

Electronic Supplementary Information (ESI): Predicting Spin States of Iron Porphyrins with DFT Methods Including Crystal Packing Effects and Thermodynamic Corrections

Mariusz Radoń*

Jagiellonian University, Faculty of Chemistry, Kraków, Poland

E-mail: mraddon@chemia.uj.edu.pl

Phone: +48-12-686-2489

Contents

List of Tables	S-2
List of Figures	S-2
1 Additional Computational Details	S-3
1.1 Molecular DFT Calculations	S-3
1.2 Periodic DFT Calculations	S-4
2 Additional Results	S-5
2.1 Optimized Geometries and Total Energies	S-5
2.2 Scalar Relativistic Corrections	S-6
2.3 Mulliken Spin Populations	S-6
References	S-7

List of Tables

S1 Scalar Relativistic Corrections	S-6
----------------------------------------------	-----

List of Figures

S1 Mulliken spin populations	S-6
----------------------------------------	-----

1 Additional Computational Details

1.1 Molecular DFT Calculations

All `Turbomole` and `Orca` calculations employed either the RIJ^{S1,S2} or (for functionals containing exact exchange) the RIJCOSX^{S3} approximation. In `Turbomole` geometry optimizations, the integration grid `m5` was used convergence threshold on forces was set to $1 \times 10^{-4} E_h a_0^{-1}$. In `Orca` calculations, default integration grid (`defgrid2`) was used. Optimized minima were verified by harmonic analysis. In the case of quartet $[\text{Fe}(\text{P})(2\text{-MeIm})_2]^+$, a tiny imaginary frequency ($i6 \text{ cm}^{-1}$) was obtained in the case of for a very soft vibration mode describing rotation of 2-MeIm axial ligand. This is regarded as unimportant computational artefact: test geometry optimization started from this structure distorted along the mode in question resulted in equivalent optimized structure and energy identical to within $0.01 \text{ kcal mol}^{-1}$. In order to facilitate analysis of spin-unrestricted orbitals, e.g. to verify that correct electronic states were obtained, `natorbs` utility^{S4} was used.

Comment on Spin–Orbit Coupling (SOC). The present calculations (for porphyrin models) include scalar-relativistic effects, but not the SOC. In Fe^{III} porphyrins, the SOC is known to cause a quantum-mechanical mixing between the sextet and quartet states,^{S5} but it cannot switch the order of these spin states if the experiment indicates predominantly sextet or quartet state based on the structure. In four-coordinate Fe^{II} porphyrin, the SOC leads to mixing of the higher energy degenerate triplet (3E) to the lowest triplet (3A) and thus it effectively contributes $\sim 1 \text{ kcal mol}^{-1}$ to stabilize the lowest triplet with respect to the quintet state.^{S6,S7} This effect is not included in the present study, but is also unlikely to significantly change our conclusions as the majority of functionals appear to recover the triplet ground state even without this correction.

1.2 Periodic DFT Calculations

QuantumEspresso calculations. Variable cell periodic optimizations in a plane-wave basis set were performed with the kinetic energy cutoff 70 Ry for the wave function (`ecutwfc`) and 560 Ry (`ecutrho`) and the following convergence thresholds: 2.0×10^{-4} Ry a_0^{-1} on forces, 2.0×10^{-4} Ry on total energy changes between two consecutive points, and 0.5 kbar for the variable-cell pressure. In subsequent single-point calculations to obtain the $\delta_{\text{CPE}}^{\text{direct}}$ correction, the kinetic energy cutoffs were set to 35 Ry (`ecutwfc`) and 280 Ry (`ecutrho`). When computing in this way the energy of a single metalloporphyrin molecule, it was placed in the cubic lattice with the cell dimension of $60 a_0$ and the Makov-Payne correction^{S8} was additionally used to correct the energy for long-range electrostatics.

Crystal17 calculations. To converge the SCF procedure to desired spin state, keyword `SPINLOCK` was used. Truncation criteria for bielectronic integrals (`TOLINTEG` keyword) were set to: 8 8 8 10 20. In the case of quintet state of [Fe(TPP)] crystal, it turned out necessary to alter orbital occupancies before initial SCF with keyword `EIGSHIFT` and such obtained correct orbitals were provided as initial guess in further optimization.

Input preparation and general remarks. Initial cells and atomic coordinates of the crystals were prepared based on the available CIF files (for refcodes, see Table 1 in the main article). The CIF files were converted to `QuantumEspresso` input format with one the tools: `cif2cell`^{S9} or `Burai`.^{S10} In a few cases some atoms were missing in the CIF (e.g., hydrogens of the CH_2Br_2 solvent molecule in DEDZER); such atoms were added manually. One specific orientation was chosen for disordered perchlorates. The conformation of isolated porphyrin is the one which is obtained from that observed in the crystal structure by performing local geometry optimization and is not necessarily the one in global energy minimum. For example, there are many possible conformations of the side chains in OEP or OETPP, i.e., many local minima, the relative energies of which were not investigated in a systematic way.

The conformation of side chains in our models is generally close to that observed in the crystal structure.

2 Additional Results

2.1 Optimized Geometries and Total Energies

Optimized geometries and total energies are provided separately in other ESI documents. A dataset of molecular geometry optimizations and `QuantumEspresso` periodic DFT calculations is available as ioChem-BD collection^{S11} under the following link: <https://doi.org/10.19061/iochem-bd-7-7>.

2.2 Scalar Relativistic Corrections

Table S1: Scalar Relativistic Corrections to Spin-State Splittings.^a

model	ΔE	nrel ^b	DK ^c	correction
[Fe ^{III} (P)(2-MeIm) ₂] ⁺	$\Delta E^{(6,2)}$	6.7	5.9	0.8
	$\Delta E^{(6,4)}$	6.8	6.7	0.1
[Fe ^{III} (P)(2-MeIm) ₂] ⁺	$\Delta E^{(6,4)}$	6.9	6.6	0.3
	$\Delta E^{(5,1)}$	-2.9	-3.8	0.9
[Fe ^{II} (P)(THF) ₂]	$\Delta E^{(5,3)}$	2.9	2.2	0.8
	$\Delta E^{(5,3)}$	7.1	6.4	0.7

^aValues in kcal mol⁻¹. ^bNonrelativistic B3LYP-D3(BJ)/cc-pVTZ.

^cRelativistic B3LYP-D3(BJ)/cc-pVTZ-DK, using Gaussian nuclear model.^{S12}

2.3 Mulliken Spin Populations

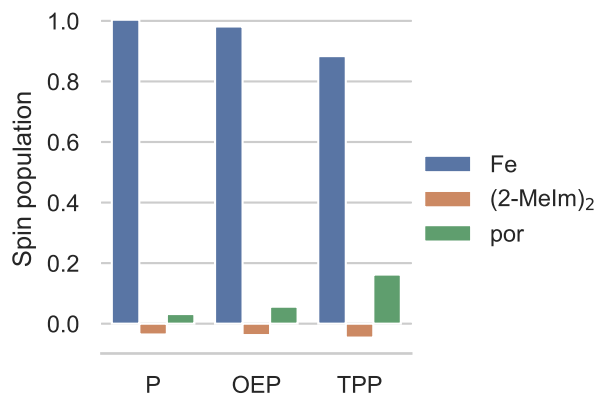


Figure S1: Mulliken spin populations on Fe, imidazoles and porphyrin ring in the optimized LS states of [Fe(por)(2-MeIm)₂]⁺ systems, where por is P, OEP or TPP. From PBE-D3(BJ)/def2-TZVP calculations.

References

- (S1) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. Auxiliary basis sets to approximate Coulomb potentials. *Chemical Physics Letters* **1995**, *240*, 283–290.
- (S2) Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.
- (S3) Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Efficient, approximate and parallel Hartree-Fock and hybrid DFT calculations. A ‘chain-of-spheres’ algorithm for the Hartree-Fock exchange. *Chem. Phys.* **2009**, *356*, 98–109.
- (S4) Radoń, M. Natorbs v1.0.2. 2022; Jagiellonian University, Krakow, Poland, available from <https://tungsten.ch.uj.edu.pl/~mradon/natorbs>.
- (S5) Maltempo, M. M.; Moss, T. H. The spin 3/2 state and quantum spin mixtures in haem proteins. *Q. Rev. Biophys.* **1976**, *9*, 181.
- (S6) Vancoillie, S.; Zhao, H.; Tran, V. T.; Hendrickx, M. F. A.; Pierloot, K. Multiconfigurational Second-Order Perturbation Theory Restricted Active Space (RASPT2) Studies on Mononuclear First-Row Transition-Metal Systems. *J. Chem. Theory Comput.* **2011**, *7*, 3961–3977.
- (S7) Radoń, M. In *Advances in Inorganic Chemistry*; van Eldik, R., Puchta, R., Eds.; Academic Press, 2019; Vol. 73; Chapter 7, pp 221–264.
- (S8) Makov, G.; Payne, M. C. Periodic boundary conditions in ab initio calculations. *Phys. Rev. B* **1995**, *51*, 4014–4022.
- (S9) Björkman, T. CIF2Cell: Generating geometries for electronic structure programs. *Computer Physics Communications* **2011**, *182*, 1183–1186.
- (S10) Nishihara, S. BURAI 1.3, a GUI for Quantum Espresso. 2018; <https://nisihara.wixsite.com/burai>.

- (S11) Álvarez-Moreno, M.; de Graaf, C.; López, N.; Maseras, F.; Poblet, J. M.; Bo, C. Managing the Computational Chemistry Big Data Problem: The ioChem-BD Platform. *J. Chem. Inf. Model.* **2015**, *55*, 95–103.
- (S12) Visscher, L.; Dyall, K. G. Dirac-Fock atomic electronic structure calculations using different nuclear charge distributions. *Atomic Data and Nuclear Data Tables* **1997**, *67*, 207–224.