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REGULAR ARTICLE

Informatics and magnetic behavior of $[Fe_6S_6]^{3+}$ superclusters

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Abstract Theoretical study on informational and magnetic behavior of a trivalent iron ion in the iron–sulfur supercluster with six Fe centers was performed based on Heisenberg exchange and double exchange (delocalisation) model. The three-valent supercluster can be modeled by three Fe(III) and three Fe(II) ions arranged within an experimental structure of prismane. Energy spectrum of the system has been calculated numerically, depending on the Heisenberg exchange J_i and double exchange b parameters. Such knowledge allows us to obtain an entropy function of the considered supercluster that makes possible effective analysis from the informatics point of view. Values of von Neumann entropy and total spin energy have been calculated for the case of fully antiferromagnetic as well as partially ferromagnetic spin interactions. On the ground of the theoretical studies, possible interpretations of available experimental EPR data for the $(Et_4N)_3Fe_6S_6Cl_6CH_3Cl$ compound are proposed.

1 Introduction

The iron–sulfur clusters have been observed in biological systems such as, e.g., metalloproteins, and play important roles in many biological living processes including enzymatic catalysis. Such clusters of mixed valence, consisting of 2, 3, 4, 6, or more iron ions, are involved in multi-electron transfer processes or multi-electron pair redox catalysis in proteins and complex enzymes. These processes are necessary for life activity of the biological systems [1–3].

Many types of the Fe–S clusters have been synthesized (such structures are simpler than natural, so easier to be examined), structurally determined and intensively investigated. In particular, prismane clusters have been considered to determine both electron transfer ability under various conditions and accompanying structural changes. For example, the crystal structure of $(Et_4N)_3$-$Fe_6S_6Cl_6CH_3Cl$ compound has been described, with the $S = 1/2$ $[Fe_6S_6]^{3+}$ core, as concluded from the EPR and Mößbauer spectra [4].

The role of metalloproteins in cellular processes and their interactions illustrate the basic feature of biological materials. Biological molecules play two distinct roles: first—specialized chemicals, and second—informational molecules. Using the analogy of computing, the chemistry corresponds to hardware, while information—to software.

In the following, we describe the results of theoretical examinations of the crystal structure of $(Et_4N)_3$-$Fe_6S_6Cl_6CH_3Cl$, quantum-informational features and magnetic features, in particular interpretations of the EPR signal.

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2 Heisenberg Hamiltonian of the $[Fe_6S_6]^{3+}$ system with resonance delocalization for the prismane superclusters

Geometry of the $[Fe_6S_6]^{3+}$ supercluster is the exactly known geometry of the synthetic $Fe_6S_6Cl_6{}^{3-}$ system, obtained from X-ray measurements [4]. It is the structure of prismane (Fig. 1).

We describe the spin model for the $[Fe_6S_6]^{3+}$ prismane system (details for $[Fe_6S_6]^{4+}$ are included in our previous publications [5–7]). The Heisenberg Hamiltonian for the $[Fe_6S_6]^{3+}$ prismane can be written as

$$\begin{aligned}\hat{H}_H = {} & J_1\left(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_6 + \hat{S}_2\hat{S}_3 + \hat{S}_4\hat{S}_5\right) + J_2\hat{S}_3\hat{S}_4 + J_3\hat{S}_5\hat{S}_6 \\ & + J_4(\hat{S}_1\hat{S}_5 + \hat{S}_3\hat{S}_5 + \hat{S}_2\hat{S}_4 + \hat{S}_4\hat{S}_6) + J_5\hat{S}_1\hat{S}_3 + J_6\hat{S}_2\hat{S}_6 \\ & + J_7\hat{S}_3\hat{S}_6 + J_8\hat{S}_1\hat{S}_4 + J_9\hat{S}_2\hat{S}_5 \qquad (1)\end{aligned}$$

where J_i is one of the Heisenberg exchange parameters. A suitable electron configuration of $3d^5$ and $3d^6$ is expected for the Fe(III) and the Fe(II) ion, respectively, thus $S_1 = S_3 = S_4 = 5/2$, $S_2 = S_5 = S_6 = 2$.

In order to calculate the Heisenberg exchange energy, the Hamiltonian (Eq. 1) should be transformed into the following equivalent form:

$$\begin{aligned}\hat{H}_H = {} & \frac{1}{2}[J_1\left(\hat{S}^2_{1236} - \hat{S}^2_{13} - \hat{S}^2_{26} - \hat{S}^2_{36} + \hat{S}^2_{45} + \hat{S}^2_3 + \hat{S}^2_6 \right. \\ & \left. -\hat{S}^2_4 - \hat{S}^2_5\right) + J_2\left(\hat{S}^2_{34} - \hat{S}^2_3 - \hat{S}^2_4\right) \\ & + J_3\left(\hat{S}^2_{56} - \hat{S}^2_5 - \hat{S}^2_6\right) + J_4\left(\hat{S}^2_{135} - \hat{S}^2_{13} - \hat{S}^2_5 + \hat{S}^2_{246}\right. \\ & \left. -\hat{S}^2_{26} - \hat{S}^2_4\right) + J_5\left(\hat{S}^2_{13} - \hat{S}^2_1 - \hat{S}^2_3\right) + J_6\left(\hat{S}^2_{26} - \hat{S}^2_2 - \hat{S}^2_6\right) \\ & + J_7\left(\hat{S}^2_{36} - \hat{S}^2_3 - \hat{S}^2_6\right) + J_8\left(\hat{S}^2_{134} - \hat{S}^2_{13} - \hat{S}^2_{34} + \hat{S}^2_3\right) \\ & +J_9\left(\hat{S}^2_{256} - \hat{S}^2_{26} - \hat{S}^2_{56} + \hat{S}^2_6\right)] \qquad (2)\end{aligned}$$

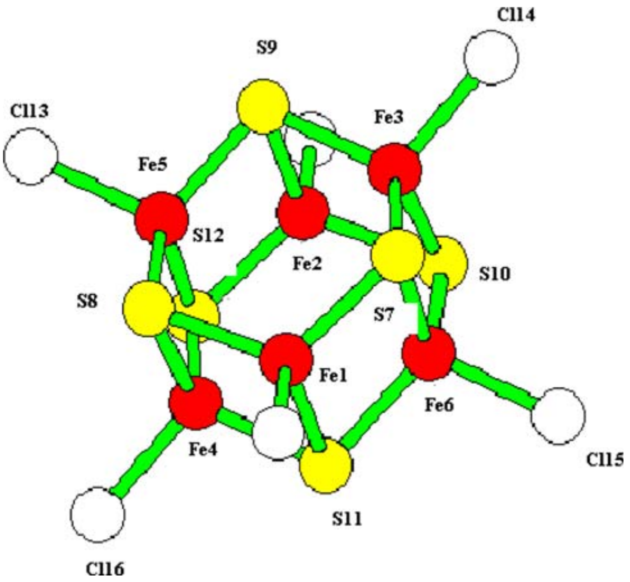

Fig. 1 Prismane structure of $Fe_6S_6X_6$ supercluster, where: *red*, *yellow* and *white* denotes Fe, S and Cl respectively

where $\hat{S}^2_{ijkl} = \left(\hat{S}_i + \hat{S}_j + \hat{S}_k + \hat{S}_l\right)^2$, $\hat{S}^2_{ijk} = \left(\hat{S}_i + \hat{S}_j + \hat{S}_k\right)^2$, $\hat{S}^2_{ij} = \left(\hat{S}_i + \hat{S}_j\right)^2$.

Since the Hamiltonian (Eq. 1) does not commute with all spin operators, it can be divided into three parts, namely $\hat{H}_0$, $\hat{H}_1$, $\hat{H}_2$, in such a way that each part consists of operators that commute with each other within a given part, i.e.,

$$\begin{aligned}\hat{H}_0 = {} & \frac{1}{2}[J_1\left(-\hat{S}^2_{13} - \hat{S}^2_{26}\right) + J_4\left(\hat{S}^2_{135} - \hat{S}^2_{13} + \hat{S}^2_{246} - \hat{S}^2_{26}\right) \\ & +J_5\hat{S}^2_{13} + J_6\hat{S}^2_{26} + J_8\left(-\hat{S}^2_{13}\right) + J_9\left(-\hat{S}^2_{26}\right)] \qquad (3a)\end{aligned}$$

$$\hat{H}_1 = \frac{1}{2}[J_1\left(\hat{S}^2_{1236} - \hat{S}^2_{36} + \hat{S}^2_{45}\right) + J_7\hat{S}^2_{36}] \qquad (3b)$$

$$\hat{H}_2 = \frac{1}{2}[J_2\hat{S}^2_{34} + J_3\hat{S}^2_{56} + J_8\left(\hat{S}^2_{134} - \hat{S}^2_{34}\right) + J_9\left(\hat{S}^2_{256} - \hat{S}^2_{56}\right)] \qquad (3c)$$

and a rest (having stable value):

$$\begin{aligned}\hat{H}_{\mathrm{const}} = {} & \frac{1}{2}[J_1\left(\hat{S}^2_3 + \hat{S}^2_6 - \hat{S}^2_4 - \hat{S}^2_5\right) + J_2\left(-\hat{S}^2_3 - \hat{S}^2_4\right) \\ & + J_3\left(-\hat{S}^2_5 - \hat{S}^2_6\right) + J_4\left(-\hat{S}^2_5 - \hat{S}^2_4\right) + J_5\left(-\hat{S}^2_1 - \hat{S}^2_3\right) \\ & + J_6\left(-\hat{S}^2_2 - \hat{S}^2_6\right) + J_7\left(-\hat{S}^2_3 - \hat{S}^2_6\right) \\ & +J_8\left(\hat{S}^2_3\right) + J_9\left(\hat{S}^2_6\right)] \qquad (4)\end{aligned}$$

Let us introduce a reduced dimensionless parameter $\alpha_i = \frac{J_{i+1}}{J_1}$ where $i = 1, 2, 3, 4, 5$.

The eigenfunctions of the total Hamiltonian (associated with the total spin S) can be presented as linear combinations of the eigenfunctions given in one of the coupling schemes (Eqs. 5, 6 or 7). We have chosen the eigenfunctions of the Hamiltonian $\hat{H}_0$ for this purpose.

$$\begin{aligned}& \psi_0(S_{13}, S_{135}, S_{26}, S_{246}, S) \\ & = |S_1S_3(S_{13})S_5(S_{135})S_2S_6(S_{26})S_4(S_{246})S\rangle \\ & = |(S_{13})(S_{135})(S_{26})(S_{246})S\rangle \qquad (5)\end{aligned}$$

the eigenfunctions of the Hamiltonian $\hat{H}_1$:

$$\begin{aligned}& \psi_1(S_{12}, S_{36}S_{1236}, S_{45}, S) \\ & = |S_1S_2(S_{12})S_3S_6(S_{36})(S_{1236})S_4S_5(S_{45})S\rangle \\ & = |(S_{12})(S_{36})(S_{1236})(S_{45})S\rangle \qquad (6)\end{aligned}$$

and the eigenfunctions of the Hamiltonian $\hat{H}_2$:

$$\begin{aligned}& \psi_2(S_{34}, S_{134}S_{56}, S_{256}, S) \\ & = |S_3S_4(S_{34})S_1(S_{134})S_5S_6(S_{56})S_2(S_{256})S\rangle \\ & = |(S_{34})(S_{134})(S_{56})(S_{256})S\rangle \qquad (7)\end{aligned}$$

Therefore, the eigenfunctions of the total Hamiltonian (1) can be expressed in terms of the eigenfunctions of the $\hat{H}_0$

$$\psi(S) = \sum_{i=i(S_{13},S_{135},S_{26},S_{246})} c_i|S_1S_3(S_{13})(S_{135})S_2S_6(S_{26})(S_{246})S\rangle \qquad (8)$$

where c_i are appropriate expansion coefficients.

The eigenfunctions of the $\hat{H}_0$ Hamiltonian can be denoted in the eigenfunctions of the $\hat{H}_1$ as

$$\begin{aligned}
&|(S_{13})(S_{135})(S_{26})(S_{246})S\rangle = \sum_{S_{45}S_{1236}} |(S_{13})(S_{26})(S_{1236})(S_{45})S\rangle \\
&\quad \times \langle (S_{13})(S_{26})(S_{1236})(S_{45})S \,|\, (S_{13})(S_{135})(S_{26})(S_{246})S\rangle \\
&= \sum_{S_{45}S_{1236}} \sum_{S_{12}S_{36}} |(S_{12})(S_{36})(S_{1236})(S_{45})S\rangle \\
&\quad \times \langle (S_{12})(S_{36})(S_{1236})(S_{45})S \,|\, (S_{13})(S_{26})(S_{1236})(S_{45})S\rangle \\
&\quad \times \langle (S_{13})(S_{26})(S_{1236})(S_{45})S \,|\, (S_{13})(S_{135})(S_{26})(S_{246})S\rangle
\end{aligned} \tag{9}$$

where

$$\begin{aligned}
&\langle (S_{13})(S_{26})(S_{1236})(S_{45})S \mid (S_{13})(S_{135})(S_{26})(S_{246})S\rangle \\
&= [(2S_{135}+1)(2S_{246}+1)(2S_{1236}+1)(2S_{45}+1)]^{\frac{1}{2}} \\
&\quad \times \begin{Bmatrix} S_{13} & S_5 & S_{135} \\ S_{26} & S_4 & S_{246} \\ S_{1236} & S_{45} & S \end{Bmatrix}
\end{aligned} \tag{10}$$

$$\begin{aligned}
&\langle (S_{12})(S_{36})(S_{1236})(S_{45})S \mid (S_{13})(S_{26})(S_{1236})(S_{45})S\rangle \\
&= [(2S_{12}+1)(2S_{36}+1)(2S_{13}+1)(2S_{26}+1)]^{\frac{1}{2}} \\
&\quad \times \begin{Bmatrix} S_1 & S_3 & S_{13} \\ S_2 & S_6 & S_{26} \\ S_{12} & S_{36} & S_{1236} \end{Bmatrix}
\end{aligned} \tag{11}$$

Instead the eigenfunctions of $\hat{H}_2$:

$$\begin{aligned}
&|(S_{13})(S_{135})(S_{26})(S_{246})S\rangle = \sum_{S_{134}S_{256}} |(S_{13})(S_{134})(S_{26})(S_{256})S\rangle \\
&\quad \times \langle (S_{13})(S_{134})(S_{26})(S_{256})S \mid (S_{13})(S_{135})(S_{26})(S_{246})S\rangle \\
&= \sum_{S_{134}S_{256}} \sum_{S_{34}} |(S_{34})(S_{134})(S_{26})(S_{256})S\rangle \\
&\quad \times \langle (S_{34})(S_{134})(S_{26})(S_{256})S \mid (S_{13})(S_{134})(S_{26})(S_{256})S\rangle \\
&\quad \times \langle (S_{13})(S_{134})(S_{26})(S_{256})S \mid (S_{13})(S_{135})(S_{26})(S_{246})S\rangle \\
&= \sum_{S_{134}S_{256}} \sum_{S_{34}} \sum_{S_{34}} |(S_{34})(S_{134})(S_{56})(S_{256})S\rangle \\
&\quad \times \langle (S_{34})(S_{134})(S_{56})(S_{256})S \mid (S_{34})(S_{134})(S_{26})(S_{256})S\rangle \\
&\quad \times \langle (S_{34})(S_{134})(S_{26})(S_{256})S \mid (S_{13})(S_{26})(S_{1236})(S_{45})S\rangle \\
&\quad \times \langle (S_{13})(S_{134})(S_{26})(S_{256})S \mid (S_{13})(S_{135})(S_{26})(S_{246})S\rangle
\end{aligned} \tag{12}$$

where

$$\begin{aligned}
&\langle (S_{13})(S_{134})(S_{26})(S_{256})S \mid (S_{13})(S_{135})(S_{26})(S_{246})S\rangle \\
&= [(2S_{135}+1)(2S_{246}+1)(2S_{134}+1)(2S_{256}+1)]^{\frac{1}{2}} \\
&\quad \times \begin{Bmatrix} S_{13} & S_5 & S_{135} \\ S_4 & S_{26} & S_{246} \\ S_{124} & S_{256} & S \end{Bmatrix}
\end{aligned} \tag{13a}$$

$$\begin{aligned}
&\langle (S_{34})(S_{134})(S_{26})(S_{256})S \mid (S_{13})(S_{134})(S_{26})(S_{256})S\rangle \\
&= (-1)^{S_1+S_4+S_{13}+S_{34}} [(2S_{13}+1)(2S_{34}+1)]^{\frac{1}{2}} \\
&\quad \times \begin{Bmatrix} S_4 & S_3 & S_{34} \\ S_1 & S_{134} & S_{13} \end{Bmatrix}
\end{aligned} \tag{13b}$$

$$\begin{aligned}
&\langle (S_{34})(S_{134})(S_{56})(S_{256})S \mid (S_{34})(S_{134})(S_{26})(S_{256})S\rangle \\
&= (-1)^{S_5+S_6+S_{26}+S_{56}} [(2S_{26}+1)(2S_{56}+1)]^{\frac{1}{2}} \\
&\quad \times \begin{Bmatrix} S_5 & S_6 & S_{56} \\ S_2 & S_{256} & S_{26} \end{Bmatrix}
\end{aligned} \tag{13c}$$

The expression in brackets in Eq. 13 denotes a 6-j and 9-j Wigner symbol, respectively [8]. In order to determine a ground state of the system, it is necessary to find total eigenenergies of a matrix $\langle i| \hat{H}_0 + \hat{H}_1 + \hat{H}_2 |j\rangle$, where $|i\rangle$ and $|j\rangle$ are eigenfunctions of one the partial Hamiltonian $\hat{H}_0$.

The resonance delocalisation can take place in systems of mixed valence. Since we have this same number Fe(II) ion and Fe(III) ion in the investigated $[Fe_6S_6]^{3+}$ system, the ions can be observed in 12 positions (Table 1), always leading to the same HDVV Hamiltonian.

In the case of the Fe–Fe distance, we can distinguish electron transfer of three types. The first one is between the nearest neighbours, i. e., 3:2 and 1:4, d_1 distance of the same energy $E1d_1$. The second type can be observed between ions localized at hexagon corners, i.e., 3:5 and 1:5, d_2 distance of the same energy $E1d_2$ of the same energy and the third type is between the most distant ions, i.e., 3:6, 1:6, d_3 distance with energy $E1d_3$. Transfers between particular states, so called electron hops are also possible. When we establish places of electron transfers causing transfer of the system from one configuration to another we assume the following: first we exclude transfers through indirect configurations and at multi-electron transfers we limit to pairs of the smallest distance.

Therefore, we will distinguish one–electron transfers, which are three because of the distance of electron transfer. The first are for the smallest distance in a cluster (marked d_1), e.g., between Fe ions in points 3 and 2, transfer from a configuration 1 to 4, and value of the transfer energy we mark as $E1d_1$. The second are for the distance longer than d_1 (d_2), e.g., between Fe ions in points 3 and 5, transfer from a configuration 1 to 5 ($E1d_2$ energy respectively). The last transfer is when the distance is longest d_3, e.g., between Fe ions in points 3 and 6, transfer from configuration 1 to 6 ($E1d_3$).

Two-electron transfers, because of the distance there are two types. First at shortest distance in a cluster d_1, e.g., first between Fe ions located in points 3 and 2. Second two-electron transfer is between Fe ions located in points 4 and 5, transition from a configuration 1 to 3 and an energy value marked as $E2d_1d_1$. Whereas when distance of a one-electron transfer amounts to d_1 between points 3 and 2 and distance of transfer of a second is longer and amounts to d_2, e.g., between Fe ions in points 1 and 5 what means transition from configuration 1 to 8 of energy $E2d_1d_2$. Three electron transfer is only one. It occurs when distances of transfers of three electrons are of the lowest value in a cluster d_1, e.g., first hop of an electron between Fe ions in

Table 1 Twenty positions leading to the same HDVV Hamiltonian

Configuration no.	1	2	3	4	5	6	7	8	9	10	11	12
Spin localisation 5/2	1, 3, 4	1, 3, 6	1, 2, 5	1, 2, 4	1, 4, 5	1, 4, 6	2, 5, 6	2, 4, 5	3, 4, 6	2, 3, 6	2, 3, 5	3, 5, 6
Spin localisation 2	2, 5, 6	2, 4, 5	3, 4, 6	3, 5, 6	2, 3, 6	2, 3, 5	1, 3, 4	1, 3, 6	1, 2, 5	1, 4, 5	1, 4, 6	1, 2, 4

points 3 and 2, second 4 and 5, third between Fe ions in points 1 and 6 what means transition from configuration 1 to 7 of an energy value amounting to $E3$ ($E3d_1d_1d_1$).

It is an important requirement that transition from one configuration to another did not cause change of eigenfunction of Heisenberg Hamiltonian, i.e., if there were no exchange interactions then each eigenfunction of Heisenberg Hamiltonian would be degenerated 12 times. Exchange interaction causes that eigenfunctions of full Hamiltonian will be combinations of those 12 own states of Heisenberg Hamiltonian.

To obtain eigenenergies of full Hamiltonian, one should solve eigenfunction of the following matrix:

$$\begin{pmatrix}
E_h & E1d_2 & E2d_1d_1 & E1d_1 & E1d_2 & E1d_3 & E3 & E2d_1d_2 & E1d_1 & E2d_1d_2 & E2d_1d_1 & E2d_1d_1 \\
E1d_2 & E_h & E2d_1d_1 & E2d_1d_2 & E2d_1d_1 & E1d_1 & E2d_1d_2 & E3 & E1d_3 & E1d_1 & E2d_1d_1 & E1d_2 \\
E2d_1d_1 & E2d_1d_1 & E_h & E1d_1 & E1d_2 & E2d_1d_2 & E1d_1 & E1d_3 & E3 & E2d_1d_2 & E1d_2 & E2d_1d_1 \\
E1d_1 & E2d_1d_2 & E1d_1 & E_h & E1d_3 & E1d_2 & E2d_1d_1 & E1d_2 & E2d_1d_1 & E2d_1d_1 & E2d_1d_2 & E3 \\
E1d_2 & E2d_1d_1 & E1d_2 & E1d_3 & E_h & E1d_1 & E2d_1d_2 & E1d_1 & E2d_1d_2 & E3 & E2d_1d_1 & E2d_1d_1 \\
E1d_3 & E1d_1 & E2d_1d_2 & E1d_2 & E1d_1 & E_h & E2d_1d_1 & E2d_1d_1 & E1d_2 & E2d_1d_1 & E3 & E2d_1d_2 \\
E3 & E2d_1d_2 & E1d_1 & E2d_1d_1 & E2d_1d_2 & E2d_1d_1 & E_h & E1d_2 & E2d_1d_1 & E1d_2 & E1d_3 & E1d_1 \\
E2d_1d_2 & E3 & E1d_3 & E1d_2 & E1d_1 & E2d_1d_1 & E1d_2 & E_h & E2d_1d_1 & E2d_1d_1 & E1d_1 & E2d_1d_2 \\
E1d_1 & E1d_3 & E3 & E2d_1d_1 & E2d_1d_2 & E1d_2 & E2d_1d_1 & E2d_1d_1 & E_h & E1d_2 & E2d_1d_2 & E1d_1 \\
E2d_1d_2 & E1d_1 & E2d_1d_2 & E2d_1d_1 & E3 & E2d_1d_1 & E1d_2 & E2d_1d_1 & E1d_2 & E_h & E1d_1 & E1d_3 \\
E2d_1d_1 & E2d_1d_1 & E1d_2 & E2d_1d_2 & E2d_1d_1 & E3 & E1d_3 & E1d_1 & E2d_1d_2 & E1d_1 & E_h & E1d_2 \\
E2d_1d_1 & E1d_2 & E2d_1d_1 & E3 & E2d_1d_1 & E2d_1d_2 & E1d_1 & E2d_1d_2 & E1d_1 & E1d_3 & E1d_2 & E_h
\end{pmatrix} \tag{14}$$

Because of the complexity of calculations, we will limit to calculation of only three energy values: $E1d_1$, $E2d_1d_1$, and $E3$ (Eqs. 18–20). The other values we neglect because of little probability of electron transfers at long distances of iron ions.

Base to double exchange sufficient to calculate each of the three above energy values is

$$\begin{aligned}
&\psi_d(S_{16}, S_{23}S_{1236}, S_{45}, S) \\
&\quad = |S_1S_6(S_{16})S_2S_3(S_{23})(S_{1236})S_4S_5(S_{45})S\rangle \\
&\quad = |(S_{16})(S_{23})(S_{1236})(S_{45})S\rangle
\end{aligned} \tag{15}$$

$$\begin{aligned}
\psi_1 = \sum_{\psi_d} &\langle S_1S_6(S_{16})S_2S_3(S_{23})(S_{1236})S_4S_5(S_{45})S \\
&\times \mid S_1S_2(S_{12})S_3S_6(S_{36})(S_{1236})S_4S_5(S_{45})S\rangle \psi_d
\end{aligned} \tag{16}$$

where

$$\begin{aligned}
&\langle (S_{16})(S_{23})(S_{1236})(S_{45})S \mid (S_{12})(S_{36})(S_{1236})(S_{45})S\rangle \\
&\quad = [(2S_{12}+1)(2S_{36}+1)(2S_{16}+1)(2S_{23}+1)]^{\frac{1}{2}} \\
&\quad\times \begin{Bmatrix} S_1 & S_2 & S_{12} \\ S_6 & S_3 & S_{36} \\ S_{16} & S_{23} & S_{1236} \end{Bmatrix}
\end{aligned} \tag{17}$$

To calculate $Ed1$ we used spin operator $\hat{H}_{d(1-6)} = b_1\left(\hat{T}_{16}\right)$.

$$\begin{aligned}
\mathrm{Ed1} &= \langle \Phi_{134}|\hat{H}_{d(1-6)}|\Phi_{634}\rangle = \langle \Phi_{134}|b_1\hat{T}_{16}|\Phi_{634}\rangle \\
&= \sum_{\psi_d} c_d^2(S_{16}, S_{23}, S_{45})\left(S_{16} + \tfrac{1}{2}\right) \times b_1
\end{aligned} \tag{18}$$

Φ_{ijk} describes eigenfunction of full Heisenberg Hamiltonian for configuration with $S_i = S_j = S_k = 2.5$, $\hat{T}_{16}$ describes operator of electron hop between ions i and j, b_1 parameter of a one-electron hop.

To calculate $E2d1d1$ we used spin operator $\hat{H}_{d(1-6,4-5)} = b_2\left(\hat{T}_{16} \circ \hat{T}_{45}\right)$, b_2 parameter of a one-electron hop.

$$\begin{aligned}
\mathrm{E2}d1d1 &= \langle \Phi_{134}|\hat{H}_{d(1-6)(4-5)}|\Phi_{635}\rangle \\
&= \langle \Phi_{134}|b_2\left(\hat{T}_{16} \circ \hat{T}_{45}\right)|\Phi_{635}\rangle \\
&= \sum_{\psi_d} c_d^2(S_{16}, S_{23}, S_{45})\left(S_{16} + \tfrac{1}{2}\right)\left(S_{45} + \tfrac{1}{2}\right) \times b_2
\end{aligned} \tag{19}$$

To calculate $E3$ we used spin operator $\hat{H}_{d(1-6,4-5,2-3)} = b_3(\hat{T}_{14} \circ \hat{T}_{45} \circ \hat{T}_{23})$ b_3 parameter of a one-electron hop.

$$\begin{aligned} E3 &= \langle \Phi_{134} | \hat{H}_{d(1-6)(4-5)(3-2)} | \Phi_{256} \rangle \\ &= \langle \Phi_{134} | b_3 (\hat{T}_{16} \circ \hat{T}_{45} \circ \hat{T}_{23}) | \Phi_{256} \rangle \\ &= \sum_{\psi_d} c_d^2 (S_{16}, S_{23}, S_{45}) (S_{23} + \frac{1}{2}) (S_{45} + \frac{1}{2}) (S_{16} + \frac{1}{2}) \times b_3 \end{aligned} \tag{20}$$

3 Theoretical information entropy

Nearly half of all proteins present in cells are specialized catalysers-enzymes. In the presence of enzymes many reactions take place under physiological conditions, i.e., at a relatively low temperature and under normal pressure, much faster (often up to 10^{10} times faster than in the presence of synthetic catalysers). Explanation of this phenomenon is very difficult. Most of the fundamental developments in physics (included quantum mechanics) in the past century have occurred without any explicit implication of the concept of information. The concept of information has played a major role in biology, the concept of energy playing a secondary role. But there are theoretical reasons to believe that full understanding of living processes including enzymatic catalysis may not be achieved without taking into account both informational and energetic aspects. As such, this information can be quantified using the theoretical information entropy. The processes in biological systems consist of selection of a message from the message source, transmission of the message through the communication channel, and the reception of the message by the receiver with the concomitant impact of the message on the receiver. In 1974, this dual requirement of energy and information for enzymatic catalysis was explicitly recognized in the formulation of the hypothesis that enzymes provide not only energy but also catalytic message [9]. The bioelectronic quantum computing is characterized, on the one hand by weak interactions, differing from chemical interactions, of biomacromolecules with the energy in the elementary act $E \ll kT$, providing their integrity, and on the other hand—by quite high selectivity. A number of molecules and molecular systems that could form part of cellular quantum information processing systems may be described as a quantum computer. The following short list [10] summarizes a selection of examples: wiring-polyene antibiotics, conductive biopolymers; storage-photosystem II, reaction centres, cytochromes, blue proteins, ferritin, collagen, DNA; gates and switches-bacteriorhodopsin, photosynthetic systems, cell receptors, ATPase. We have listed the examples of quantum processes as are attributable to biological materials, such as the iron–sulfur systems, present in enzymes which can be found in numerous bacteria and other biological systems [1–3]. Use of quantum mechanics to process information may lead to new effects, which were not found in the classic theory of information. Entanglement is a new, non-classic element introduced to the processing information by quantum informatics [11–14]. Unfortunately, there is no entirely accepted definition of entanglement [15]. There are many ways of designating entanglement criteria. Pursuit of classifying entanglement states leads to the notion of entanglement measure. In sending and processing information entanglement is a very valuable resource. In the case of carrying out an algorithm by a quantum computer (biological system), it is interesting to note how many entanglements we have at our disposal and how many we use while performing the task. Because of the lack of criteria of entanglement of multi-component systems (although in the recent literature there has appeared information giving general construction of entanglement measure in multi-component systems [16]) we use in this works measures allowing to calculate the degree of entanglement for two subsystems of a complex system. The measure of entanglement may be treated as a physical value. The most important measure for pure states is the reduced von Neumann entropy. Reduced von Neumann entropy for a pure state $|\psi\rangle\langle\psi|$ can be described as

$$\begin{aligned} S_{vN}(|\psi\rangle\langle\psi|) &= -Tr_B(Tr_A(|\psi\rangle\langle\psi|)\log(Tr_A(|\psi\rangle\langle\psi|)) \\ &= -Tr_A Tr_B(|\psi\rangle\langle\psi|)\log((Tr_B(|\psi\rangle\langle\psi|)) \end{aligned} \tag{21}$$

where $|\psi\rangle$l is a unit vector in a Hilbert space of the complex system $H = H_A \otimes H_B$.

In our case we have eigenfunctions of Hamiltonian (1), described by the Eq. 22.

$$\psi(S) = \sum_{i=i(S_{13},S_{135},S_{26},S_{246})} c_i | S_1 S_3 (S_{13}) (S_{135}) S_2 S_6 (S_{26}) (S_{246}) S \rangle \tag{22}$$

To obtain matrix of density of mixed states ($\rho = |\psi\rangle\langle\psi|$) we will divide our system into two parts (A and B), i.e., on a system, e.g., described by a spin S_{13}, and a system comprising the other spins. Then, after the other spins we will carry out summing up in this way, we will obtain a mixed state because of the spin S_{13}.

So far in this chapter, to keep the text legible, we assumed that our iron ions may be located in two states, what means that they represented qubits. In reality we have a multi-level system (qubit theory). For our further considerations it is essential that we may bring these systems to circuits with gates built on qubits. Moreover, one should note that a qubit system may include more information than a qubit, by a $\log_2 n$ factor.

Quantum computing of the irons superclusters could in principle be performed by array of systems, such as single electron spins, coupled via the Heisenberg (or “exchange”) interaction. Heisenberg interaction can effectively lead to

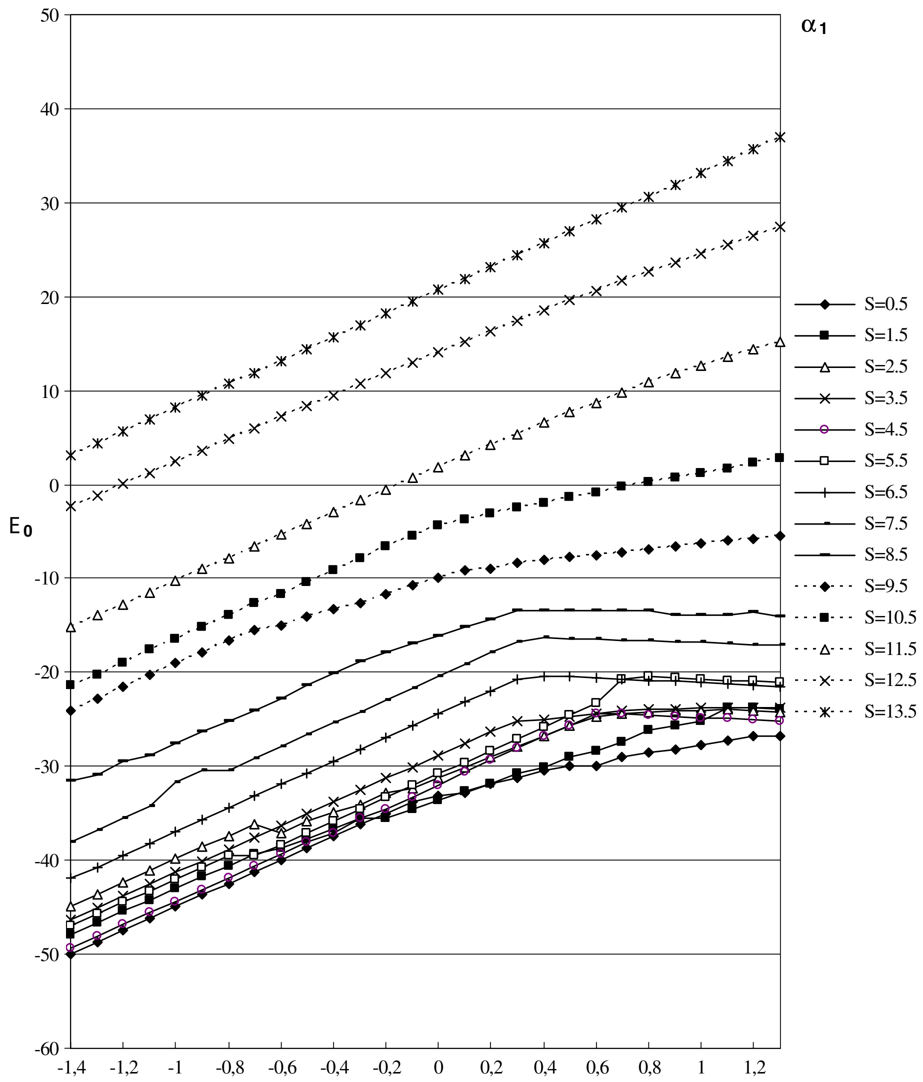

Fig. 2 Correlation energy diagram for the lowest spin states without resonance delocalization: $S = 0.5, \ldots, 13.5$, $\alpha_2 = -1$, $\alpha_3 = -0.2$, $\alpha_4 = \alpha_5 = \alpha_6 = \alpha_7 = \alpha_8 = 0.1$, $b = 0J_1$

inversion of electron spins. To the calculations of reduced von Neumann entropy we used a function Eq. 22, which was designated by using Heisenberg Hamiltonian, taking into consideration a double exchange. Numerical calculations were performed using our own HMVC-RE package [17].

4 Discussion of numerical calculations of eigenenergies and information entropy

The total Hamiltonian including the double and treble electron exchange takes the following form:

$$\hat{H}_{\text{total}} = \sum_i \hat{H}_i + \hat{H}_d \tag{23}$$

where $\hat{H}_i$ is a HDVV operator that acts on the ψ_i state only.

Calculations with changes of parameter α_i were made. The changes of α_i corresponded to different states, for example with fully antiferromagnetic interactions, where $\alpha_1 = 1.5$, $\alpha_2 = 0.2$, $\alpha_3 = \alpha_4 = \alpha_5 = 0.1$, or with partially ferromagnetic interactions with $\alpha_1 = -1.5$, $\alpha_2 = 0.2$, $\alpha_3 = \alpha_4 = \alpha_5 = 0.1$. The results of numerical calculations of the energies for the spin states of the prismane structure are presented in Figs. 2, 3. The total energy (including only Heisenberg exchange) is expressed in the units of the parameter J_1 (i.e., $E0 = E/J_1$). The double exchange energy is expressed in the units of the parameter b ($Ed0 = Ed/b$). In the case of neglecting the double exchange (Fig. 2) and for $\alpha_1 = -1.5$ there are different states with similar energies for the total spin from $S = 0.5$ to 5.5. Within the range of α_1 values ranging from 0.1 to 1.5 (ferromagnetic interactions) the ground-state energy is achieved for the total spin $S = 1/2$. The experimental total spin of $S = 1/2$ (the same as that in our theoretical model) was found for the synthetic $[Fe_6S_6]^{3+}$ ion [4]. If the double exchange is taken into account (Fig. 3) the correlation diagram of spin-state energy-changes only slightly

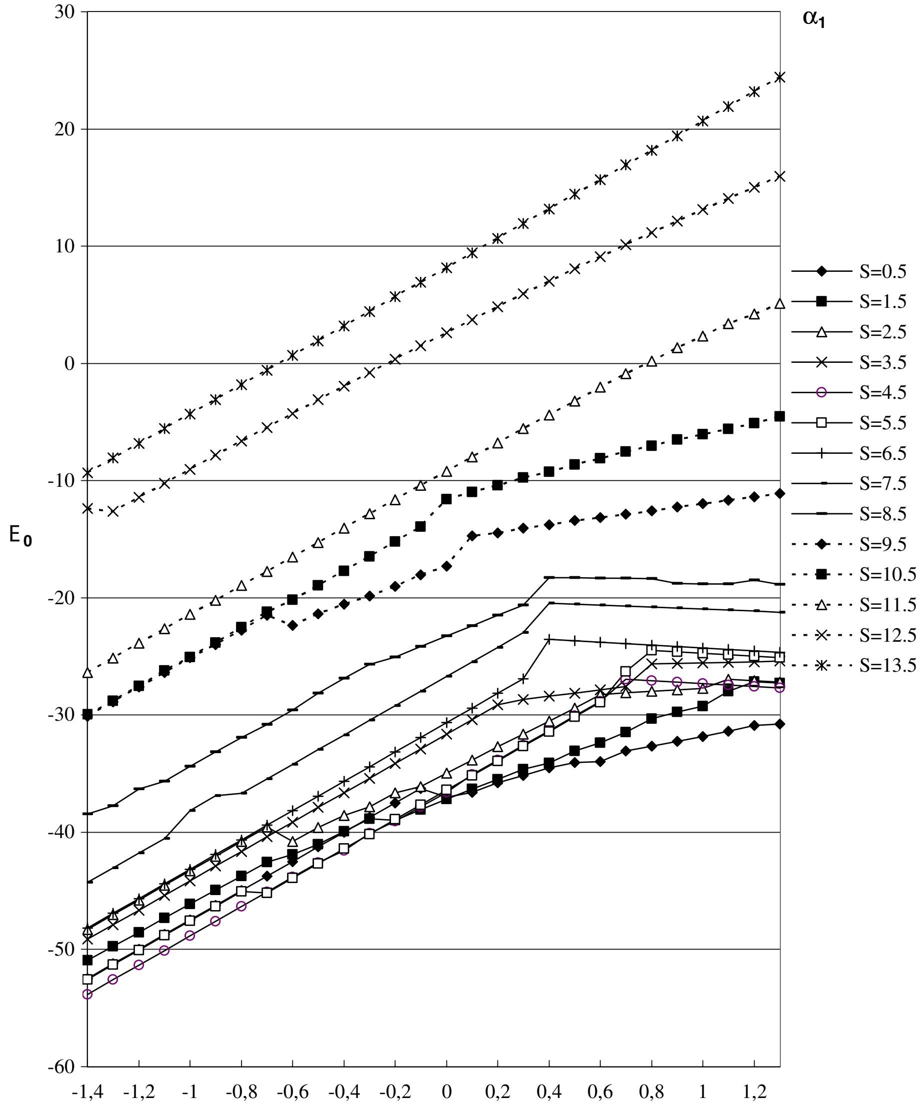

Fig. 3 Correlation energy diagram for the lowest spin states with resonance delocalization: $S = 0.5, \ldots, 13.5$, $\alpha_2 = -1$, $\alpha_3 = -0.2$, $\alpha_4 = \alpha_5 = \alpha_6 = \alpha_7 = \alpha_8 = 0.1$, $b1 = 0.5J_1$, $b2 = 0.2J_1$, $b3 = 0.1J_1$

displaces in relation to the previous case. In the ferromagnetic area this picture shows that the order of the energy states is correlated with the total spin values and is this same as in the exchange model. Moreover, there is a general rule that the energies of states for ferromagnetic interactions are larger than the antiferromagnetic ones.

In Figs. 4, 5 we present correlation between the reduced von Neumann entropy for a subsystem connected with two spins located on the iron ion, and the total spin of the supercluster. Analysis of the calculation results provides valuable information and may help to explain the mechanism of functioning of enzymes. Here we can see how the value of reduced von Neumann entropy depends on the symmetry, distances between the iron ions or charges on the iron ions. Particular pairs of iron ions can be characterized by other degree of entanglement with the other part of the supercluster. This entanglement depends also on the total spin of the whole system. In all the cases we can see some similarities. Generally, we can say that entanglement decreases with the increase in the total spin (the increase in the spin increases the energy of the system). The entanglement is different for iron ions designated as 1 and 3 of 5/2 spins. In this case entanglement does not exceed 0.5, i.e., it is by four times lower than in other cases; moreover, in the states of the total spin in the range from 2.5 to 7.5 the entanglement amounts to zero what means that the system is in the pure state. In all the cases (except for S_{13}) the entanglement is high and exceeds 1.0, but it dramatically decreases in the states of the total spin over $S = 10.5$. Except for the state $S = 3.5$ for coupling between the ions No. 4 and 5, and 3 and 6, entanglement decreases to 0.2. In Fig. 5 we observe a correlation between entropy and temperature. We can precisely see very fast increase in the entropy with the increase in temperature. In temperatures over the room temperature, the increase is practically independent of it. Different interactions of entanglement

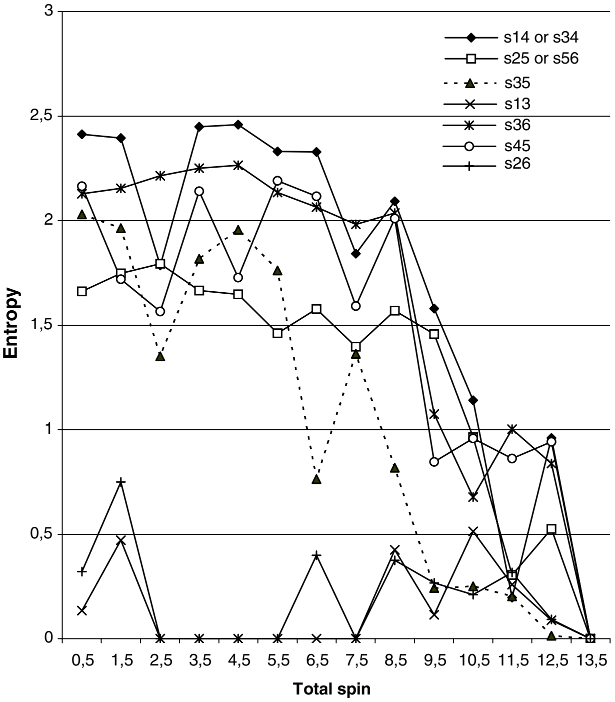

Fig. 4 Entropy for a few subsystems in relation to total spin

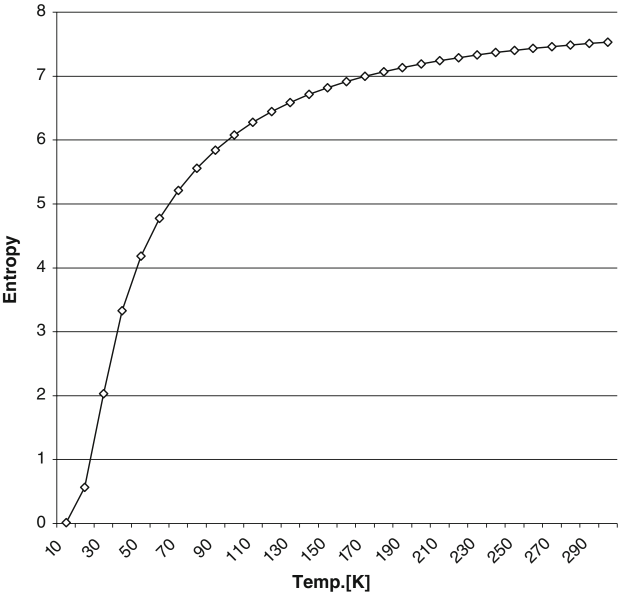

Fig. 5 Entropy of total cluster in relation to temperature

for particular parts of the supercluster, depending on the state (total spin), may be explained by the above mentioned selectivity of the center of an active enzyme, whereas correlation between entropy and temperature allows to assume the systems will be most effective in room temperatures.

5 Conclusions

Theoretical study of Heisenberg exchange and double exchange effects in the iron–sulfur supercluster of six iron ions has been performed. The prismane model of the $[Fe_6S_6]^{3+}$ cluster allows us to predict the total spin of ground state, depending on the Heisenberg direct exchange and double exchange parameters. The total spin of $S = 1/2$ is expected in the case when fully antiferromagnetic interactions and double exchange are included. This is in agreement with the available EPR literature data for synthetic systems having an iron–sulfur core of the prismane type in the $(Et_4N)_3Fe_6S_6Cl_6CH_3Cl$ compound. Analysis of the results of calculations of reduced von Neumann entropy, based on the obtained spin density within the theory using the Heisenberg Hamiltonian, allowed us to interpret qualitatively selectivity and temperature requirements for metallic systems built into enzymes.

References

1. Lowenberg W (1977) Iron–sulfur proteins, vol 1–3. Academic Press, New York
2. Matsubara H, Katsube Y, Wada K (1987) Iron–sulfur protein research. Springer, Berlin
3. Cammack R, Dickson DPE, Johnson CE (1977) In: Lovenberg W (ed), Iron–sulfur proteins, vol 3. Academic Press, New York, p 283
4. Pierik AJ, Hagen WR, Dunham WR, Sands H (1992) Eur J Biochem 206:705
5. Matusiewicz M, Czerwiński M, Kasperczyk J, Kityk IV (1999) J Chem Phys 111:6446
6. Matusiewicz M, Czerwinski M, Kasperczyk J (2002) J Clust Sci 12:537
7. Czerwiński M (1999) Int J Quantum Chem 72:39
8. Jucys AP, Badzaitis AA (1977) Theory of angular momentum in quantum mechanics (in Russian). Moklas, Vilnius, p 175
9. Ji S (1974) Energy and negentropy in enzymic catalysis. NY Acad Sci 227:419
10. Ji S (2000) BioSystems 54:107
11. Schrödinger E (1935) Die gegenwärtige situation in der Quantenmechanik. Naturwissenschaften 23:807
12. Silverman MP (1995) More than one mystery: explorations in quantum interference. Springer, Berlin
13. Bell JS (1990) Phys World 3:33
14. Bouwmeester D, Ekert A, Zeilinger A (2001) The Physics of quantum information. Springer, Berlin
15. Bruss D (2002) J Math Phys 43:4327
16. Mintert F, Kuś M, Buchleintner A (2005) Phys Rev Lett 95:260502
17. Czerwiński M, Matusiewicz M (2006) Computer package Heisenberg mixed valence calculation, HMVC-RE