Metal–Metal Interactions in 2-Fe Ferredoxins; SCF-Xα-SW Calculations

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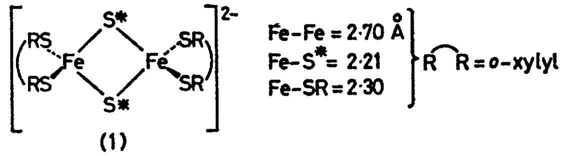
Summary SCF–Xα–SW calculations on $Fe_2S_2(SH)_4{}^{2-}$ show that (i) the antiferromagnetism of 2–Fe ferredoxins is due to superexchange rather than direct Fe–Fe overlap; (ii) the weak direct Fe–Fe bonding present is concentrated not in the Fe 3d band, but in a lower lying, mainly Fe–(bridging S) orbital.

We present here some conclusions from an overlapping-sphere SCF–Xα–SW calculation on $Fe_2S_2(SH)_4^{2-}$, a theoretical model for the active site of oxidized 2–Fe ferredoxin proteins. Previously we have reported such calculations for 1–Fe[1] and 4–Fe[2] iron-sulphur protein models (the latter being mainly work of our co-authors). The nature of Fe–Fe interaction in the 2–Fe proteins, and its influence on their properties, has been widely disucussed.[3] Structures of synthetic models for the oxidized proteins[4] (**1**) show



(1)

them to be members of the large class of compounds where two metals are bridged by two ligands. We have gained some insights about Fe–Fe bonding in this environment by combining explicit calculations with general theoretical concepts previously developed for $M_2(\mu\text{–}X)_2$ compounds.[5–7] Our own prior conclusions concerning $Rh_2Cl_2(CO)_4$[7] prove particularly applicable to the present case.

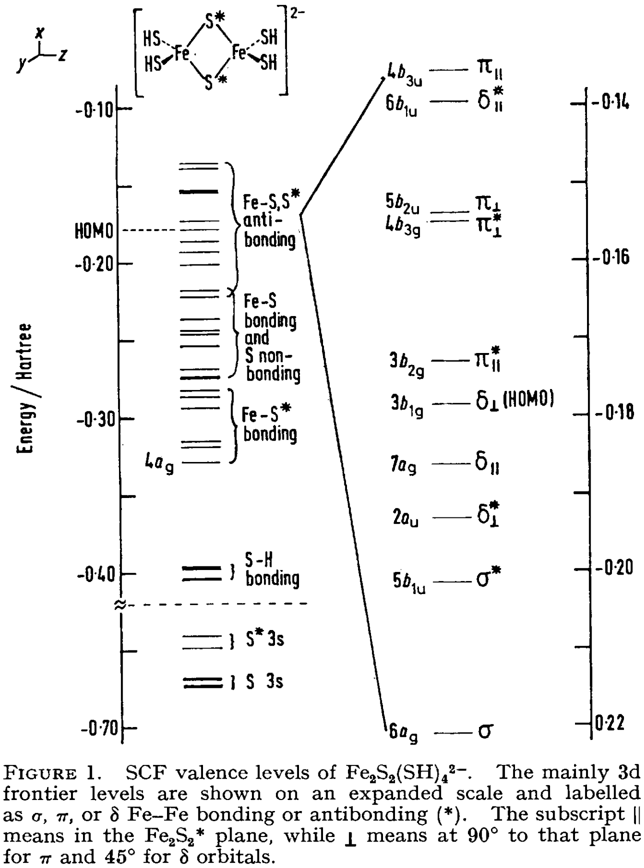


Figure 1. SCF valence levels of $Fe_2S_2(SH)_4^{2-}$. The mainly 3d frontier levels are shown on an expanded scale and labelled as σ, π, or δ Fe–Fe bonding or antibonding (*). The subscript $\parallel$ means in the Fe_2S_2* plane, while $\perp$ means at 90° to that plane for π and 45° for δ orbitals.

$Fe_2S_2(SH)_4^{2-}$ was calculated in D_{2h} symmetry using planar Fe–S–H groups and averaged dimensions from the synthetic model (**1**).† Figure 1 shows resulting valence energy levels. As expected from the temperature-dependent magnetic moment,[8] the Fe 3d-band orbitals at the top of the diagram‡ are very closely spaced. The essential point about their ordering is that the ligand-field splitting is much greater than the metal–metal splitting. That is, the direct Fe–Fe interaction in these orbitals is so weak that their ordering is determined not by this interaction, but by how favourably or unfavourably a particular 3d–3d combination interacts with the ligands. The exact ordering is in fact consistent with a previous general analysis of ligand effects on the metal–metal orbitals of tetrahedral $M_2(\mu\text{–}X)_2$ dimers.[9a] The consequence of this ligand-imposed ordering is little, if any, net Fe–Fe bonding in these orbitals. The σ bonding in $6a_g$, (Figure 2) is effectively cancelled by σ^* character in $5b_{1u}$. Formally, the calculation predicts

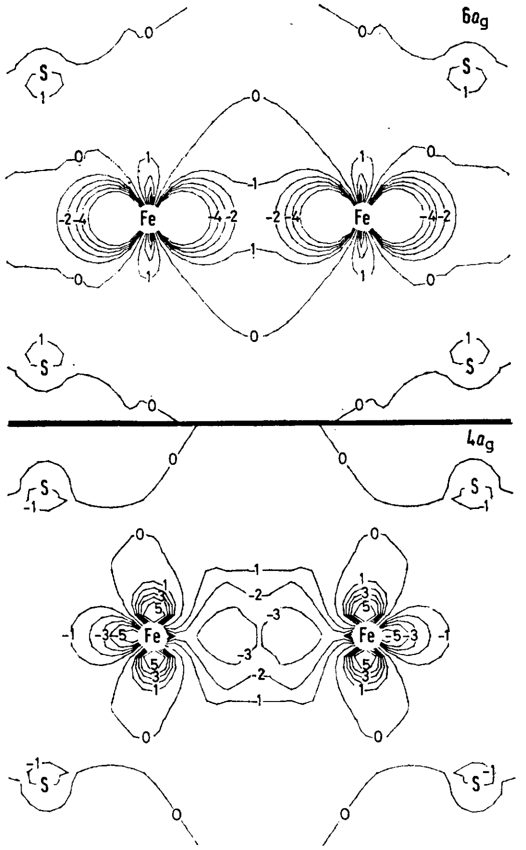


Figure 2. Contour maps of wavefunctions for the $4a_g$ and $6a_g$ orbitals of $Fe_2S_2(SH)_4^{2-}$. The plane perpendicular to the bridging sulphur atoms is used to avoid ambiguities due to their density. Contour values (electrons/Bohr^3)$^{1/2}$ are 0, ±1, ±2, ±3, ±4, and ±5 = 0, $\pm0{\cdot}050$, $\pm0{\cdot}075$, $\pm0{\cdot}100$, $\pm0{\cdot}125$, and $\pm0{\cdot}160$, respectively.

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† Sphere radii (Bohrs) were Fe, 2·313; S*, 2·384; S, 2·374; H, 1·278; outer, 9·535. They were chosen by our nonempirical method (J. G. Norman, Jr., *Mol. Phys.*, 1976, **31**, 1191). Schwarz's α_{HF} parameters (K. Schwarz, *Phys. Rev. B*, 1972, **5**, 2466) were used, with outer and intersphere $\alpha = 0{\cdot}72472$. Spherical harmonics through l = 4, 2, 2, and 0 were used to expand outer, Fe, S, and H wavefunctions, respectively.

‡ The lower five occupied orbitals in this band have 65—96% Fe character, the upper five empty orbitals 55—68%.

a net 3d–3d δ bond, which is insignificantly weak at this Fe–Fe distance. The observed antiferromagnetic coupling of the two $3d^5$ Fe^{3+} centres, leading to diamagnetism at absolute zero,[3b,8] is thus due to a superexchange rather than direct-overlap mechanism.[9b]

Examination of contour maps of the Fe–S* bonding orbitals shows, however, that the 3d band does not contain all metal–metal interaction in this system. These orbitals have 31–50% Fe character which is considerable, but much less than the 65—96% in the occupied part of the 3d band. However, the lowest, $4a_g$, shows much more direct Fe–Fe overlap than any other orbital in the molecule (see Figure 2). Although the charge density is not that of a normal σ bond, at the Fe–Fe midpoint it is *ca.* 50% of that in the main Rh–Rh σ orbital of $Rh_2(O_2CH)_4(H_2O)_2$, where a single bond is present.[10,§] Moreover, this is the single significant Fe–Fe interaction not cancelled by a corresponding antibonding interaction in some other orbital.[¶] This implies that one can change the 3d-band occupation of 2–Fe proteins thermally *or by oxidation–reduction* without significantly affecting any Fe–Fe bonding present.

This situation parallels that in $Rh_2Cl_2(CO)_4$.[7] There, the important, unbalanced metal–metal interaction which causes the folding of the molecule along the Cl–Cl bridge occurs in one of the Rh–Cl bonding orbitals, not in the higher energy Rh 4d band. It may be generally true for $M_2(\mu\text{-}X)_2$ systems that, where the metal–metal interaction is weak, any bonding will be strongly mediated by the bridging ligands, and centred more deeply in energy than the frontier orbitals.

A subsequent paper will compare the 1-Fe, 2-Fe, and 4-Fe calculations in detail and assign spectra.[**] Briefly, a noteworthy difference between $Fe(SH)_4^-$ and $Fe_2S_2(SH)_4^{2-}$ is that the highest occupied orbitals of the former are mainly S,[1,11] while those of the latter are mainly Fe. This is a consequence of the five unpaired electrons in $Fe(SH)_4^-$;[1] even our spin-polarized calculations for a reduced 2–Fe model, $Fe_2S_2(SH)_4^{3-}$, show mainly Fe HOMO's. The one large difference in orbital character between $Fe_4S_4(SH)_4^{2-}$ [2] and $Fe_2S_2(SH)_4^{2-}$ is that the Fe–SH bonds are much more covalent for the former.[††] This is consistent with the shorter Fe–SR distances observed in the synthetic tetramer structures.[12] One might expect each corner of the $Fe_4S_4^{2+}$ core to draw more electrons from its single RS^- ligand than each side of the $Fe_2S_2^{2+}$ core would from either of its two RS^- ligands.

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[§] The total Fe–Fe interaction is sufficiently weak that a valence-bond treatment would probably show less total Fe–Fe overlap. However, absolute magnitude of the interaction is not our main concern.

[¶] The five higher Fe–S* orbitals, in order of increasing energy, have $\delta^*_{\parallel}$, $\pi_{\parallel}$, $\pi^*_{\parallel}$, $\pi_{\perp}$, and $\delta_{\perp}$ Fe–Fe symmetry. The $\pi_{\perp}$ orbital ($3b_{2u}$) has insignificant Fe–Fe overlap relative to $4a_g$.

[**] The calculations predict 3d→3d, Fe–S→3d, and Fe–S*→3d transitions in the ranges 0.5—2.3, 2.1—4.2, and 3.9—5.7 eV, respectively. We thus assign the intense bands observed at 2.1, 2.7sh, 3.0, 3.7, and 4.2 eV in the synthetic model (ref. 4) to mainly Fe–S→3d charge transfer transitions, with the last perhaps having chiefly Fe–S*→3d character. The weak band at 1.7 eV in the oxidized protein (J. Rawlings, O. Siiman, and H. B. Gray, *Proc. Nat. Acad Sci. U.S.A.*, 1974, **71**, 125) is similarly assigned to a 3d→3d transition.

[††] The eight Fe–S bonding and S nonbonding orbitals in $Fe_2S_2(SH)_4^{2-}$ have 0—46% Fe character.

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