Modelling of EMR data for Fe$^{2+}$ ($S=2$) ions in a [2Fe-2S] cluster in the reduced ferredoxin

Abstract. The modelling techniques employed in this study utilize structural data to enable correlation of EMR data – described by the spin Hamiltonian (SH) and optical spectroscopy data – described by the crystal field (CF) Hamiltonian. These techniques enable also to predict magnetic and spectroscopic properties of 3$d^6$ ions, especially 3$d^6$ and 3$d^8$ ions, in various systems. Specific applications are considered for [Fe$^{2+}$ and Fe$^{3+}$] binuclear centres in [2Fe-2S] cluster in the reduced ferredoxin and related biological molecules. The background for model calculations of the zero-field splitting (ZFS) parameters and/or crystal field parameters and the capabilities of the two major techniques used will be presented in the full paper. Here, we present preliminary results of the microscopic spin Hamiltonian (MSH) modelling for Fe$^{3+}$ (3$d^6$) ions in the reduced ferredoxin.

Keywords: [2Fe-2S] cluster • electron magnetic resonance (EMR) • Fe$^{2+}$ ions • microscopic spin Hamiltonian (MSH) • zero field splitting (ZFS) parameters
parameters has been presented in [16]. Two major techniques employed are: (i) the package MSH/VBA [18] developed in Visual Basic in Application (VBA) in Excel environment based on the microscopic spin Hamiltonian (MSH) theory, which includes also graphical capabilities and is especially useful for the 3$d^7$ and 3$d^6$ ($S = 2$) ions at tetragonal, trigonal, and orthorhombic symmetry sites [19] and (ii) the CF analysis (CFA) package [11] which is suitable for the 3$d^6$ ions at arbitrary symmetry sites in crystals, and includes the MSH module for axial symmetry cases. Preliminary microscopic modelling results for the Fe$^{3+}$(3$d^7$) ions with spin $S = 2$ in the reduced forms of rubredoxin (Rd$_{\text{red}}$) are presented here. Illustrative examples of potential applications of these techniques for other 3$d^7$ and 3$d^6$ ($S = 2$) ions in biological systems will be discussed in the full paper together with a comparative analysis of our results with the pertinent ones obtained using DFT techniques [10, 21].

### Theoretical background

Iron-sulphur [2Fe-2S] proteins are characterized by the presence of polynuclear metallic systems containing sulphide ions, in which the iron ions have variable oxidation states. The simplest polynuclear system is constituted by two iron ions bridged by two sulphide ions, coordinated by four cysteinyl ligands in Fe$_2$S$_2$ ferredoxins [4] or by two histidine and two cysteines ligands. Spectroscopic properties of the 3$d^6$ ions in crystals are determined by the CF energy levels and states. The energy levels scheme of the Fe$^{2+}$ ions in Rd$_{\text{red}}$ systems correspond to the energy levels \{\Delta_i\} scheme denoted cOHII in the package MSH/VBA [18, 19] with \Delta_1, \Delta_2, \Delta_3 corresponding to \Delta_{\text{ex}}, \Delta_{\alpha}, \Delta_{\tau} in [20], respectively. Additionally, the correlation of the wave functions yields the mixing coefficient \theta used in [18, 19] corresponding to \((\pi/2 - \theta)\) in [20]. Detailed analysis of the energy levels, wave functions, and mixing coefficients will be presented in the full paper.

### Results and discussion

#### Selected sets of model parameters

The energy levels and mixing coefficient ($s$) adopted from Ref. [20] for calculations of the Zeeman $g$-factors and the ZFS parameters [18, 19] are listed in Table 1. Shubin and Dikanov in their Table 1 [20] have provided the minimum and maximum values of the mixing angle $\theta$ for each set of parameters obtained during the fitting of the experimental g-tensors for the [2Fe-2S] cluster. The intervals ($\theta_{\text{max}} - \theta_{\text{min}}$) are rather small and vary slightly for their sets I to III, which were considered as most reasonable, whereas are larger and vary significantly for their sets IV to VII, which were considered as deficient in some respects by some authors [20]. In order to reduce the modelling calculations to a manageable number of input datasets, we have selected only the energy levels $\Delta_i$ given in their sets I to III and denoted them as sets 1 to 3 in our Table 1, respectively. For the same reason, we have adopted the average values of the mixing angles $\theta_{av} = (\theta_{\text{max}} + \theta_{\text{min}})/2$, as listed in Table 1, and recalculated them for the mixing coefficients $s_{av} = \sin(\pi/2 - \theta_{av})$ [18, 19]. In order to consider variations of the spin Hamiltonian parameters with the microscopic

<table>
<thead>
<tr>
<th>Set</th>
<th>$\Delta_1$</th>
<th>$\Delta_2$</th>
<th>$\Delta_3$</th>
<th>$\Delta_4$</th>
<th>$\theta_{av}$</th>
<th>$s_{av}$</th>
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<td>15 000</td>
<td>650</td>
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<td>2497</td>
<td>30 526</td>
<td>640</td>
<td>31 026</td>
<td>0.8961</td>
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<td>616</td>
<td>18 090</td>
<td>347</td>
<td>18 590</td>
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<td>-43.15</td>
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The following variants of parameter sets are included in our calculations (in cm⁻¹): (A) with \( \lambda = -80, \rho_A = 0.18 \) and differing by \( \Delta_4 \): (Ai) \( \Delta_4 \equiv \text{Max} + 500 \) and (Ai) \( \Delta_4 \equiv \text{Max} + 1000 \), and (B) differing by \( \rho_B \): (Bi) and (Bii) with \( \rho_B = 1.00 \) and other respective parameters as in sets (Ai) and (Aii), respectively. By ‘Max’ we denote the available maximum energy of the third excited state for a given set.

### Table 2. The calculated Zeeman factors (\( i = x, y, z \)) for Fe²⁺-[2Fe-2S]: \( g_{zi} \) – contributions due only to the second-order spin-orbit coupling, \( g_{zit} \) – the total values, and the relative percentage differences \( \Delta g_{zi} \) defined in text; \( g_e = 2.0023 \)

<table>
<thead>
<tr>
<th>Set</th>
<th>( g_x = g_e + \Delta g_x(\lambda) )</th>
<th>( g_y = g_e + \Delta g_y(\lambda) )</th>
<th>( g_z = g_e + \Delta g_z(\lambda) )</th>
<th>( g_{xT} = g_{zit} - \Delta g_x(\lambda) )</th>
<th>( g_{yT} = g_{zit} - \Delta g_y(\lambda) )</th>
<th>( g_{zT} = g_{zit} - \Delta g_z(\lambda) )</th>
<th>( \Delta g_x(%) )</th>
<th>( \Delta g_y(%) )</th>
<th>( \Delta g_z(%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0977 2.0449 2.2172 2.0421 1.9766 2.1601 2.7</td>
<td>3.3</td>
<td>2.6</td>
<td>2.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2</td>
<td>2.0810 2.0232 2.1993 2.0309 1.9640 2.1484 2.4</td>
<td>2.9</td>
<td>2.3</td>
<td>2.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>3</td>
<td>2.0896 2.0358 2.8650 1.6942 1.5875 2.4654 18.9</td>
<td>22.0</td>
<td>14.0</td>
<td>18.3</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Our calculations reveal that for all variants, the relative percentage differences \( \Delta g_x \) are around 3% for the set 1 and 2, whereas around 19% for the set 3 (Table 2).

### Table 3. The total ZFS parameters \( b_{ki} \) for Fe²⁺-[2Fe-2S]

<table>
<thead>
<tr>
<th>Set</th>
<th>( b_{0} )</th>
<th>( b_{2} )</th>
<th>( b_{4} )</th>
<th>( b_{6} )</th>
<th>( b_{8} )</th>
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<tr>
<td>1</td>
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<td>-0.4243</td>
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<td>0.4763</td>
<td>0.2848</td>
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<tr>
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<td>0.1065</td>
<td>0.3309</td>
<td>0.1775</td>
</tr>
<tr>
<td>3</td>
<td>-19.3302</td>
<td>-8.7285</td>
<td>5.9851</td>
<td>6.5630</td>
<td>1.1052</td>
</tr>
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</table>

Our calculations reveal that for all variants, the relative percentage differences \( \Delta g_x \) are around 3% for the set 1 and 2, whereas around 19% for the set 3 (Table 2).

The total standardized [15–17] ZFS parameters for Fe²⁺ in the [2Fe-2S] proteins for the variant Ai are presented in Table 3. Note that the calculated ZFS parameters for the sets 1 to 3 from Table 1 are standard and nearly the same for the variants Ai (Bi) and Aii (Bii), thus showing that these quantities depend only slightly on the variables \( \Delta_4 \) and \( \rho \) [18]. Hence, we refrain from presenting the results for the type (ii) variants.

For illustration, the variations of the total second-rank ZFS parameters \( b_{0} \) and \( b_{2} \) for Fe²⁺-[2Fe-2S] with the spin-orbit coupling constant \( \lambda \) for the sets 1 to 3 from Table 3 and using the variant \( A \) with \( \rho_A = 0.18 \) cm⁻¹ are presented in Fig. 1. The variations of the fourth-rank ZFS parameters \( b_{4} \) have also been considered and will be presented in the full paper.

### Calculated spin Hamiltonian parameters

In order to visualize the role of the additional contributions to the Zeeman \( g \) factors included in the extended perturbation expressions [18, 19] \( g_{zit} \) with respect to the second-order spin-orbit coupling contributions, \( g_z \), only included by other authors [5, 20] the relative percentage differences are defined as follows

\[
\Delta g_{zi} = \frac{|g_{zit} - g_{zi}|}{g_{zi}} \times 100\%
\]

Fig. 1. Variation of the total second-rank ZFS parameters \( b_{0} \) and \( b_{2} \) for Fe²⁺-[2Fe-2S] with \( \lambda \) for the sets 1 to 3 (Table 1) and the variant \( A \) (\( \rho_A = 0.18 \) cm⁻¹).

Our calculations reveal that for all variants, the relative percentage differences \( \Delta g_x \) are around 3% for the set 1 and 2, whereas around 19% for the set 3 (Table 2).
It is seen in Figs. 1a and 1b that for the set 1 and 2, the value of $|b_2^b|$ and $|b_2^q|$ decrease while the absolute value of $|\lambda|$ decreases and remain standard [15–17] in the range of $\lambda$ considered. For the set 3, some peculiarities are observed, which arise due to orthorhombic standardization since the package MSH/VBA [18, 19] transforms automatically the ZFS parameters from a non-standard region to the standard region $S1$ [15–17]. Overall after standardization the values of non-standardized parameter $\alpha$ decrease for $\lambda$ in the range $(–120, –102)$ cm$^{-1}$ and negative for $\lambda \alpha (–102, –40)$ cm$^{-1}$ (Figs. 1c and 1d). However, the non-standardized parameter $b_y^b$ changes the sign first at about $\lambda = –117$ cm$^{-1}$ due to the transformation from the $S5$ to $S2$ region, whereas the apparent jumps for the set 3 at about $\lambda = –102$ cm$^{-1}$ are due to the transformation from the $S2$ to $S1$ region. The results for several other data sets and their detailed analysis will be presented in the full paper.

Conclusions

The capabilities of the modelling technique, i.e. the package MSH/VBA based on microscopic spin Hamiltonian (MSH) theory, have been demonstrated using as a case study model calculations of the spin Hamiltonian parameters for Fe$^{2+}$ ions in the reduced ferrodoxin. The preliminary results for the Zeeman $g$ factors and the second-rank zero field splitting (ZFS) parameters are presented here. The variation of the total second-rank ZFS parameters $b^b_2$ and $b^q_2$ for Fe$^{2+}$ in the [2Fe-2S] cluster with the spin-orbit coupling constant $\lambda$ reveals that for certain parameter sets obtained by Shubin and Dikanov [20] intricate aspects related to orthorhombic standardization must be considered. Detailed analysis of the extended results will be presented in the full paper. Our comparative analysis will enable bridging the gap between DFT and crystal-field based techniques for modelling of EMR and optical spectroscopic data.

References