Project Title:

Density Functional Theory modeling of Fe-containing Metalloporphyrins.

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Background:

Some of the most important proteins are Heme metalloproteins (e.g. Myoglobin, Hemoglobin) whose biological activity are partly constrained by the spin state of the central iron atom (see e.g. STRICKLAND & HARVEY, 2007). It is however well known that DFT usually predict an incorrect spin state for the ground state of many porphyrins (BIKIEL *et al.*, 2006), and this was recently linked with an incorrect description of the electronic correlation and coulomb interaction (SCHERLIS *et al.*, 2007). The goal of our study is to use DFT calculation as a starting point for a further modeling of these systems using quantum Monte-Carlo methods in the Extended Haldane-Anderson model framework (J. Phys. Soc. Japan, 2003, 72, 2029-2032). The asked computational time will be used for DFT calculations only.

Estimation of the needed computational time:
1.000.000 h/proc per year

Preliminary results:

As a starting point on this project, we checked our capability in reproducing some of the known properties of the active site of Myoglobine (Fig. 1). Thus, we computed the electronic ground state of a simplified model in which the active site heme B was replaced by porphine and the proximal ligand histidine was replaced by an imidazol group. These substitutions are usually considered to have a negligible effect in DFT (Rovira & Parinello, 1999 ; Liao et al., 2010).
Thus, we used GAUSSIAN 03 code in the DFT-hybrid GGA approximation (B3LYP functional), using for the basis functions a Pople-type basis set (6-31G(d,p)) and an effective core potential on the iron atom (LANL2DZ) to compute the electronic ground state of imidazol-bonded porphine (thereafter noted ImFeP). The effects of the bonding of O_2 and CO to ImFeP was investigated as well, and the fig. 2 presents and allow to compare the geometry of the last populated electronic level (HOMO) and the first unoccupied electronic level (LUMO) as well as the density of states of these three case.

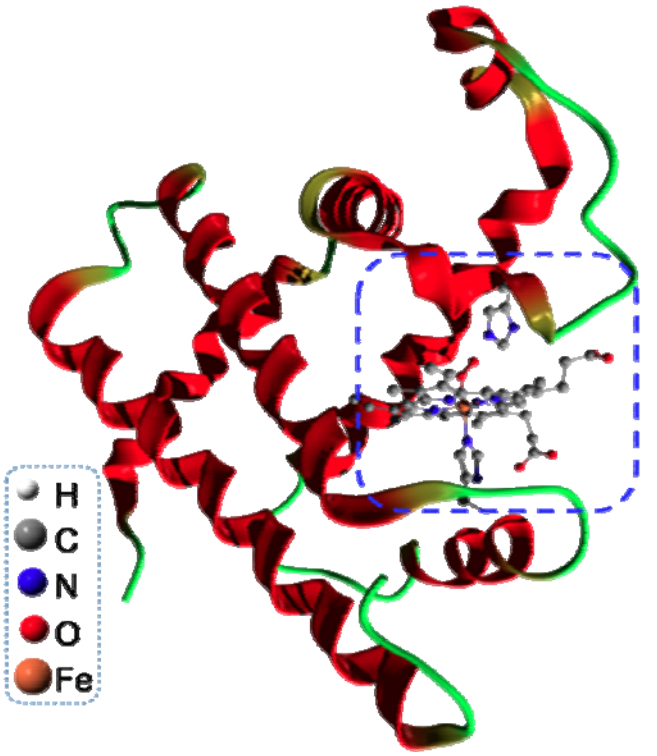

Fig. 1: Structure of the Myoglobin protein. Only the atoms from the active site are represented in ball-and-sticks (blue square)

In this work, we used GAUSSIAN 03 code in the DFT-hybrid GGA approximation (B3LYP functional), using for the basis functions a Pople-type basis set (6-31G(d,p)) and an effective core potential on the iron atom (LANL2DZ) to compute the electronic ground state of imidazol-bonded porphine (thereafter noted ImFeP). The effects of the bonding of O_2 and CO to ImFeP was investigated as well, and the fig. 2 presents and allow to compare the geometry of the last populated electronic level (HOMO) and the first unoccupied electronic level (LUMO) as well as the density of states of these three cases.
In ImFeP case, the optimized structure consist in a bended porphine unit, with the iron atom displaced 0,3 Å out of the plane. The central iron is in a 2+ electronic state, with a optic gap of about 3,5 eV. Iron bonding with CO or O_2 restore the flatness of the prophine unit, but

while Fe-C-O is linear, the Fe-O-O angle is close to 130°. CO bonding affects mainly the HOMO state, while O_2 bonding affects strongly the LUMO as well, reducing the optic gap to about 2 eV. All these results are in good agreement with data from the literature (Rovira & Parinello, 1999 ; Liao et al., 2010).

Thus, we proved our ability to correctly describe such systems using hydrid DFT.

Future goals:

The results obtained on these system will be refined in order to get extremely well converged results with respect to basis set size, energy, electronic density. We will investigate as well the effect of several types of exchange-correlation functionals, as e.g. PBE0 and OPBE, which are known to be more accurate for the description of the ground state of such iron-based molecular systems.

The ground state, one particule full Hamiltonian of the system will be extracted, and we will use it to build a Anderson impurity model of the protein to accound correctly for the many-body interactions occurring through the prophyrin ring ; this should allow us to compute accurately the ground state magnetic properties of these systems, that DFT is not able to predict correctly to this day.

Bibliography:

Bikiel, Boechi, Capece, Crespo, De Biase, Di Lella, Gonzalez Lebrero, Marti, Nadra, Perissinotti, Scherlis & Estrin (2006). *Phys. Chem. Chem. Phys.* **8**, 5611.

Liao, Huang & Watts (2010). *J. Phys. Chem. A* **114**, 9554.

Rovira, Kunc, Hutter, Ballone & Parrinello (1997). *J. Phys. Chem. A* **101**, 8914.

Scherlis, Cococcioni, Sit & Marzari (2007). *J. Phys. Chem. B* **111**, 7384.

Strickland & Harvey (2007), *J. Phys. Chem. B*, **111**, 841.

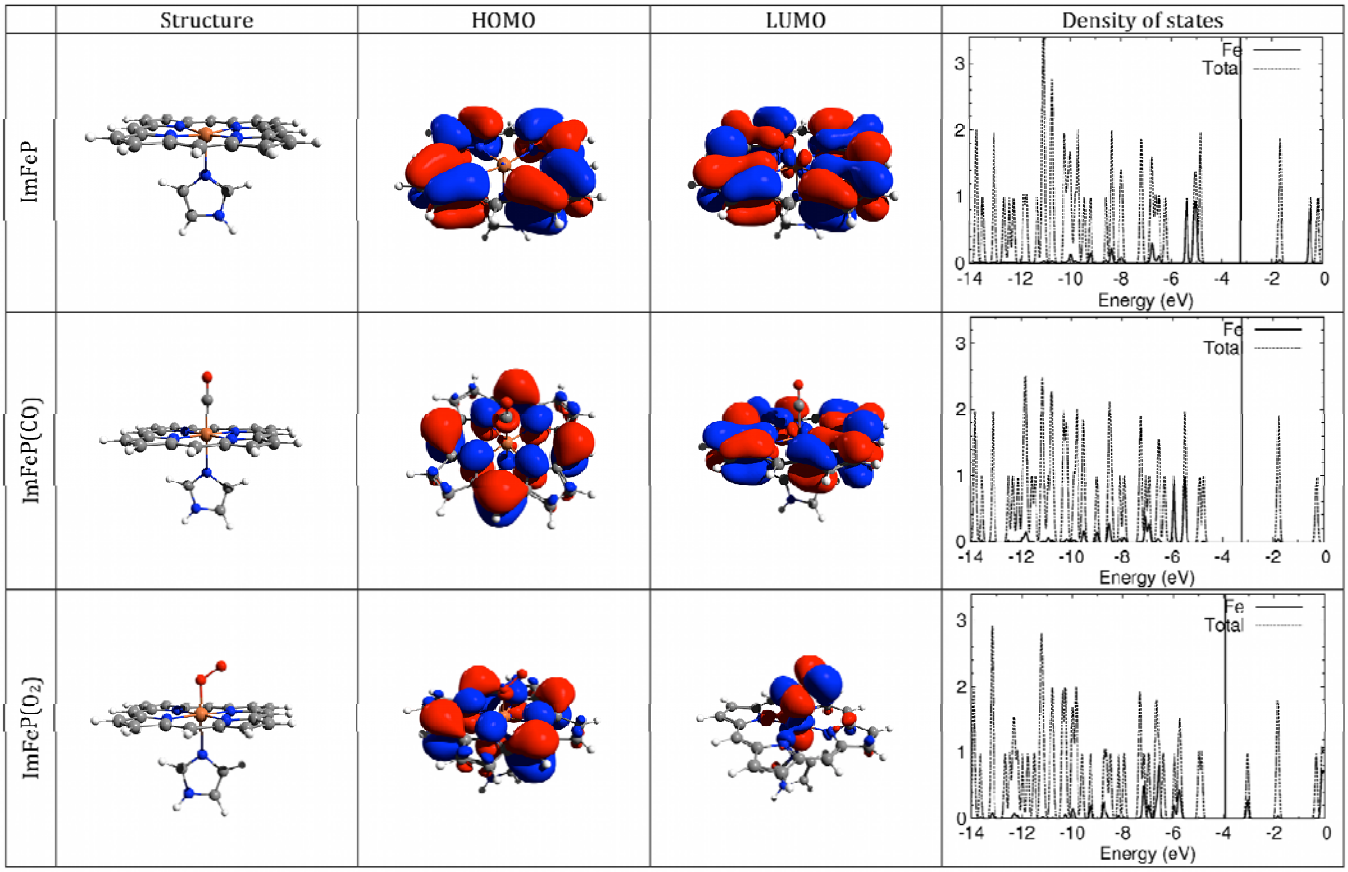

Fig. 2: Geometry-optimized structure, HOMO, LUMO and density of states of the three cases ImFeP, ImFeP(CO) and ImFeP(O_2).