software and hardware, initial attempts were able to achieve an essentially qualitative description only.⁹ More recently, use of computational approaches that extensively introduce the instantaneous electron-electron interactions, or electronic correlation, has enabled a better, nearly quantitative, description. In some special cases such as La_2CuO_4 , a cluster-model approach including only two magnetic centers permits one to recover 80–90 % of the experimental value.^{10,15-17} However, in other systems such as KNiF_3 (Refs. 11–14) or NiO ,¹⁸ a similar approach is able to explain only roughly 50–60 % of the total magnetic interaction. Although these previous theoretical studies have enlightened

some important physical mechanisms of antiferromagnetism, the origin of the difference between calculated and experimental values is not completely understood. To explain the shortcoming of the cluster-model approach many factors have to be considered. Among others, we quote the possible role of collective effects implicit in the two-body effective operator of the Heisenberg Hamiltonian, insufficient inclusion of electronic correlation, or limited representation of the cluster environment.

At a first sight it may seem that band-theory calculations, which implicitly take into account the extended nature of the solid, may be able to provide a more accurate description than that offered by the cluster-model approach. However, band-structure calculations encounter another series of problems. First, we note that, in band theory, the computation of the magnetic coupling constant is carried out by comparing the energy of two unrestricted, or spin-polarized, Hartree-Fock (UHF) solutions. These solutions correspond to the ferromagnetic and antiferromagnetic phases, the latter being indeed a broken-symmetry solution obtained by doubling the unit cell. As is well known, the UHF wave functions are not eigenfunctions of the total square spin operator. Therefore, a mapping between UHF solutions and Heisenberg eigenstates is not convenient and other model spin Hamiltonians have to be used. Moreover, methods based on the local-density approximation (LDA) approach fail to appropriately describe these strongly correlated systems, which are often predicted to be metallic instead of insulators.¹⁹ It has been claimed that better results could be obtained by introducing corrections such as the self-interaction correction^{20,21} or on-site Coulomb repulsion²²⁻²⁴ U to the LDA formalism; however, the use of such approaches so far has been rather limited. An alternative approach is to use the periodic Hartree-Fock formalism, in its unrestricted or spin-polarized version, because exchange interactions are treated as nonlocal as in standard molecular calculations.²⁵ However, this approach completely neglects dynamical correlation effects, which are known to be very important in determining the actual magnitude of J , in a given system. In fact, recent periodic Hartree-Fock studies of both KNiF_3 (Ref. 26) and K_2NiF_4 (Ref. 27) perovskites

report values that are only 30% (Ref. 28) of the experimental values reported in Refs. 6–8.

In order to achieve a better understanding of the different factors determining the magnetic coupling in ionic solids, we present in this paper a detailed comparative theoretical *ab initio* study of antiferromagnetism in KNiF_3 and K_2NiF_4 . On the one hand, this comparative study will permit us to see whether the good value obtained for La_2CuO_4 using the cluster approach is due to its effective two-dimensional magnetic order or, on the contrary, KNiF_3 and K_2NiF_4 are found to behave similarly as suggested by the periodic Hartree-Fock calculations.^{26,27} On the other hand, the study of both perovskites will permit a direct comparison between cluster and periodic calculations. Such comparison will no doubt add more information about the adequacy of the cluster-model approach.

This paper is organized as follows. In Sec. II we explain the mapping between *ab initio* exact nonrelativistic and spin Hamiltonians; in particular we discuss the relationship between Heisenberg and Ising model Hamiltonians and how comparisons between model and *ab initio*, cluster or periodic, calculations should be carried out. In Sec. III we briefly report the cluster models used to represent KNiF_3 and K_2NiF_4 , while Sec. IV presents a short description of the computational details used in this work. Section V discloses the calculated results for both perovskites comparing the present cluster approach with previous periodic Hartree-Fock results reported in Refs. 26 and 27. Section VI presents an analysis of the role played by the ligands surrounding the magnetic centers. Finally, in Sec. VII we present our conclusions.

II. MAPPING EXACT AND MODEL HAMILTONIANS

To restrict this section to a minimum extent, while including the material necessary to understand the contents of this work and its relationship with previous periodic calculations, let us consider the particular case of two Ni^{2+} cations. We start by noting that the magnetic interaction of two Ni^{2+} cations can be simply considered as resulting from two particles of total spin $S=1$ (see also Refs. 11–14). In the Heisenberg approach the interaction of these two particles can be described by a model Hamiltonian that is usually written as

$$\hat{H} = -J\hat{S}_1\hat{S}_2, \quad (1)$$

where J is the magnetic coupling constant. With the present choice, a negative value of J in Eq. (1) means antiferromagnetic order and $\hat{S}_1, \hat{S}_2$ are the total spin operators for particles 1 and 2, respectively. Making use of the well-known ladder operators $\hat{S}_+, \hat{S}_-$, the above equation may be written as

$$\hat{H} = -J\left\{\frac{1}{2}(\hat{S}_+\hat{S}_- + \hat{S}_-\hat{S}_+) + \hat{S}_{z_1}\hat{S}_{z_2}\right\}, \quad (2)$$

where $\hat{S}_+ = \hat{S}_{+1} + \hat{S}_{+2}$, $\hat{S}_- = \hat{S}_{-1} + \hat{S}_{-2}$, and $\hat{S}_{+1}$ ($\hat{S}_{-1}$) are the spin-up (spin-down) operator for particle 1 and $\hat{S}_{z_1}, \hat{S}_{z_2}$ are the operators for the z component of spin for particles 1 and 2, respectively. As shown in previous work,^{11–14} the eigenfunctions of Eq. (1) for two particles of spin 1 are a singlet $|S\rangle$, a triplet $|T\rangle$, and a quintet $|Q\rangle$. In order to com-

pare with the periodic calculations we prefer here to denote these eigenfunctions also as $|S, M_S\rangle$, with S being the total resulting spin and M_S its z component. Obviously, there is a single eigenfunction for the singlet: $|S\rangle = |0,0\rangle$ at energy $2J$; three energy degenerate states at $E=J$ for the triplet, $|1,1\rangle$, $|1,0\rangle$, and $|1,-1\rangle$; and five degenerate states at $E=-J$ for the quintet, $|2,2\rangle$, $|2,1\rangle$, $|2,0\rangle$, $|2,-1\rangle$, and $|2,-2\rangle$.

Given the ionic nature of these materials,²⁹ in the *ab initio* cluster-model calculations, each of these two Ni^{2+} cations can be effectively regarded as a 3F state arising from the d^8 open-shell configuration. These two triplet states may be coupled singlet, triplet, and quintet and we see that there is a one-to-one mapping between the *ab initio* states and the eigenfunctions of the Heisenberg Hamiltonian given by Eq. (1) or (2). This one-to-one mapping is precisely what permits one to compute J from the energy difference from well-defined states. It is straightforward to show that, independently of the value of the M_S component, one has

$$E_{|S\rangle} - E_{|T\rangle} = J, \quad E_{|T\rangle} - E_{|Q\rangle} = 2J. \quad (3)$$

However, in the band-structure calculations the use of an UHF wave function, which is not an eigenfunction of the total square spin operator, does not allow the use of the mapping described above and other relationships have to be sought. In the recent periodic Hartree-Fock studies reported in Refs. 26 and 27. The authors make use of the Ising model Hamiltonian that results from neglecting the ladder operator terms in Eq. (2). For a two-particle system the Ising Hamiltonian is simply given by

$$\hat{H}^{\text{Ising}} = -J\hat{S}_{z_1}\hat{S}_{z_2}. \quad (4)$$

In order to compare cluster and periodic calculations it is necessary to find a mapping between electronic states representing approximate eigenfunctions of the exact nonrelativistic Hamiltonian and the eigenfunctions of the Ising model Hamiltonian. To this end let us first note that the eigenfunctions of the Heisenberg Hamiltonian (1) or (2) are not, in general, eigenfunctions of the Ising Hamiltonian given by Eq. (4). Moreover, different spin eigenfunctions that are degenerate with respect to either the exact or the Heisenberg Hamiltonian exhibit different expectation values for the Ising Hamiltonian. For instance, one has $\langle 20|\hat{H}^{\text{Ising}}|20\rangle = J/3$, and $\langle 22|\hat{H}^{\text{Ising}}|22\rangle = -J$, whereas for exact and Heisenberg Hamiltonians, $|20\rangle$ and $|22\rangle$ are obviously exactly degenerate. However, after some simple algebra it can be proved that some particular eigenfunctions of the Heisenberg Hamiltonian are also eigenfunctions of the Ising model Hamiltonian. In fact, it can be shown that

$$\hat{H}^{\text{Ising}}|22\rangle = -J|22\rangle, \quad \hat{H}^{\text{Ising}}|10\rangle = +J|10\rangle. \quad (5)$$

Now, let us inspect the $|22\rangle$ and $|10\rangle$ spin eigenfunctions more closely by recalling first that each $|SM_S\rangle$ originates by coupling $|S_1M_{S_1}\rangle$ and $|S_2M_{S_2}\rangle$ and may also be written as $|S_1S_2M_{S_1}M_{S_2}\rangle$. From the Clebsch-Gordan series we know that

$$|22\rangle = |11\rangle|11\rangle = |1111\rangle, \quad (6)$$

which simply shows that the eigenfunction corresponding to the highest eigenvalue of both the Heisenberg and Ising spin

models corresponds simply to an eigenstate that represents the ferromagnetic coupling of the two Ni^{2+} cations; hereafter we will use $|22\rangle$ and $|F\rangle$ as synonyms. Indeed, notice that for both model Hamiltonians the eigenvalue corresponding to the antiferromagnetic coupling is the same. Similarly, one finds that

$$\begin{aligned} |10\rangle &= \frac{1}{\sqrt{2}} \{ |11\rangle |1-1\rangle + |1-1\rangle |11\rangle \} \\ &= \frac{1}{\sqrt{2}} \{ |111-1\rangle + |1-111\rangle \}, \end{aligned} \quad (7)$$

which shows that the lowest root of the Ising model is precisely the symmetry-adapted combination of the two possible antiferromagnetic states resulting of reversing either the left- $|1-111\rangle$ or right- $|111-1\rangle$ hand side total spin of the given Ni^{2+} cation. We must stress the fact that, within this two-magnetic-center-cluster model, the antiferromagnetic state is a triplet. As in the previous case we will use either $|10\rangle$ or $|A\rangle$ to indicate the antiferromagnetic state.

The previous analysis shows that, if the appropriate spin states are chosen, a correspondence (not one-to-one) between Heisenberg and Ising models exists. Indeed, in the latter case, the energy difference between the ferromagnetic and antiferromagnetic spin arrangements is precisely twice the magnetic coupling constant J . In other words,

$$E_{|A\rangle} - E_{|F\rangle} = 2J. \quad (8)$$

Now it is important to see that the two states in Eq. (7) are degenerate and orthogonal. Therefore, one may think of using just one of the two components of the symmetry-adapted antiferromagnetic state, thus obtaining a broken-symmetry solution. This is precisely the basis of a method suggested earlier by Noodleman³⁰ and Noodleman and Davidson³¹ to deal with magnetic coupling in transition-metal dinuclear complexes. These authors have shown that for these transition-metal dimers, a relationship exists between the UHF solution for the ferromagnetic or high-spin state and a broken symmetry solution for the lowest value of the M_S quantum number that will lead to the antiferromagnetic coupling. According to these authors and using the definition of the Heisenberg Hamiltonian given by Eq. (1), one will have

$$E_{S_{\max}} - E_{\text{broken}} = -S_{\max}^2 \frac{J}{2}, \quad (9)$$

which in the present case will lead to

$$E_{S_{\max}} - E_{\text{broken}} = -2J, \quad (10)$$

where $S_{\max}$ is the maximum value of the total spin resulting from coupling S_1 and S_2 . It is obvious that the information in Eqs. (8) and (10) is exactly the same if spin-restricted orbitals are used. Notice, however, that we presently derived Eq. (8) from a completely different point of view and that our derivation of Eq. (8) or (10) does not need to assume an UHF wave function for the broken-symmetry solution. However, if spin contamination, inherent to the UHF procedure, is small, it can be appropriate to use the UHF broken-symmetry solution to represent the antiferromagnetic state. In that case,

the above discussion serves to illustrate how UHF broken-symmetry solutions can be compared to the proper spin eigenfunctions of the Ising Hamiltonian and also to the appropriate eigenfunctions of the Heisenberg Hamiltonian. Here we must point out that Eq. (9) differs by a factor 2 from the one reported in Refs. 30 and 31. This is due to the different choice of the Heisenberg Hamiltonian used by several authors. Given the fact that for two electrons in two degenerate orbitals (e.g., two atoms at $10r_e$) the singlet-triplet separation is twice the exchange integral, some authors prefer to write the expression (1) as

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 \quad (11)$$

and J in Eq. (2) is just half the value of that in Eq. (11). As we will show below, the existence of these two choices, Eqs. (1) and (11), is at the origin of some errors in the recent literature.

Now let us return to the Ising model, but assuming that instead of two interacting cations one needs to deal with an infinite solid. If we assume additivity of the two-body interactions and that each cation is interacting with z neighbors instead of one, Eq. (8) or (10) will reduce to

$$E_{|A\rangle} - E_{|F\rangle} = 2zJ, \quad (12)$$

which is precisely the equation used by Ricart *et al.*²⁶ and Dovesi *et al.*²⁷ in their periodic Hartree-Fock study of magnetic coupling in KNiF_3 and K_2NiF_4 . We must point out that Eq. (12) is consistent with the form (1) of the Heisenberg Hamiltonian. This point will be of importance in the forthcoming discussion when comparing cluster to periodic calculations. In particular, we will show that because of an improper comparison, the periodic Hartree-Fock results are barely similar to cluster results.

In this section we have shown that while a one-to-one mapping exists between the eigenstates (or suitable approximations) of exact nonrelativistic and Heisenberg Hamiltonians, such a mapping does not exist, in general, between either exact or Heisenberg and Ising Hamiltonians. However, a mapping between certain appropriate states of both exact or Heisenberg and Ising exists. This permits one to compare cluster and periodic calculations and, since the algebra involved in the Ising model is simpler than that of the Heisenberg Hamiltonian, it will also facilitate the calculation of J when clusters involving more than two magnetic centers are used.

III. CLUSTER MODELS FOR KNiF_3 AND K_2NiF_4

Both KNiF_3 and K_2NiF_4 have perovskitelike structure and exhibit antiferromagnetic order. The former crystallizes in a cubic structure where Ni cations are at the centers of the cube, F anions at the face centers, and K cations at the cube corners (Fig. 1), whereas K_2NiF_4 consists of Ni_2F layers separated by KF layers (Fig. 2). Moreover, KNiF_3 is a prototypical antiferromagnetic compound with nearest-neighbor interactions only. Hence KNiF_3 is ideal for a cluster-model study. Similarly, K_2NiF_4 is a model of two-dimensional magnetic order also with nearest-neighbor exchange interactions only. The minimum cluster representation of magnetic interaction for both compounds is Ni_2F embedded in an array of point charges to adequately provide the appropriate point

FIG. 1. Schematic representation of the KNiF_3 crystalline structure: small dark spheres represent Ni^{2+} , small light spheres K^+ cations, and large spheres F^- anions.

symmetry and the electrostatic or Madelung potential. However, previous work on KNiF_3 and other systems¹⁰⁻¹⁸ has shown that the F ligands surrounding each Ni cation play a very important role in determining the magnitude of the magnetic coupling constant and hence they have to be explicitly included in the model. This leads to Ni_2F_{11} cluster models for both compounds. This cluster is further embedded in an appropriate environment to represent the rest of the crystal. This environment consists of two well-defined different regions. In the first one, total ion potentials³² (TIP's) are used to represent the K^+ cations near the cluster atoms and also to represent the Ni^{2+} cations directly connected to the cluster anions. These TIP's have a charge of either +1 or +2 depending on whether K^+ or Ni^{2+} cations are represented. The second region of the environment consists of an array of point charges placed at the ion sites and using the experimental structure. The point charges are chosen to adequately represent the crystal Madelung potential; formal ionic charges of -1, +1, and +2 are used for all the ions represented by point charges except for those situated at the cluster edge, where the fractional charge method of Evjen³³ has been adopted in order to guarantee a good convergence for the truncated Madelung series.³⁴ Now it is easy to understand the need of the TIP's placed in the first region: They simply prevent an artificial polarization of the cluster anion electrons towards the nearest positive point charges.³⁵

Taking into account the previous discussion, we present the final cluster models used in this work to study magnetic

FIG. 2. Schematic representation of the K_2NiF_4 crystalline structure: small dark spheres represent Ni^{2+} , small light spheres K^+ cations, and large spheres F^- anions.

FIG. 3. Ni_2F_{11} -cluster model used to represent KNiF_3 . Also shown are the total ion potentials for the nearest K^+ and Ni^{2+} cations surrounding the Ni_2F_{11} cluster. Thick lines link cluster atoms, while thin lines link cluster atom to TIP's, small dark spheres represent Ni^{2+} , small light spheres K^+ cations, and large spheres F^- anions.

coupling in KNiF_3 and K_2NiF_4 . For KNiF_3 our cluster contains a total of 35 centers (Fig. 3), 13 atoms corresponding to the Ni_2F_{11} unit, which are explicitly treated, plus the TIP's representing the 12 K^+ and 10 Ni^{2+} cations nearest the Ni_2F_{11} unit. This 35-center cluster is further embedded in a total of 430 point charges as described above. A 35-center cluster, also having a central Ni_2F_{11} unit, is used for K_2NiF_4 as well (Fig. 4), but in this case there are 16 K^+ and 6 Ni^{2+} cations represented by TIP's plus a total of 1154 point charges.

IV. COMPUTATIONAL DETAILS

Ab initio cluster-model wave functions of increasing complexity were obtained to describe the electronic structure of the central Ni_2F_{11} unit of the KNiF_3 and K_2NiF_4 cluster models. In both cases, nonempirical pseudopotentials³⁶⁻³⁸ are

FIG. 4. Ni_2F_{11} 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_2F_{11} cluster. Thick lines link cluster atoms, while thin lines link cluster atom to TIP's; small dark spheres represent Ni^{2+} , small light spheres K^+ cations, and large spheres F^- anions.

used to represent the $[1s^2]$ and $[1s^22s^22p^63s^23p^6]$ inner cores of F and Ni, respectively. While recent work on NiO has shown that the use of pseudopotentials has some influence on the final calculated value of J , this influence is not crucial, especially in the present work where the main goal is a comparison of antiferromagnetism in two similar compounds using similar cluster models. The total number of electrons being explicitly treated is 104, 16 arising from the d^8 shell of each Ni^{2+} cation plus 88 from the $2s^22p^6$ of each F^- anion. Notice that the number of electrons corresponds to that of perfect ionic system. However, the wave functions chosen in this work to describe these valence electrons are flexible enough so as to represent any possible degree of covalence. Indeed, it has been shown that the covalent involvement in the bond is very small.^{25,26,29} Finally, we must point out that the final cluster models, including real atoms, TIP's, and point charges, are electrically neutral.

The cluster wave functions are obtained by making use of atomic basis sets expressed in terms of contracted Gaussian-type orbitals. These basis sets are as follows: for Ni we use a $(3s3p6d/2s2p3d)$ basis, for the bridge F anion at the bridge site the basis set is $(5s5p1d/3s3p1d)$, while for the remaining ligands we use a $(5s5p/2s2p)$ set. For the Ni_2F moiety the present basis is the same as that used in our previous studies,^{11–14,29} whereas that of the external ligands is now a double- ζ contraction of the primitive set, while it was a minimal basis set in the previous works. We must add that extensive work on the basis-set dependence¹² has shown that, beyond the present basis-set quality, calculated values for J are rather insensitive to basis-set improvements. Using these basis sets, a preliminary restricted open-shell Hartree-Fock self-consistent-field calculation is carried out on the quintet state to generate a set of molecular spin orbitals. The first type of wave function that we consider is a complete active space configuration interaction (CASCI) expansion. This CASCI contains all the Slater determinants that, using the molecular orbitals described above, can be built by distributing the active electrons in the active orbitals in all possible ways. As usual, the active orbitals are those corresponding to the partially filled d shell in each Ni^{2+} cation. In both compounds, the d manifold exhibits a crystal-field splitting leading to a filled t_2^6 and a half-filled e^2 shell. The active space is that formed by the four orbitals of e symmetry and contains four active electrons. As discussed in Sec. II, each of the two e^2 shell is locally a triplet, and both triplets can be coupled to quintet, triplet, and singlet. The CASCI description reproduces the so-called Anderson model,^{39,40} which indeed contains the necessary ingredients to obtain superexchange. However, the Anderson model neglects terms that involve excitations out of the complete active space (CAS). These excitations are generally referred to as external correlation, although it is possible to use the diagrammatic form of many-body perturbation theory to investigate the importance of the terms that are missing in the Anderson model. An exhaustive list of second-order diagrams was reported by de Loth *et al.* in their study of copper-diacetate complexes.^{41,42}

It is quite clear that improving the CASCI description requires one to further extend the configuration-interaction expansion. The simplest, manipulable, way to deal with such extended expansion is by using second-order perturbation theory and considering the quintet, triplet, and singlet

CASCI wave functions as zeroth-order wave functions. This second-order procedure involves all single and double excitations out of each occupied spin orbital in each Slater determinant in the CASCI wave function towards the virtual space. Among the different existing multireference second-order procedures we employ the one followed in the CIPSI algorithm, but using a CASCI wave function as reference.^{43–46} As in previous work,¹⁴ the second-order results will be indicated as CAS+2ND. Now we may note that many of the double excitations out of the CASCI contribute equally to the quintet, triplet, and singlet wave functions and hence do not improve the value of J that is obtained at the CASCI level.⁴⁷ This fact was exploited by Miralles *et al.* in deriving their difference dedicated configuration interaction (DDCI) method.^{48,49} The determinants used in the DDCI are *selected* as those that contribute to J , or the energy differences in Eq. (3), up to second order. We must stress that the DDCI method is not aimed at optimizing the energies of the individual quintet, triplet, and singlet states, but rather at giving, in a computationally efficient fashion, an accurate, correlated energy difference. Hence the determinants entering into the DDCI list are found following the arguments proposed by Miralles *et al.*^{48,49} This method has been successfully tested in a large variety of cases including difficult problems involving small energy differences arising from magnetic coupling in molecules^{50,51} and solids^{11–14,16,18} as well in intricate transition energies such as $10Dq$ in NiO .⁵² In the present paper we will compute J by including the effect of the determinants in the DDCI list either up to second order, CAS+S2ND, or variationally, DDCI. All calculations were carried out using the PSHF-CIPSI chain of programs, developed at the University of Toulouse, France; the University Rovira i Virgili, Tarragona, Spain; and the University of Barcelona, Spain.⁵³

V. MAGNETIC COUPLING IN KNiF_3 AND K_2NiF_4

We start this section by summarizing the experimental results for both KNiF_3 and K_2NiF_4 . Both exhibit antiferromagnetic order and, with the definitions of the spin Hamiltonians given by Eq. (1) or (4) in Sec. II, J is negative. For KNiF_3 the reported experimental value for J is -95 ± 7 K; for K_2NiF_4 the reported interval is -100 ± 4 K.^{6–8} As noted earlier, both compounds have similar values for J in spite of being prototypes of three- and two-dimensional antiferromagnetic order.

Calculated values for the magnetic coupling constant obtained using the Ni_2F_{11} cluster model for both KNiF_3 and K_2NiF_4 are reported in Table I at the various levels of theory described in Sec. IV. First, we note that the Anderson model of superexchange, reproduced at the CASCI level, effectively predicts the compounds to be antiferromagnetic. However, the CASCI value is, for both compounds, too small by a factor ~ 4 . In spite of the disagreement on the absolute value of the CASCI value for J , it is remarkable to realize that this simple model already predicts a value of J that is larger, in absolute value, for K_2NiF_4 than for KNiF_3 ; indeed the calculated ratio for J in the two compounds is very similar to the experimental one. The CASCI value is too small because, as pointed out by several authors,^{31,41,42} there are important physical mechanisms that are lacking in the

TABLE I. Calculated J between different electronic states corresponding to different spin couplings of the Ni_2F_{11} cluster model used to simulate KNiF_3 and K_2NiF_4 [see Eq. (3) and Sec. III]. Results are in K; 1 hartree=315 773.21 K.

Method	Compound			
	KNiF_3		K_2NiF_4	
	$E_S - E_T$	$(E_T - E_Q)/2$	$E_S - E_T$	$(E_T - E_Q)/2$
CASCI	-20.5	-20.5	-22.7	-22.8
CAS+2ND	-50.2	-50.2	-54.4	-54.8
CAS+S2ND	-45.5	-45.5	-49.5	-49.8
DDCI	-47.6	-48.0	-52.7	-52.2
Expt. value ^a	-95 ± 7		-100 ± 4	

^aReferences 6–8.

Anderson model. Those mechanisms are often referred to as ligand-spin polarization, dynamic spin polarization, double spin polarization, etc., and their names come from a detailed study of the second-order terms³¹ or diagrams^{41,42} involved in the second-order energy corrections, although higher-order terms may also be important. Here we will refer to these terms as external correlation and use the CAS+2ND, CAS+S2ND, and DDCI methods to explore its relative importance. Results in Table I show that these external correlation effects are very important, largely reducing the discrepancy between calculated and experimental values. The importance of external correlation can be understood from simple considerations based on the widely used Hubbard model Hamiltonian. It is well known that second-order perturbation theory on the Hubbard model shows that $J \approx t^2/U$, where t is the hopping integral and U the on-site Coulomb repulsion. In the Hartree-Fock, CASCI, or CAS self-consistent field approaches the estimate of the hopping integral is, in general, rather good. However, the on-site Coulomb repulsion, which can be roughly estimated as the energy difference between the ionization potential and the electron affinity on the atom, is too large unless orbital relaxation is included. These arguments have been numerically tested for La_2CuO_4 (Ref. 54) and it is very likely that the same arguments hold for the two nickel crystals studied in this work.⁵⁵ Since the CASCI wave function is invariant under unitary transformation, we may make our reasoning in terms of localized orbitals. In this localized framework the CASCI, or Anderson model, is nothing but the mixing of neutral and ionic valence bond components (see Ref. 48). The exceedingly large value of U resulting from the use of the same orbital set for all neutral and ionic valence-bond determinants does not allow an efficient mixing of ionic and neutral forms and hence the CASCI calculated J is too small. External correlation acts to lower the U determined from the Hartree-Fock orbitals and the final result is a much larger calculated value of J . The above arguments also explain the success of the approaches based on nonorthogonal configuration interaction (CI), where orbitals are optimized for each configuration entering into the CI expansion.^{15,17}

In spite of the large improvement over the CASCI result resulting from explicit inclusion of external correlation, the calculated value is only 50–60 % of the experimental value. Before trying to understand the origin of the remaining

calculated-experimental difference, it is worth noting that the three estimates of external correlation lead to almost identical values. This shows the effective cancellation of many second-order terms as predicted by Malrieu.⁴⁷ Also, the fact that CAS+S2ND and DDCI lead to nearly the same result means that the higher-order contribution arising from second-order terms is not important to determine the magnetic coupling constant of these highly ionic materials. If the difference between calculated and experimental results is due to incomplete evaluation of external correlation, it would be more appropriate to include third- and fourth-order terms than summing up the DDCI second-order terms up to infinite order.

In previous studies a small Ni_4F_4 four center cluster was also used to extract the magnetic coupling constant. Compared to the value resulting from Ni_2F , the Ni_4F_4 cluster showed a considerable increase on the calculated J . This was interpreted as the identifying characteristic of the collective effects hidden in the effective two-body operator of the Heisenberg, or Ising, model Hamiltonian and was used to justify the calculated-experimental difference remaining at the correlated level. This result, however, needs to be considered with caution because these small clusters lack the surrounding ligands that are found to have a very large effect on the calculated J value.^{11–14,16,18} Better conclusions could be extracted if calculations were carried out on a Ni_4F_{20} cluster model. However, this cluster is too large to be handled beyond the CASCI level with the present software capabilities and work is in progress to modify the computer codes to enable such a large, and important, calculation to be carried out. In this work we will investigate the role of collective effects indirectly by comparing the cluster-model results to the periodic Hartree-Fock calculations by Ricart *et al.*²⁶ and Dovesi *et al.*²⁷ From the UHF results for ferromagnetic and antiferromagnetic, doubling unit cell broken symmetry solutions and using Eq. (12), these authors report values of -29.8 K for KNiF_3 and -31.3 K for K_2NiF_4 . Unfortunately, these authors compare these calculated values with the experimental ones reported by de Jongh and co-workers,^{7,8} who uses the Heisenberg Hamiltonian in the form of Eq. (11). These lead to the erroneous conclusion that the periodic unrestricted Hartree-Fock calculations were able to account for ≈ 60 –65 % of the experimental result. Now, it is clear that the results from periodic unrestricted Hartree-Fock method are rather close to the CASCI results for Ni_2F_{11} and the small differences can be attributed to the differences between CASCI and UHF wave function. The closeness of cluster and periodic results seems to indicate that, contrary to previous beliefs, collective effects are not important in determining the magnetic coupling constant. This is a very important point and merits a more detailed analysis. Therefore, we proceeded to obtain *ab initio* unrestricted Hartree-Fock wave functions for the Ni_2F_{11} -cluster models of KNiF_3 and K_2NiF_4 . Hence we obtained UHF wave functions for the ferromagnetic and antiferromagnetic coupling; in the latter case a broken-symmetry solution was used. In order to make a meaningful comparison, an all-electron approach was used where the basis sets are similar to those used in the periodic calculations. We also used much larger basis sets, again with no noticeable effects on J . Using the UHF results and Eq. (10), we found values of J of -31.4 and -33.6 K for KNiF_3

and K_2NiF_4 , respectively. These results differ from the periodic ones by less than 5%. Considering that these differences are of the order of ≈ 3 K, the agreement is remarkable. This cluster-periodic model comparison seems to indicate that J is in fact a genuine two-body quantity. At first glance, the fact that cluster and periodic calculations lead to the same J may be surprising, but we note that it is also consistent with other findings from the periodic calculations. In fact, in the work of Ricart *et al.*²⁶ and Dovesi *et al.*²⁷ additivity of the magnetic interaction is assumed by using Eq. (12). Moreover, these authors use different unit cells to verify the hypothesis of additivity and the results do indeed support it. Now, notice that Eq. (12) simply shows that J scales linearly with the number of interacting magnetic centers, thus meaning that the same J will be obtained whether two or more centers are used. Calculations on other systems using as well cluster models containing more than two magnetic centers will help to settle this question. From the present study, we venture to predict, however, that clusters having two, three, or more magnetic centers will lead to the same J value.

Before ending this section we would like to stress the fact that the energy differences in Table I do in fact accurately follow the relationships given in Eq. (3). While this may seem to be a confirmation of the validity of the Heisenberg Hamiltonian, earlier phenomenologically proposed and later derived using very restrictive conditions, rather it is a test of the adequacy of the present models since from the earlier work of Nesbet^{57–59} it follows that two particles with spin S must indeed interact according to the Heisenberg Hamiltonian; a comprehensive and complete review on this topic has been given by Herring.⁶⁰

VI. ROLE OF LIGANDS REVISITED

Results in the preceding section strongly suggest that the magnetic coupling between Ni^{2+} cations in both KNiF_3 and K_2NiF_4 may in fact be described as a two-body interaction. Therefore, it is difficult to understand the importance of the ten ligands surrounding the basic unit Ni_2F containing the two interaction cations and the bridging ligand. In fact, previous work has shown that results from the Anderson, or CASCI, model in the Ni_2F cluster, embedded in an appropriate point charge array plus a representation of Ni^{2+} and K^+ as TIP's, gives roughly half the value obtained using the larger Ni_2F_{11} cluster. In the present work we have also used such a small Ni_2F cluster model for KNiF_3 and K_2NiF_4 and found the same behavior. The influence of the ligands was studied in previous works^{11–14,16} by making use of the constrained space orbital variation (CSOV) method.^{61–63} The CSOV approach permits one to obtain different sets of orbitals in which well-defined physical interactions are turned on or off, thus allowing one to study each effect separately. Starting with the molecular orbitals resulting from the superposition of the Hartree-Fock densities for Ni_2^{4+} and F_{11}^{11-} , each fragment in the appropriate environment of point charges, and TIP's resulting in a zero net charge, only a weak antiferromagnetic interaction is found. The introduction of intraunit polarization or interunit charge transfer involving closed shell orbitals does not modify the small value of J obtained using the frozen orbitals arising from the superposition of the charge density of both fragments. How-

ever, a large increase in the magnetic interaction is found when the open-shell magnetic orbitals of the Ni_2^{4+} unit are allowed to mix with the closed-shell orbitals of the F_{11}^{11-} unit; this is interpreted as the delocalization of the magnetic orbitals into the anion p band.^{11–14,16} Again, it is difficult to reconcile this effect with the apparent two-body nature of the interaction arising from the previous discussion. Although not reported here to avoid an exceedingly long paper, the complete set of results for the CSOV decomposition is available upon request to the authors.

In a recent study on the magnetic interaction on NiO , de Graaf *et al.*¹⁸ suggested that a different partition of the similar Ni_2O_{11} cluster can be used to further decompose the magnetic interaction, which helps to find the leading mechanisms. These authors suggested to start the CSOV decomposition from Ni_2O and O_{10} units. They found that the CASCI value for J obtained using the frozen molecular orbitals resulting from the superposition of the Hartree-Fock densities of both Ni_2O and O_{10} units was almost the same as that obtained using the fully relaxed Hartree-Fock orbitals obtained using the whole Ni_2O_{11} cluster. Therefore, we decided to carry out a similar study on the Ni_2F_{11} unit cluster models of KNiF_3 and K_2NiF_4 . Starting from the orbitals resulting from the superposition of the electronic Hartree-Fock densities of the Ni_2F and F_{10} units, the CASCI value for KNiF_3 and K_2NiF_4 is -18.4 and -20.2 K, respectively, to be compared with -20.5 and -22.8 K (Table I) corresponding to the Anderson model value obtained when using the fully relaxed Hartree-Fock orbitals. These results clearly show that delocalization of the magnetic orbitals is of rather local character; in fact, it appears to be already included in the Ni_2F unit. This result strongly suggests that a mechanism responsible for the magnetic interaction is precisely the bonding covalent contribution arising from the mixing of the magnetic orbitals and the orbitals of the bridging anion. In the cluster model, the effect of the remaining ligands is essentially environmental. A further indirect proof of this environmental effect can be obtained by recalling that K_2NiF_4 is best described as a two-dimensional system. This is because the F anions perpendicular to the NiF_2 planes are not involved in a direct antiferromagnetic interaction (see Fig. 2). Therefore, it would be possible to ignore these apical ligands and use a smaller Ni_2F_7 cluster with all the atoms in the same plane. However, it turns out that the calculated value for J , either at the CASCI or the correlated level, is much smaller than the value reported in Table I for the Ni_2F_{11} cluster. This is contrary to previous findings for La_2CuO_4 , where Cu_2O_7 and Cu_2O_{11} clusters give essentially the same result.¹⁶ The reason for these differences is easily understood by simply examining the space orientation of the magnetic orbitals. In La_2CuO_4 each Cu cluster may be thought of as a Cu^{2+} cation with a d^9 electronic configuration; the magnetic interaction arises then from the unfilled $d_{x^2-y^2}$ orbital that lies in the CuO plane. However, in K_2NiF_4 and also in KNiF_3 , the magnetic orbitals are $d_{x^2-y^2}$ and d_{z^2} ; $d_{x^2-y^2}$ is in the NiF plane, but d_{z^2} is perpendicular to it and hence very sensitive to environmental changes. This is a clear indication of the environmental role of the ligands not directly involved in a magnetic interaction. In addition, this is fully consistent with results in Sec. V, with the fact that cluster and periodic cal-

culations lead to the same results, and with the ideas of the superexchange mechanism.

VII. CONCLUSION

In this paper we used cluster models and sophisticated *ab initio* techniques to study the origin of magnetic coupling in two different ionic insulators KNiF_3 and K_2NiF_4 , representative of three- and two-dimensional antiferromagnetic systems. By a detailed study of the mapping between the appropriate eigenstates of exact nonrelativistic and model spin Hamiltonians it is possible to compare cluster-model results to experimental values and also to compare cluster model and periodic unrestricted, or spin-polarized, Hartree-Fock calculations. From these comparisons we learned that magnetic interactions in KNiF_3 and K_2NiF_4 have a similar origin. At the CASCI, or Anderson model, level the two compounds are predicted to be antiferromagnetic, in agreement with experimental evidence. Moreover, when properly compared, the CASCI cluster-model results appear to be very close to the periodic calculations results.^{26,27} That this coincidence is not fortuitous is clearly seen when comparing the UHF cluster-model results for the ferromagnetic and antiferromagnetic broken-symmetry solutions with those of the periodic UHF calculations; the calculated magnetic coupling constants resulting from both approaches are almost identical. This coincidence seems to indicate that the magnetic coupling is in fact a local, two-body interaction. Additional work on larger clusters, containing more magnetic centers and their corresponding ligands is needed to further prove this interpretation. From the present analysis we predict that different clusters will indeed lead to the same value for J .

However, in spite of the good agreement between cluster and periodic calculations, the value for J resulting from the Anderson models is only $\approx 25\%$ of the experimental value for both compounds. While in the periodic calculations it is hard to improve this result, the cluster model permits one to go beyond the Anderson model by simply using second-order perturbation theory or the difference dedicated configuration-interaction method described above. These methods are able to introduce the dynamical correlation effects that are lacking at the CASCI (or UHF) levels. In fact, the CASCI accounts for only a small part of the electronic correlation effects, the so-called left-right, or more properly nondynamical, correlation. Introduction of dynamical electronic correlation effect through either CAS+2ND, CAS+S2ND, or DDCI largely improves the calculated results, which are now $\approx 50\text{--}60\%$ of the experimental value. To explain the remaining difference with respect to experiment we must first point out that, according to the present work, J

appears to be dominated by two interactions. Therefore, the origin of the difference with respect to the experiment may reflect limitations of the present cluster-model approach. In fact, for a quantitative description, one limitation is the use of pseudopotentials to describe the metal-atom cores. Recent work on NiO (Ref. 18) has shown that although pseudopotential and all-electron calculations lead to similar results, the effect on J is noticeable. Another limitation arises from the representation of the cluster environment. The present analysis has shown that ligands not directly involved in a given superexchange interaction have a purely environmental effect. This effect is to determine the spatial extent of the magnetic orbitals and may need to be better represented. From the present and previous results, we know that the magnetic coupling constant is not very sensitive to the basis of the ligand. However, the spatial extent of the electron density of the ligands, and indirectly that of the magnetic orbitals, is affected by the representation of the remaining of the crystal as TIP's plus point charges. Finally, we must note that only second-order terms are included in CAS+2ND, CAS+S2ND, or DDCI. Given the important role of electron correlation effects, it is likely that some higher-order terms will be responsible for a noticeable part of the difference with respect to experiment.

In summary, a detailed comparison of *ab initio* cluster-model and periodic calculations show that the magnetic coupling constant is strongly determined by the two-body interaction. This is a surprising, unexpected result that can be further tested using cluster models, which explicitly include three or more metal magnetic centers; this project is currently being developed.⁵⁶ Also of importance is the effect of the ligands surrounding the basic metal-ligand-metal interacting unit. However, the alternative CSOV analysis used in this work has enabled us to show that this effect is basically environmental. Finally, we must stress the very large effect of electronic correlation in determining the final value of the magnetic coupling constant.

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