A Haldane-Anderson impurity model study for the spin- and charge-states of iron in heme proteins

Vivien Badaut1, Tomonori Shirakawa1,2,3, and Seiji Yunoki1,2,3

1 Computational Condensed Matter Physics Lab., RIKEN ASI, Wako, Saitama 351-0198 Japan
2 CREST, Japan Science & Technology Agency, Kawaguchi, Saitama 332-0012 Japan
3 Computational Materials Science Research Team, RIKEN AICS, Kobe, Hyogo 650-0047 Japan
E-mail: vivien.badaut@riken.jp

Abstract. To understand the spin and charge properties of iron(II) heme-proteins like myoglobin, we formulated a Haldane-Anderson impurity model within the closed-shell DFT-hybrid-GGA approximation. We employed a mean-field approximation to solve a simple model of myoglobin active site, the iron porphyrin-imidazol complex FeP(Im), which was found to reproduce some of the known spin-charge states of myoglobin. We also computed the spin-charge phase diagram of iron in FeP(Im) with and without O2 attached to the central iron, and found that the spin-charge states for FeP(Im) is much more sensitive to the local correlations than that for FeP(Im)(O2).

1. Introduction
Iron(II) heme proteins are controlling some of the main biological functions in mammals, like oxygen transport (e.g. hemoglobin, myoglobin) or electron transfer (e.g. cytochrome P450). Their prosthetic group consists of a substituted iron(II) porphyrin, which is linked to the protein chain by an amino-acid-to-iron bond. Their biological activity is partly determined by the spin state of the central iron [1]. In the case of myoglobin, whose main role is oxygen transport in the muscles, the prosthetic group of the active form deoxymyoglobin has a high-spin (HS) ground-state. When oxygen binds to the active site to form oxymyoglobin, it induces a transition to a low-spin (LS) ground state [2].

The pentacoordinated iron(II) porphyrin-imidazol complex FeP(Im) is a simple and extensively studied model of the prosthetic group of myoglobin (see e.g. [3]). It can bind an oxygen to form the hexacoordinated FeP(Im)(O2) complex. To this day, the common approximations allowing the ab initio calculation of the electronic states in extended systems, e.g. Hartree-Fock (HF) and Density Functional Theory (DFT), are unable to correctly predict the aforementioned spin transition between these two complexes [4]. In the DFT approximation, it was argued that this is caused by the local density approximation to the exchange interactions [5]. Hybrid-functionals [6] and LDA+U (see e.g. [7]) both have been used to try to solve the myoglobin spin-transition problem, with unsatisfactory results [5]. In the hybrid-functional approximation, the fraction of exact (Hartree-Fock) exchange interactions was observed to be system-dependent, and thus could not be determined unambiguously for both systems. In the LDA+U approximation, the exact exchange interactions of the localized electrons are computed after subtracting their DFT exchange energy, called double-counting correction. The double-counting correction is
estimated within a mean-field approximation of the Hubbard model, using the screened local coulomb repulsion \( U \) and Hund’s coupling \( J \) terms, whose values can be determined \textit{ab initio} [8]. However in this approximation, the structure of FeP(Im)(O\(_2\)) is not in agreement with experiments [5]. This failure suggests a lack of full understanding of the mechanisms responsible for the HS-LS transition in myoglobin.

In this paper, we present the first step of our attempt to understand this spin transition. We first computed the DFT closed-shell ground state of the complexes FeP(Im) and FeP(Im)(O\(_2\)) and used the resulting Hamiltonian elements to build a Haldane-Anderson impurity model [9]. This procedure is described in section 2. Using a mean-field approximation, the Haldane-Anderson impurity model was solved and the spin-charge phase diagram of iron in the FeP(Im) and FeP(Im)(O\(_2\)) complexes is presented in section 3. The limitations of our approach are briefly discussed in section 4.

2. Model and Approximations

2.1. \textit{Ab initio} determination of the Hamiltonian matrix

We used the code GAUSSIAN 03 [10] for the determination of the Hamiltonian matrices of the FeP(Im) and FeP(Im)(O\(_2\)) complexes, whose structures have been extensively studied and will not be shown here (see e.g. [3]). For the exchange-correlation functional, we used the hybrid B3LYP [6]. In order to keep the total number of basis functions as low as possible, a LANL2DZ effective core potential [11] was used for iron in combination with a light Pople-type 6-31*G basis for all other elements. The electronic and geometric constraints were fully released in the closed-shell approximation, without any numerically-enforced symmetry operations (keyword \textit{nosymm}), and the ground-state Fock (\( F \)) and overlap (\( S \)) matrices of the system were obtained (keyword \textit{iop}(3/33=1,3/36=-1,5/33=4)). The orthogonalized Fock matrix \( F_{orth} \) was obtained via an unitary transformation matrix \( \chi \), which was generated iteratively, starting from \( l = 1 \),

\[
\chi_{l,l} = \frac{S_{l,l} - \sum_{j=1}^{l-1} \chi_{l,j} \cdot \chi_{l,j}^*}{\sqrt{1 - \sum_{j=1}^{l-1} \chi_{l,j} \cdot \chi_{l,j}^*}}
\]  

(1)

The dimensions of \( F_{orth} \) are 460 × 460 and 488 × 488 for FeP(Im) and FeP(Im)(O\(_2\)) complexes, respectively, and the full elements of \( F_{orth} \) will be presented elsewhere.

2.2. Anderson Impurity Model

To treat correctly the effects of the local Coulombic correlations of Fe as well as the hybridization between Fe and its surroundings, we constructed a Haldane-Anderson-type impurity model [9]

\[
\mathcal{H} = \mathcal{H}_0 + U \sum_{\sigma} \sum_{m,m'} n_{m\sigma} \cdot n_{m'\sigma} + (U - J) \sum_{\sigma} \sum_{m,m'} \langle n_{m\sigma} \rangle \cdot n_{m'\sigma}
\]

\[
-U \sum_{\sigma} \sum_{m,m'} \langle n_{m\sigma}^0 \rangle \cdot n_{m'\sigma} + (U - J) \sum_{\sigma} \sum_{m,m'} \langle n_{m\sigma}^0 \rangle \cdot n_{m'\sigma}
\]

(2)

where \( \mathcal{H}_0 \) is obtained from the orthogonalized Fock matrix as \( \mathcal{H}_0 = \begin{pmatrix} F_{orth} & 0 \\ 0 & F_{orth} \end{pmatrix} \). \( U \) is the intra-atomic Coulomb repulsion and \( J \) is the Hund’s coupling between the localized 3d electrons on iron. \( n_{m\sigma} = c_{m\sigma} \cdot c_{m\sigma}^\dagger \) is the number operator of d orbital \( m \) (\( d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2} \), and \( d_z \)) with spin \( \sigma \). This model was solved in a mean-field approximation with \( \langle n_{m\sigma} \rangle \) as mean-fields. The expectation values of the number operators forms the occupation matrix. The second line
3. Numerical results

3.1. Initial occupation matrix

Because of the localization effects due to the Coulomb repulsion term, the converged electronic structure was often observed to depend on the initial occupations. Thus, the self-consistent iterations were started from seven different assumptions of the occupation matrix, corresponding respectively to the LS state, the IS (intermediate-spin) state, and the five possible HS states.

3.2. Spin-charge state diagram

The local charge \( Q = \sum_{m,\sigma} \langle n_{m\sigma} \rangle \) and spin \( S = \sum_{m,\uparrow} \langle n_{m\uparrow} \rangle - \sum_{m,\downarrow} \langle n_{m\downarrow} \rangle \) of iron were determined from the ground state occupation matrix. Sudden spin transitions were observed to occur with small \( U \) and \( J \) variation. The transition points were determined for each value of \( U \) and \( J \) within \( \Delta = \pm 0.025 \text{ eV} \). The obtained spin-charge phase diagram of the iron are presented Figure 1. This diagram is the superimposition of the results for both complexes.

Six distinct phases are observed in the investigated range of \( U \) and \( J \) values. For small \( U \) and \( J \) values, a \( d^6 \) LS (\( S = 0 \)) state was obtained. The electrons are localized in the \( d_{xy}, d_{xz}, \) and \( d_{yz} \) basis, in agreement with the non spin-polarized DFT ground state [2]. For intermediate (respectively large) values of \( U \) and small values of \( J \), a \( d^6 \) IS (\( S = 1 \)) state was obtained in FeP(Im) (resp. FeP(Im)(O\(_2\))). The majority-spin electrons are localized into the \( d_{xy}, d_{xz}, d_{yz}, \) and \( d_{yz} \) basis.
and $d_{z^2}$ basis while the minority-spin electrons are localized into the $d_{xz}$ and $d_{yz}$ basis. Thus, this state is equivalent to the (incorrect) ground state of FeP(Im) in open-shell DFT-B3LYP calculations \[4\]. For large $U$ and $J$ values, several $d^6$ HS ($S = 2$) state were obtained. In the dominant HS phase, which was observed for both system, the minority-spin electron is localized in the $d_{yz}$ basis function. The population of the $d_{yz}$ basis function decreases with increasing $J$ but is practically independent of $U$. In FeP(Im) case, two other HS phases were observed, with the minority-spin electron localized in the $d_{xy}$ basis function for intermediate values of $U$ or in the $d_{z^2}$ basis function for larger values of $U$. Finally, in the FeP(Im) system only, a $d^5$ HS ($S = \frac{5}{2}$) state was obtained for $J > 3$ eV and for all values of $U$ investigated here.

4. Discussion and Conclusion

In this paper, we have proposed a simple procedure to describe the active site of heme proteins using a Haldane-Anderson-type impurity model. The conduction band of the model was obtained by a quantum chemical calculations using DFT, and the local Coulombic correlations of Fe were included explicitly in the model. To demonstrate our scheme, we have studied as examples the spin and charge states of Fe in FeP(Im) with and without O$_2$ attached. Our model, constructed from the DFT closed-shell ground state, was able to reproduce the existence of the experimentally-assessed IS and HS states of iron porphyrins, and the important difference of spin states between FeP(Im) and FeP(Im)(O$_2$). However, the absence of the experimental ground state of FeP(Im), the $d^6$ HS state with the minority-spin electron localized in the $d_{xy}$ basis function \[2\], is an important issue. Moreover, the $d^6$ LS state obtained for FeP(Im)(O$_2$), being a closed-shell singlet, is different from the open-shell singlet ground-state previously reported \[5\]. These issues will be addressed in future study.

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