Ab Initio Study of the Magnetic Coupling in $Na_6Fe_2S_6$

Martin Mödl,[†,‡] Àngels Povill,[†] Jaime Rubio,[†] and Francesc Illas*[,†]

Departament de Química Física, Universitat de Barcelona, E-08028 Barcelona, Spain, and
Max-Planck-Institut für Physik komplexer Systeme, D-01308 Dresden, Germany

Received: June 18, 1996; In Final Form: October 14, 1996[⊗]

For the ternary thioferrate crystal $Na_6Fe_2S_6$, ab initio quantum chemical calculations using a cluster model ansatz have been performed to examine the magnetic coupling of the two half-filled Fe 3d shells in the isolated dimeric $[Fe_2S_6]^{6-}$ complexes having the structure of edge-linked double tetrahedra. The active-electron approach using complete active space configuration interaction (CASCI) with 10 electrons in 10 orbitals yields the multiplet splitting of a two-center Heisenberg Hamiltonian with an antiferromagnetic coupling constant $J = -19$ cm^{-1}, which is by a factor of 5 smaller than the experimental value. Correlation effects are essential for the magnetic coupling, as the application of multireference second-order Møller−Plesset perturbation theory based on the CIPSI algorithm (CAS-2nd) and the recently proposed difference-dedicated CI method lead to values $J(4\rightarrow5) = -158$ and -66 cm^{-1}, respectively, which clearly agree better with experiment. The different electronic contributions to the chemical bonding in the binuclear transition metal complex have been investigated using the constrained space orbital variation method.

1. Introduction

The theoretical investigation of magnetic interactions in ionic solids by means of rigorous ab initio calculations is an interesting and recent research field for quantum chemists. Often the energy difference between the electronic states involved in these interactions is very small (usually <1000 cm^{-1}) compared to other electronic energy scales, like the bonding energies, for example. Furthermore, instantaneous electron−electron interactions, or electronic correlation, play a crucial role in determining the magnitude of the magnetic coupling constant, and therefore high efforts and elaborate methods are necessary for the calculation of these small energy differences.

In the last years, Bronger and co-workers synthesized a series of thioferrates(III), all of them being composed of tetrahedral FeS_4 structural units. Depending on the stoichiometry, their structures range from isolated tetrahedral $[FeS_4]^{5-}$ anions[1] to one-dimensional $^{1}_{\infty}[FeS_{4/2}]$ chains of edge-linked tetrahedra.[2] An important link between Na_5FeS_4 with its isolated magnetic moments and $NaFeS_2$, a one-dimensional magnet, is made by the crystal $Na_6Fe_2S_6$, as it consists of isolated $[Fe_2S_6]^{6-}$ anions with two magnetic Fe centers.[3,4] For this reason the dimeric complex $[Fe_2S_6]^{6-}$, which has the structure of edge-linked double tetrahedra, is an interesting object of investigation to both experimentalists and theoretical chemists. X-ray diffraction studies have shown that the real geometry of the $[Fe_2S_6]^{6-}$ complex exhibits D_{2h} point group symmetry only approximately because the edge-linked double tetrahedra are slightly distorted from a regular D_{2h} structure. The six sulfur atoms occupy the corners and the two iron ions, each having a $3d^5$ configuration, the centers of the tetrahedra.

For the $[Fe_2S_6]^{6-}$ dimer both magnetic susceptibility measurements[5] and neutron scattering experiments[6] yield an antiferromagnetic coupling of the two Fe ions which can be described through a Heisenberg model Hamiltonian with a coupling constant of $J = -95$ cm^{-1}. In the framework of this model Hamiltonian, the two $3d^5$ cations give rise to a multiplet splitting between the singlet ground state $S = 0$ and the excited states with $S = 1, 2, 3, 4,$ and 5. In addition, from the magnetic susceptibility measurements, a local medium-spin state $S_i = {}^3/_2$ for the Fe ions has been deduced for the dimer (whereas the same authors have found a local high-spin state $S_i = {}^5/_2$ for the Fe ions in the monomer complex).

Previous studies on the $[Fe_2S_6]^{6-}$ dimer have used the semiempirical extended-Hückel approach[7] or the spin-unrestricted Hartree−Fock (UHF) method.[8] The UHF studies of magnetic coupling are based on the use of broken symmetry solutions, and dynamical electronic correlation effects are either neglected or approximately introduced by means of correlation functionals.[9] In spite of these limitations, rather good results have been obtained on polynuclear sulfur-bridged iron complexes.[10−14] However, Schmidtke et al.[8] could not report about the magnetic coupling constant in the dimer. This is probably because these simple studies do not treat the correlation effects thoroughly enough. Intensive quantum chemical studies for the monomer and the dimer have been performed by Mödl et al.[15,16] For the dimer $[Fe_2S_6]^{6-}$ the active-electron approach based on the complete active space self-consistent field (CASSCF) method with 10 active electrons and 10 active orbitals, performed with large basis sets of one-electron functions, leads to a significant deviation from the empirical Heisenberg Hamiltonian, as the coupling constants range from $J(4\rightarrow5) = -18$ cm^{-1} to $J(0\rightarrow1) = -28$ cm^{-1}. Furthermore an analysis of the CASSCF wave functions by expectation values of local operators has been presented[17] allowing for the calculation of the local spin state on either Fe site and for a discussion of interatomic and intraatomic correlation effects. It has been shown that the local spin configuration on both Fe ions is a high-spin state $S_{\rm i} = {}^5/_2$ and not a medium-spin state. Going beyond the active-electron approach, improved correlation calculations with MRCI and ACPF have been carried out by applying an approximation based on increments. This results in a coupling constant of $J(4\rightarrow5) = -65$ cm^{-1} (see ref 16).

As shown above and in many other examples, the active-electron approach is not able to yield quantitatively correct magnetic coupling constants. This is because important physical effects such as potential exchange, kinetic exchange, dynamic spin polarization, and charge transfer, as well as polarization of the ionic forms, are not included in the simple active electron

---

[†] Universitat de Barcelona.

[‡] Max-Planck-Institut.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

S1089-5639(96)01811-7 CCC: $14.00

approach. A complete list of the missing, up to second order, contributions have been reported by De Loth et al.[17,18] and Daudey et al.[19] The ab initio calculation of the magnetic coupling of two transition metal ions beyond the CASSCF approach becomes most complicated when both d shells are half-filled, which is the case for the complex $[Fe_2S_6]^{6-}$ as this gives rise to a huge number of determinants in the complete active space (CAS). Using the exact crystallographic atomic coordinates and hence C_1 point group symmetry, the singlet ground state is built by 63 504 determinants. As the deviation from the exact D_{2h} geometry is only small, a symmetrized cluster model can be considered. As has already been shown, the symmetrization of the cluster geometry has only weak influence on the electronic structure and, hence, on the magnetic coupling[16] but reduces the CAS for the ^1A_g ground state to only 7992 determinants. This is, however, a too large expansion to be used as reference space. Moreover, truncation or selection techniques cannot be applied because of the very small energy differences involved.

In the present work we have performed highly correlated calculations for the excited states $S = 3$, $S = 4$, and $S = 5$, by considering a specific subset of the single and double excitations on each determinant belonging to the CAS and allowing for excitations from all 24 valence orbitals of the sulfur ligands.

2. Computational Details

Due to the fact that the thioferrate complexes $[Fe_2S_6]^{6-}$ are isolated and well separated in the crystal, a cluster approach is doubtless appropriate and straightforward to model this system. This cluster model approach allows one to use molecular ab initio methods for the investigation of magnetic coupling in the bulk $Na_6Fe_2S_6$ system. In our calculations, we have considered one thioferrate anion $[Fe_2S_6]^{6-}$ as a cluster where the atoms are indeed treated by pseudopotentials and a finite basis set. For a correct embedding of the cluster in the crystal environment we have added 1040 point charges, which have been optimized to model the electrostatic Madelung field of the crystal. Since our calculations have only been feasible by exploiting the D_{2h} point group symmetry, we have used the D_{2h}-symmetrized geometry instead of the real C_1 symmetry of the complex. A more detailed description of the point charge optimization procedure and the D_{2h} symmetrization has been described in ref 16. A similar modeling of the crystal Madelung field by an array of optimized point charges has already been proposed by Illas et al.[20] Since only the thioferrate complex $[Fe_2S_6]^{6-}$ itself (and also the Madelung field) but not the remaining crystal atoms have nearly D_{2h} symmetry, it is not compatible with the use of D_{2h} symmetry to increase the cluster size and include the next-nearest Na ions to the cluster.

In our ab initio calculations we used the large-core pseudopotentials derived by Durand et al.[21−23] The pseudopotential for Fe was constructed from Fe^+ and previously used to study FeH and FeH^+ molecules[24,25] and the $Fe^+ + H_2$ potential energy surface.[26] We must remark that this Fe pseudopotential is derived from relativistic Dirac−Fock atomic calculations and, hence, scalar relativistic effects are included. For S we also use a pseudopotential of the form reported by Durand et al.[21−23] The (4s4p6d|3s2p3d) basis set for Fe is the one used in previous studies;[24−26] i.e., it is of valence-triple-ζ (VTZ) quality. The basis set for S is (4s4p1d|2s2p1d), which is a valence-double-ζ (VDZ) basis previously used in ref 27, but we have added a diffuse p function with exponent 0.03. With these two basis sets for Fe and S, the total dimension of the finite basis set for the $[Fe_2S_6]^{6-}$ cluster is 126 atomic orbitals (AOs). In a previous work[16] on the thioferrate crystal $Na_6Fe_2S_6$ we have shown that it is not the size of the basis set but the proper treatment of correlation which is crucial for a correct quantitative result of the magnetic coupling constant. The recent investigations by Illas et al. on $KNiF_3$ and La_2CuO_4 also confirm that the basis set is not the crucial part of the problem.[28,29]

The simplest model and a widely used ansatz in solid-state physics for the magnetic interaction of two localized spins $\vec{S}_1$ and $\vec{S}_2$ is the Heisenberg Hamiltonian

$$\mathbf{H} = -2J\vec{S}_1 \cdot \vec{S}_2 \tag{1}$$

where J is the magnetic coupling constant. This effective Hamiltonian was first derived by Heisenberg[30] and Dirac[31] assuming certain restrictions on the exchange integrals between orbitals on different atoms. Several attempts to remove some of these constraints were later carried out. In particular, we must quote the work of Nesbet[32] and Herring[33] which provided a basis for a broader validity of eq 1 (for a thorough review, see ref 34). We must finally mention that spin Hamiltonians can be deduced more rigorously using the quasi-degenerate perturbation theory (see ref 35 and references therein).

In the pioneering work of Nesbet,[36,37] it was already suggested that accurate ab initio calculations have to be able to predict J. For the two-center spin-only Hamiltonian in eq 1, the eigenvalues

$$E(S) = -J[S(S+1) - S_1(S_1+1) - S_2(S_2+1)] \tag{2}$$

are immediately expressed by the total spin quantum number $S = |S_1 - S_2|, ..., |S_1 + S_2|$ as $\mathbf{H}$ is already diagonal in the eigenfunctions to $\vec{S}^2$ and $\vec{S} = \vec{S}_1 + \vec{S}_2$ holds. From this follows the Landé interval rule $E(S) - E(S-1) = 2JS$ for the multiplet splitting of the two coupled spins. Establishing a link to our ab initio calculations, the Landé rule serves us as a definition of $J(S-1 \rightarrow S)$ for arbitrary multiplet energies $E(S)$.

As has already been shown[16] and is reconfirmed by our calculations, both Fe ions carry a local high-spin $S_i = {}^5/_2$, which is expected from Hund's rule although it strictly applies to the ground state of free ions only and not to ions in a crystal field. In our ab initio approach for the investigation of magnetic coupling we start, following a widely used strategy, from the ferromagnetically coupled state $S = 5$ of a spin-restricted open-shell Hartree−Fock (ROHF) calculation. This one-determinant wave function consists of 10 singly occupied molecular orbitals (MOs) which are seen to be linear combinations of mainly 3d atomic orbitals with a small mixture of ligand 3s and 3p atomic orbitals (LCAO); this is the justification to denote the configuration of the two equivalent Fe ions in the complex as $3d^5$. Due to the Abelian D_{2h} point group, these singly occupied 3d-like MOs are nondegenerate and belong to the one-dimensional irreducible representations (irreps) a_g, a_g, b_{1u}, b_{1u}, b_{3u}, b_{2g}, b_{2u}, b_{3g}, b_{1g}, and a_u. The ferromagnetic ROHF state $S = 5$ is therefore $^{11}B_{1u}$.

It can be shown that the remaining states $S = 0, ..., 4$ of the multiplet belong to the same irrep B_{1u} if the total spin quantum number S is odd and belong to the totally symmetric irrep A_g if S is even; i.e., the six multiplet states are $^{11}B_{1u}$, ^9A_g, $^7B_{1u}$, ^5A_g, $^3B_{1u}$, and ^1A_g. In our complete active space configuration interaction (CASCI) calculations, the ROHF MOs of the $^{11}B_1$ ferromagnetic state have been used to obtain the CI expansions corresponding to each value of S, in contrast to CASSCF. This is because of the need to have a fixed model space within which the model Heisenberg Hamiltonian will be built up. The determinants of the CAS have been selected (1) by the z-component S_z of the vector of the total spin $\vec{S}$ and (2) by the irreducible representation of the determinants, i.e., by exploiting spinor and spatial symmetry, respectively. For $S_z = 5$ the CAS contains one determinant and therefore is equivalent to ROHF, whereas it consists of 7992 determinants for $S_z = 0$. In particular, all six multiplet energies can be found theoretically by considering the three, two, and one lowest energy eigenvalues for $S_z = 0$, $S_z = 2$, and $S_z = 4$ and A_g, respectively, and for $S_z = 1$, $S_z = 3$, and $S_z = 5$ and B_{1u}, respectively. The redundant information may be used to check that the different roots of the CASCI matrix obtained from the Davidson procedure are in fact those which one wants to compute effectively.

The CASCI wave function contains many important physical effects, such as the direct exchange and the superexchange via the bridging ligands. The latter goes back to Anderson[38] and is also referred to as kinetic exchange as it originates from charge fluctuations between the two Fe 3d shells intermediate by the sulfur orbitals. For a quantitative description of magnetic coupling, however, CASCI is not appropriate as it lacks very important correlation effects. Following De Loth et al.[18] and Daudey et al.,[19] these terms may be classified as potential exchange, kinetic exchange, dynamic spin polarization, and charge transfer, as well as polarization of the ionic forms. We have introduced these correlation effects by considering the appropriate single and double excitations out of all 24 sulfur valence orbitals (2s and 2p) using the CASCI wave functions as references. This is because direct application of multireference CI (MRCI-SD), with single and double excitations, for our system, however, is too complicated, as even for the two simplest multiplet states $^{11}B_{1u}$ and $^{9}A_g$, which consist of 1 and 14 CAS reference determinants, respectively, the use of the above described basis set leads to a MRCI expansion containing 3.6×10^5 and 4.9×10^6 determinants, respectively. While it is possible to find the first root by direct diagonalization it is quite difficult to obtain the second, and to obtain a third one is out of question. Therefore we have applied two different methods which can be thought of as good approximations to the full MRCI-SD wave function. The first method, hereafter referred to as CAS-2nd, is a second-order multireference perturbation theory based approach which uses the barycentric Møller−Plesset partition of the Hamiltonian and the CASCI eigenfunction as zeroth-order wave function.[39] The second method may be described as a difference-dedicated configuration interaction and will be denoted as DDCI. The DDCI method was first proposed by Miralles et al. for the variational calculation of singlet−triplet energy differences and bond energies[40,41] and has successfully been applied to investigation of magnetic coupling constants in ionic solids[28,29,42−45] and inorganic complexes.[46−48] Since the application of the DDCI approach to magnetic exchange coupling in polynuclear complexes has already been reviewed by Handrick et al.[49] we only briefly restate the main features.

The basic concept of DDCI is the reduction of the CI space by a clever selection of determinants for the evaluation of energy differences. The CAS×full(S+D) space (i.e. of a MRCI-SD calculation) originates from the CAS space by single and double substitutions, $S^+_{p,i} = a^+_i a_p$ and $D^+_{pq,ij} = a^+_i a^+_j a_p a_q$, respectively. Since the set of all orthogonal molecular orbitals (MOs) can be partitioned into the three disjunct sets of n_C inactive occupied or core MOs (labeled *p*, *q*, ...), n_A active MOs (labeled *a*, *b*, ...), and *n*v inactive virtual MOs (labeled *i*, *j*, ...), the double substitutions have either 1 degree of freedom ($ab \rightarrow cj$, $ap \rightarrow cd$), 2 degrees of freedom ($ab \rightarrow ij$, $pa \rightarrow cj$, $pq \rightarrow cd$), 3 degrees of freedom ($pa \rightarrow ij$, $pq \rightarrow cj$), or 4 degrees of freedom ($pq \rightarrow rs$). On the basis of arguments derived from the quasi-degenerate perturbation theory (QDPT), Miralles et al.[40,41] have shown, by constructing a second-order corrected effective Hamiltonian, $\mathbf{H}_{\text{eff}}$, that the 4-degrees-of-freedom substitutions, which are the most numerous ones and bring most of the correlation energy, do not contribute to energy differences in second order and can therefore be left out. That they do not contribute to the difference energy was already proven by Malrieu[50] as early as 1967.

TABLE 1: Heisenberg Coupling Constants *J* for Transitions $S \rightarrow S + 1$ between the Four Highest Multiplet States (in cm^{-1})

transition	CASCI	CAS-2nd(4)	CAS-2nd(3)	CAS-2nd(2)	DDCI2
4 → 5	−18.57	−157.9	−154.9	−155.1	−66.0
3 → 4	−18.57	−121.7	−118.6		
2 → 3	−17.85				

The so-selected CI space with substitutions of only up to 3 degrees of freedom is called T space. In the case discussed above, the T space selection reduces the MRCI-SD space for $^{11}B_{1u}$ to 1.5×10^5 and for $^{9}A_g$ to 2.0×10^6 determinants, i.e., to less than half. For a full variational treatment, the DCCI3 space (or T space) may still be too large. Miralles et al. have therefore suggested to restrict the T space to 1 and 2 degrees of freedom,[41] and the resulting Cl may be denoted as DDCI2. For a magnetic problem in a fully degenerate model space the DDCI2 contains indeed all the determinants that contribute to the energy difference up to second order; these determinants are indeed those responsible for the potential exchange, kinetic exchange, dynamic spin polarization, and charge transfer, as well as polarization of the ionic forms (see refs 18 and 19). In the present case the DDCI2 expansion includes only 20 584 determinants for $^{11}B_{1u}$ and 5.0×10^5 determinants for $^{9}A_g$. We will indeed show that the DDCI3 terms not included in DDCI2 do make only a modest contribution to the second-order energy difference as computed using the barycentric Møller−Plesset partition of the electronic Hamiltonian as in the CIPSI algorithm.[39] We will be able discuss and confirm this assumption by considering the dependence of the energy differences upon the CI space selection by second-order Møller−Plesset perturbation theory. With CAS-2nd(*n*) we mean that the selected CI space contains double substitutions with up to *n* degrees of freedom, but the determinants out of the CAS are treated perturbatively to second order ($n = 4, 3, 2$).

All quantum chemical calculations have been performed using a locally modified version of the PSHF-CIPSI system of programs[51] in combination with program modules for the DDCI[52] and for direct-CI.[53,54]

3. Results and Discussion

In this section we will first discuss the results obtained using the Anderson model; this is the active-electron approach or CASCI method. These are also compared to CASSCF calculations, which have been performed earlier, and a connection to the Heisenberg Hamiltonian is shown. Then we discuss the influence of correlation to the magnetic coupling constant *J* regarding selected CI spaces of different sizes and applying both perturbative and variational methods, i.e., CAS-2nd(*n*) and DDCI2, respectively. Finally a constrained space orbital variation (CSOV) analysis is used to quantitatively discuss the electronic contributions to the chemical bonding in the $[Fe_2S_6]^{6-}$ complex and examine their influence on the magnetic coupling constant *J*.

In Table 1 we report the magnetic coupling constant *J* as obtained from various multiplets. In particular we have used the states $^{11}B_{1u}$, $^{9}A_g$, and $^{7}B_{1u}$. These results show that applying the ROHF orbitals of the $^{11}B_{1u}$ state, the CASCI energies reproduce the behavior expected from the Heisenberg Hamiltonian; according to the discussion in section 2, this is by no means a surprise. Similar results can be obtained for the remaining multiplicities, and they will not be reported here. We have not been able to successfully apply the Davidson diagonalization for the states $S = 0$ and $S = 1$, as root-flipping problems occurred and the convergence of the algorithm has been too poor in these cases. For the same reason also the CASCI energy for $S = 2$ and hence $J(2\rightarrow3)$ might be contaminated with little error, and we conclude that the Heisenberg coupling constant from CASCI using the MOs of the state $S = 5$ is $J = -18.6$ cm^{-1}.

This finding seems to be, at first sight, in contradiction to previous CASSCF results for $[Fe_2S_6]^{6-}$, because they yield different coupling constants for each transition $S \rightarrow S + 1$, ranging from $J(0\rightarrow1) = -27.8$ cm^{-1} to $J(4\rightarrow5) = -18.2$ cm^{-1}, and therefore give a deviation from the Heisenberg Hamiltonian,[15,16] eq 1. Those CASSCF calculations used the same cluster geometry but pseudopotentials with a smaller core and basis sets of comparable quality, which justifies comparison of the CASCI and CASSCF results. Again, we must recall the theoretical works of Nesbet[32,35-37] and Herring[33,34] which strongly suggest that a system of two interacting spin angular momenta can be properly described by a Heisenberg Hamiltonian as given by eq 1. Therefore the CASSCF results appear to be quite difficult to understand. However, we must point out that the Heisenberg Hamiltonian may be in fact thought as an effective Hamiltonian which is constructed by the appropriate mapping of accurate ab initio energies. This mapping must be coherent, using always the same model space. This is guaranteed when applying the CASCI orbitals for all the states, but it is not the case when using the CASSCF approach because in this case the one-electron basis changes from one multiplicity to another, thus changing the model space in which the effective Hamiltonian is built up. In a given Hilbert subspace, the energy splitting exhibited by the exact or full CI energies will of course show the behavior of the Heisenberg Hamiltonian, but this will not be the case for the CASSCF wave functions. In the CASSCF wavefunction the orbitals are adapted to each state and may differ substantially from one state to another. In previous studies on $KNiF_3$, Illas et al.[28] have shown that the difference between CASCI or CASSCF was quite small. In the present case, however, the difference is much larger and indicates the importance of nondynamical correlation effects, which are larger for the $[Fe_2S_6]^{6-}$ complex. This is not surprising because the ionicity of this system is lower than that of $KNiF_3$.

An interesting question which now arises from our discussion above is the behavior of the magnetic coupling $J(S\rightarrow S+1)$ for CASCI wave functions using MOs which are optimized for the singlet state ^1A_g instead of using MOs of the state $^{11}B_{1u}$, i.e., which are taken from the CASSCF wave function for $S = 0$. Following Nesbet's arguments we expect to have an effective Heisenberg Hamiltonian, i.e., with constant J. If we furthermore assume that for the neighboring state $S = 1$ the CASCI energy is not drastically higher than the variational energy—similar as for the transition $4\rightarrow5$ in the above case—we would predict the coupling to be close to -28 cm^{-1}. These is exactly the result found in a previous CASSCF study[28] and shows that for the present system the orbital space is very important, and the resulting CASCI values for J shift from -18 to -28 cm^{-1} as a result of the nondynamical correlation effects included in the CASSCF wave function. This allows us to separate the correlation effects into two well-separated parts. This separation is difficult to carry out using other approaches. In fact, the results from DCCI2 are much less affected by the orbital space, simply because they already contain a part of nondynamic correlation, which appears from the single excitations out of the CAS and the diexcitations with one degree of freedom.

In order to gain further understanding of the origin of the magnetic coupling, we have performed a constrained space orbital variation (CSOV) analysis[55-57] of the magnetic interaction. The basic idea is to perform the CASCI calculations using again a set of molecular orbitals obtained for the ferromagnetic $^{11}B_{1u}$ state but with different constraints. The CASCI results for J depend, of course, on the set of molecular orbitals which are used to build the configurations; changes in J due to well-defined changes on the molecular orbitals enable identification of the chemical contributions to magnetic coupling. This technique starts from the SCF wave functions of two fragments, $[Fe_2]^{6+}$ and $[S_6]^{12-}$, and finally creates the ROHF wave function for $^{11}B_{1u}$ in several well-defined steps, each of which is defined by the orbitals to be varied and the space where these orbitals are allowed to vary. Each variation or step can be associated with a given physical effect. The $[Fe_2]^{6+}$ fragment is calculated with total spin $S = 5$, and the six sulfur atoms are replaced by $-2e$ point charges plus a pseudopotential that takes into account the finite size of the anions although in an approximate way. The $[S_6]^{12-}$ fragment is considered as a closed-shell system with the Fe ions replaced by point charges $+3e$ plus pseudopotentials for Fe^+. The surrounding point charges, which model the Madelung field, remain unchanged for both fragments. Starting by superimposing the electronic densities for the two fragments, an initial set of orbitals, hereafter referred to as frozen orbital (FO), is built. From these FO initial CASCI wave functions for $S = 5$, 4, and 3 are obtained, and from the energy splitting a first estimate of J is extracted; the same procedure is repeated using each one of the sets of orbitals obtained through the steps described in the following. The polarization of the Fe^{3+} cations lowers the energy of the $^{11}B_{1u}$ state by 0.32 eV; this is a small fraction of the total contribution of about 26.4 eV which separates the energy of the $^{11}B_{1u}$ state as computed by using the FO or the ROHF orbitals. The second contribution is the charge transfer donation from the $[Fe_2]^{6+}$ to the $[S_6]^{12-}$ unit, but since the valence shell of the ligands are already filled, this small effect, which is of about 0.07 eV, must therefore be ascribed to the basis set superposition error (BSSE). The variation of the orbitals of the $[S_6]^{12-}$ unit in its own orbital space accounts for about 6.7 eV and illustrates the importance of the polarization of the ligand orbitals in response to the presence of the Fe^{3+} cations. The next two energy contributions, which are of about 13.9 and 5.4 eV, are ascribed to covalent bonding. The first one is formally the charge donation from $[S_6]^{12-}$ to $[Fe_2]^{6+}$. For ionic systems such as MgO to BaO this contribution is small,[58,59] hence indicating that the covalent effects make only a modest contribution. However, a large contribution does not necessarily indicate covalent bonding and may be interpreted as further polarization of the $[S_6]^{12-}$ unit. In fact, if the energy of the $[S_6]^{12-}$ unit is computed in the presence of the basis set of $[Fe_2]^{6+}$, the effect of the "ghost" basis on the energy is as large as when the real Fe^{3+} ions are present. At first sight this large contribution may be ascribed to BSSE, but this cannot be that large and the physical effect associated by this variation is better described as a mixing between real charge transfer and anion polarization. We must point out that the calculation of $[S_6]^{12-}$ with the ghost basis cannot be considered as BSSE simply because there is the $+3e$ charge at the cation site. In any case we will show later that as far as J is concerned this step is not crucial. Finally we consider the mixing of the $[S_6]^{12-}$ closed-shell orbitals with the open-shell cation orbitals. This is an important covalent contribution to the energy and we will show that it is a leading mechanism

TABLE 2: Constrained Space Orbital Variation (CSOV) Energy Decomposition (Cumulative Δ_1/Incremental Δ_2) (in eV) for the Ferromagnetic SCF State $S = 5$ and Origin of the Magnetic Coupling J for the Transitions 4 → 5 and 3 → 4 (in cm^{-1})

orbital variation	physical contribution	Δ_1	Δ_2	$J(4\rightarrow5)$	$J(3\rightarrow4)$
FO	frozen orbital	0.000	0.000	−1.54	−1.54
V(Fe; Fe)	cation polarization	0.316	0.316	−2.40	−2.40
V(Fe; all)	cation donation (BSSE)	0.386	0.070	−2.42	−2.42
V(S; S)	anion polarization	7.097	6.711	−2.19	−2.19
V(S; all)	anion donation	20.969	13.872	−2.35	−2.35
V(open; closed)	open-shell delocation				
Full SCF	remaining terms	26.444	5.475	−18.57	−18.57

TABLE 3: Energies E of the Four Highest Multiplet States, with Reference to the Electronic Energy $E(S{=}5) = -339.217\,693$ au of the Ferromagnetic State (in au)

spin S	state	CASCI	CAS-2nd(4)	CAS-2nd(3)	CAS-2nd(2)	DDCI2
5	$^{11}B_{1u}$	0.000 000	−0.644 571	−0.282 131	−0.184 261	−0.080 761
4	$^{9}A_{g}$	−0.000 846	−0.651 767	−0.289 188	−0.191 328	−0.083 767
3	$^{7}B_{1u}$	−0.001 523	−0.656 202	−0.293 511		
2	$^{5}A_{g}$	−0.002 008				

to the magnetic coupling. In Table 2 we present a summary of the different physical contributions to the chemical bond in $Na_6F_2S_6$. This summary includes the cumulative, Δ_1, and the incremental, Δ_2, energy contributions to the final ROHF energy for the $^{11}B_{1u}$ state for the distinct CSOV steps i, defined as

$$\Delta_1 = E_{\text{step } i} - E_{\text{FO}} \quad \text{and} \quad \Delta_2 = E_{\text{step } i} - E_{\text{step } (i-1)} \tag{3}$$

following our denotation in the very detailed description shown in ref 45.

In Table 2 we also report the different values of J calculated using the MOs obtained at each CSOV step. The antiferromagnetic order appears even using the FO description although J is by far too small. Moreover, this small value of J does not change until the magnetic orbitals are allowed to mix with the valence orbitals of the ligand $[S_6]^{12-}$ unit. This indicates that a large part of the magnetic coupling is due to a certain delocalization of the Fe 3d orbitals into those of the $[S_6]^{12-}$ unit; this is a clear consequence of the covalent mixing.

So far we have discussed the Anderson model or active-electron approach including only the determinants of the complete active space (CAS), i.e., with all 24 ligand valence orbitals doubly occupied and 10 active electrons in the 10 3d-like MOs. Neither CASCI nor CASSCF approaches include the external electronic correlation, which is due to electron excitations from the core and active orbitals to the virtual ones. While in some cases, mainly in ionic solids, the active-electron approach is enough to determine the qualitative behavior of a material, the quantitative description requires explicit accounting for these external correlation effects; this is clear from the theoretical analysis of de Loth et al.[18] and Daudey et al.[19] For the $[Fe_2S_6]^{6-}$ complex we find that the magnetic coupling constant from CASCI is a factor of 5 too small when compared to the experimental results. A similarly large shortcoming of the active-electron picture has been reported by Wang et al.,[60] who studied the superexchange coupling in binuclear oxygen-bridged Ni(II) complexes, and has also been seen in previous studies for $KNiF_3$[28,42−45] and La_2CuO_4.[29]

The results for the perturbational and the variational treatment of external correlation energy applying the above described methods CAS-2nd(n) and DDC12 are also listed in Table 3. The correlation energies are at least 2 orders of magnitude larger than the magnetic splitting of the multiplet states. The systematic reduction of the space of the external determinants from CAS-2nd(4) to CAS-2nd(2) is accompanied by a decrease of the correlation energy. However, whereas the number of external determinants for the states $^{11}B_{1u}$ and $^{9}A_g$ falls by a factor of 18 and 10, respectively, when going from $n = 4$ to $n = 2$, the perturbative correlation diminishes only by a factor of about 3, which indicates that the DDCI space determinants are important for both the absolute and the differential correlation energies. Comparing the variational and the perturbative results for the same CI space, DDCI2 and CAS-2nd(2), we see that, in this case, perturbation theory overestimates the correlation energy by more than 100%. This large deviation is certainly an artifact of perturbation theory caused by near degeneracies of CAS determinants with external determinants. Among the different systems which have been previously studied using a similar approach,[28,29,42−45] the present one is the first where second-order results largely differ from variational DDCI2 ones.

In Table 1 we report the magnetic coupling constants J using both multireference second-order Møller−Plesset perturbation theory and the variational DDCI2 method. In the case of using localized magnetic orbitals, second-order quasi-degenerate perturbation theory shows that CAS-2nd(4) and CAS-2nd(3) should give the same results. The fact that both results differ by less than 2.5% shows that higher-order effects do not indeed play an essential role for the magnetic coupling. Furthermore, since CAS-2nd(3) and CAS-2nd(4) give almost the same result, we recognize that the external determinants with 3 degrees of freedom contribute very weakly to the transition energies. This justifies the neglect of the determinants with 3-degrees-of-freedom substitutions as assumed by the DDCI2. The perturbatively calculated coupling constants $J(4\rightarrow5) = -158\ cm^{-1}$ and $J(3\rightarrow4) = -122\ cm^{-1}$ turn out to be 66% and, respectively, 28% larger than the experimental result $J = -95\ cm^{-1}$. The variational method, however, yields $J(4\rightarrow5) = -66\ cm^{-1}$, which is 31% smaller than the experimental value. In particular, both the variational and the perturbative treatment of correlation lead to a much better agreement with experiment than the CASCI and CASSCF methods discussed above, and they clearly show, once again, the need to go beyond the active-electron approach for quantitatively accurate results. We want to add here that the variational DDCI2 method gives nearly the same coupling constant $J(4\rightarrow5)$ as the increment-based ACPF-scheme reported elsewhere.[16]

In order to estimate the goodness of the difference-dedicated CI method with respect to the experiment, we want to indicate that DDCI was able to give 50% of the magnetic coupling constant for $KNiF_3$[28,42−45] and 80% for La_2CuO_4.[29] Since the first system is three-dimensional and the second two-dimensional, the error can be ascribed to the collective effects which may play a role and are not treated by the cluster model approach. However, for the thioferrate crystal $Na_6Fe_2S_6$ collective effects are less likely, because the $[Fe_2S_6]^{6-}$ units are well separated from each other. Therefore one should expect a better value for J in our system. The difference between the experimental and calculated results, however, may be caused by the need to use a larger basis set, to include higher-order determinants or, to a lesser extent, by the model used to represent the real system. We must point out that the electronic density may change slightly when including the Na counterions and may depend also on the Madelung field used in the model. However, we remark that calculations of J using point charges which are 50% of the ones previously described give almost the same results for the magnetic coupling as reported above.

4. Conclusions

The origin of magnetism in $Na_6Fe_2S_6$ has been studied by means of a cluster model and several newly developed theoretical techniques. These techniques allowed not only to computationally obtain a reasonable estimate for the magnetic coupling constant but also to understand its physical origin. This has been possible thanks to the ideas of the constrained space orbital variation (CSOV) method and the philosophy of the difference-dedicated configuration interaction (DDCI). We have explored the DCCI space by means of multireference second-order perturbation theory and have been able to variationally treat a large DCCI space through the use of a newly developed direct-CI method which can handle any general CI space.

In summary, the DDCI method has been successfully applied for the first time to a system with two half-filled d shells. Considering the difficulty of the problem, the present results are in good agreement with experiment. We would like to point out that, in the authors opinion, more important than reproducing the experimental value is to be able to understand the physical origin of magnetic coupling in these thioferrates. The set of theoretical analysis presented in this work has enabled the origin of the magnetic coupling in $Na_6Fe_2S_6$ to be shown.

Acknowledgment. This research has been supported by the Human Capital and Mobility Programme, Access to Large Installations, under contract CHGE-CT92-0009 “Access to supercomputing facilities for european researchers” established between the European Community and CESCA/CEPBA and to the projects of DGICYT number PB92-0766-C02-01 and PB95-0847-C02-01. We also thank Dr. R. Caballol, Dr. O. Castell, Prof. Dr. P. Fulde, Prof. Dr. H. Stoll, and Dr. M. Dolg for support and many discussions on this subject.

References and Notes

(1) Klepp, K. O.; Bronger, W. *Z. Anorg. Allg. Chem.* **1986**, *532*, 23.

(2) Schmidtke, H.-H.; Packroff, R.; Bronger, W.; Müller, P. *Chem. Phys. Lett.* **1988**, *150*, 129.

(3) Müller, P.; Bronger, W. *Z. Naturforsch.* **1979**, *34b*, 1264.

(4) Bronger, W.; Ruschewitz, U.; Müller, P. *J. Alloys Compd.* **1992**, *187*, 95.

(5) Ruschewitz, U. Ph.D. Thesis, RWTH Aachen, 1992.

(6) Welz, D.; Bennington, S. M.; Müller, P. *Physica B* **1995**, *213/214*, 339.

(7) Silvestre, J.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 4108.

(8) Schmidtke, H.-H.; Rosellen, U.; Diehl, M. *Mol. Phys.* **1994**, *83*, 1191.

(9) Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737.

(10) Norman, J. G., Jr.; Ryan, P. B.; Noodleman, L. *J. Am. Chem. Soc.* **1980**, *102*, 4279.

(11) Noodleman, L.; Baerends, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 2316.

(12) Noodleman, L.; Norman, J. G., Jr.; Osborne, J. H.; Aizman, A.; Case, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 3418.

(13) Mouesca, J. M.; Noodleman, L.; Case, D. A.; Lamotte, B. *Inorg. Chem.* **1995**, *34*, 4347.

(14) Mouesca, J. M.; Noodleman, L.; Case, D. A. *Int. J. Quantum Chem.*, Quantum Biol. Symp. **1995**, *22*, 95.

(15) Mödl, M. Ph.D. Thesis, Universität Stuttgart, 1995.

(16) Mödl, M.; Dolg, M.; Fulde, P.; Stoll, H. Submitted to J. Chem. Phys.

(17) Mödl, M.; Dolg, M.; Fulde, P.; Stoll, H. J. Chem. Phys., in press.

(18) de Loth, Ph.; Cassoux, P.; Daudey, J. P.; Malrieu, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 4007.

(19) Daudey, J. P.; de Loth, P.; Malrieu, J. P. In *Magnetic Structural Correlation in Exchange Coupled Systems*; NATO Symposium; Gatteschi, D., Kahn, O., Willett, R. D., Eds.; Reidel: Dordrecht, 1984.

(20) Sousa, C.; Casanovas, J.; Rubio, J.; Illas, F. *J. Comput. Chem.* **1993**, *14*, 680.

(21) Durand, P.; Barthelat, J. C. *Theor. Chim. Acta* **1975**, *38*, 283.

(22) Pelissier, M.; Durand, P. *Theor. Chim. Acta* **1980**, *55*, 43.

(23) Barthelat, J. C.; Pelissier, M.; Durand, P. *Phys. Rev. A* **1981**, *21*, 1773.

(24) Sodupe, M.; Lluch, J. M.; Oliva, A.; Illas, F.; Rubio, J. *J. Chem. Phys.* **1989**, *90*, 6436.

(25) Sodupe, M.; Lluch, J. M.; Oliva, A.; Illas, F.; Rubio, J. *J. Chem. Phys.* **1990**, *92*, 2478.

(26) Sodupe, M.; Lluch, J. M.; Oliva, A.; Illas, F.; Rubio, J. *J. Chem. Phys.* **1990**, *94*, 4352.

(27) Aguilar, A.; González, M.; Illas, F.; Rubio, J.; Sayós, R. *Chem. Phys.* **1992**, *161*, 99.

(28) Casanovas, J.; Illas, F. *J. Chem. Phys.* **1994**, *100*, 8257.

(29) Casanovas, J.; Rubio, J.; Illas, F. *Phys. Rev. B* **1996**, *53*, 945.

(30) Heisenberg, W. *Z. Phys.* **1928**, *49*, 619.

(31) Dirac, P. A. M. *The Principles of Quantum Mechanics*, 3rd ed.; Clarendon: Oxford, 1947; Chapter IX.

(32) Nesbet, R. K. *Ann. Phys.* **1958**, *4*, 87.

(33) Herring, C. *Rev. Mod. Phys.* **1962**, *34*, 631.

(34) Herring, C. *Magnetism*; Rado, G. T., Shul, H., Eds.; Academic Press: New York, 1965; Vol. 2B.

(35) Maynau, D.; Durand, Ph.; Daudey, J. P.; Malrieu, J. P. *Phys. Rev. A* **1983**, *28*, 3193.

(36) Nesbet, R. K. *Phys. Rev.* **1960**, *119*, 658; *Ibid.* **1960**, *122*, 1497.

(37) Nesbet, R. K. *Phys. Rev.* **1960**, *135*, A460.

(38) Anderson, P. W. *Phys. Rev.* **1959**, *115*, 2.

(39) Huron, B.; Rancurel, P.; Malrieu, J. P. *J. Chem. Phys.* **1973**, *75*, 5745.

(40) Miralles, J.; Daudey, J.-P.; Caballol, R. *Chem. Phys. Lett.* **1992**, *198*, 555.

(41) Miralles, J.; Castell, O.; Caballol, R.; Malrieu, J. P. *Chem. Phys.* **1993**, *172*, 33.

(42) Illas, F.; Casanovas, J.; Garcia-Bach, M. A.; Caballol, R.; Castell, O. *Phys. Rev. Lett.* **1993**, *71*, 3549.

(43) Casanovas, J.; Illas, F. *J. Chem. Phys.* **1994**, *101*, 7683.

(44) Casanovas, J.; Rubio, J.; Illas, F. In *New Challenges in Computational Quantum Chemistry*; Broer, R., Aerts, P. J. C., Bagus, P. S., Eds.; Groningen, 1994; pp 214−226.

(45) Casanovas, J.; Illas, F. *Phys. Rev. B* **1994**, *50*, 3789.

(46) Handrick, K.; Malrieu, J. P.; Castell, O. *J. Chem. Phys.* **1994**, *101*, 2205.

(47) Castell, O.; Caballol, R.; Subra, R.; Grand, A. *J. Phys. Chem.* **1995**, *99*, 154.

(48) Castell, O.; Miralles, J.; Caballol, R. *Chem. Phys.* **1994**, *179*, 377.

(49) Handrick, K.; Malrieu, J. P.; Castell, O. *J. Chem. Phys.* **1994**, *3*, 101.

(50) Malrieu, J. P. *J. Chem. Phys.* **1967**, *47*, 4555.

(51) PSHF-CIPSI package written by J.-P. Daudey, J. P. Malrieu, D. Maynau, M. Pelissier, F. Spiegelmann, R. Caballol, S. Evangelisti, F. Illas, and J. Rubio.

(52) Program written by Oscar Castell, Rosa Caballol, Jean Paul Malrieu, Klaus Handrick, and Victor Manuel García, 1995.

(53) Povill, A.; Rubio, J.; Illas, F. *Theor. Chim. Acta* **1992**, *82*, 22.

(54) Povill, A.; Rubio, J. *Theor. Chim. Acta* **1995**, *92*, 305.

(55) Bagus, P. S.; Hermann, K.; Bauschlicher, C. W. *J. Chem. Phys.* **1984**, *80*, 4378.

(56) Bagus, P. S.; Hermann, K.; Bauschlicher, C. W. *J. Chem. Phys.* **1984**, *81*, 1966.

(57) Bagus, P. S.; Illas, F. *J. Chem. Phys.* **1992**, *96*, 8962.

(58) Illas, F.; Lorda, A.; Rubio, J.; Torrance, J. B.; Bagus, P. S. *J. Chem. Phys.* **1993**, *99*, 389.

(59) Pacchioni, G.; Sousa, C.; Illas, F.; Parmigiani, F.; Bagus, P. S. *Phys. Rev. B* **1993**, *48*, 11573.

(60) Wang, C.; Fink, K.; Staemmler, V. *Chem. Phys.* **1995**, *192*, 25.