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Spin Population Analysis and Local Spin Hamiltonian Parameters in Exchange-Coupled Systems

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The different contributions to the spin density of coupled polynuclear metal systems are analysed in the framework of perturbation theory. The main contribution consists in a weighted superposition of normalized local spin densities arising from each metal site, the weights being given by usual spin coupling matrix elements. When this analysis is applied to the spin densities calculated for the high-spin and broken symmetry states of $[Fe_2S_2(SH)_4]^{2-}$ and $[Fe_2S_2(SH)_4]^{3-}$, it appears that the local spin densities differ significantly from those calculated for the $[Fe(SCH_3)_4]^-$ and $[Fe(SCH_3)_4]^{2-}$ monomers. In particular, the spin densities on the iron atoms are markedly smaller in the dinuclear systems. Although these results were obtained on model centers, they are fully consistent with the spectroscopic characteristics of these centers in proteins.

Introduction

The magnetic properties of exchange-coupled polynuclear metal systems are currently the subject of intense experimental and theoretical investigations.[1-5] Their interpretation is usually based on an appropriate spin Hamiltonian, which comprises an Heisenberg term describing the exchange interactions, along with different local terms which describe the magnetic properties of each metal site. The physical observables of the coupled system are then expressed in terms of the local parameters by standard angular momentum algebra. This so-called vector coupling procedure is supported by the success of semiempirical approaches, in which parameters measured in closely related mononuclear centers are used as local parameters.[2] However, it is well-known that the exchange phenomenon arises from the overlap of magnetic orbitals centered on different metal sites. In the presence of strong exchange interactions, it is then expected that these sites lose at least in part their individuality, so that the local parameters become ill-defined.

The concept of spin density can be used to shed some light on this problem. The spin Hamiltonian parameters of a mononuclear metal center are closely related to the distribution of its normalized spin density $d(\vec{r})$. For example, the isotropic contact component of the hyperfine interactions with a magnetic nucleus located at $\vec{r}_N$ is proportional to $d(\vec{r}_N)$, and the anisotropic components are also largely determined by the $d(\vec{r})$ distribution.[6] Likewise, the $\tilde{g}$ and zero-field splitting tensors depend primarily on the nature of the metal ion and the symmetry of the center, but they are also sensitive to the delocalization of the magnetic orbitals onto the ligands. When such a metal center belongs to a polynuclear system, its spin density distribution reflects the modulation of the local properties brought about by delocalization effects within the system and consequently the values of the local spin Hamiltonian parameters *in the coupled system*.

In this paper, the different contributions to the spin density of a weakly coupled polynuclear metal cluster are analyzed in the framework of perturbation theory. For a trapped-valence system, the main contribution is simply given by a weighted superposition of normalized local spin densities arising from each metal site. Owing to the superexchange coupling, residual amounts of spin density are also transferred on adjacent sites. The extension to the case of delocalized valence is explicited for dinuclear systems. The formalism is then applied to extract local spin densities from the spin populations calculated by Noodleman et al.[7] for mononuclear and dinuclear iron–sulfur centers. It turns out that these local spin densities can be used to predict the ^{57}Fe isotropic hyperfine constants for reduced 2Fe2S ferredoxins, from a McConnell type relation calibrated for rubredoxin.

The Model

We first consider a mononuclear metal center comprising n magnetic orbitals φ_i ($i = 1, ..., n$) which are assumed to be normalized and orthogonal. These orbitals are centered on the metal and are delocalized onto the surrounding ligands. The different states can be represented by the functions

$$\psi_{S,M}(1, ..., n) = \mathcal{A}\,[\varphi_1(1) \ldots \varphi_n(n)\, X_{S,M}(1, ..., n)]/(n!)^{1/2} \tag{1}$$

where $X_{S,M}$ is a n-electron spin function and $\mathcal{A}$ is an antisymmetrization operator. The spin density in state $\psi_{S,M}$ defined by

$$\rho_{S,M}(\vec{r}) = \langle \psi_{S,M} | \sum_{i=1}^{n} 2\delta(\vec{r}_i - \vec{r}) s_{iz} | \psi_{S,M} \rangle \tag{2}$$

is given by

$$\rho_{S,M}(\vec{r}) = \sum_{i=1}^{n} |\varphi_i(\vec{r})|^2 \langle X_{S,M} | 2 s_{iz} | X_{S,M} \rangle \tag{3}$$

This expression can be simplified by using the Wigner–Eckart theorem

$$\rho_{S,M}(\vec{r}) = 2M \sum_{i=1}^{n} |\varphi_i(\vec{r})|^2 (S\|s_i\|S) \tag{4}$$

where $(S\|s_i\|S)$ is a reduced matrix element. It is useful to consider the *normalized* spin density $d_S(\vec{r})$

$$d_S(\vec{r}) = \langle \psi_{S,M} | S_z^{-1} \sum_{i=1}^{n} \delta(\vec{r}_i - \vec{r}) s_{iz} | \psi_{S,M} \rangle$$

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which is independent of M and is related to $\rho_{S,M}$ by[8]

$$\rho_{S,M}(\vec r) = 2Md_S(\vec r)$$

$d_S(\vec r)$ is normalized to unity. For the ***high-spin*** state with $S = S_{\max} = n/2$, it is easy to show that the reduced matrix element involved in (4) is equal to $1/(2S_{\max}) = 1/n$, so that the normalized spin density is simply equal to

$$d_{S_{\max}}(\vec r) = (2S_{\max})^{-1}\sum_{i=1}^{n}|\varphi_i(\vec r)|^2 \qquad (5)$$

We now consider a polynuclear system made of several interacting units labeled with $\alpha = A, B, C, ...$, each unit being centered on a ***high-spin*** metal ion with spin S_α. In this section, we restrict the study to the case of trapped-valence sites. Using perturbation theory, Noodleman and Case have shown that the wave functions describing such a system can be expanded in terms of determinants built upon *orthogonal* orbitals[4]

$$\psi_{S,M} = (\Phi^0_{S,M} + \sum_u a_u\Phi^u_{S,M} + \sum_v a_v\Phi^v_{S,M})/N^{1/2}$$

where N is a normalization constant. $\Phi^0_{S,M}$ is the principal determinant corresponding to the ground configuration, which can be defined as the lowest energy solution to the open-shell restricted Hartree–Fock equations. It is built on a set of orbitals φ_i, comprising doubly occupied ligand orbitals and magnetic orbitals φ^0_i which here reduce to metal d orbitals. The terms Φ^u arise from the transfer of electrons from the ligands to the metal d orbitals, which leads to other sets φ^u_i of magnetic orbitals. These terms are responsible for covalency effects, and for the ligand spin polarization contribution to the exchange interactions. The terms Φ^v arise from the transfer of electrons from a d orbital to another d orbital centered on an adjacent metal, which leads to new sets φ^v_i of magnetic orbitals. These terms are responsible for a weak transfer of spin density from one metal to another and for the Anderson superexchange contribution.

The essential part of the spin density is determined by $\Phi^0_{S,M}$ and by the mixing with the ligand spin polarization terms $\Phi^u_{S,M}$ which accounts for metal–ligand covalency. Using the definition given in (2), it is shown in the Appendix that this part $\rho^{\text{cov}}_{S,M}$ can be written

$$\rho^{\text{cov}}_{S,M}(\vec r) = \sum_\alpha \langle X_{S,M}|2S_{\alpha z}|X_{S,M}\rangle d_\alpha(\vec r) \qquad (6)$$

$X_{S,M}$ is the spin function associated with $\Phi^0_{S,M}$ and the ligand spin polarization terms $\Phi^u_{S,M}$, and $d_\alpha(\vec r)$ represents a local spin density arising from the magnetic orbitals $\varphi^0_{i\alpha}$ and $\varphi^u_{i\alpha}$ of unit α:

$$d_\alpha(\vec r) = (2S_\alpha)^{-1}(\sum_i|\varphi^0_{i\alpha}(\vec r)|^2 + \sum_u|a_u|^2|\varphi^u_{i\alpha}(\vec r)|^2)/N \qquad (7)$$

According to expression 6, $\rho^{\text{cov}}_{S,M}(\vec r)$ represents a weighted superposition of normalized spin densities arising from each metal site, the weights being given by the usual spin coupling matrix elements. This expression is isomorphic to well-known relations derived by the vector coupling procedure,[2] in which the hyperfine and g tensors of the system are expressed in terms of corresponding local parameters $\tilde a_\alpha$ and $\tilde g_\alpha$:

$$\tilde A_\alpha = [\langle X_{S,M}|2S_{\alpha z}|X_{S,M}\rangle/2M]\tilde a_\alpha \qquad (8)$$

$$\tilde g = \sum_\alpha [\langle X_{S,M}|2S_{\alpha z}|X_{S,M}\rangle/2M]\tilde g_\alpha \qquad (9)$$

Thus, $\tilde a_\alpha$ and $\tilde g_\alpha$ can be interpreted as the spin Hamiltonian parameters of a mononuclear center characterized by the normalized spin density $d_\alpha(\vec r)$. Strictly speaking, the residual spin densities transferred on site α from all adjacent sites by the superexchange mechanism[9] also contribute to the hyperfine interactions (see Appendix). In a spin Hamiltonian description, these contributions are represented by transferred hyperfine terms like[10]

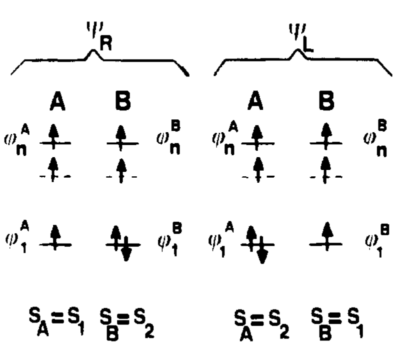

Figure 1. Two possible electronic configurations of a binuclear mixed-valence system. S_1 and S_2 are respectively equal to $n/2$ and $(n-1)/2$.

$$\mathcal{H}_{\text{THF}} = \sum_{\beta\neq\alpha}\vec S_\beta\cdot\tilde a'_{\beta\alpha}\cdot\vec I_\alpha$$

However, these terms are expected to be much smaller than the direct one $\vec S_\alpha\cdot\tilde a_\alpha\cdot\vec I_\alpha$ and are very difficult to detect experimentally.[10]

Extension to Mixed-Valence Systems

In the preceding section, the expression of the spin density was obtained by assuming that a well-defined spin value S_α could be attributed to each site α of the polynuclear system. This is no longer possible when valence delocalization effects are significant. In order to illustrate how the expressions have to be modified, let us consider the simple case of a dinuclear center comprising two sites, A and B. Each site can receive n unpaired electrons, and an extra electron can localize either on A or B (Figure 1). This defines two different configurations, giving states labeled ψ_L and ψ_R respectively. The states of the system are sought in the form

$$\psi_{S,M} = C_R\psi^R_{S,M} + C_L\psi^L_{S,M}$$

where $\psi^R_{S,M}$ and $\psi^L_{S,M}$ are functions similar to those of the preceding section. Usually, the mixing coefficients C_R and C_L are calculated variationnally by minimizing the energy of $\psi_{S,M}$. Their value is determined by (i) the diagonal elements $H^{RR}_{S,M}$ and $H^{LL}_{S,M}$, which are sensitive functions of the geometry of the system and which vary with S according to the Landé interval rule, and (ii) the off diagonal element $H^{RL}_{S,M}$ which is proportional to $(S + {}^1/_2)$ in the weak overlap limit.[3,11] If the overlap between φ^A_1 and φ^B_1 is sufficiently weak that cross terms can be neglected, the spin density in state $\psi_{S,M}$ is given by

$$\rho_{S,M}(\vec r) = |C_R|^2\rho^R_{S,M}(\vec r) + |C_L|^2\rho^L_{S,M}(\vec r)$$

where $\rho^R_{S,M}$ and $\rho^L_{S,M}$ are trapped valence spin densities which can be expanded according to expression 6.

$$\rho^R_{S,M}(\vec r) = \langle X^R_{S,M}|2S_{Az}|X^R_{S,M}\rangle d^R_A(\vec r) + \langle X^R_{S,M}|2S_{Bz}|X^R_{S,M}\rangle d^R_B(\vec r)$$

$$\rho^L_{S,M}(\vec r) = \langle X^L_{S,M}|2S_{Az}|X^L_{S,M}\rangle d^L_A(\vec r) + \langle X^L_{S,M}|2S_{Bz}|X^L_{S,M}\rangle d^L_B(\vec r)$$

Finally, the spin density is cast in the form

$$\rho_{S,M}(\vec r) = \langle X_{S,M}|2S_{1z}|X_{S,M}\rangle[|C_R|^2d^R_A(\vec r) + |C_L|^2d^L_B(\vec r)] + \langle X_{S,M}|2S_{2z}|X_{S,M}\rangle[|C_R|^2d^R_B(\vec r) + |C_L|^2d^L_A(\vec r)] \qquad (10)$$

Applying to this expression the isomorphism defined previously,

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we obtain for the hyperfine and g tensors of the mixed-valence system

$$\begin{aligned} \tilde{A}_{\mathrm{A}} &= K_1|C_{\mathrm{R}}|^2\tilde{a}_{\mathrm{A}}^{\mathrm{R}} + K_2|C_{\mathrm{L}}|^2\tilde{a}_{\mathrm{A}}^{\mathrm{L}} \\ \tilde{A}_{\mathrm{B}} &= K_2|C_{\mathrm{R}}|^2\tilde{a}_{\mathrm{B}}^{\mathrm{R}} + K_1|C_{\mathrm{L}}|^2\tilde{a}_{\mathrm{B}}^{\mathrm{L}} \end{aligned} \tag{11}$$

and

$$\tilde{g} = K_1\tilde{g}_1 + K_2\tilde{g}_2$$

$$\tilde{g}_1 = |C_{\mathrm{R}}|^2\tilde{g}_1^{\mathrm{R}} + |C_{\mathrm{L}}|^2\tilde{g}_1^{\mathrm{L}} \tag{12}$$

$$\tilde{g}_2 = |C_{\mathrm{R}}|^2\tilde{g}_2^{\mathrm{R}} + |C_{\mathrm{L}}|^2\tilde{g}_2^{\mathrm{L}}$$

with

$$K_\alpha = \langle X_{S,M}|2S_{\alpha z}|X_{S,M}\rangle/2M \qquad \alpha = 1,2$$

The following notations are used: $\tilde{a}_{\mathrm{A}}^{\mathrm{R}}$ and $\tilde{a}_{\mathrm{A}}^{\mathrm{L}}$ are the hyperfine tensors for site A associated with the local spin densities $d_{\mathrm{A}}^{\mathrm{R}}$ and $d_{\mathrm{A}}^{\mathrm{L}}$ respectively, while $\tilde{g}_1^{\mathrm{R}} \equiv g_{\mathrm{A}}^{\mathrm{R}}$ and $\tilde{g}_1^{\mathrm{L}} \equiv g_{\mathrm{B}}^{\mathrm{L}}$ represent the **g** tensors of the site with spin S_1, in states ψ^{R} and ψ^{L}, respectively. Although expressions equivalent to (11) and (12) have already been given in the literature,[12,13] it is worth noting that they are deduced in the present work by reference to an orbital model. In the trapped-valence limit where $|C_{\mathrm{R}}|^2 = 1$ and $|C_{\mathrm{L}}|^2 = 0$, (11) and (12) reduce to (8) and (9), respectively. The forms of expressions 11 and 12 indicate that the hyperfine tensor is expected to be much more affected by valence delocalization effects than the **g** tensor. This can be illustrated by considering the special case of equivalent sites:

$$\tilde{a}_{\mathrm{A}}^{\mathrm{R}} = \tilde{a}_{\mathrm{B}}^{\mathrm{L}} = \tilde{a}_1 \qquad \tilde{a}_{\mathrm{B}}^{\mathrm{R}} = \tilde{a}_{\mathrm{A}}^{\mathrm{L}} = \tilde{a}_2$$

$$\tilde{g}_1^{\mathrm{R}} = \tilde{g}_1^{\mathrm{L}} = \tilde{g}_1 \qquad \tilde{g}_2^{\mathrm{R}} = \tilde{g}_2^{\mathrm{L}} = \tilde{g}_2$$

In this case, expression 12 for the **g** tensor no longer depends on the mixing coefficients and reduces to (9), while (11) *does not* reduce to (8). In particular, when delocalization is complete

$$|C_{\mathrm{R}}|^2 = |C_{\mathrm{L}}|^2 = {}^1/_2$$

and the following simple relation applies

$$\tilde{A}_{\mathrm{A}} = \tilde{A}_{\mathrm{B}} = (K_1\tilde{a}_1 + K_2\tilde{a}_2)/2$$

which is indeed very different from eq 8.

Application to 2Fe2S Clusters

2Fe2S clusters play an important role as redox centers in a great variety of biological systems. In these centers, each high-spin iron is coordinated by a distorted tetrahedron of sulfur ligands, and the two sites are coupled by strong antiferromagnetic exchange interactions in both the oxidized [Fe(III), Fe(III)] and reduced [Fe(III), Fe(II)] forms. Their magnetic properties have been extensively investigated by a number of techniques.[14-16] In a series of papers, Noodleman and co-workers have interpreted those properties through LCAO-Xα valence bond calculations.[7,9,11] They have especially emphasized the importance of a broken symmetry state, the spin function of which is given by $X_{\mathrm{BS}} = X_{S_{\mathrm{A}}}^{S_{\mathrm{A}}}X_{-S_{\mathrm{B}}}^{S_{\mathrm{B}}}$, where S$_{\mathrm{A}}$ and S$_{\mathrm{B}}$ are the spins of the two irons ($S_{\mathrm{A}} \geqslant S_{\mathrm{B}}$). In particular, this state can be used together with the highest-spin multiplet $X_{\mathrm{HS}} = X_{S_{\mathrm{A}}}^{S_{\mathrm{A}}}X_{S_{\mathrm{B}}}^{S_{\mathrm{B}}}$ to evaluate the exchange parameter J.[9,11] Noodleman and co-workers have also developed Xα valence bond scattered-wave calculations on different iron–sulfur model systems including Fe(SCH$_3$)$_4$$^{1-,2-}$ and Fe$_2$S$_2$(SH)$_4$$^{2-,3-}$, which mimic the active sites of rubredoxins and 2Fe2S proteins, respectively.[7] For these systems, a population partitioning algorithm was used to determine the spin population on every atomic site q. In the case of dinuclear centers, the calculations were carried out for both the high-spin and broken symmetry states (Table I). Since they have been obtained at the same level of theoretical calculations, it is particularly interesting to apply to these data the analysis presented in the previous sections.

Table I. Spin Populations Computed in Reference 7 for Mononuclear and Dinuclear Iron–Sulfur Models[a]

	Fe(SCH$_3$)$_4$$^{1-}$			Fe(SCH$_3$)$_4$$^{2-}$		
spin state	2S	Fe(III)	2S	2S	Fe(II)	2S
$X_{S_{\max}}^{S_{\max}}$	0.48	3.64	0.48	0.2	3.30	0.2
			Fe$_2$S$_2$(SH)$_4$$^{2-}$			
spin state	2S	Fe(III)	2S*	Fe(III)	2S	
X_{HS}	0.66	3.29	1.16	3.29	0.66	
X_{BS}	0.54	3.00	0	−3.00	−0.54	
			Fe$_2$S$_2$(SH)$_4$$^{3-}$			
spin state	2S	Fe(III)	2S*	Fe(II)	2S	
X_{HS}	0.48	3.19	0.90	3.15	0.44	
X_{BS}	0.48	3.13	0.26	−2.74	−0.30	

[a] For convenience, the spin population on the sulfur ligands is given for 2S.

Table II. Local Spin Densities Calculated from the Data of Table I, with the Method Described in the Text

	Fe(SCH$_3$)$_4$$^{1-}$			Fe(SCH$_3$)$_4$$^{2-}$		
spin density	2S	Fe(III)	2S	2S	Fe(II)	2S
$d_{S_{\max}}$	0.092	0.728	0.092	0.05	0.825	0.05
			Fe$_2$S$_2$(SH)$_4$$^{2-}$			
spin density	2S	Fe(III)	2S*	Fe(III)	2S	
d_{A}	0.12	0.63	0.116	0.029	0.012	
d_{B}	0.012	0.029	0.116	0.63	0.12	
			Fe$_2$S$_2$(SH)$_4$$^{3-}$			
spin density	2S	Fe(III)	2S*	Fe(II)	2S	
$d_{\mathrm{A}}^{\mathrm{R}}$	0.12	0.63	0.116	0.029	0.012	
$d_{\mathrm{B}}^{\mathrm{R}}$	0.03	0.004	0.08	0.721	0.09	

In the case of the mononuclear complex Fe (SCH$_3$)$_4$$^{1-,2-}$, this is simply achieved by dividing the quoted spin populations by 2M, which is equal to 5 and 4 for the oxidized and reduced forms, respectively. The normalized spin densities so obtained differ notably in the two redox species (Table II), which is probably related to their quite different bonding scheme.[17] Next, we consider the diferric form Fe$_2$S$_2$(SH)$_4$$^{2-}$ of the dinuclear cluster. Application of expression 6 gives

$$\begin{aligned} \rho_{\mathrm{HS}}^{\mathrm{cov}}(q) &= 5d_{\mathrm{A}}(q) + 5d_{\mathrm{B}}(q) \\ \rho_{\mathrm{BS}}^{\mathrm{cov}}(q) &= 5d_{\mathrm{A}}(q) - 5d_{\mathrm{B}}(q) \end{aligned} \tag{13}$$

The local spin densities d_{A} and d_{B} overlap only on the bridging sulfur ligands and are almost spin independent. Therefore, $\rho_{\mathrm{HS}}^{\mathrm{cov}}$ and $\rho_{\mathrm{BS}}^{\mathrm{cov}}$ are expected to have the same magnitude on the terminal sulfur ligands. This is observed with a good approximation on the spin populations given for these states by the Xα

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method (Table I). The different spin populations calculated for the ferric atoms in these states are presumably due to the superexchange contribution which leads to a residual transfer of spin density from one metal to the other. According to the equations given in the Appendix, this contribution should be written

$$\begin{aligned} \rho^{\mathrm{se}}_{\mathrm{HS}}(q) &= 4d_{\mathrm{A}}'(q) + 4d_{\mathrm{B}}'(q) \\ \rho^{\mathrm{se}}_{\mathrm{BS}}(q) &= 4d_{\mathrm{A}}'(q) - 4d_{\mathrm{B}}'(q) \end{aligned} \qquad (14)$$

Application of eqs 13 and 14 to the data of Table I gives $d_{\mathrm{A}} = 0.63$ and $d_{\mathrm{B}}' = 0.036$ for the covalent and superexchange contributions to the spin density of $\mathrm{Fe_A(III)}$, respectively. Very similar results are obtained if the spin populations of Table I are analyzed only in terms of eq 13: inverting these equations leads to the "local" spin densities d_{A} and d_{B} reported in Table II, which now contain a residual part transferred on the other site. Owing to the near equality of the weighting factors appearing in (13) and (14), this transferred part represents a good approximation of the superexchange contribution. In the following, ρ^{se} will not be explicitely considered in the analysis, and the weak transfer of spin density on the adjacent metal allowed by the superexchange mechanism will be accounted for by a residual delocalization of d^{A} and d^{B}.

The situation is a priori more involved for $\mathrm{Fe_2S_2(SH_4)^{3-}}$ which is a mixed-valence system. When reduced $[\mathrm{2Fe2S}]^+$ clusters are embedded in a protein medium, the two iron sites appear valence-trapped on the Mossbauer time scale.[14] Although this could originate from asymmetric environments imposed by the protein, the observation of similar effects occuring spontaneously for synthetic analogs in solution[18] suggests a more intrinsic origin. In the model studied by Noodleman et al.,[7] a structural asymmetry was introduced by allowing a 0.07-Å increase of all Fe–S bonds at the B site, compared to the geometry of $\mathrm{Fe_2S_2(SH)_4^{2-}}$. Although such a marked asymmetry is expected to impose well-trapped-valence sites for the doublet ground state and the broken symmetry state, the highest spin state is likely substantially delocalized due to the $(S + {}^1/_2)$ dependence of the resonance term $H^{\mathrm{LR}}_{\mathrm{S,M}}$.[11] In such a situation, the spin density is given by expression 10, which involves too many unknown parameters to be useful. In the broken symmetry state, the spin density on atom q is given by

$$\rho_{\mathrm{BS}}(q) = 5d^{\mathrm{R}}_{\mathrm{A}}(q) - 4d^{\mathrm{R}}_{\mathrm{B}}(q)$$

where the suffix R recalls that the extra electron is localized on the right (B) site (Figure 1). Since the structure of the unreduced A site is the same in both oxidation states, it is reasonable to assume that $d^{\mathrm{R}}_{\mathrm{A}}(q)$ is essentially equal to $d_{\mathrm{A}}(q)$ in $\mathrm{Fe_2S_2(SH)_4^{2-}}$. This hypothesis leads to the local spin densities reported in Table II.

Discussion

According to expression 6, the main part of the spin density of weakly coupled polynuclear systems can be expressed as a weighted superposition of local spin densities arising from each site, the weights being given by appropriate spin coupling matrix elements. These local spin densities are almost spin independent, and can be used to define local spin Hamiltonian parameters *in the coupled system*. This formulation is of course congruent with the general intuition one may have of a spin coupled system. However, our derivation based on the perturbation approach of Noodleman and Case[4] emphasizes that it only applies in the weak coupling limit.

Table III. Experimental Value (in MHz) of the Isotropic Component of the ^{57}Fe Hyperfine Tensor in Mononuclear and Dinuclear Centers of Iron–Sulfur Proteins

center	protein	Fe(III)	Fe(II)	ref
mononuclear	rubredoxin	−22.6	−23.3	21, 22
	desulforedoxin	−21	−21.3	23
	av	$a_1 = -22$	$a_2 = -22.3$	
dinuclear	parsley ferredoxin	−46.4	+19.6	24, 25
	spinach ferredoxin	−47.4	+21.0	24, 25
	Synechococus lividus ferredoxin	−47.9	+21.5	26
	adrenodoxin	−49.7	+25.3	25
	putidaredoxin	−49.7	+23.3	27
	av	$A_1 = -48.2$	$A_2 = +22.1$	

We proceed by examining if the local spin densities reported in Table II, which were calculated for model iron–sulfur centers, reflect the magnetic properties of these centers in proteins. We first observe that the spin density transferred from the B site of the dinuclear system is much smaller in the reduced state than in the oxidized state. This is in keeping with the large decrease of the superexchange interactions that occurs upon reduction. Furthermore, the local spin density at the iron atoms appears significantly smaller in the dinuclear system than in the monomer, both at the ferric and the ferrous site. Noodleman and co-workers have already noted that covalency effects are more pronounced in polynuclear complexes, so that spin Hamiltonian parameters measured for the mononuclear center of rubredoxin should not be directly transferrable to the polynuclear clusters of ferredoxins.[7] This important point can be studied quantitatively, by considering the isotropic components of the ^{57}Fe hyperfine tensors measured by Mossbauer and ENDOR spectroscopies in rubredoxin and 2Fe2S ferredoxins (Table III). Some dispersion is apparent within both groups of centers, which is likely due to structural variations imposed by the different proteins. Accordingly, only the average values reported in Table III will be compared in the following. The data quoted for the dinuclear centers concern the localized doublet ground state. For this state, application of the vector coupling procedure leads to

$$A_1 = (7/3)a_1 \qquad A_2 = (-4/3)a_2$$

a_1 and a_2 being local parameters for the ferric and ferrous site, respectively. Taking for these parameters the average of the values measured in rubredoxin and desulforedoxin, we get $A_1 = -51$ MHz and $A_2 = +30$ MHz. Although the agreement with the experimental data is satisfactory for A_1, the calculated value of A_2 is much too large.

The isotropic hyperfine component is essentially of contact or core polarization origin, and is therefore expected to be proportional to the total spin density on the iron atom according to a McConnell type relation. The proportionality factor Q can be calibrated from the normalized spin density calculated for the monomeric model complex (Table II) and the average a_i ($i = 1, 2$) used above. This leads to $Q_1 = -30$ MHz and $Q_2 = -27$ MHz for the ferric and ferrous atom respectively. If the superexchange term ρ^{se} is omitted, the spin density on atom q of the binuclear center in the doublet ground state is given by

$$\rho_{\mathrm{LS}}(q) = (7/3)d^{\mathrm{R}}_{\mathrm{A}}(q) - (4/3)d^{\mathrm{R}}_{\mathrm{B}}(q)$$

By applying to $\rho_{\mathrm{LS}}(q)$ evaluated at the ferric and ferrous atoms the proportionality factors Q_1 and Q_2, we get $A_1 = -44$ MHz and $A_2 = +24$ MHz. We have checked that very similar results are obtained if the ρ^{se} terms are explicitely considered. The overall agreement is then significantly improved by this procedure, although it is based on spin densities calculated for model systems. The agreement would certainly be better if the spin density calculations were carried out for the real structures of the different centers quoted in Table III.

It is worth noting that the increase of covalency effects in the dinuclear system is also apparent when one considers the **g** and zero-field splitting tensors of the ferrous site: in semiempirical ligand field models used to describe their variations, it is necessary

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to assume that the absolute value of the ferrous spin–orbit constant λ is reduced by covalency to 80 cm^{-1} in dinuclear centers,[16] while it is only reduced to 100 cm^{-1} in mononuclear centers.[19]

Conclusion

The spin density analysis presented in this paper brings a new perspective on the validity and the significance of local terms in the spin Hamiltonian description of exchange-coupled systems. From a practical point of view, this approach provides a tool for evaluating semiempirically the isotropic component of hyperfine tensors in polynuclear clusters. The method, which is based on the theoretical determination of local spin densities and their calibration to an appropriate monomeric complex, was illustrated in the present study by a reinterpretation of the spin populations calculated by Noodleman et al. for mononuclear and dinuclear iron–sulfur centers. Its application to higher nuclearity iron–sulfur centers seems especially promising. For example, the calculation of local spin densities in $[Fe_3S_4]^+$ clusters could explain why an isotropic ferric component $a = -18$ MHz, significantly smaller than the values reported in Table III for rubredoxin and desulforedoxin, accounts for the hyperfine ^{57}Fe tensors measured for these centers in proteins.[20] The situation is certainly more complicated for $[Fe_3S_4]^0$, $[Fe_4S_4]^{3+}$, and $[Fe_4S_4]^+$, which are delocalized mixed-valence systems. In this case, we have seen that it is necessary to consider more than one local spin density for each metal site. Their determination will certainly require spin density calculations for several broken symmetry states.

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Appendix

The spin density in state $\psi_{S,M}$ is given by

$$\rho_{S,M} = (\rho^0_{S,M} + \sum_u |a_u|^2 \rho^u_{S,M} + \sum_v |a_v|^2 \rho^v_{S,M})/N$$

where cross terms have been neglected due to the orthogonality of the orbitals. $\rho^j_{S,M}$ represents the spin density in state $\Phi^j_{S,M}$, which is given by an expression similar to (3):

$$\rho^j_{S,M}(\vec{r}) = \sum_i |\varphi^j_i(\vec{r})|^2 \langle X^j_{S,M}|2s_{iz}|X^j_{S,M}\rangle \quad j = 0, u, v$$

For a weakly coupled polynuclear system, the main contribution to $\rho_{S,M}$ arises from the principal determinant $\Phi^0_{S,M}$ and from the spin polarization terms $\Phi^u_{S,M}$. All these states have the same spin functions[4] $X_{S,M}$, which can be expanded in terms of the spin functions $X^{S_\alpha}_{M_\alpha}$ associated with the local spins S_α:

$$X_{S,M} = \sum_{M_A, M_B, M_C} C(M_A, M_B, M_C, ...) X^{S_A}_{M_A} X^{S_B}_{M_B} X^{S_C}_{M_C} \cdots$$

For these states application of the Wigner–Eckart theorem yields

$$\langle X^{S_\alpha}_{M_\alpha}|s_{iz}|X^{S_\alpha}_{M_\alpha'}\rangle = \delta(M_\alpha, M_\alpha')M_\alpha/S_\alpha$$

so that the spin densities $\rho^0_{S,M}$ and $\rho^u_{S,M}$ can be expressed as a weighted superposition of contributions arising from the different units α

$$\rho^j_{S,M}(\vec{r}) = \sum_\alpha \langle X_{S,M}|2S_{\alpha z}|X_{S,M}\rangle d^j_\alpha(\vec{r})$$

with

$$d^j_\alpha(\vec{r}) = (2S_\alpha)^{-1} \sum_i |\varphi^j_{i\alpha}(\vec{r})|^2$$

for $j = 0, u$. The spin functions $X'_{S,M}$ associated with the superexchange terms $\Phi^v_{S,M}$ have a different structure.[4] For example, in the case of a dinuclear system $X_{S,M}$ results from the coupling of S_A, S_B whereas $X'_{S,M}$ results from the coupling of $(S_A - {}^1/_2)$ with $(S_B - {}^1/_2)$. Therefore, these terms must be treated separately. Finally, the whole spin density can be written

$$\rho_{S,M}(\vec{r}) = \rho^{cov}_{S,M}(\vec{r}) + \rho^{se}_{S,M}(\vec{r}) \tag{A1}$$

$$\rho^{cov}_{S,M}(\vec{r}) = \sum_\alpha \langle X_{S,M}|2S_{\alpha z}|X_{S,M}\rangle d_\alpha(\vec{r})$$

$$d_\alpha(\vec{r}) = (d^0_\alpha(\vec{r}) + \sum_u |a_u|^2 d^u_\alpha(\vec{r}))/N$$

$$\rho^{se}_{S,M}(\vec{r}) = \sum_\alpha \langle X'_{S,M}|2S'_{\alpha z}|X'_{S,M}\rangle d_\alpha'(\vec{r})$$

$$d'_\alpha(\vec{r}) = \sum_v |a_v|^2 d^v_\alpha(\vec{r})/N$$

In eq A1, the dominant part of the spin density arises from the first term, which accounts for metal–ligand covalency, while the superexchange contribution $\rho^{se}_{S,M}$ leads only to a residual transfer of spin density from one metal to the other. This is illustrated in the text by the example of 2Fe2S clusters.

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