The Electronic Structure of the $Fe_4S_4^{3+}$ Cluster in Proteins: The Importance of Double Exchange Parameter

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Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday

The recently obtained Mössbauer and EPR parameters of the $Fe_4S_4^{3+}$ polymetallic center in the High Potential Iron-Sulfur Protein (HiPIP) II from *E. halophila* have been reproduced with models based on pure Heisenberg exchange. The role of double exchange versus *J*-inequivalence is discussed. An evaluation of the upper limit of the double exchange parameter in the $Fe_4S_4^{3+}$ bimetallic center is also presented. The present calculations shed further light on the electronic structure of the $Fe_4S_4^{3+}$ center.

Key words: Heisenberg exchange; Double exchange; Iron-sulfur proteins.

1. Introduction

High potential iron-sulfur proteins formally contain three iron(III) and one iron(II) in $Fe_4S_4^{3+}$ cubane, in which the irons are tetrahedrally arranged (Fig. 1A) [1]. Mössbauer [2–6], EPR [6–11], MCD [12] and ENDOR [13] studies, both on proteins and model compounds [14–19] are available. Characteristic features can be rationalized in terms of a total spin ground state $S = 1/2$. Mössbauer [5, 20] and ENDOR [15, 17] data also indicate that the ferrous ion delocalizes its extra electron onto one of the ferric ions, giving rise to a pair of $Fe^{2.5+}$ ions (mixed valence pair). The usual picture is that the total spin ground state $S = 1/2$ is obtained from antiferromagnetic coupling between two subspins, S_{12} and S_{34}, the former referred to the ferric Fe_1-Fe_2 pair and the latter to the mixed Fe_3-Fe_4 valence pair (Fig. 1A) [5]. Extensive analysis of the NMR data on several HiPIPs from different sources [21–25] has shown that the ground state description in terms of the two S_{12} and S_{13} pairs is qualitatively correct, as long as one allows either for a partial inclusion of a third spin into the electron delocalization scheme [22] or, more likely, for the presence of an equilibrium between (at least) two species differing by the localization of the mixed valence

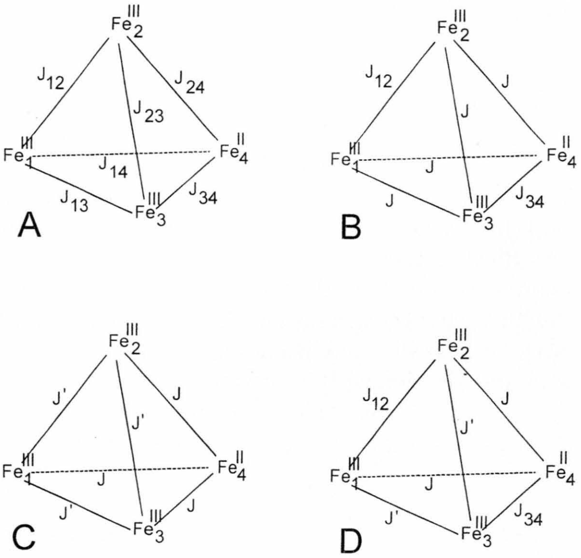

Fig. 1. Arrangement of the ferric and ferrous ions, and of their Heisenberg exchange parameters, in oxidized HiPIP under various symmetries. A) generic case of C_1 symmetry. B) C_{2v} symmetry (the C_2 axis passing through the center of the tetrahedron and perpendicular to the Fe_1-Fe_2 and Fe_3-Fe_4 edges). C) C_{3v} symmetry (the C_3 axis passing through Fe_4 and the center of the $Fe_1-Fe_2-Fe_3$ triangular face. D) C_s symmetry obtained by slight distortion of the C_{3v} symmetry (the mirror plane containing the Fe_3-Fe_4 edge and bisecting the Fe_1-Fe_2 edge).

Reprint requests to Professor I. Bertini pair [24]. EPR data on model systems confirm that, even within the same crystal, different localizations of the mixed valence pair may coexist [17]. EPR data on most HiPIPs also suggest the presence of more than one species [25].

Recently, NMR data on the HiPIP II from *E. halophila* [26] provided the only example of delocalization strictly confined to one pair, even at room temperature. Consistently, the EPR spectrum [6] is unique among the EPR spectra of HiPIPs up to now investigated in being clearly due to only one species. The Mössbauer parameters [6] confirm the two subspin description. Therefore, it appears that the above protein constitutes the only suitable system to attempt a quantitative rather than a qualitative analysis of the spectroscopic parameters. The relevant spectroscopic parameters of *E. halophila* HiPIP II are summarized in Table 1.

We are going to interpret the data in Table 1 through various theoretical approaches [28–33], and we are going to discuss the values of the double exchange parameter and its importance in $Fe_4S_4^{3+}$ centers.

2. High symmetry and C_{2v} models

The generally accepted simplified description of the $Fe_4S_4^{3+}$ cluster in terms of $|S_{12}, S_{34}, S\rangle$ wavefunctions [5, 22, 23, 31] has the advantage of 1) providing analytical solutions of the Heisenberg exchange Hamiltonian and 2) allowing the introduction of a double exchange term on the S_{34} pair to account for electron delocalization, while still retaining analytical solutions [29, 30, 34]. This description imposes a C_{2v} symmetry to the system, with the C_2 axis passing through the center of the tetrahedron of the four irons in the cubane and perpendicular to the S_1-S_2 and the S_3-S_4 edges. The complete Hamiltonian for the C_{2v} case is

$$\boldsymbol{H} = J\sum_{i,j} \boldsymbol{S}_i \boldsymbol{S}_j + \Delta J_{12} \boldsymbol{S}_1 \boldsymbol{S}_2 + {}^{(3)}\Delta J_{34}\,{}^{(3)}\boldsymbol{S}_3\,{}^{(3)}\boldsymbol{S}_4 \boldsymbol{O}_3 + {}^{(4)}\Delta J_{34}\,{}^{(4)}\boldsymbol{S}_3\,{}^{(4)}\boldsymbol{S}_4 \boldsymbol{O}_4 + B_{34} \boldsymbol{T}_{34}, \tag{1}$$

where ΔJ_{12} and ΔJ_{34} are the deviations of J_{12} and J_{34} from the other J values (Fig. 1 B), B_{34} is the double exchange parameter, $\boldsymbol{T}_{34}$ is the operator of the electron transfer between the centers 3 and 4, $\boldsymbol{O}_3$ and $\boldsymbol{O}_4$ are occupation operators, and the superscripts (3), (4) indicate the situations when the electron is localized on center 3 or 4, respectively.

The $S=1/2$ ground state can easily be reproduced with this Hamiltonian within a large range of parameters. We have discussed at length the covariance between the double exchange parameter B_{34} and ΔJ_{34} [22, 23, 35]. The larger the B_{34} value, the smaller the effective J_{34} value. Indeed, in an attempt to reduce the number of parameters, it has been often assumed that $\Delta J_{34}=0$ [31, 36], which implicitly required a relatively large double exchange term to obtain qualitatively acceptable descriptions of the system. The reverse is also true: the same ground states can be obtained by using a negative ΔJ_{34} value and neglecting the contribution of double exchange [22–24, 26].

Within C_{2v} symmetry two ground states have been found to give qualitatively acceptable values for Mössbauer, EPR and ENDOR parameters: these are described by the $|4, 9/2, 1/2\rangle$ [31] and the $|3, 7/2, 1/2\rangle$ [16] ground state functions. Both can be obtained with or without inclusion of double exchange. However, while the former exists within a wide range of parameters, the latter solution is extremely unstable unless relatively large B_{34} values are used. This is illustrated in Figure 2. It is interesting to note that, among the various cluster species observed in ENDOR, one is more consistent with the former and another with the latter ground state [16]. Magnetic susceptibility data on a model system have been reproduced by both states at essentially the same energy, practically representing a degenerate ground state [36]. On the other hand, the *E. halophila* HiPIP II parameters are definitely in better agreement with a well isolated $|3, 7/2, 1/2\rangle$ ground state, as shown in Table 1. Therefore, if the C_{2v} symmetry approximation is indeed adequate for the description of the natural system, we should conclude that the $|3, 7/2, 1/2\rangle$ ground state is the correct one, as already suggested [16].

Table 1. Comparison of experimental hyperfine constants and g_{av} values for the oxidized form of *E. halophila* HiPIP II [6] with values calculated[a] by different models.

	Exp. values	C_{2v} $\|4,9/2,1/2\rangle$	C_{2v} $\|3,7/2,1/2\rangle$	C_{3v}	$C_{3v}\rightarrow C_s$[b]
A_{12}(MHz)	21.4 ± 1.5	26.7	20.0	−3.1	21.5
A^c_{34}(MHz)	-31.5 ± 1.0	−38.3	−31.5	8.9	−33.1
g_{av}	2.07	2.054	2.042	2.065	2.066

[a] All calculations are performed using monomer hyperfine constants $a_{Fe}^{3+} = -20$ MHz and $a_{Fe}^{2+} = -22$ MHz [27].
[b] Calculated using $J' = 2J$, $\Delta J_{12} = \Delta J_{34} = -0.1\,J$ (Fig. 1 D).
[c] Average value of A_3 and A_4.

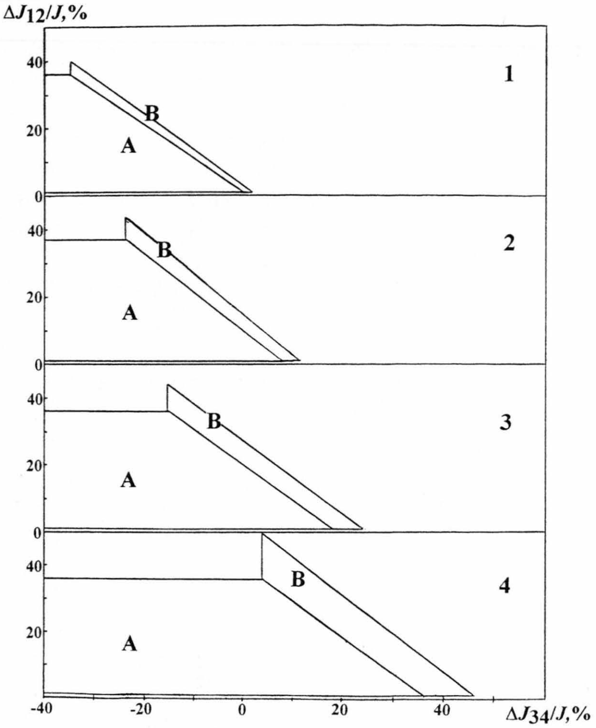

Fig. 2. The regions of stability of the $|4, 9/2, 1/2\rangle$ (A) and the $|3, 7/2, 1/2\rangle$ (B) ground states (C_{2v} model, Fig. 1 B) in the space of the Heisenberg parameters for different values of the ratio B_{34}/J (J = interpair coupling constant). 1: $B_{34}/J=0$, 2: $B_{34}/J=0.4$, 3: $B_{34}/J=0.8$, 4: $B_{34}/J=1.6$.

Recent theoretical work [37] has also pointed out that the introduction of relatively strong vibronic coupling into a strongly and uniformly delocalized cluster of T_d symmetry leads to the formation of six equivalent ground states, in each of which the extra electron is delocalized over one of the six possible metal pairs. This theoretical finding further justifies the model based on C_{2v} symmetry. In this picture, the lowering of symmetry induced by the protein would easily stabilize delocalization over one of the six pairs.

3. The C_{3v} model

There is another analytical solution to the coupling scheme of a four-S system that is described by a C_{3v} symmetry [29, 30, 32–34] (Fig. 1 C). In this scheme, three spins, for instance $S_1 - S_3$, share three equal antiferromagnetic coupling constants, $J' = J + \Delta J_{123}$, and a fourth spin, S_4, is antiferromagnetically coupled to the first three spins again by three equal J values. The relative Hamiltonian is

$$H = J \sum_{i,j} \boldsymbol{S}_i \boldsymbol{S}_j + \Delta J_{123} (\boldsymbol{S}_1 \boldsymbol{S}_2 + \boldsymbol{S}_1 \boldsymbol{S}_3 + \boldsymbol{S}_2 \boldsymbol{S}_3). \quad (2)$$

This Hamiltonian has the advantage of representing the reasonable situation of one ferrous ion (S_4) more weakly coupled to the three ferric ions (positive ΔJ_{123} values). Indeed, we expect that J will be smaller in Fe(II)–Fe(III) than in Fe(III–Fe(III) pairs. However, this choice of parameters yields a strongly degenerate ground state and unreasonable values for the experimental quantities in Table 1. The results are not unexpected, because in the above symmetry there is no special pair of irons that can be taken as representative of the mixed valence pair.

The symmetry of (2) could in fact be lowered, and analytical solutions still maintained, by making one of the three pairs in the $S_1 - S_2 - S_3$ triangle different from the others [29, 30, 34]; this also allows inclusion of double exchange. However, this choice requires placing the ferrous ion in either site 1 or 2, in contradiction with its original localization in site 4 to account for its starting smaller J values. For this reason, this analytical solution has not been taken into consideration when dealing with HiPIPs and their models, although it has been tentatively applied to the reduced ferredoxin $Fe_3S_4^+$ case [32, 33] and was, later, successfully used to interpret Fe_3MS_4 heterometallic systems [38–40].

4. A distorted C_{3v} model

We will show here that the C_{3v} model is a good starting point that can be easily adapted to yield a good description of the electronic properties of HiPIPs. We take advantage of the known covariance between J_{ij} and B_{ij} for any particular pair in the cluster (see also later) [22, 23, 35], and use this notion to avoid the introduction of double exchange by lowering the corresponding J_{ij} value, as it has been done in the past [22]. This choice is only dictated by ease of calculations and does not *a priori* deny the possible importance of double exchange. We recall that a purely Heisenberg exchange picture can be solved numerically for even six different J_{ij} values (Fig. 1 A), according to the general Hamiltonian

$$H = \sum_{i,j} J_{ij} \boldsymbol{S}_i \boldsymbol{S}_j . \quad (3)$$

We have already described a computer program designed to accomplish this task [22]. The program arranges the basis set of 1080 wavefunctions constructed from the projections of the individual spin states in blocks of equal total M_S, thereby reducing the largest matrix to be diagonalized to an affordable 125×125 dimension.

We then look for the minimal perturbation, using the minimum number of different J values that can provide a ground state that would reproduce the Mössbauer data and the EPR values.

We find that four different J_{ij} values in the arrangement shown in Fig. 1 D give very good agreement with the experimental values (Table 1). The temperature dependencies of the hyperfine shifts of the β-CH_2 cysteine protons are also satisfactorily reproduced (not given). The arrangement in Fig. 1 D corresponds to a C_s symmetry. The J values differ little from those in the starting C_{3v} symmetry (Table 1) and are therefore still consistent with the expectation that J will be smaller in the Fe(II)–Fe(III) than in Fe(III–Fe(III) pairs. In particular, the values of Table 1 are obtained for $J'=2J$, $\Delta J_{12}=\Delta J_{34}=-0.1\,J$. This set of values provides a ground state function $\psi=0.95\,|4,9/2,1/2\rangle-0.30\,|4,7/2,1/2\rangle$. This function does not contain the $|3,7/2,1/2\rangle$ function but yields very similar hyperfine values.

In essence, the experimental hyperfine values of *E. halophila* HiPIP II are reproduced reasonably well by the $C_{2v}(|3,7/2,1/2\rangle$ ground state) and $C_s(\psi=0.95\,|4,9/2,1/2\rangle-0.30\,|4,7/2,1/2\rangle)$ models; less satisfactorily by the $C_{2v}(|4,9/2,1/2\rangle$ ground state) model; and not at all by the high symmetry C_{3v} model. The $g_{av.}$ parameter is less sensitively, but still better reproduced by the C_s (and even by its high symmetry "precursor", C_{3v}) model. This observation, by itself, should at least teach us that the C_{2v} approximation is not an obligate choice. The C_{2v} model tends to stress the importance of double exchange, while the C_s model tends to stress the initial localization of individual oxidation states. As a consequence, any claim about the magnitude of the double exchange parameter is expected to be strongly model-dependent.

The C_s model has the advantage of accounting for the role of the protein part that is expected to determine which of the four iron (III) ions of a hypothetical superoxidized protein is most reducible in order to obtain the actual $Fe_4S_4^{3+}$ center; furthermore the model implies that the protein is able to induce such distortions as to have one set of J values with a ground energy sizably lower than that of all other possible sets. In this symmetry, the double exchange phenomenon would manifest itself on the pair having the smallest J value, e.g. the Fe_3–Fe_4 pair. In this way, stabilization through electron delocalization is maximized. As the Fe_3–Fe_4 pair has the highest possible spin multiplicity, any small value of B_{34} (provided it is larger than the hyperfine coupling with ^{57}Fe) is able to make the Fe_3 and Fe_4 iron ions equivalent.

5. A comment on the values of the parameter *B*

It is well documented that the Fe^{3+}–Fe^{2+} states in $Fe_2S_2^+$ plant ferredoxins are strongly localized [41]. Reliable estimates of J for the oxidized and reduced forms are 290 and 200 cm^{-1}, respectively [42]. It has previously been shown [28] that the reduced form of these systems would show delocalization only if $B \geq 4.5\,J$, i.e. for $B \geq 900$ cm^{-1}. We believe this upper limit can be sizably lowered. The argument is as follows: while $J=290$ cm^{-1} for the oxidized form is truly due to antiferromagnetic coupling, the smaller $J=200$ cm^{-1} value for the reduced form can be ascribed partly to the usual decrease caused by iron reduction and partly to the effect of double exchange. We can thus define an effective J value, J_{eff}, given by a true antiferromagnetic value diminished by a contribution from double exchange.

For a dimeric system the energy matrix can be written as

$$\begin{matrix} 1/2\,JS(S+1)+\Delta E & B(S+1/2) \\ B(S+1/2) & 1/2\,JS(S+1)\,, \end{matrix} \tag{4}$$

where ΔE is the difference in non-spin energies for the different localizations of the extra electron, and B is the double exchange parameter. We can then calculate magnetic susceptibility data for different temperatures using the energy levels obtained after diagonalization of matrix (4). The generated data are fitted by using a pure Heisenberg exchange interaction, which for a dimer is described by the Hamiltonian

$$\boldsymbol{H}=1/2\,J_{\text{eff}}\,\boldsymbol{S}(\boldsymbol{S}+1)\,. \tag{5}$$

Therefore, from the J_{eff} values obtained for different values of J, ΔE and B one can estimate a reasonable range for the latter parameter. Acceptable values of J only range from 200 cm^{-1} (no contribution from double exchange) to 290 cm^{-1} (upper limit set by the

Table 2. J_{eff} Heisenberg exchange parameters calculated for different values of ΔE, cm^{-1} and B, cm^{-1}. $J = 290$ cm^{-1}.

$B \backslash \Delta E$	0	10	20	40	80	160	320	640	1280
10	289	289	289	289	289	289	289	290	290
20	287	287	287	287	287	288	288	289	289
40	280	280	280	280	281	281	283	285	288
80	257	257	257	257	257	259	264	272	282
160	199	199	199	199	200	202	211	230	253
240	148	148	148	148	149	151	159	180	215

J value of the oxidized form). We also consider ΔE values larger than 10^3 cm^{-1} (corresponding to a difference in microscopic reduction potentials of more than 100 mV) to be unlikely. Table 2 shows the J values obtained from the fitting for the most unfavorable J value of 290 cm^{-1}. It appears that B can hardly be larger than 150 cm^{-1} and will be even smaller if $J < 290$ cm^{-1}. This estimated upper limit for B is also consistent with the recent Mössbauer data and analysis on a partially delocalized $Fe_2S_2^+$ model compound [43–45].

It would be surprising if B were much larger in $Fe_4S_4^{3+}$ systems, where the geometric relationships between the iron and bridging sulfide ions responsible for magnetic coupling are so similar to those in $Fe_2S_2^+$ systems.

6. Concluding remarks

The above theoretical considerations tend to describe the $Fe_4S_4^{3+}$ center as derived from four Fe^{3+} ions plus one extra electron which is shared by one pair of ions. The protein decides which pair. This result can be obtained either through Hamiltonian (1) (C_{2v} model) or through Hamiltonian (3), the latter with four different J values (C_s model). In the latter case, double exchange of the extra electron on two iron sites is eventually needed. In the C_{2v} model the $|3, 7/2, 1/2\rangle$ ground state reproduces at best the hyperfine coupling values (see Table 1). This ground state is obtained as a stable solution only for relatively large B values. In C_s model the ground state is a mixture of $|4, 9/2, 1/2\rangle$ and $|4, 7/2, 1/2\rangle$ states. The C_s approach seems to provide a good agreement with the experimental hyperfine values under a broader range of parameters and, in particular, without the need to impose a large B value. The upper value of B, here estimated, is shown to be relatively small.

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