HARTREE–FOCK–SLATER–LCAO CALCULATIONS ON \([\text{Fe}_4\text{S}_4(\text{SH})_4]^{0,2,3-}\): A MODEL FOR THE 4-Fe ACTIVE SITE IN HIGH POTENTIAL IRON PROTEIN AND FERREDOXIN

P.J.M. GEURTS, J.W. GOSSELINK, A. VAN DER AVOIRD
Institute of Theoretical Chemistry, University of Nijmegen, Nijmegen, The Netherlands

and

E.J. BAERENDS and J.G. SNIJDERS
Scheikundig Laboratorium der Vrije Universiteit, Amsterdam, The Netherlands

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The electronic structure of the complexes \([\text{Fe}_4\text{S}_4(\text{SH})_4]^{0,2,3-}\) which model the 4-Fe active site in high potential iron protein and ferredoxin, has been calculated with the Hartree–Fock–Slater–LCAO method (in its frozen core and core pseudopotential versions). Results are in agreement with the measured electronic absorption spectrum and magnetic behaviour. The electric field gradient on the Fe nuclei is larger than expected from the observed Mössbauer quadrupole splitting, but the (small) change in this quantity in going from the dianion to the trianion is well described. The Fe–S bonding is mainly covalent and direct Fe–Fe bonding is weak; these conclusions also follow from extended Hückel calculations which we have made in parallel. The self-consistent HFS-LCAO calculations show that in redox reactions the Fe atoms act as charge redistributors. The core pseudopotential version of the method yields results which generally agree with those of the frozen core calculations.

1. Introduction

The non-heme iron–sulphur proteins with 1-Fe, 2-Fe and 4-Fe active sites play an important role as electron carriers in many biological systems [1–3]. Especially, the 4-Fe active sites of the two biocatalysts high potential iron protein (HP) and ferredoxin (Fd) and their synthetic analogues, \([\text{Fe}_4\text{S}_4(\text{SR})_4]^{2,3-}\) (R = alkyl, aryl) which have been prepared recently [4–7] have been subject to much experimental study (see also refs. [1–7]): X-ray diffraction [4,8–10], electrochemical measurements [6,8,11,12], electronic absorption spectroscopy [6,8,9,11–14], XPS [8,13], Mössbauer spectroscopy [5,8,10,13–15], magnetic susceptibility measurements [5,8,10] and \(^1\text{H}\) NMR shifts [8,9,16,17].

The relationship between the biologically important oxidation states of the proteins and their analogues is indicated in the following scheme (s-red = super-reduced, red = reduced, ox = oxidized, s-ox = super-oxidized):

\[
\begin{align*}
\text{Fd}_\text{red} & \leftrightarrow \text{Fd}_\text{ox} \leftrightarrow \text{Fd}_\text{s-ox}, \\
\text{HP}_\text{red} & \leftrightarrow \text{HP}_\text{ox} \\
[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-} & \leftrightarrow [\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-} \leftrightarrow [\text{Fe}_4\text{S}_4(\text{SR})_4]^{-}.
\end{align*}
\]

The central role is played by \(\text{Fd}_\text{ox}, \text{HP}_\text{red}\) and the dianion analogue \([\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}\). Formally the latter can be viewed as a mixed valence compound with two of the Fe atoms in the 2+ and two in the 3+ oxidation state (bridging S\(^2-\) and terminal SR\(^-\)); in Mössbauer spectroscopy [8,13–15] only one quadrupole splitting (doublet), has been observed, however, which shows the four iron atoms to be equivalent (formal oxidation state Fe\(^{2.5+}\)). From these Mössbauer data, but also from NMR and magnetic susceptibility measurements at low temperature [8,16] it follows further that the dianion has a singlet spin ground state (\(S = 0\)) with antiferromagnetically coupled iron centres; at higher temperatures the increasing \(^1\text{H}\) NMR shifts and susceptibilities point to
the population of non-singlet states. A qualitative MO
description of the iron core (4-Fe^{2.5+}) results in the
electron configuration (a_1 + e + t_2)^{12} (e + t_1 + t_2)^{10}
(t_1 + t_2)^{0} with the second set of orbitals neither bond­
ing nor antibonding [4]. In Mössbauer spectra of the
other biologically important oxidation state, the tri­
anion, in first instance a broadened quadrupole dou­
blet [14,15] has been observed. Later on two doublets
have been found with on the average a similar splitting
as for the dianion (at low temperature) [5,10]; this is
indicative for two inequivalent subsites in
\[ \text{[Fe}_4\text{S}_4\text{(SR)}_4]^{3–} \text{ and localization of the extra elec­}

tron at one subsite. Magnetic susceptibilities [5,10]
are consistent with an antiferromagnetic spin doublet
ground state \( S = \frac{1}{2} \) but again indicate the popula­
tion of higher spin states, even at the lowest tempera­
tures in this case [10].

In this work we investigate the
\[ \text{[Fe}_4\text{S}_4\text{(SH)}_4]^{3–,2–,0} \text{ cubane cluster by three dif­}

derent molecular orbital methods: the restricted
Hartree–Fock–Slater-LCAO-frozen core (HFS-FC)
method [18] and the same method but using a core
pseudopotential [19] (HFS-PS) instead of the frozen
core and the extended Hückel (EH) method [20].
The reason that we also include the (biologically ir­
relevant) neutral cluster in our study is to examine
the influence of the negative charge on the calculated
positive occupied orbital energies in the dianion; see
sections 3.2 and 3.3.

The purpose of this study is twofold. On the one
hand to obtain more information about the electron­
ic structure of the cubane cluster and to interpret
the optical excitation spectrum, the Mössbauer param­
eters and the temperature behaviour of the magnetic
moment and the \(^1\text{H}\) NMR shifts. On the other hand,
we wanted to test the core pseudopotential version
of the HFS-LCAO method and to compare this meth­

od with the HFS-scattered wave (SW) method [21,22]
(which has been applied recently [23] to the re­
lated cluster \[ \text{[Fe}_4\text{S}_4\text{(SCH}_3)_4]^{2–} \] and the EH meth­

od on a realistic test system with more than one tran­
sition metal atom. This analysis is important in view
of other possible applications of these methods, for
instance to the study of chemisorption clusters.

Other theoretical studies of Fe–S non-heme pro­
teins have concentrated on the 1-Fe active site using
EH [24–28], HFS-SW [29] and GVB [30,31] meth­

ods and on the 2-Fe active site using the EH [32,33] ·
and HFS-SW [34] methods.

2. Method and calculations

In all three computational methods used in this
study (HFS-FC, HFS-PS and EH) only valence elec­

trons are treated variationally; we have considered the
3d and 4s electrons on Fe, the 3s and 3p electrons on
S and the 1s electron on H; the Slater type orbital (STO)
basis was taken from the tables of Clementi
and Roetti [35]: double zeta quality with an addi­
tional set of 4p functions on Fe (the exponents of
the 4p basis functions were taken equal to those of
the 4s functions).

As one can find detailed information about the
HFS-LCAO method elsewhere, regarding the principles
[18,19,36] and the application to small molecules
and transition metal complexes [36], we will mention
here only the basic features. The HFS-LCAO matrix
elements are calculated numerically; the scaling pa:
parameter \( \alpha \) in the local exchange (J\( \phi \cdot \)) potential is taken
to be equal to 0.7. Mainly to simplify the calculation
of the Coulomb potential in each integration point,
the electron density,
\[
\rho(1) = \sum_{\mu,\nu} P_{\mu,\nu} X_{\mu}(1) X_{\nu}(1),
\]
is expanded in one-centre fit functions \( \psi \) with angular
parts including \( l \neq 0 \) (in contrast to the HFS-SW meth­

od we do not introduce the muffin-tin approximation).
This electron density is iterated to self-consistency.
In the HFS-FC version the core orbitals are frozen
(using double zeta STO’s [35]) and the valence orbit­
als are orthogonalized to the core by adding extra
core functions to the basis (single zeta STO’s [35]);
this of course requires additional density fit func­
tions. In the HFS-PS version a pseudopotential is ad­
ded to the one-electron HFS operator, which makes
the core orbitals degenerate with the valence orbital
to be calculated; the problem of which valence or­
bital has to be chosen is essentially solved by taking
the average energy of the occupied valence levels and
applying a perturbation correction to the valence or­
bital energies through second order [19]; the advan­
tage of the pseudopotential approach is that we need
less basis and fit functions.

We have compared the HFS-FC and HFS-PS meth­
ods, we have tested different density fit bases and we
have investigated the effect of the perturbation cor­
rection in case of HFS-PS. All these tests were first
performed for FeS, which can be considered as a subunit of the main cluster, and then for the
[Fe_4S_4(SH)_4]^2^- dianion.

For FeS the internuclear distance has been taken equal to 2.45 Å [37]. The HFS calculations on
[Fe_4S_4(SH)_4]^3-,2-,0 were carried out in Td symmetry (fig. 1; sulphur atoms which bridge iron atoms
are indicated as S*), although the real structure of the complex deviates slightly from Td and actually
has D_{2d} symmetry; by means of EH calculations (which were done in both Td and D_{2d} symmetry),
we have shown that this approximation has no drastic influence on the results.

The coordinates of the Fe and S atoms in the D_{2d} symmetry were taken from parameters for the crystal
structure of [(CH_3CH_2)_4N]^2+ [Fe_4S_4(SCH_2C_6H_5)_4] [4]; in Td symmetry they were determined by aver­
aging. The coordinates of the H atoms were chosen such that the S—H distances are equal to those in the
H_2S molecule [38]; in Td the Fe—S—H angle is 180° (imposed by symmetry) and in D_{2d} it is equal to the
Fe—S—C angle in

\[(\text{CH}_3\text{CH}_2)_4\text{N}]_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{C}_6\text{H}_5)_4] [4] (\approx100°)\,.

Calculations on the 1-Fe and 2-Fe active sites have shown that replacing CH_3 groups by H atoms [25,
29,32] does not influence the results essentially.

A problem we have in our calculations is to deter­
mine the electronic ground state configuration of the complexes [Fe_4S_4(SH)_4]^n-. In principle one could
do this by comparing, for different electron configu-
ration, the total energies. These are defined in the
HFS scheme just as in the Hartree—Fock (HF) method
except that the HF total exchange energy has been re­
placed by a statistical expression depending on the
electron density only (=\rho^{6/3}) [21]. In practice the
HFS total energies are affected by two kinds of errors
(in addition to the errors present in the HF total en­
ergies):

(1) the inaccuracy caused by the numerical inte­
gration scheme and by the electron density fit proce­
dure (explained above);

(2) for open shell electron configurations the HFS
method does not calculate the total energies of the
different possible spin multiplet states but some aver­
age over these states [36,39].

For the large [Fe_4S_4(SH)_4]^n- clusters where the
number of numerical integration points and density
fit functions are necessarily rather limited, while dif­
ferent possible electron configurations lie very close
in energy, the comparison of total energies is not a
good criterion to decide which is the electronic ground
state. Instead, we have defined the ground state as
the state where all the molecular orbitals with the
lowest energies are occupied with electrons, in a fully
self-consistent manner.

3. Results and discussion

3.1. FeS

In order to test the core pseudopotential and the
density fit basis to be used we have performed several
calculations on FeS in the valence configuration
\(\sigma^2\sigma^2\sigma^2\pi^4\pi^2\delta^1\). Results for the orbital energies and
the Mulliken population analysis [40,41] calculated
with the most extensive fit bases are shown in table 1.

It can be concluded that there is good agreement
between HFS-FC and HFS-PS. The perturbation cor­
ections to the pseudopotential improve the orbital
energies by less than 5% (about 0.02 hartree), which
is in agreement with the conclusions in the literature
[19].

The influence of the fit basis is the following. The
differences between the energies calculated with only
s-type fit functions and those calculated with s- and
p-type functions are 6% at most. Adding a d-type fit
function has almost no effect (3%) on the \(\sigma\) and \(\pi\)
Table 1
Orbital energies and population analysis for FeS with spdfg
fit basis *

<table>
<thead>
<tr>
<th>Method</th>
<th>HFS-FC</th>
<th>HFS-PS a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>orbital and energy (hartree)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>σ</td>
<td>-0.542</td>
<td>-0.546</td>
</tr>
<tr>
<td>σ</td>
<td>-0.235</td>
<td>-0.233</td>
</tr>
<tr>
<td>σ</td>
<td>-0.169</td>
<td>-0.176</td>
</tr>
<tr>
<td>π</td>
<td>-0.191</td>
<td>-0.189</td>
</tr>
<tr>
<td>π</td>
<td>-0.153</td>
<td>-0.154</td>
</tr>
<tr>
<td>δ</td>
<td>-0.194</td>
<td>-0.180</td>
</tr>
<tr>
<td>gross atomic charges</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>-0.39</td>
<td>0.33</td>
</tr>
<tr>
<td>gross atomic orbital populations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe : 3d</td>
<td>6.13</td>
<td>6.20</td>
</tr>
<tr>
<td>4s</td>
<td>1.22</td>
<td>1.21</td>
</tr>
<tr>
<td>4p</td>
<td>0.25</td>
<td>0.27</td>
</tr>
<tr>
<td>S : 3s</td>
<td>1.97</td>
<td>1.96</td>
</tr>
<tr>
<td>3p</td>
<td>4.43</td>
<td>4.37</td>
</tr>
<tr>
<td>net atomic and atom-atom overlap populations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-S</td>
<td>7.44</td>
<td>7.45</td>
</tr>
<tr>
<td>S</td>
<td>6.23</td>
<td>6.10</td>
</tr>
<tr>
<td>Fe-S</td>
<td>0.33</td>
<td>0.45</td>
</tr>
</tbody>
</table>

a) HFS-PS results with perturbation corrections.

levels but improves the δ level by 15% which is still
less than 0.03 hartree. The changes caused by adding
fit functions of still higher angular momentum, f- and
g-type (and at the same time some more s- and p-
type functions), are minor (3%). The influence of
the fit basis on the populations is negligible. Clearly
the charge density can be fitted with functions which
need not necessarily go as high in angular momentum
as the basis functions would suggest (otherwise atomic
orbitals up to d-type would require charge density
functions up to g).

In the large cubane cluster we have limited the fit
basis to s- and p-type functions only.

3.2. HFS-FC calculations on [Fe₄S₄(SH)₄]²⁻

Calculations have been done with s-type fit functions
only (s fit basis) and with s- and p-type fit functions
(sp fit basis). We have investigated three different
valence electron configurations: 3t₁⁹e⁴t₂⁰, 3t₁⁶e⁰t₂⁴ and 3t₁⁴e⁴e⁰t₂⁴, the first one gives rise to
a singlet spin state, whereas the second and third configura-
tions can lead to singlets and triplets.

The HFS-SW calculation of Yang et al. [23] for
the similar complex [Fe₄S₄(SCH₃)₄]²⁻ resulted in
the ground state configuration t₁⁹e⁴t₂⁰. In our calculations,
independently of the fit basis used (s or sp), we have found
the ground state (defined by a self-consistent occupation
of the lowest orbitals, see section 2) to be t₁⁹e⁴t₂⁰; the other two configurations led to
empty orbitals lying lower than occupied ones. So,
our ground state configuration disagrees with that
found by HFS-SW for the methyl analogue of the
cluster, but it is in agreement with our EH calculations
(for T₄d and D₂d symmetry).

Comparing the results for the three different con-
figurations with each other (using the sp fit basis) we
observe that the orbital energies are shifted to lower
values going from t₁⁹e⁴t₂⁰ to t₁⁷e⁴t₂⁰ (by about 0.4 eV)
and again from the latter to t₁⁵e⁴t₂⁰ (about 0.2 eV).
The effect of enlarging the fit basis from s to sp is an
almost constant shift of all levels (upwards by about
1.5 eV for the higher valence levels).

In fig. 2 we have shown the MO scheme correspond-
ing to the t₁⁷e⁴t₂⁰ configuration in the sp fit basis. The
character of the orbitals indicated in this figure was
determined by a Mulliken population analysis [40,
41]; the uppermost valence levels have mainly Fe(3d)
character and they are separated by a gap of about 1
eV from levels which mainly consist of S(3p) orbitals;
another gap of about 1 eV separates the latter from
a cluster of mainly S* (3p) levels. The occupation of
the MO's with mainly Fe(3d) character: 5a₂, 7t₂,
3e⁴, 4e⁴, 3t₁⁹, 8t₂⁰, 4t₁⁰, 9t₂⁰, confirms the qualitative
MO description [4] (a₁ + e + t₂)⁰ (e + t₁ + t₂)⁰
(t₁ + t₂)⁰. In the HFS-SW calculation [23] only one
distinct gap is found with a somewhat greater width,
while the highest occupied orbitals consist of a mix-
ture of orbitals with predominantly Fe(3d) character
and orbitals with Fe(3d)—S(3p) character. Whereas
the HFS-SW results [23] in these respects seem to be
sensitive to the exact occupation of the highest va-
lence levels, our results do not change qualitatively,
and only slightly quantitatively, when changing the
electron configuration (e.g. from t₁⁷e⁴t₂⁰ to t₁⁵e⁴t₂⁰).

A peculiar point in the calculation of the dianion
[Fe₄S₄(SH)₄]²⁻ is the large number of positive or-
itral energies.

Schwarz [42] has found for the O⁻ and F⁻ ions
that local density schemes, such as HFS, yield positive
orbital energies, while in Hartree–Fock (HF) theory
P.J.M. Geurts et al./HFS-LCAO calculations on $[\text{Fe}_4\text{S}_{4}(\text{SH})_4]^{0,2-}$

<table>
<thead>
<tr>
<th>eV</th>
<th>HFS-FC: $t_1^5e^4t_2^0$</th>
<th>HFS-PS: $t_1^6e^4t_2^0$</th>
<th>HFS-FC: atoms</th>
</tr>
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<tbody>
<tr>
<td>8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>$9t_2$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$5t_2$</td>
<td></td>
<td>$3t_2$</td>
</tr>
<tr>
<td>1</td>
<td>$1t_1$</td>
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<td>$1t_1$</td>
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<tr>
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<td>$5t_1$</td>
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<td>$5t_1$</td>
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<tr>
<td>-1</td>
<td>$4t_2$</td>
<td>$3t_2$</td>
<td>$4t_2$</td>
</tr>
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<td>-2</td>
<td>$4a_1$</td>
<td>$3t_1$, $Fe(4s)$, S(3p), H(1s), S*(3s)</td>
<td>$3a_1$</td>
</tr>
<tr>
<td>-3</td>
<td>$3t_2$</td>
<td>S*(3p), H(1s)</td>
<td>$3t_2$</td>
</tr>
<tr>
<td>-4</td>
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<td>-8</td>
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<tr>
<td>-9</td>
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<td>$2a_1$</td>
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</tr>
<tr>
<td>-11</td>
<td></td>
<td>$1a_1$</td>
<td>$1a_1$</td>
</tr>
</tbody>
</table>

Fig. 2. MO level scheme and characterization of orbitals for HFS calculations in $T_d$ symmetry; on request a list of detailed information about MO coefficients or MO population data is available from the authors.
all orbital energies are negative; he concluded that this difference in the energies practically does not lead to a difference in the wavefunctions. In general, positive orbital energies are reached with smaller ion-icity in HFS than in HF theory, because of the higher orbital energies in the former. HFS-DV (discrete variational) calculations for the (MgO6)10~ cluster [43] also showed positive orbital energies for the occupied levels. If the crystal field of bulk MgO was included in the calculation, however, all levels were stabilized (showing an almost constant downward shift of about 55 eV).

3.3. HFS-FC calculations on [Fe4S4(SH)4]0,3~

In order to investigate the origin of the positive orbital energies obtained for the dianion without taking into account the stabilizing field of the positive counterions explicitly we have performed a calculation on the neutral cluster with configuration t^e2^ in the sp fit basis; the results are presented in fig. 2. Note that in essence all levels are shifted by a constant amount (~8 eV) to lower energies, such that all occupied orbitals have negative energies; also the relation with atomic Fe, S and H levels can be seen now; the cluster valence levels are somewhat stabilized compared to the corresponding free atom levels, due to bonding interactions. So the positive orbital energies in the dianion are correlated with the overall net charge and can be expected to vanish when the positive counterions are taken into account explicitly.

The calculations on the trianion (configuration t^e41^2) show a further shift of the levels of the dianion towards positive energy. The magnitude of this shift (2— to 3—) is indeed about half of the shift (0 — 2—).

3.4. HFS-PS calculations on [Fe4S4(SH)4]2~

The pseudopotential calculations have been performed with an sp fit basis for the configuration t^e41^2 without and with perturbation corrections (see section 2) and for the configuration t^e41^2 with corrections; the level scheme for t^e41^2 with corrections is shown in fig. 2.

The corrected energies of the occupied orbitals do not differ significantly from the uncorrected ones, mostly by less than about 0.5 eV or 0.02 hartree; this is in agreement with the findings for FeS. Larger differences have been found for the virtual levels: without perturbation, the empty 6e1 orbital lies between the filled 7t2 and 3e orbitals, whereas in the scheme with perturbation (see fig. 2) this 6e1 orbital (not drawn) has moved up above the filled levels and now the empty 8t2 and 9t2 orbitals lie between the filled 3e and 4e levels.

The presence of these virtual orbitals between the occupied ones could not be removed by choosing a different orbital occupancy; always the self-consistent result showed a level ordering which was not consistent with the occupancy. So we must conclude that the PS method in this case does not lead to a unique ground state as defined in section 2. The case of [Fe4S4(SH)4]2~ is a difficult one, however, since the highest occupied and the lowest empty orbitals lie very close indeed (cf. the situation in metals with partly filled bands). Moreover, we have found that the PS method is still useful even for this system, since the different electron configurations only show a more or less constant energy shift of the occupied MO levels and the electronic charge distribution (section 3.6) calculated with the PS method (for all these configurations) is in good agreement with the FC results. In other possible applications of the PS method, e.g. to chemisorption clusters the precise occupation of the highest (metal) levels is not important (see also section 4).

3.5. EH calculations on [Fe4S4(SH)4]2~

As already mentioned we have used an idealized Td structure of the complex in all HFS calculations in order to save computation time. To study the effect of this idealization we have performed two non-iterative EH calculations, one in Td and the other in the real D^2d symmetry. Table 2 gives the VSIP's and basis functions (STO's) as taken from ref. [44,45]; the 3d orbital on Fe is represented by a contracted set of two d functions; the Wolfsberg–Helmholz parameter κ was set to 2.5 [45].

When comparing the EH-MO scheme for Td symmetry in fig. 3 with the HFS schemes in fig. 2, we see the great differences between the two methods;
Table 2
Parameters for extended Hückel calculations a)

<table>
<thead>
<tr>
<th>Atom</th>
<th>AO</th>
<th>VSIP</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>3d</td>
<td>-8.70</td>
<td>5.35/2.20 b)</td>
</tr>
<tr>
<td>Fe</td>
<td>4s</td>
<td>-7.90</td>
<td>1.40</td>
</tr>
<tr>
<td>Fe</td>
<td>4p</td>
<td>-4.55</td>
<td>1.56</td>
</tr>
<tr>
<td>S*, S</td>
<td>3s</td>
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<td>2.1223</td>
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<tr>
<td>S*, S</td>
<td>3p</td>
<td>-11.58</td>
<td>1.8273</td>
</tr>
<tr>
<td>H</td>
<td>1s</td>
<td>-13.60</td>
<td>1.0</td>
</tr>
</tbody>
</table>

a) From refs. [44,45].

b) The contraction coefficients are: 0.565088 and 0.584953.

For instance the large gap in EH between Fe(3d) and S(3p), S*(3p) levels separates into two smaller gaps in HFS; the latter level distribution corresponds much better with the experimental electronic spectrum (section 3.7). The ground state configuration derived from the EH results is the same, however, as that from the HFS-FC results: $t^e_4t^o_2$. Also the splitting between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) differs little, but note that in EH the LUMO is the $4t^1_1$ orbital whereas in HFS it is the $8t^2_2$ orbital.

Finally, we see from fig. 3 that in going from $T_4$ to $D_{2d}$ symmetry, the MO scheme does not change much; the obvious effect is a (small) lifting of degeneracy. Also the charge distribution is not much affected (section 3.6). So one can safely use results from calculations in $T_4$ symmetry also in case of the HFS calculations.

3.6. Population analysis and electron density plots

We have represented the charge distribution of the cluster by a Mulliken population analysis [40, 41] (see tables 3 to 5). The character of each MO as indicated in figs. 2 and 3 was obtained by analyzing these data per MO. Moreover, we have made some electron density and density difference plots (density of the complex, minus the sum of atomic densities) for several planes through the $[Fe_4S_4(SH)_4]^2-$ cubane. Results for two planes are shown in figs. 4 and 5.

Looking at tables 3 to 5 and comparing the electron density plots (not shown) for different HFS calculations, we see that there is generally good agreement between these calculations. The results for the FC s fit basis (not shown) deviate somewhat. The perturbation correction in the HFS-PS calculations has no significant effect on the populations. A minor effect is obtained by changing the electron configuration: going from $t^e_4t^o_2$ via $t^e_4t^o_4$ to $t^e_4t^o_6$ one finds mainly an increase of Fe net population and a decrease of the Fe–Fe, Fe–S* and S–H overlap populations. This can be understood from the Fe(3d) and S(3p) character of the orbitals involved (see fig. 2).

The two EH calculations (in $T_4$ and $D_{2d}$ symmetry) also agree very closely. Qualitatively the EH results show the same features as the HFS results but there are some discrepancies regarding the net and overlap populations discussed below.

From table 3 we see that the atomic charges on Fe ($\approx -0.25$), S* ($\approx -0.30$) and S ($\approx -0.60$) are much smaller than their ionic values, Fe$^{2+}$, S$^{2-}$. This indicates mainly covalent bonding. From table 4 it appears that 0.55 electron is donated by the sulphur ligands to the 4s orbital of Fe, 0.89 electron to the 4p orbitals (both of which are empty in Fe$^{2+}$) and 0.80 electron to the Fe 3d shell (in addition to the 5.5 d electrons in Fe$^{2+}$). The outer S atoms possess a larger electron density than the bridging S* atoms, which clearly originates from the populations of the 3p orbitals. In agreement with this, figs. 4a and 5a show that the density is polarized along the Fe–Fe and Fe–S bonds more than along the Fe–S* bond. The population of the Fe 4p orbitals, which indicates a strong sp hybridization on Fe, confirms the picture of directional Fe–S bonds. Also, the greater Fe–S overlap population compared to that of Fe–S* (table 5) underlines this conclusion.

In table 5 we observe a remarkable difference between HFS and EH. In particular, there is a rather large shift of electrons from the Fe net to the Fe–Fe overlap population. The same shift has been found to a smaller extent between different HFS calculations (see above). A detailed analysis has shown that the large negative Fe–Fe overlap population and the extremely high Fe net population in HFS, are caused mainly by the $4t^2(S^*(3p), Fe(4s))$ and $7t^2(Fe(3d))$ orbitals, suggesting an antibonding Fe–Fe interaction. The density difference plots in figs. 4b and 5b demonstrate the contrary however, namely a slight accumulation of electron density between the Fe atoms. So one can conclude that the four Fe atoms...
Fig. 3. MO level scheme and characterization of orbitals for EH calculations in $T_d$ and $D_{2d}$ symmetry. Comparison of HOMO-LUMO splittings.
Table 3
Gross atomic charges a)

<table>
<thead>
<tr>
<th>Complex:</th>
<th>[Fe₄S₄(SH)₄]²⁻</th>
<th>[Fe₄S₄(SH)₄]⁰</th>
<th>[Fe₄S₄(SH)₄]³⁻</th>
<th>[Fe₄S₄(SH)₄]²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method:</td>
<td>HFS-FC</td>
<td>HFS-PS b)</td>
<td>HFS-FC</td>
<td>EH-Td</td>
</tr>
<tr>
<td>Configuration:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.26</td>
<td>0.27</td>
<td>0.29</td>
<td>-0.05</td>
</tr>
<tr>
<td>S</td>
<td>-0.31</td>
<td>-0.31</td>
<td>-0.11</td>
<td>-0.16</td>
</tr>
<tr>
<td>S</td>
<td>-0.60</td>
<td>-0.58</td>
<td>-0.47</td>
<td>-0.35</td>
</tr>
<tr>
<td>H</td>
<td>0.15</td>
<td>0.12</td>
<td>0.29</td>
<td>0.07</td>
</tr>
</tbody>
</table>

a) HFS results with sp fit basis.

b) HFS-PS results with perturbation corrections.

in the tetrahedral arrangement are non-bonding or weak bonding. As observed earlier [46] the Mulliken population analysis loses some of its significance when used with a larger than minimal basis set.

The population analysis of the model clusters for 1-Fe [25,28] and 2-Fe [32,33] active sites shows the same overall results for gross atomic charges and orbital populations. The weak direct Fe–Fe bonding has been reported also for a 2-Fe active site using the HFS-SW method [34].

Finally, we compare the results for the diatomic and neutral cluster. From tables 3 to 5 it is clear that the two outgoing electrons originate almost entirely from the S*(3p)–S(3p)–H(1s) part of the cluster. This, at first sight, is unexpected since these two electrons are taken from the 4e level which has mainly Fe(3d) character. Apparently, after removal of the double negative charge, the orbitals relax in such a way that the total charge density around the Fe centres is not changed essentially; this is confirmed by a population analysis. Going to the trianion, the third electron goes into the 8t₉ level, which has almost purely Fe(3d) character. Again we observe the same trend, namely that also in this case the Fe atoms act mainly as charge redistributors. Thus we can understand the almost unchanged quadrupole splitting (cf. section 3.8H) upon electron addition or removal [5,8,10,13–15]. Similar observations have been made for the 1-Fe and 2-Fe active site clusters, [Fe(SH)₄]¹⁻,²⁻ [31] and [Fe₂S₂(SH)₄]⁰,¹⁻ [32] and in the series

Table 4
Gross atomic orbital populations a)

<table>
<thead>
<tr>
<th>Complex:</th>
<th>[Fe₄S₄(SH)₄]²⁻</th>
<th>[Fe₄S₄(SH)₄]⁰</th>
<th>[Fe₄S₄(SH)₄]³⁻</th>
<th>[Fe₄S₄(SH)₄]²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method:</td>
<td>HFS-FC</td>
<td>HFS-PS b)</td>
<td>HFS-FC</td>
<td>EH-Td</td>
</tr>
<tr>
<td>Configuration:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe 3d</td>
<td>6.30</td>
<td>6.30</td>
<td>6.30</td>
<td>6.35</td>
</tr>
<tr>
<td>Fe 4s</td>
<td>0.55</td>
<td>0.60</td>
<td>0.52</td>
<td>0.53</td>
</tr>
<tr>
<td>Fe 4p</td>
<td>0.89</td>
<td>0.81</td>
<td>0.92</td>
<td>1.17</td>
</tr>
<tr>
<td>S 3s</td>
<td>1.93</td>
<td>1.95</td>
<td>1.91</td>
<td>1.57</td>
</tr>
<tr>
<td>S 3p</td>
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<td>4.16</td>
<td>4.49</td>
<td>4.60</td>
</tr>
<tr>
<td>S 3p</td>
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<td>4.16</td>
<td>4.49</td>
<td>4.60</td>
</tr>
<tr>
<td>H 1s</td>
<td>0.85</td>
<td>0.71</td>
<td>0.95</td>
<td>0.93</td>
</tr>
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</table>

a) HFS results with sp fit basis.

b) HFS-PS results with perturbation corrections.
Table 5
Net atomic and atom–atom overlap populations a)

<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Method:</td>
<td>HFS-FC</td>
<td>HFS-PS b)</td>
<td>HFS-FC</td>
<td>EH-Td</td>
</tr>
<tr>
<td>Configuration:</td>
<td>$t_1^6e_4^4t_2^0$</td>
<td>$t_1^6e_4^4t_2^0$</td>
<td>$t_1^6e_4^4t_2^1$</td>
<td>$t_1^6e_4^4t_1^0$</td>
</tr>
<tr>
<td>net</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>13.64</td>
<td>11.68</td>
<td>13.79</td>
<td>14.27</td>
</tr>
<tr>
<td>S*</td>
<td>6.24</td>
<td>6.29</td>
<td>6.03</td>
<td>6.37</td>
</tr>
<tr>
<td>S</td>
<td>6.25</td>
<td>6.22</td>
<td>6.06</td>
<td>6.40</td>
</tr>
<tr>
<td>H</td>
<td>0.77</td>
<td>0.82</td>
<td>0.54</td>
<td>1.01</td>
</tr>
<tr>
<td>overlap</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–Fe</td>
<td>-4.14</td>
<td>-2.84</td>
<td>-4.28</td>
<td>-4.49</td>
</tr>
<tr>
<td>Fe–S*</td>
<td>0.21</td>
<td>0.16</td>
<td>0.19</td>
<td>0.19</td>
</tr>
<tr>
<td>Fe–S</td>
<td>0.64</td>
<td>0.62</td>
<td>0.58</td>
<td>0.63</td>
</tr>
<tr>
<td>S–H</td>
<td>0.42</td>
<td>0.39</td>
<td>0.53</td>
<td>0.22</td>
</tr>
</tbody>
</table>

a) HFS results with sp fit basis.
b) HFS-PS results with perturbation corrections.
c) Averaged over non-equivalent pairs.

$[\text{Fe}_2(\text{CO})_6(\text{PH}_2)]^n$, $n = 0, -1, -2$ [47]. These results should be quite important in explaining the redox behaviour of the Fe–S proteins (and their synthetic analogues).

3.7. Electronic excitation spectrum

In the experimental optical absorption spectrum of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ in solution [6,8,11,14] two bands,
Fig. 5. Electron density plot (a) and electron density difference plot (b) in $S_{3}^{+}$-$Fe_{4}$-$S_{4}$ plane for $[Fe_{4}S_{4}(SH)]^{2-}$ calculated with the HFS-FC method in the $t_{1}^{6}e_{t}^{4}$ configuration with an sp fit basis; values in e/bohr$^3$. 
P.J.M. Geurts et al./HFS-LCAO calculations on \([\text{Fe}^\text{S}(\text{SH})_4]^{2-}\)

Fig. 6. Calculated electronic transitions (HFS-FC, \(t_1^0 e^{4}_2\), sp fit basis) of \([\text{Fe}_4\text{S}_4(\text{SH})_4]^{2-}\) (vertical bars) compared with experimental electronic absorption spectra of \([\text{(CH}_3\text{CH}_2)_4\text{N}]_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{C}_6\text{H}_5)_4] (- - -)\) in acetonitrile solution (a) [6,14] and as a thin film (b) [13] and of \([\text{(CH}_3\text{CH}_2\text{CH}_2)_4\text{N}]_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{CH}_3)_4] (- - -)\) in DMF solution (c) [11] and as a thin film (d) [13]. Dotted vertical bars represent transitions which are symmetry forbidden in \(T_d\) but which will be allowed in \(D_{2d}\).

at 4.2 eV and 3.0 eV, have been attributed to \(S \rightarrow Fe\) charge transfer transitions; shoulders have been observed around 3.5 eV and at 1.9 eV. In addition, the spectrum of the solid [13] shows absorption bands at 2.5 eV and 1.6 eV. See fig. 6.

We have calculated excitation energies: (a) from the ground state levels (GS); (b) from transition state calculations [21,48] for some excitations (TS).

The transition state procedure accounts for the orbital relaxation effects which occur upon excitation (in this respect it is similar to the \(\Delta\text{SCF}\) method [49]), and it has shown to yield results in quantitative agreement with the experimental spectra for a series of transition metal oxo-complexes [50]. The subtraction of ground state energy levels (method a) cannot be justified theoretically, but the results show that there is very little difference (less than 3%) between (a) and (b). This is related to the observation (sections 3.2 and 3.3) that changes in the electron configuration just cause a practically constant shift of all levels in this large complex. Fig. 6 shows all possible symmetry-allowed excitations from the \(t_1^0 e^{4}_2\) ground state corresponding with the HFS-FC results in the sp fit basis.

By looking at the character of the orbitals involved (fig. 2) one can assign the experimentally observed bands at 1.9 and 1.6 eV to \(\text{Fe}(3d) \rightarrow \text{Fe}(3d)\) transitions. The bands at 3.0 and 2.5 eV are \(\text{S}(3p) \rightarrow \text{Fe}(3d)\) charge transfer excitations, probably mixed with the relatively high lying \(5a^1 \rightarrow 4t_1 \) and \(5a^1 \rightarrow 9t_2 \) d—d transitions; also the shoulder around 3.5 eV will be a charge transfer band. The absorption around 4.2 eV has mainly \(S^*(3p) \rightarrow \text{Fe}(3d)\) charge transfer character. From our calculations we predict some symmetry-allowed d—d transitions at lower energies as well, but we have not calculated the intensities. A lower energy band is observed in the spectrum of HPersed at 1.2 eV [51] but it seems to have no counterpart in \([\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}\).

An analysis for other configurations or from the PS results is hampered by the circumstance that some
of the empty levels are lying lower than filled ones; disregarding these empty levels yields, as could be expected, an incomplete and less satisfactory picture.

An analysis of the EH results (see fig. 3) shows immediately that these do not agree with the measured electronic spectrum although the correct order of the bands is predicted. In particular they yield much too high frequencies for some of the charge transfer bands; e.g. no absorptions are found in the range from 2.2 to 3.8 eV due to the large gap discussed in section 3.5.

In the experimental spectrum of the trianion \([\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}\) one observes a shift of about 0.4 eV, relative to the dianion spectrum, of the band at 3.0 eV to higher energy, while the other bands stay practically at the same positions [6,14]. In our HFS-FC calculations on the trianion (ground state) we observe a change in the excitation energies which reflects this behaviour almost quantitatively.

### 3.8. Quadrupole splitting

From Mössbauer measurements on \([\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}\) at low temperature (4.2 K) [8,13—15] a quadrupole splitting of the \(^{57}\text{Fe}\) Mössbauer levels of 1.26 mm/s has been obtained. Moreover, one has derived that the electric field gradient on the Fe nucleus has a positive principal component \(V_{zz}\) and an asymmetry parameter,

\[
\eta \equiv (V_{xx} - V_{yy})/V_{zz} < 0.4
\]

From the fact that only one quadrupole doublet was observed, it has been concluded that all four Fe atoms are equivalent to each other. For the trianion the situation is different. At first, a broadened spectrum with a similar quadrupole splitting as for the dianion has been seen at low temperature [14,15]. Subsequent experiments [5] and especially a detailed analysis [10] have shown that the spectrum consists of two distinct quadrupole doublets, indicating two inequivalent subsites in \([\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}\). In our calculations we have applied symmetry restrictions to the nuclear framework and to the electron distribution which prevent us from distinguishing between both subsites. Therefore we can compare our calculated quadrupole splitting for the trianion only with an average of the two splittings observed experimentally. Specifically, this average for \([\text{CH}_3\text{CH}_2\text{N}]_{3} [\text{Fe}_4\text{S}_4(\text{SCH}_2\text{C}_6\text{H}_5)_4]^{0.2 - 3-}\) in frozen solution (again at 4.2 K) amounts to 1.57 mm/s [10]; the average value of 1.17 mm/s for the crystalline compound corresponds with a more strongly distorted structure [10].

We have calculated the electric field gradient from the HFS molecular orbitals in the following way. Each STO in the atomic orbital basis has been expanded as a linear combination of 3, 4 or 5 gaussian type orbitals (GTO's) using the exponents and coefficients from Stewart's maximum overlap fits [52]. These expansions have been substituted into the MO's obtained from the HFS calculations and the components and principal values of the electric field gradient tensor on the Fe nucleus have been calculated with the one-electron properties package of the program POLYATOM [53] including all multi-centre contributions. The one-centre contributions have been directly calculated with the STO basis also, in order to verify that the STO-3, -4 or -5GTO expansion did not significantly influence the results. For the EH molecular orbitals we have only calculated these one-centre terms (after first orthogonalizing the EH basis orbitals to the core orbitals [44]) since the multi-centre contributions appeared to be small (less than 20%).

From table 6 where the results are listed we observe that particularly the HFS absolute values for the Fe quadrupole splitting are much too large. However, the HSF calculations predict correctly that the change in the quadrupole splitting in going from the dianion to the trianion is small [5,8,10,13—15]. This is consistent with the picture emerging from these calculations that the Fe atoms mainly act as charge redistributors for the extra electron. The results from different HFS calculations on the same (2-) complex, FC or PS, different density fit bases, different electron configurations do not vary much.

The overestimate of the quadrupole splitting can be ascribed in part to the lack of core polarization effects in the HFS-FC and HFS-PS calculations as well as in the EH calculation. Correcting for these effects by the use of an approximate Sternheimer factor, which has been calculated for a 3d-electron in the Fe\(^{2+}\) ion, [55,56], brings the EH results into reasonable agreement with experiment; the HFS values are still too high. This is probably related to the very high Fe net atomic population and negative Fe—Fe overlap population resulting from the HFS but not from the EH calculations (see section 3.6). The Mössbauer
quadrupole splitting is a very sensitive measure of the charge distribution around the Fe atom (it depends mainly on the differences in 3d orbital populations). The HFS results with the charge density represented only by s- and p-type fit functions (during the iterations to self-consistency) may not be sufficiently accurate to reproduce this detailed d-electron charge distribution. The good agreement with experiment, for the much simpler EH method must then be regarded as fortuitous, although it seems to occur more generally [24,26,28,33].

3.9. Magnetic properties

From the Mössbauer spectra [8,13–15], the $^1H$ NMR shifts of SCH$_2$ protons [8,16] and the magnetic susceptibility [8] at low temperature it follows that the ground state of the complex $[Fe_4S_4(SR)_4]^{2-}$ is a singlet spin state or, in other words, that the Fe centres are antiferromagnetically coupled. At higher temperature the $^1H$ NMR shifts and the susceptibility increase [8,16], indicating a thermal population of excited non-singlet spin states. The magnetic moment per iron atom nearly obeys an exponential law $M \sim \exp(-\Delta \epsilon/kT)$ in the temperature range 140 K $< T < 300$ K with an excitation energy $\Delta \epsilon$ of about 0.02 eV.

From the HFS calculations as well as from the EH calculations we have found indeed a singlet closed shell (3$^t$4$^e$) ground state. The distance $\Delta \epsilon$ to the first excited level is 0.29 eV in the HFS-FC results *(in Td symmetry), but this value will probably be reduced somewhat by the symmetry lowering to D$_{2d}$, (see fig. 3; in EH there is indeed such a reduction of $\Delta \epsilon$ from 0.33 eV to 0.26 eV). What is more important is that, in contrast with the optical spectrum where we look at singlet—singlet transitions, we are interested here in the excitation energy $\Delta \epsilon$ to the lowest non-singlet state (e.g. triplet) which is lower (according to Hund’s rule) than the excitation energy calculated by the restricted HFS method which in fact lies in between the singlet—triplet and the singlet—singlet excitation energies. Therefore we can only consider the HFS value $\Delta \epsilon = 0.29$ eV as an upper bound for the excitation energy $\Delta \epsilon$. The result $\Delta \epsilon < 0.29$ eV is not very useful in practice but at least it is not in contradiction with the experimental result $\Delta \epsilon \approx 0.02$ eV.$^\dagger$

### Table 6

<table>
<thead>
<tr>
<th></th>
<th>$[Fe_4S_4(SR)_4]^{2-}$</th>
<th></th>
<th>$[Fe_4S_4(SR)_4]^{3-}$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>HFS-FC a)</td>
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<td>HFS-PS a)</td>
</tr>
<tr>
<td></td>
<td>$T_d$</td>
<td></td>
<td>$T_d$</td>
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<tr>
<td></td>
<td>one-centre</td>
<td>total STO-3GTO</td>
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<tr>
<td></td>
<td>STO</td>
<td>STO-3GTO</td>
<td>STO</td>
</tr>
<tr>
<td>$V_{zz}$ (10$^{22}$ N/mC)</td>
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<td>3.0 e)</td>
<td>3.4 3.3 f)</td>
</tr>
<tr>
<td>$\eta$ g)</td>
<td>0 0 0 0</td>
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<td>7.4 7.1</td>
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<tr>
<td>quadrupole splitting h)</td>
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<td>(4.2)</td>
<td>(4.7) (4.5)</td>
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</tbody>
</table>

a) Values are given for the configuration $t^6 \bar{e}^4 \bar{c}^2$ calculated with an sp fit basis.

b) From ref. [8,13–15].

c) From ref. [10]; see also text.

d) STO-4GTO expansion: $V_{zz} = 4.0$; STO-5GTO expansion: $V_{zz} = 4.1$.

e) STO-4GTO expansion: $V_{zz} = 3.2$.

f) STO-4GTO expansion: $V_{zz} = 3.3$; STO-5GTO expansion: $V_{zz} = 3.3$.

g) In $T_d$ symmetry $\eta = 0$ since the local symmetry on Fe is $C_3v$.

h) Calculated with $Q = 0.21$ barns (quadrupole moment of the $I = 3/2$ excited state of the $^{57}$Fe nucleus [54]; values in brackets have been obtained by correcting for core polarization using the approximate Sternheimer factor $(1 - R) = 0.64$ [55,56].

$^\dagger$ The excitation energy $\Delta \epsilon$ should in fact be obtained as the level difference $\Delta \epsilon$ in a transition state calculation but this will not much affect the result (cf. section 3.7).
In the HFS-SW calculations [23] the lowest energy in $T_d$ symmetry was found to correspond with the $t_{2g}^6e_{g}^{14}$ configuration, leading to a non-singlet ground state. By invoking the symmetry distortion to $D_{2d}$ symmetry [23] one could obtain a closed shell (antiferromagnetically coupled) ground state in agreement with experiment.

4. Conclusions

Summarizing, we can conclude that the Hartree—Fock—Slater-LCAO method yields results for the $[\text{Fe}_4\text{S}_4(\text{SH})_4]^{2-,3-}$ complex which are in fair agreement with the experimental electronic absorption spectrum and magnetic behaviour. Extended Hückel results are not in agreement with the optical spectrum. The HFS value for the electric field gradient on the Fe nucleus is considerably larger than the experimental value from Mössbauer quadrupole splitting; this may be due to the insufficient accuracy of the present HFS calculation (which uses only s- and p-type functions for representing the electronic charge density during the iterations) in describing the detailed charge distribution around the Fe nucleus. It is probably fortuitous that the EH value for this electric field gradient agrees better with experiment. The small relative change in quadrupole splitting when going from the dianion to the trianion is correctly predicted by the HFS method.

The Fe—S bonding in this Fe—S cubane complex is mainly covalent; the charges on the Fe atoms and especially the bridging S* atoms are quite small. Direct Fe—Fe bonding or antibonding is weak. In relation to the practically important redox behaviour of this complex in the biocatalysts high potential iron protein and ferredoxin it is interesting that we have found that electrons taken away from or added to this complex will originate mainly from or will be going to the sulphur ligands, although the molecular orbitals which donate or receive these electrons are composed strongly of Fe(3d) orbitals in the original complex; the Fe atoms mainly act as charge redistributors.

About the HFS-core pseudopotential (PS) method we can conclude the following. Most results agree closely with the frozen core (FC) calculations: electronic charge distribution, Mössbauer quadrupole splitting, positions of the occupied levels. This holds even if we omit the perturbation procedure to correct the pseudopotential for the position of each individual valence level (starting with a pseudopotential for the average valence energy). Somewhat larger deviations occur for some of the virtual levels. For the large 4-Fe complex considered here, with only a very small gap between the highest occupied levels and the lowest virtual ones, some of the virtual levels are found between the occupied ones in the PS calculation. Since this occurs for any electron configuration chosen during the iteration to self-consistency it is not possible to determine the ground state configuration by the PS method. Although we do not wish to disregard this problem, we observe, on the other hand, that the PS method can still be very useful since some rearrangement of electrons between the MO's around the “Fermi level” hardly changes the overall charge distribution and the relative positions of the occupied MO's. We have reached the same conclusion in HFS calculations for the chemisorption of acetylene on transition metal clusters, where the exact occupancy of the levels in the metal “d-bands” practically did not affect the results found for the acetylene bonding.

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