Structure and Spin-State Energetics of an Iron Porphyrin Model: An Assessment of Theoretical Methods

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ABSTRACT: The ability of unrestricted Hartree–Fock (UHF), Møller–Plesset (MP2),
density functional theory (DFT), and hybrid density functional/Hartree–Fock
methodologies to describe the structure and spin-state energetics of iron porphyrins was
assessed. In the first place, these techniques have been applied to Fe, Fe\(^+\), Fe\(^{2+}\), and Fe\(^{3+}\)
for which HF calculations overestimate energy gaps, favoring stabilization of higher
multiplicity states. DFT shows the opposite trend at the GGA level, with some
improvement using the hybrid schemes B3LYP and half-and-half. We use the hybrid
functionals to explore the dependence of the spin state with the iron displacement out of
the porphyrin plane in the five-coordinate system, for which a high-spin ground state has
been experimentally determined. The possibility of spin crossover, proposed in previous
studies, is examined. Finally, the hybrid methodologies are applied to the computation of
the oxyhemoglobin model. The B3LYP description of the electronic structure of both penta
and hexa coordinate model systems is consistent with previous theoretical calculations
and with experimental information of deoxy and oxy hemoglobin. © 2002 John Wiley &

Key words: spin-state energetics; DFT; porphyrin; hemoglobin; B3LYP

Introduction

Iron porphyrins have been extensively studied, both from the experimental and theoretical
viewpoints, because they play a central role in un-

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derstanding the reactivity of many physiologically
relevant systems. Among the most typical biomole-
cules containing iron porphyrins, we can mention
the proteins hemoglobin and myoglobin. These pro-
teins contain an iron(II) protoporphyrin IX, called
the heme group, attached to the polipeptidic chain
through a linkage between the iron and the nitro-
gen atom of the aminoacid histidine [1] (Fig. 1).
In order to shed light into the structural, spectral
properties, and ligand binding energetics of metal
porphyrins, a variety of ab initio, density functional theory (DFT), and semiempirical electronic structure calculations have been performed in the last years on model systems of the heme unit [2 – 5]. Due to its good performance for systems containing transition metals [6] and its relative low cost, DFT has probably been the scheme most widely applied to these kinds of systems.

Normal hemoglobins are in the iron(II) oxidation state and are five-coordinated, having a single axial imidazole ligand from the so-called proximal histidine. The iron atom in heme binds to the four nitrogens in the center of the porphyrin ring (Fig. 1), and besides it can form two additional bonds, one on either side of the heme plane. In myoglobin and hemoglobin one of these bonding sites connects the iron to a nitrogen atom of the proximal histidine, and the other remains free to bind molecular oxygen or other ligands. While in oxyhemoglobin the metal is hexacoordinated and low spin, in the deoxy form it is pentacoordinated and in a high spin state [7, 8]. These high-spin species have also been characterized in synthetic model compounds of pentacoordinated Fe(II) porphyrins [9 – 11]. It is then critical that the splittings of the low-lying states of iron are well described if a quantum chemical method is intended to be reliable, especially in this system where a spin transition takes place when the bond is formed. In order to find a reliable treatment of the electronic structure of iron porphyrins, in this work we examine the performance of Hartree–Fock and various DFT approaches in different cases, starting from isolated atomic iron and ions, and continuing with porphyrin model structures for the deoxy and oxyhemoglobin. We investigate geometrical properties and its relationship with spin-state energetics as well.

### Computational Methods

#### MODEL STRUCTURE

We have employed a porphyrin model proposed previously [12, 13] (Fig. 2), in which the porphyrin macrocycle was replaced by two amidinato ligands, thus keeping both the coordination environment on the iron and the π electron delocalization of the macrocycle. Because one of our main interests is to find a method suitable to describe the active site of hemoglobin and myoglobin, the computations were done on the iron(II) complex, that is, the formal oxidation state of the metal in these heme proteins. In such oxidation state the system has no net charge and the total number of electrons is even; therefore the possible spin states are $S = 0, 1, 2,$ and so on. The geometrical parameters of the porphyrin ring correspond to average distances and angles of model compounds compiled by Marques et al. [14]. To model the pentacoordinated heme in hemoglobin, an imidazole ligand is bound to the Fe atom. Partial optimizations have been performed on the pentacoordinated models. There is experimental and theoretical evidence that due to the rigidity of the ring the internal coordinates of the porphyrin hardly change with the nature of the ligand, nor with the spin state [5, 14]. Taking this into account, in our calculations the geometrical parameters related to the atoms of the cycle were kept fixed, while...
the position of the iron, together with the distances and angles between the heme and the ligands, were allowed to relax without symmetry constraints. This procedure aims to introduce in the optimization of the model structure the same degrees of freedom that the heme moiety has within the quaternary structure of the protein.

**ELECTRONIC STRUCTURE CALCULATIONS**

Calculations have been carried out using the Gaussian 98 program [15], at the unrestricted (UHF) level and assessing the stability of the obtained wavefunctions in all cases. The basis employed for iron was a triple-zeta valence (TZV) contracted Gaussian-type set developed by Schäfer, Huber, and Ahlrichs [16] with a contraction pattern (621/41/1) for contracted Gaussian-type set developed by Schäfer, Huber, and Ahlrichs [16] with a contraction pattern (621/41/1) for carbon, nitrogen, and oxygen, and (41) for hydrogen.

To examine the influence of relativistic effects, a number of calculations were performed on Fe, Fe+, Fe2+, and Fe3+ using the Stuttgart/Dresden effective core potential (DZVP) basis sets designed for DFT by Godbou and coworkers [17], with contraction patterns (621/41/1) for carbon, nitrogen, and oxygen, and (41) for hydrogen.

Several methodologies were tested and compared: Hartee–Fock (HF), Møller–Plesset [19] perturbation theory truncated at second order [20 – 23] (MP2), DFT, and hybrid schemes mixing HF and density functional theory. Pure DFT calculations have been accomplished within the generalized gradient approximation (GGA), using the Becke’s 1988 exchange functional [24] in combination with either the Perdew [25] or the Lee–Yang–Parr [26] correlation functionals, conventionally denoted BP86 and BLYP, respectively.

The hybrid method brings Hartee–Fock exchange together with DFT exchange correlation, so that the exchange correlation energy may be expressed in the following general form:

\[
E_{\text{XC}}(\text{hybrid}) = c_1 E_X(\text{HF}) + c_2 E_X(\text{LSDA}) + c_3 \Delta E_X(\text{nonlocal}) + c_4 E_C(\text{LSDA}) + c_5 \Delta E_C(\text{nonlocal})
\]

where \(E_X\) and \(E_C\) refer to exchange and correlation energies, and LSDA to the local spin density approximation [27]. \(\Delta E_{\text{nonlocal}}\), which is equal to \(E(\text{GGA}) - E(\text{LSDA})\), stands for gradient corrections. In this work we make use of two different implementations of the hybrid technique, both proposed by Becke: the B3LYP [28] and the half-and-half [29] functionals. The first one has a semiempirical origin, as the \(c_i\) coefficients of Eq. (1) were fitted using thermochemical data. The second one has been derived as a linear interpolation of the adiabatic connection formula [30 – 33]. This approach results in the equal mixture of the Hartree–Fock exchange and DFT exchange correlation, and using an LSDA estimate of the latter yields the following expression:

\[
E_{\text{XC}}(\text{half-and-half}) = \frac{1}{2} E_X(\text{HF}) + \frac{1}{2} E_X(\text{LSDA}) + \frac{1}{2} E_C(\text{LSDA})
\] (2)

**Results and Discussion**

**RELATIVE SPIN STATE ENERGETICS OF Fe, Fe+, Fe2+, AND Fe3+**

A fundamental requirement for any electronic structure scheme intended to be applied to transition metal systems, and particularly to processes in which there may be a spin-state change, is its ability to describe correctly the relative spin energetics of the neutral atom and ions. Computed transition energies of the isolated ferric ion at the all-electron unrestricted DFT level using a GGA functional have been reported by Harris, Loew and Komornicki [34] to be in good agreement with experimental results. However, it seems that the accord is because the HF and DFT reported values correspond to restricted open shell calculations (ROHF), which differ significantly from spin unrestricted values. Excitation energies for Fe and Fe+ have also been computed by Holthausen et al. using B3LYP calculations [35].

In Table I we present calculated and experimental [36] energy gaps between the low-lying spin states of the atomic and ionic Fe species. In the cases of Fe and Fe2+, the lowest accessible spin states correspond to a triplet and a quintuplet. For Fe+ and Fe3+ these are a quartet and a sextet. The information of Table I shows that DFT techniques at the GGA level systematically underestimate the energy gaps, favoring the stabilization of the lowest multiplicity states. Hartree–Fock calculations provide a good agreement with experiment for Fe3+, reasonable for Fe2+ and fairly bad for Fe+ and Fe. This is probably because the neglect of correlation effects is more important for the neutral and the single-charged systems. The inclusion of dynamical correlation through MP2 calculations leads to a decrease in the energy gaps. This decrease is very pronounced in the Fe and Fe+ cases.
TABLE I
Calculated and experimental [36] energetic separations (kcal/mol) between the two lowest accessible spin states of Fe\(^0\), Fe\(^+\), Fe\(^{2+}\), and Fe\(^{3+}\) in the gas phase.

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>MP2</th>
<th>BLYP</th>
<th>BP86</th>
<th>B3LYP</th>
<th>half-and-half</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S = 1)</td>
<td>59.7</td>
<td>21.3</td>
<td>21.4</td>
<td>23.5</td>
<td>26.5</td>
<td>40.4</td>
<td>34.2</td>
</tr>
<tr>
<td>(S = 2)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe(^+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S = 3/2)</td>
<td>41.1</td>
<td>1.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.3</td>
<td>18.5</td>
<td>5.4</td>
</tr>
<tr>
<td>(S = 5/2)</td>
<td>0.0</td>
<td>0.0</td>
<td>4.8</td>
<td>3.3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S = 1)</td>
<td>59.0</td>
<td>54.8</td>
<td>34.8</td>
<td>36.1</td>
<td>38.5</td>
<td>51.1</td>
<td>55.5</td>
</tr>
<tr>
<td>(S = 2)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S = 3/2)</td>
<td>93.6</td>
<td>87.4</td>
<td>56.8</td>
<td>57.6</td>
<td>62.7</td>
<td>80.8</td>
<td>92.2</td>
</tr>
<tr>
<td>(S = 5/2)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Let us now consider the hybrid DFT/HF functionals. These methods have been reported to perform very well in a variety of biochemical problems involving transition metal atoms [6]. In this case, the results obtained with B3LYP show minor improvements compared to those corresponding to GGA calculations. Better agreement with experiment is achieved with the implementation of the half-and-half functional. It is clear that in all considered methodologies the observed errors are significant. The use of more sophisticated schemes, such as multireference CI calculations probably would reduce these errors significantly. However, such calculations would be impossible to perform even for the smaller model systems of physiologically relevant porphyrins [6].

Since relativistic effects may often be significant in transition metal atoms, the use of effective core potentials (ECP) which implicitly include these effects [18] has also been explored. The results, pre-

TABLE II
Energetic separations (kcal/mol) between the two lowest accessible spin states of the different iron species, calculated with the relativistic Stuttgart/Dresden effective core potential.

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>MP2</th>
<th>BLYP</th>
<th>BP86</th>
<th>B3LYP</th>
<th>half-and-half</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S = 1)</td>
<td>59.1</td>
<td>32.4</td>
<td>19.1</td>
<td>20.6</td>
<td>23.0</td>
<td>39.2</td>
<td>34.2</td>
</tr>
<tr>
<td>(S = 2)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe(^+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S = 3/2)</td>
<td>43.7</td>
<td>9.5</td>
<td>0.0</td>
<td>1.5</td>
<td>2.4</td>
<td>22.4</td>
<td>5.4</td>
</tr>
<tr>
<td>(S = 5/2)</td>
<td>0.0</td>
<td>0.0</td>
<td>2.2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S = 1)</td>
<td>54.5</td>
<td>56.2</td>
<td>34.2</td>
<td>35.0</td>
<td>37.9</td>
<td>52.9</td>
<td>55.5</td>
</tr>
<tr>
<td>(S = 2)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S = 3/2)</td>
<td>88.4</td>
<td>88.6</td>
<td>56.0</td>
<td>56.2</td>
<td>61.7</td>
<td>83.7</td>
<td>92.2</td>
</tr>
<tr>
<td>(S = 5/2)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
sented in Table II, do not differ substantially from the all-electron calculations, and show, in agreement with previous DFT computations of Fe and Fe\(^{+}\) [37, 38] and of iron(II) porphyrin [39], that the consideration of relativistic effects through the use of ECPs do not alter significantly the relative energies of spin states of iron containing species.

**THE FIVE-COORDINATED COMPLEX**

In Table III we present the energetic separations between the three lowest accessible spin states of the pentacoordinated model (Figure 2) computed using Hartree–Fock, DFT (BP86), and the two hybrid methods. Table III also shows two relevant structural parameters, the distance of the iron atom to the plane defined by the nitrogen atoms of the porphyrin model, also called the iron out-of-plane displacement \((d_{Fe-p})\), and the bond distance between Fe and the nitrogen atom of the imidazole \((d_{Fe–Nim})\).

We have optimized the coordinates of the Fe atom and the relative position of the imidazole with respect to the porphyrin. The N-Fe–N\(_{im}-C\) torsion was kept fixed, since in physiological situations it has been assumed that for steric constraints the protein prevents the rotation of the heme unit around the Fe–N\(_{im}\) axis [10].

The HF and half-and-half schemes predict a quintuplet as the ground state for the pentacoordinate model. On the other hand, BLYP and B3LYP predict it to be a triplet. These results are consistent with the underestimation of the transition energies of the atomic species discussed above. Our results are also consistent with those reported by Rovira et al. for a full porphyrin model [5], in which by using a BLYP functional in a Car–Parrinello scheme a triplet ground state was found. We can find a simple interpretation of this in the context of the ligand field theory, which explains the electronic structure of transition metal complexes in terms of the distortion of the \(d\)-orbitals of the isolated metal. If the gap between the high and the intermediate spin state is too small in the isolated iron species, the perturbation induced by the ligand field may be enough to stabilize the triplet configuration below the quintuplet, hence inverting the order. On the other hand, if this gap is overestimated, as in the case of the Hartree–Fock computations, the energetic gap between the quintuplet and the triplet is likely to also result too large in the model compound. The values in Table III make evident the importance of an accurate treatment of the isolated atomic species. Of course we cannot assess the quality of the transition energies obtained by the different methods, since no experimental results are available for these systems. Nevertheless, it can be argued that the bias in the atomic Fe species would become manifest in the complex energetics.

It has been proposed [41] that a thermal equilibrium arises between two different spin states, as measured in some porphyrin derivatives [42] or other iron complexes [43, 44]. This argument would justify the fact that B3LYP and BLYP computations yield a triplet as the ground state of the pentacoordinated heme at 0 K, since experiments show that deoxy hemoglobins and model systems are in a high-spin ground state. According to this hypothesis, as temperature increases the high-spin state is observed due to the fluctuations of the iron around its equilibrium position: a spin crossover will take place whenever the distortion in geometry is such that the quintuplet becomes the ground state. In order to shed light on this issue, we have performed a series of calculations using the B3LYP

<table>
<thead>
<tr>
<th>TABLE III</th>
<th>Energetic separations and selected geometrical parameters for the different spin states of the five-coordinated system.(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{rel})</td>
<td>(d_{Fe-p})</td>
</tr>
<tr>
<td>HF</td>
<td></td>
</tr>
<tr>
<td>singlet</td>
<td>52.6</td>
</tr>
<tr>
<td>triplet</td>
<td>37.9</td>
</tr>
<tr>
<td>quintuplet</td>
<td>0.0</td>
</tr>
<tr>
<td>BLYP</td>
<td></td>
</tr>
<tr>
<td>singlet</td>
<td>11.4</td>
</tr>
<tr>
<td>triplet</td>
<td>0.0</td>
</tr>
<tr>
<td>quintuplet</td>
<td>15.7</td>
</tr>
<tr>
<td>B3LYP</td>
<td></td>
</tr>
<tr>
<td>singlet</td>
<td>15.1</td>
</tr>
<tr>
<td>triplet</td>
<td>0.0</td>
</tr>
<tr>
<td>quintuplet</td>
<td>8.2</td>
</tr>
<tr>
<td>half-and-half</td>
<td></td>
</tr>
<tr>
<td>singlet</td>
<td>36.3</td>
</tr>
<tr>
<td>triplet</td>
<td>15.6</td>
</tr>
<tr>
<td>quintuplet</td>
<td>0.0</td>
</tr>
<tr>
<td>Exp.(^d)</td>
<td></td>
</tr>
<tr>
<td>quintuplet</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\(^a\) Energies in kcal/mol and distances in Å.
\(^b\) Relative energy with respect to the ground state.
\(^c\) Distance from the Fe atom to the porphyrin plane.
\(^d\) Data from Refs. [40, 45], corresponding to values measured in synthetic and native five-coordinated hemes.
and half-and-half functional, in which we optimized the high and intermediate spin states of the pentacoordinated model for several fixed $d_{\text{Fe-p}}$ values.

For the half-and-half functional the quintuplet state remains far below the lower multiplicity states at all $d_{\text{Fe-p}}$ values (Fig. 3). On the other hand, the results for the B3LYP functional support the hypothesis of a spin crossover: the quintuplet potential energy surface is very shallow, and at large displacements the triplet state becomes lower in energy. The B3LYP results are in agreement to those found in a full porphyrin model calculation performed at the BP86 level by Rovira et al. [5]. Both scenarios, the one found in the half-and-half calculations and the one found at the B3LYP level, are consistent with the experimental results. However, considering that both hybrid schemes showed significant errors in the evaluation of the atomic species spin energetics, it is not possible at this point to assess which one is correct.

The optimized out-of-plane displacements of the Fe atom in the quintuplet state exhibit an important dependence on the level of theory, ranging from 0.25 to 0.52 Å (Table III). This is a natural consequence of the shallowness of the potential energy surface discussed above and is also consistent with the fact that Fe motion along the Fe–N$_{\text{im}}$ axis is usually assigned to a low-frequency normal mode. These results are in agreement with experimental structures of imidazole-substituted iron porphyrins (of heme proteins and model compounds) in which the measured values of the iron out of plane displacement vary in the interval of 0.3–0.6 [40, 45]. It is interesting to remark that regarding structural parameters, the hybrid functional yield results pretty close to experimental and previous BLYP data (Table III).

We want to draw attention to the variation of the Fe–N$_{\text{im}}$ bond length as a function of the out-of-plane displacement of iron, shown in Figure 4. It can be noted that the Fe–N distance significantly decreases as the iron moves away from the plane. This trend supports the idea that the major cause of the Fe out-of-plane displacement is the nonbonded interaction between the axial ligand and the N orbitals of the porphyrin, and not the expansion of the iron atom as multiplicity increases, as commonly argued. In fact, DFT computations [5] yield for the isolated high-spin porphyrin a displacement of 0.08 Å, while in the presence of an axial imidazole this distortion becomes four times bigger. Thus, the magnitude of $d_{\text{Fe-p}}$ seems to be more likely the result of a balance between the attractive Fe–N and the repulsive nonbonded interactions [46], than a consequence of the size of the iron atom.
THE SIX-COORDINATED MODEL

To test the applicability of the hybrid methods to the investigation of the O₂ binding process in hemoproteins, we have used both the half-and-half and the B3LYP functionals to optimize a model structure of the oxyheme at different spin multiplicities. In this system, shown in Figure 5, the iron is hexacoordinated, and according to experiments, the O₂ molecule is axially bound in an angular configuration, exhibiting the so-called end-on geometry. The partial optimizations included the same structural degrees of freedom minimized in the five-coordinated model, plus the coordinates of the oxygen molecule. In Table IV we show selected geometrical parameters, together with the energetic gaps between spin states.

B3LYP yields an open-shell singlet as the ground state, with a closed-shell singlet, a triplet and a quintuplet lying at 19.7, 3.0, and 10.8 kcal/mol, respectively. The total spin density in the open-shell singlet ground state is close to zero on all atoms except on the iron and on the oxygen atoms: on Fe it is about −1, counterbalanced by the sum over both oxygens, which gives approximately 1. This

![Figure 5. Six-coordinated porphyrin model structure.](image)

<table>
<thead>
<tr>
<th>Energetic separations and selected geometrical parameters for the different spin states of the six-coordinated system.**</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>E</strong>&lt;sub&gt;rel&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>B3LYP open-shell singlet</td>
</tr>
<tr>
<td>singlet</td>
</tr>
<tr>
<td>triplet</td>
</tr>
<tr>
<td>quintuplet</td>
</tr>
<tr>
<td>half-and-half singlet</td>
</tr>
<tr>
<td>triplet</td>
</tr>
<tr>
<td>quintuplet</td>
</tr>
<tr>
<td>Exp.</td>
</tr>
</tbody>
</table>

<sup>a</sup> Energies in kcal/mol, distances in Å and angles in degrees.<br /><sup>b</sup> Relative energy with respect to the ground state.<br /><sup>c</sup> Data from crystallographic structure [48].
picture resembles the model proposed by Goddard to describe the Fe–O₂ bond [46, 47], consisting of a diamagnetic state with two singly occupied orbitals, one of them with \( d \) and the other with \( \sigma_\pi \) characters. Rovira and Parrinello [49], on the other hand, report also an open-shell singlet to be the ground state of the six-coordinated complex, with a spin distribution of +0.88/−0.88 localized on the \( d \) orbitals of Fe and the \( \pi^* \) orbitals of O₂.

The half-and-half functional predicts a quintuplet ground state, followed by an open-shell singlet, triplet and closed-shell singlet states lying at 20.7, 23.7, and 53.8 kcal/mol, respectively. These results seem to be in disagreement with experimental evidence, which has established that the electronic structure of the oxyheme and of hexacoordinated model systems corresponds to a singlet configuration [7, 8, 40]. This is consistent with the bias in the half-and-half functional in favoring high-spin configurations, observed in the Fe and Fe⁺ species. With this in mind, we expect that DFT at the GGA level would yield a singlet ground state, and in fact, Rovira et al. [5, 49] got both closed-shell and open-shell singlets very close in energy and much more stable than the higher multiplicity states by employing a BP86 scheme for a full porphyrin model.

**Conclusions**

We have shown that there are significant differences in the predicted spin energetics of the penta and hexa coordinated model systems computed by employing HF and different DFT schemes. These results may be understood in terms of ligand field theory as related to the errors in the description of the isolated metal. The neglect of correlation effects leads to significant errors in the transition energies, as can be seen by inspecting the results of Hartree–Fock calculations. The half-and-half DFT scheme yields results consistent with experimental information for the atomic species as well as for the five-coordinated system, but is not accurate when applied to the six-coordinated model. B3LYP calculations yield a reasonable picture of the hexa coordinated model systems, but in order to explain the high spin of the ground state of the penta coordinate model, a spin crossover should be assumed. To summarize the situation, we can say that those methods with a trend to stabilize high-spin configurations in atomic and ionic iron will perform qualitatively right in the case of the pentacoordinated system and will fail to describe the six-coordinated porphyrin. The opposite will be true for those schemes that favor a low-spin electronic structure. We expect that better results could be achieved within the DFT formalism by further improving the exchange correlation functionals. In this sense exploration of exact exchange functionals [50] may become a valuable tool to treat transition metal systems such as this one, where the spin state is the result of subtle electronic and bonding effects.

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