

Origin of magnetic coupling in La_2CuO_4

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The *ab initio* cluster model approach has been used to study the origin of the magnetic coupling in La_2CuO_4 and, also, its pressure dependence. Use of different cluster models and different *ab initio* wave functions permits the identification of the three leading mechanisms of magnetic coupling. These are the delocalization of the magnetic orbitals into the anion “*p*” band, the electronic correlation effects, and the collective effects hidden in the two-body operator of the Heisenberg Hamiltonian. The first two mechanisms are almost equally important and account for 80% of the experimental magnetic coupling constant value, the remaining 20% being due to the third effect. For the pressure dependence we predict $J \propto r^{-n}$ with $n \approx 8.4$ in agreement with experiment. Surprisingly enough these mechanisms are exactly the same previously found for KNiF_3 but with different contributions to the value of the magnetic coupling constant.

I. INTRODUCTION

The discovery of high- T_c cuprate superconductors has largely stimulated the study of their stoichiometric parent compounds. One of the main characteristics of these fascinating compounds is their large antiferromagnetic coupling. The experimental value for the magnetic coupling constant, J , of La_2CuO_4 is of ≈ 130 meV,¹⁻⁴ or about 14 times larger than that reported for the isostructural K_2NiF_4 crystal.⁵ The pressure dependence of J for La_2CuO_4 follows a $J \propto r^{-n}$ power law as in many other perovskite related compounds but with $n = 6.4 \pm 0.8$ (Ref. 6) whereas $n \approx 12$ has been reported for K_2NiF_4 and KNiF_3 .⁷

In spite of the large body of literature dealing with the electronic structure and magnetic order of La_2CuO_4 , the origin of the large J value and of its dependence with the pressure is still a matter of controversy. It is well known that the widely used standard local-density approximation (LDA) fails to reproduce the antiferromagnetic ground state of parent undoped materials.⁸ In the LDA framework, it is necessary to explicitly introduce some corrections to properly reproduce the antiferromagnetic ordering of La_2CuO_4 . Among the several possibilities we mention the self-interaction correction (SIC) either on cluster models⁹ or extended systems,¹⁰ and the so-called on-site Coulomb interaction U correction.¹¹⁻¹³ However, even after considering these corrections, the physical mechanism of antiferromagnetism is unclear. In fact, LDA+SIC or LDA+ U antiferromagnetic ground states are obtained by forcing a spin-polarized, or unrestricted Hartree-Fock, solution which is not an eigenfunction of the \hat{S}^2 spin operator. Moreover, the magnetic coupling constant J cannot be easily calculated and the comparison with experiment is done by considering the calculated magnetic moment which is, in turn, usually computed in a very poor way; i.e., as the difference between α and β d populations⁹ as obtained from the Mulliken population analysis. We must advert, however, that this population par-

titution is arbitrary and may lead to very unrealistic results.¹⁴

The difficulties encountered in the LDA approaches described above prompted many authors to model the electronic structure of La_2CuO_4 and related materials using model Hamiltonians. In these approaches the model Hamiltonian is usually written in second quantized form and only some terms are explicitly introduced. Among these models we can quote the well-known single-band Hubbard model or the three-band one introduced by Emery¹⁵ to explain the electronic structure of the high- T_c superconductors. These models have been widely used in solid state physics and, in particular, to describe the electronic structure of superconducting cuprates. A possible weak point of these models is that the parameters entering into the definition of the model Hamiltonian cannot be directly obtained from the model itself, and are usually estimated from experiment. In some cases, special limiting situations are considered to obtain analytical solutions for these model Hamiltonians. A detailed study of the three-band model in the “realistic” region of the parameters has been reported recently.¹⁶ In both, single-band and three-band models, perturbation theory is often used to obtain the magnetic coupling constant. In the first case, and up to second order, one obtains the $J = 4t^2/U$ expression corresponding to the original Anderson superexchange theory.¹⁷ Here t and U are the hopping integral and the on-site interaction parameters of the Hubbard model Hamiltonian. For the Emery model Eskes and Jefferson have carried perturbation theory up to fifth order.¹⁸ These authors claim that fourth order is not enough and suggest that the t_{pp} (or oxygen-oxygen hopping) term, appearing precisely at the fifth order, is responsible for a large part ($\sim \frac{2}{3}$) of the total exchange interaction. As commented above, the values of t and U (or t_{pp}) cannot be predicted by the Hamiltonian models approaches and their values constitute an external input to the theoretical model.

In contrast with the LDA (LDA+SIC or LDA+ U) or model Hamiltonian based approaches the traditional *ab initio*

methods of quantum chemistry (Hartree-Fock self-consistent field, single- or multiconfigurational, wave functions followed by a suitable configuration interaction expansion) are of general applicability to either atoms, molecules, clusters, or solids. The full electronic Hamiltonian is considered and all electrons (or all valence electrons) are explicitly contemplated. The second quantized form of the *ab initio* electronic Hamiltonian is, of course, very similar to that of the current model Hamiltonians. It contains a sum of one- and two-electron operators with matrix elements which, contrary to the model Hamiltonian approaches, are explicitly calculated with the aid of a finite basis set describing the atomic orbitals. It might be claimed that the basis set is again an external input. Notice that basis sets are also directly obtained from *ab initio* atomic calculations and they can be systematically improved with the only limitation being computer capability. Once all the integrals are calculated the eigenfunctions of the Hamiltonian are approximately obtained using variational or perturbational methods or both (See for instance Refs. 19 and 20). In other words, in the *ab initio* approaches there are no parameters external to the theoretical model and, more importantly, for a given problem they allow the identification of the leading physical terms and permit a theoretical estimate of the parameters entering into a possible model Hamiltonian. The power of such an approach to the study of extended systems has been shown in a series of recent works by Lepetit *et al.*^{21–25}

In the case of superconductor cuprates *ab initio* methods properly predict that in La_2CuO_4 the antiferromagnetic spin coupling is the lowest electronic state. Also, if a finite cluster model is used, they permit the direct calculation of J as the difference between calculated energies corresponding to different spin eigenstates. In fact, the *ab initio* cluster model approach was applied to La_2CuO_4 by Guo *et al.*²⁶ who used a $[\text{Cu}_2\text{O}_{11}]^{18-}$ cluster model surrounded by point charges and a generalized valence bond (GVB) *ab initio* wave function. The GVB calculations correctly predict La_2CuO_4 to be antiferromagnetically coupled and a J value of 36 meV. A similar approach and an identical cluster model has been used recently by Martin.^{27–29} The calculated value of J being 38 meV at the GVB level and 70 meV after explicit inclusion of electron correlation through a configuration interaction including all single and double excitations, i.e., a SDCI wave function. These results show the capability of the *ab initio* cluster model approach to properly predict the antiferromagnetic ground state of La_2CuO_4 and related materials. However, none of these works has explored the origin of the calculated J value.

The aim of this work is, precisely, a detailed investigation of the physical origin of antiferromagnetism in La_2CuO_4 . We will rely on theoretical techniques³⁰ and specifically designed first principles, or *ab initio*, cluster model wave functions, similar to those used in Refs. 30–33. These wave functions are based on the well-known configuration interaction (CI) approach. Our theoretical techniques permit us to separately investigate the different contributions to J and to identify the leading mechanisms of antiferromagnetic coupling. In particular, we will show that there is nothing mysterious in the antiferromagnetic coupling of La_2CuO_4 . Our theoretical analysis will univocally show that the leading terms are essentially the same as those that have been recently shown to

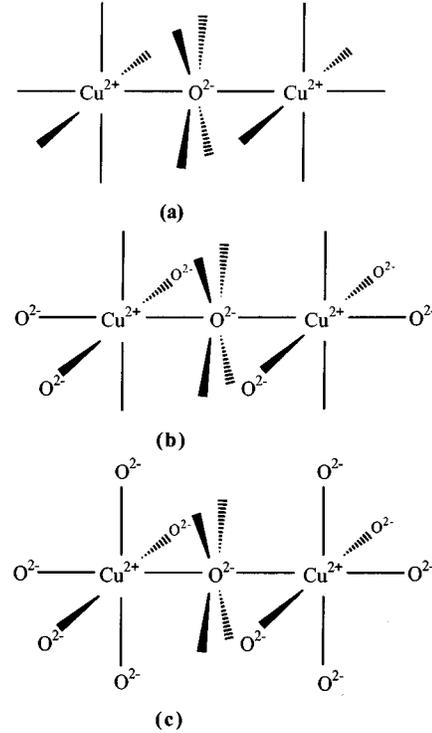


FIG. 1. Schematic representation of the (a) $[\text{Cu}_2\text{O}]^{2+}$, (b) $[\text{Cu}_2\text{O}_7]^{10-}$, and (c) $[\text{Cu}_2\text{O}_{11}]^{18-}$ cluster models of La_2CuO_4 .

originate antiferromagnetism in the much less fashioned KNiF_3 compound.^{30–33} Also, we will show that our approach allows us to predict a rather accurate value for the magnetic coupling constant and illustrate the quantitative importance of each physical effect.

II. CLUSTER MODELS AND COMPUTATIONAL DETAILS

To investigate the different contributions to the antiferromagnetic coupling in La_2CuO_4 we use three different finite cluster models and *ab initio* wave functions which explicitly include the instantaneous electron-electron interactions. These clusters have two metal atoms and differ in the number of ligands. The first cluster is $[\text{Cu}_2\text{O}]^{2+}$ and includes only the oxygen bridging the two magnetic centers. Our second model, $[\text{Cu}_2\text{O}_7]^{10-}$, adds all the oxygen atoms in the CuO_2 plane and finally, we consider the $[\text{Cu}_2\text{O}_{11}]^{18-}$ model, which also includes the apical oxygens. These clusters are further surrounded by an appropriate set of ≈ 700 point charges to account for the Madelung potential. A schematic representation of these models is given in Fig. 1.

The Cu and O atoms of the above described clusters are explicitly included in the *ab initio* calculations, each of the four La^{3+} cations surrounding the central oxygen are represented by a pseudopotential without basis set, and the number of electrons considered is that corresponding to the formal Cu^{2+} and O^{2-} ions. The three cluster models share the common characteristic of having two possible magnetic centers. In fact, for a fully ionic situation the electronic ground state of each Cu^{2+} cation corresponds to a d^9 configuration. Because of the crystal-field splitting, the hole is mainly located in the $d_{x^2-y^2}$ atomic orbital. Therefore, each Cu^{2+} cat-

ion can be considered as a particle with spin $S = \frac{1}{2}$.

In order to establish a link between the *ab initio* cluster model approach and the usual solid state physics approach let us now assume that the interaction of these two $\frac{1}{2}$ -spin particles can be modeled by a Heisenberg Hamiltonian,

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

It is easy to show that for the states with zero total S_z spin components there are two combinations that are eigenfunctions of \hat{H} and of the \hat{S}^2 spin operator. These two spin states have spin eigenvalues of 2 and 0 a.u., respectively. In the first case, the two $\frac{1}{2}$ -spin states have been ferromagnetically coupled through \hat{H} (and/or \hat{S}^2) and the corresponding state, $|T\rangle$, has triplet multiplicity. In the second case, the coupling is antiferromagnetic and the final state, $|S\rangle$, is a singlet. Moreover, one can readily show that

$$E(|S\rangle) - E(|T\rangle) = J. \quad (2)$$

If we now turn back to the *ab initio* cluster model approach we will realize that the magnetic coupling constant J corresponding to our cluster models is simply the energy difference between the cluster analogs of these two spin states (See Refs. 30–33). It must be adverted that covalence may change the above description (*vide infra*).

To compute J we first construct *ab initio* wave functions for the singlet and triplet states. Following the strategy used in our early study of antiferromagnetism in KNiF_3 (Refs. 30–33) we first obtain a set of one-electron functions, or molecular orbitals. This is done by performing a restricted open-shell Hartree-Fock (ROHF) calculation for the triplet state. The self-consistent field (SCF) ROHF wave function is obtained by using the LCAO approach in which the molecular orbitals are obtained as linear combinations of atomic orbitals which, in turn, are represented by a set of fixed Gaussian-type orbitals. Here, we use nonempirical pseudopotentials to describe the [Ar], [He], [Xe] cores of Cu, O, and La atoms, respectively. The valence orbitals of Cu have been described using a $[3s, 3p, 5d/2s, 2p, 3d]$ basis set. For the cluster central oxygen we use a $[6s, 6p, 1d/3s, 3p, 1d]$ basis set. For the remaining oxygens we use two different basis sets. The first one is a minimal basis set contraction of the $(6s, 6p)$ primitive set; this $[6s, 6p/1s, 1p]$ basis will be referred to as basis 1. In our previous study of magnetic interactions in KNiF_3 we have shown that increasing the basis set of noncentral ligands had a very small effect. However, it is well known that KNiF_3 is a highly ionic compound³³ while in La_2CuO_4 the situation is less clear. This prompted us to extend the ligands basis set to double- ζ quality in all the noncentral cluster oxygen atoms; this augmented $[6s, 6p/2s, 2p]$ basis will be referred to as basis 2. From the set of self-consistent one-electron functions corresponding to the triplet state complete active space configuration interaction wave functions (CASCI) are constructed for the triplet and for the singlet using the two combinations of the open-shell $d_{x^2-y^2}$ orbitals as active. We have to be precise in stressing that by construction the CASCI wave function is invariant with respect to any unitary transformation on the active orbitals, i.e., localized versus delocalized magnetic orbitals. Also, notice that the CASCI wave function already includes

a part of the electronic correlation energy; the so-called non-dynamical or internal correlation energy.^{34,35}

In the present case the CAS only involves two electrons in two active orbitals. Moreover, due to the D_{2h} symmetry point group exhibited by the different cluster models, the two active orbitals are the symmetric (a_{1g}) and antisymmetric (b_{1u}) combinations of the $d_{x^2-y^2}$ orbitals of each of the two Cu cluster atoms. Therefore, the CASCI contains four Slater determinants with total $S_z = 0$. These determinants may be indicated as

$$|\cdots(a_{1g}\alpha)(b_{1u}\beta)\rangle, \quad (3)$$

$$|\cdots(a_{1g}\beta)(b_{1u}\alpha)\rangle, \quad (4)$$

$$|\cdots(a_{1g}\alpha)(a_{1g}\beta)\rangle, \quad (5)$$

$$|\cdots(b_{1u}\alpha)(b_{1u}\beta)\rangle. \quad (6)$$

Now, notice that determinants (5) and (6) are of A_{1g} symmetry and can mix through configuration interaction (CI) leading to two singlet ${}^1A_{1g}$ states. It is rather simple to show that the lowest ${}^1A_{1g}$ state corresponds precisely to the antiferromagnetic coupling of the unpaired electrons. In fact, if the SCF a_{1g} and b_{1u} orbitals obtained for the triplet state are localized to near atomic $d_{x^2-y^2}$ orbitals on each Cu^{2+} cation, the lowest ${}^1A_{1g}$ state appears largely dominated by the “neutral” determinants with one unpaired electron on each cation and antiferromagnetically coupled. However, because of the configuration-interaction mixing it also contains the so-called “ionic” situations with ten d electrons in one Cu cluster atom and eight d electrons in the other one. This non-trivial CI mixing makes an important contribution to the magnetic coupling constant and it is the only way to describe the magnetic coupling in a delocalized, symmetry-adapted description. This is why Guo *et al.*²⁶ claim that restricted (closed-shell) Hartree-Fock wave functions; i.e., determinant (5) alone, is inadequate to study the magnetic coupling and the simplest description requires a two-configuration wave function [See also Ref. 29(b)]. Determinants (3) and (4) lead to ${}^1B_{1u}$ and ${}^3B_{1u}$ electronic states. The ${}^3B_{1u}$ state represents the ferromagnetic coupling of the two unpaired spins and, as commented above, is the one used to obtain the molecular orbitals. Therefore, the lowest ${}^1A_{1g}$ and the ${}^3B_{1u}$ states are precisely those to be used in Eq. (2) to obtain the magnetic coupling constant. Finally, notice that in a localized approach the highest ${}^1A_{1g}$ and the ${}^1B_{1u}$ states correspond to physical situations dominated by the “ionic” determinants.

Two different methods have been used to introduce electronic correlation effects not included in CASCI wave functions. In both cases we consider single and double excitations that contribute to the triplet-singlet energy difference up to the second order. A list of all many-body diagrams contributing to the energy difference up to second order may be found in Ref. 36. In the first method, hereafter referred to as CAS+2nd, the terms entering into the second-order diagrammatic expansion of the triplet-singlet energy difference are evaluated perturbatively up to second order. In the second method, CAS+VAR, the contribution of these terms is taken into account up to infinite order, i.e., by diagonalization of the corresponding CI Hamiltonian matrix. It is important to note that, for Cu_2O_{11} , the total number of Slater de-

TABLE I. Calculated values of the magnetic coupling constant J (meV) for different cluster models and different levels of theory (see text).

Cluster model	Basis set	CASCI	CAS+2nd	CAS+VAR
Cu ₂ O	1	10.35	22.58	25.36
Cu ₂ O ₇	1	35.12	83.09	86.99
	2	33.87	88.73	91.21
Cu ₂ O ₁₁	1	34.18	84.14	93.39
	2	35.01	88.79	97.58

terminants generated by allowing all single and double excitations out of the CASCI reference wave function is of $\approx 8 \times 10^6$. However, use of diagrammatic techniques permits us to show that only $\approx 10^4$ contributes to the triplet-singlet energy difference. A detailed description of these theoretical approaches is given in Refs. 30–38.

III. RESULTS AND DISCUSSION

It is interesting to note that the singlet antiferromagnetic coupling is found to be the ground state for all cluster models and at all theoretical levels. A summary of the calculated J values obtained from the *ab initio* singlet and triplet energies and making use of Eq. (2) is reported in Table I. According to these results all the theoretical approaches employed in the present work are able to predict that La₂CuO₄ exhibits an antiferromagnetic ordering. However, in the forthcoming discussion we will show that the extent of antiferromagnetic coupling is very sensible to the level of computation.

First, let us consider the CASCI results. The fact that the J value for the Cu₂O₇ and Cu₂O₁₁ is very similar indicates that the main effect is due to the in-plane oxygen anions. Moreover, the value for the larger clusters is really different than that of the simplest Cu₂O one. This is a clear indication that at the CASCI level the J value is dominated by the delocalization of the active magnetic orbitals into the oxygen $2p$ band. To prove that this is the case we have computed the CASCI value of J of Cu₂O₁₁ using three different sets of orbitals (using basis 2). These sets of orbitals are sequentially obtained by using the constrained space orbital variation (CSOV) method.^{39–41} The CSOV method allows one to obtain the restricted open-shell Hartree-Fock (ROHF) calculation for the triplet state but with some artificial constraints. One may for instance prevent the covalent mixing or the intraunit polarization by switching some interactions on or off. To carry out a CSOV calculation one needs first the orbitals of two separate fragments. Here we consider the [Cu₂]⁴⁺ and [O₁₁]²²⁻ units and carry out separate Hartree-Fock calculations for each unit. For the Cu₂O₁₁ we then construct a first set of orbitals by simply superimposing the separately calculated Hartree-Fock electronic densities of the [Cu₂]⁴⁺ and [O₁₁]²²⁻ units. Notice that at this step there is no variational freedom, the orbitals are simply those of the two interacting units properly orthogonalized and are kept frozen. The resulting wave function, for the triplet state, corresponds to a fully ionic description where electrostatic attraction and Pauli repulsion is accounted for, but where no intraunit polarization nor interunit donation has occurred. We will refer to this wave function as the frozen orbital (FO) wave func-

tion. In the second set we start the variational process from the FO wave function and now allow the closed-shell orbitals of the two units to mix with each other and to the virtual orbitals but maintaining the two open-shell orbitals fixed as they are in the [Cu₂]⁴⁺ unit. This variation introduces both intraunit polarizations and interunit donations but, as mentioned above, does not allow the open-shell orbitals to vary. Notice that in the two sets of orbitals just described, the magnetic moment of each Cu²⁺ cation is forced, by construction, to be $1\mu_B$. To obtain the third set of orbitals we remove the remaining constraints of the variational process and the resulting wave function is simply the unconstrained ROHF one.

Using the three sets of orbitals described above we have constructed the CASCI wave functions and obtained the energies for the singlet and triplet states. The J values obtained from the different CASCI wave functions, corresponding to each orbital set, are 4.03, 4.43, and 35.01 meV. This result strongly suggests that one of the leading physical mechanisms of the magnetic coupling in La₂CuO₄ is precisely the delocalization of the magnetic orbitals. In terms of the Hubbard Hamiltonian this effect may be effectively included into the t hopping integral. It is worth pointing out that this result shows that the reduction of the magnetic moment from $1\mu_B$ to the experimentally measured value $0.4\mu_B$ (Ref. 42) is due to covalent mixing. This reduction is precisely responsible for the enhancement of the J value. This is in agreement with previous LDA+SIC calculations¹⁰ but here we can further identify the origin of this reduction and show that the existence of a magnetic moment in the cations is not enough to understand the magnitude of the magnetic coupling constant. The importance of delocalization into the oxygen p band has also been pointed out by several authors. For instance, according to model Hamiltonian approaches the large value for J is largely due to a large Cu-O hybridization.^{43,44} Our conclusion is on the line of these previous investigations but here it arises in a natural way; without any previous assumption. Moreover, the present approach permits us to quantify the importance of this Cu-O hybridization. If it is not taken into account that the compound is predicted to be antiferromagnetic but with $J \approx 5$ meV whereas covalent mixing of the magnetic orbitals with the p orbitals of the oxygen bridging the two copper ions leads to $J \approx 10$ meV and covalent mixing with all the oxygen neighbors leads to $J \approx 35$ meV. Also, we can see that only the oxygen ions in the Cu-O₂ planes are of importance. This fact has been generally assumed; the present *ab initio* cluster model calculations add further support to this interpretation.

The results discussed hitherto do not include the contribution of external electronic correlation to the magnetic coupling constant. This is because the complete active space does only include the two active orbitals and excitations either from the active orbitals to the virtual external space, from the inactive occupied to the external virtual space, or from the inactive occupied to the active space are not considered. However, second-order many-body perturbation theory shows that the excitations commented above contribute to the triplet-singlet energy difference and, hence, to the magnetic coupling constant.⁴⁵ These effects are explicitly considered in the CAS+2nd and CAS+VAR calculations. Results on Table I show that both, CAS+2nd and CAS

+VAR, largely improve the CASCI calculated J . These calculated values are about two times larger than those obtained from the CASCI wave function. This clearly shows that electronic correlation is a second physical mechanism which must be taken into account to properly describe J . At this level of theory the present values are in very good agreement with those reported by Martin using a very similar computational approach.^{27–29} Our best value is 97.6 meV to be compared with the 83 meV as reported by Martin.^{27–29}

The large effect of electronic correlation may also be understood in the framework of the Hubbard Hamiltonian. In fact, since in the Hubbard approach one finds $J=4t^2/U$, introduction of the electronic correlation will decrease the on-site U interaction which is overestimated at the Hartree-Fock level of theory, thus leading to a larger J . Our analyses also show that, if the CASCI is taken as a zero-order wave function, the second-order contributions are the leading terms. Here, we must point out that the importance of correlation has been pervading all the literature on the cuprate superconductors and one may wonder what is the novelty of the present result. Again, we emphasize that our approach allows us to quantify the importance of this physical mechanism from an *ab initio* point of view. In the study of the electronic structure of cuprates, correlation effects have been almost exclusively treated in the framework of model Hamiltonians.^{16,46,47} Our estimation of the importance of electronic correlation contribution to J is obtained from the exact nonrelativistic Hamiltonian and, therefore, without making reference to the importance of any term entering into the definition of the electronic Hamiltonian. In the present work, the terms explicitly considered are, of course, those already defined in Anderson's original work.¹⁷ Here we present a model to compute these terms from a first-principles-parameter-free point of view. The terms entering into the second-order energy difference may be represented by the habitual many-body perturbation theory diagrams. Use of diagrammatic techniques permits us to univocally find the appropriate second-order contributions.³⁶ The present *ab initio* approach enabled us to conclude that $\approx 50\%$ of the value of J is precisely due to the electronic correlation effects. This conclusion can hardly be obtained from a model Hamiltonian approach. Moreover, our approach may help to define the parameters entering into these Hamiltonians.

Using a computational model that explicitly includes the best possible description of both physical effects, magnetic orbital delocalization and electronic correlation, one obtains a J calculated value of 97.6 meV or $\approx 80\%$ of the experimental quantity. We must mention that our calculated value represents the best up-to-date *ab initio* estimation of J . Also, we notice that using similar cluster models and *ab initio* wave functions, the level of accuracy reached for La_2CuO_4 is much better than that reported for KNiF_3 . This is simply because La_2CuO_4 is effectively a two-dimensional (2D) magnetic system⁴⁸ whereas KNiF_3 exhibits a 3D magnetic ordering. The difference between our value and the experimental value can be assigned to the collective effects which are hidden in the two-body effective operator of the Heisenberg Hamiltonian. In fact, the Heisenberg picture contains only two-body operators where the real systems contain many body terms. Moreover, our model systems do not include the non-nearest-neighbor exchange interactions. Therefore, there

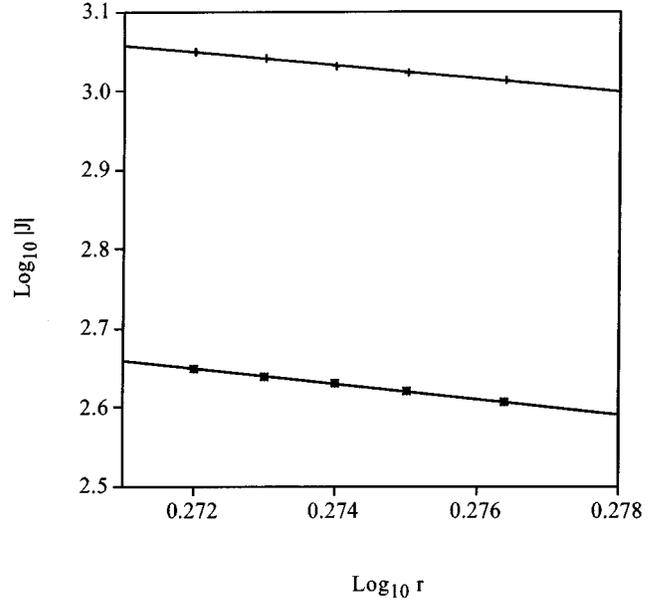


FIG. 2. Representation of $\log|J|$ versus $\log r$ for the Cu_2O_{11} cluster model as obtained from CASCI (*) and CAS+2nd (+) calculation.

are two effects that are missing in our models. These are precisely collective effects due to the fact that each magnetic center is interacting simultaneously with four in-plane magnetic centers and the next-nearest-neighbor exchange interactions. Previous results concerning antiferromagnetism in KNiF_3 (Refs. 30–32) and, also, semiempirical calculations on La_2CuO_4 (Ref. 49) suggest that two-center models are not enough for a quantitative description of J . The present *ab initio* results reinforce this idea.

The results presented so far indicate a close similarity between the mechanism of magnetic coupling in KNiF_3 and La_2CuO_4 . In order to further illustrate this point we will consider the variation of J with the external pressure. In the high-pressure Raman-scattering experiments of Aronson *et al.*⁶ a $J \approx r^{-n}$ relationship between the magnetic coupling constant J and the Cu-O distance r is proposed. This pressure dependence can also be simulated in the *ab initio* cluster model calculations by simply computing J for the Cu_2O_{11} cluster model at different values of the lattice parameters; in a range similar to that used in the experimental work. Following the experimental work we have plotted $\log J$ versus $\log r$ (Fig. 2). For both computational approaches, CASCI and CAS+2nd, the resulting plot is linear and the slope is $n \approx 9.7$ (CASCI) or 8.4 (CAS+2nd) whereas the experimental value is $5.6 < n < 7.2$.⁶ The calculated value is somehow larger but the important point is that the *ab initio* cluster model approach is able to predict a power law of the type $J \propto r^{-n}$ in agreement with experiment. The pressure dependence of J has been also briefly discussed by Eskes and Jefferson.¹⁸ These authors justify the experimental pressure dependence by using a fifth-order perturbation expansion of the Emery three-band model, assuming that only t_{pd} vary significantly with r , that $t_{pp} \approx t_{pd}^{2/3}$ and a given set of parameters. Once again, we must bring up the fact that the present approach permits us to predict the pressure dependence from an *ab initio* approach. Our model calculations also permit us to differentiate the n values corresponding to KNiF_3 and

La₂CuO₄. In fact, the calculated value for KNiF₃ was $n \approx 11.4$ (Ref. 50) against an experimental value of $n \approx 12$.⁷ This is an extremely important point because it shows that the same approach, with no empirical parameters and without any other modification, can be used to explain the different magnetic behavior of different compounds.

IV. CONCLUSIONS

The previous discussion has shown that the *ab initio* cluster model approach can be effectively used to gain understanding on the mechanism of magnetic coupling in ionic solids. According to the present approach there are two important mechanisms contributing to the large J value of La₂CuO₄. These are the covalent mixing of the magnetic orbitals into the anion “ p ” band and the external correlation effects involving simultaneous processes in the magnetic centers and neighbor ions, i.e., double-spin polarization, charge-transfer, or kinetic exchange polarization terms which are only included when the wave function goes beyond the CASCI approach. These two mechanisms have been found to almost equally contribute to the final calculated J value. The prominence of the two mechanisms has been recognized for a long time but the quantitative importance of each one was not previously known. Likewise, the pressure dependence of J has been analyzed and we have been able to show that, although many algebraic fits are possible, the experimental behavior may be deduced from *ab initio* considerations only,

the $J \approx r^{-n}$ experimental law appearing as a natural consequence of the electronic structure.

Also, we have shown that the physical origin of magnetism in KNiF₃ and La₂CuO₄ is essentially the same. The only important difference concerns the role of collective effects which is larger for KNiF₃ due to its three-dimensional magnetic behavior. In our opinion, the fact that the origin of magnetic coupling in these two compounds is so similar is an important conclusion which has not been recognized previously.

Finally, we would like to remark that the present *ab initio* approach is of general applicability. It may be used for any existing or hypothetical compound without any previous knowledge of its electronic structure or related properties. It permits the identification of the quantitative importance of different contributions to the magnetic coupling constant and may help to define *ab initio* parameters to be used in model Hamiltonian based approaches.

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