Ground State of the Fe(II)-porphyrin Model System Corresponds to the Quintet State: A DFT and DMRG-based Tailored CC Study

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Fe(II)-porphyrins (FeP) play an important role in many reactions relevant to material science and biological processes, due to their closely lying spin states. However, this small energetic separation also makes it challenging to establish the correct spin state ordering. Although the prevalent opinion is that these systems possess the triplet ground state, the recent experiment on Fe(II)-phthalocyanine under conditions matching those of an isolated molecule points toward the quintet ground state. We present a thorough study of FeP model by means of the density functional theory and density matrix renormalization group based tailored coupled clusters, in which we address all previously discussed correlation effects. We examine the importance of geometrical parameters, the Fe—N distances in particular, and conclude that the system possesses the quintet ground state, which is in our calculations well-separated from the triplet state.

Porphyrins are conjugated aromatic systems composed of four pyrrole rings connected at their Cα atoms by CβH groups (see Figure 1). Their metal-derivates, in particular Fe(II) porphyrins based on Fe(II)-porphin (FeP, Fig. 1a) (Fe(II)-phtalocyanine (FePc, Fig. 1b) and Fe(II)-porphyrazine (FePz, Fig. 1c)), play an important role in reactions related to material science and biological processes due to the near degeneracy of their high-spin (quintet), intermediate-spin (triplet) and low-spin (singlet) states. A well-known example is the triplet to singlet spin crossover upon binding of molecular oxygen to the Fe(II) active site of hemoglobin. Despite the huge efforts over the years, the exact mechanism of this reaction has not yet been established.

The major obstacle in the investigation of the heme molecule (especially hemoglobin) is its size, which renders the use of high-level calculations, necessary for definitive assignment of its ground state, challenging. For this reason, only the core formed by FeP is used to model this system. However, since it does not exist in an unsubstituted state, similarly to FePz, the reliability of computational methods based on the comparison with experiment cannot be assessed. Existing experimental studies of four-coordinated Fe(II) embedded in substituted porphyrin systems have assigned mostly the triplet ground state, with the exception of the high-spin quintet ground state of Fe(II)-octamethyl-tetrabenzoporphyrin that has been assigned by the Mössbauer spectroscopy. These experiments have been performed either in the crystal phase or in polar solvent, which might affect the ground state and currently make highly correlated calculations not directly comparable with experiment. Gas phase studies in which an isolated molecule is investigated were limited to high temperatures which alter the ordering of closely lying spin states.

The effect of different environments on the FePc ground state was recently investigated in our laboratory by means of a combined experimental and computational study. We measured Mössbauer spectra in crystalline form and in the dimethyl-formamide (DMF) and monochlorobenzene solvents, which are characterized by different dielectric constants (D) and dipole moments (µ_dip). (DMF: D ∼ 37, µ_dip = 3.9 D; monochlorobenzene: D ∼ 6, µ_dip = 1.5 D). The low solubility and polarity of monochlorobenzene closely resemble the gas phase conditions of computational studies; the isolated nature of FePc is confirmed also by the zero Weiss temperature. The observed characteristics, i.e. the isomer shift (δ) and quadrupole splitting (∆E_Q) have unambiguously indicated the triplet ground state of FePc in the crystalline form and dissolved in DMF, and the quintet when dissolved in monochlorobenzene. The quintet ground state was also confirmed by the multireference density matrix renormalization group (DMRG) calculations. These findings clearly contradict the prevalent opinion in the literature.

The experimental observations of Fe(II) porphyrins guided several follow-up computational studies per-
formed on FeP and FePz with the single-reference density functional theory (DFT) \cite{16,17,18} and multireference methods.\cite{20,21} Depending on the functional, DFT calculations have assigned either quintet or more frequently triplet ground-state for FeP and FePz. On the contrary, the complete active space perturbation theory (CASPT2)\cite{25} has predicted the quintet ground-state which has lead to the discussion of various computational aspects, mainly the Fe(3s,3p) electron correlation.\cite{26,27} Its evaluation with CASPT2 and coupled clusters (CC) with singles, doubles and perturbative triples (CCSD(T)) puts triplet 0.15 kcal/mol below quintet.\cite{28} An unambiguous answer to the state ordering has not been found even with the DMRG method\cite{29,30,31} or Heat-bath Configuration Interaction quantum Monte Carlo or Heat-bath Configuration Interaction algorithm coupled with the multiconfiguration self-consistent field methods, which are able to correlate a relatively large number of electrons. It should be noted that due to the size of FePc neither the DMRG calculations provide a full description of the electron correlation,\cite{32} although they predict the quintet ground state in agreement with the experiment.

The effects of different contributions to electron correlation,\cite{33,34,35} have recently been investigated by calculations on model system of Fe(II)-porphyrin in which the bridging Cβ-H groups are replaced by hydrogen atoms (model 1, Fig. 1). In the recent work of Li Manni et al.\cite{36} the complete active space (CAS) was constructed from 32 electrons in 34 orbitals, in particular, the Fe(3d), Fe(4d), σ lone pairs, and all π orbitals of the porphyrin model ring to cover the valence correlation. These orbitals describe the σ-donation/π-back-donation interaction with the ring, which significantly contributes to the triplet stabilization with respect to quintet. The active space was then augmented by the semi-core Fe(3s,3p) orbitals resulting in CAS(40,38) and a minor increase in the quintet-triplet gap. The inclusion of beyond-active-space correlation by employing the coupled cluster approach further stabilized the triplet ground state and provided the final estimate of the triplet-quintet energy gap as 5.7 kcal/mol. This result contradicts our findings on FePc,\cite{37} discussed above and once again opens the question of reliability of computational methods, especially regarding the extent of the electron correlation in the multireference approach, but also the role of other parameters which may influence the ground state predictions.

Among such parameters, a special attention should be paid to the structure and geometry of FeP model and related systems. The Fe—N bond distance ($R_{FeN}$) has been discussed by several authors,\cite{38,39} with some proposing that the increase in $R_{FeN}$ stabilizes quintet states via the relaxation of $d_{z^2}$-type orbitals.\cite{40} The calculated Fe—N bond distances obtained for the quintet states typically range from 2.0 to 2.1 Å\cite{41,42,43}. In comparison, the value of 1.972 Å taken from the X-ray diffraction of Fe(II) tetraphenylporphine (FeTPP)\cite{44} is closer to the value of 1.989 Å obtained for the FeP triplet state by employing the PBE0 functional in DFT optimization.\cite{45} This result confirms the suggestion discussed in Ref.\cite{11} for Fe(II)-Pc, according to which the ground spin state observed in the crystalline form of Fe(II) porphyrins very likely differs from the ground state of an isolated molecule in the gas phase.

This discussion on various effects influencing the spin state ordering raises the following question: Does the improved electron correlation treatment result in the same changes in the triplet-quintet state ordering of the FeP model regardless of whether the triplet optimized ($R_{FeN} = 1.989$ Å\cite{43}) or quintet optimized ($R_{FeN} > 2$ Å) distance is used?

To resolve this issue, apart from the DFT calculations with the B97 functional, we investigated the electronic structure of 1 by means of the DMRG method and its extension in the form of tailored CC (DMRG-TCCSD, DMRG-TCCSD(T))\cite{46,47}. Here, we only outline the main ideas behind the DMRG-TCC method as its detailed description and mathematical background is available in one of our previous works.\cite{48,49,50}

DMRG is a well-established and very powerful approach suitable for treatment of strongly correlated problems that require large active spaces not accessible by the exact diagonalization.\cite{51,52} However, despite its favorable

**FIG. 1:** Structures of Fe(II)-porphin (a), Fe(II)-phtalocyanine (b), Fe(II)-porphyrazine (c) and a model system 1 of Fe(II)-porphyrin (d). Color key: iron (gray, large), nitrogen (blue), carbon (gray, small), hydrogen (white).
scaling, it is still computationally prohibitive to treat the dynamic correlation solely with DMRG. As a possible solution, we have introduced the DMRG-TCCSD method, in which the CC wave function is externally corrected using the information extracted from the DMRG calculation.\textsuperscript{56,57,58}

The general form of the TCC wave function reads: \textsuperscript{54}

\[ |\Psi_{\text{TCC}}\rangle = e^{T}|\Phi_0\rangle = e^{T_{\text{ext}} + T_{\text{CAS}}}|\Phi_0\rangle, \]

where \( T_{\text{CAS}} \) represents the active space amplitudes and \( T_{\text{ext}} \) comprised the rest of the cluster operator composed of the amplitudes that have at least one orbital index outside of CAS. In the case of DMRG-TCCSD, the active space amplitudes corresponding to the single and double excitations with respect to \( |\Phi_0\rangle \) are efficiently obtained from the pre-calculated DMRG wave function.\textsuperscript{59}

These amplitudes, which are responsible for a proper description of non-dynamic correlation, are kept constant (not iterated) during the subsequent CC procedure. On the other hand, the external amplitudes responsible for the main portion of the dynamic correlation, are iterated in the usual manner. Note that within this scheme, the DMRG-TCCSD method employs the single-reference CC formalism with a single Hartree-Fock determinant as a Fermi vacuum. However, by introducing the external information from DMRG, which is a genuine multireference method, it is able to describe both non-dynamic and dynamic correlation in a balanced way.\textsuperscript{14,16}

Due to the scaling of the CCSD part, the DMRG-TCCSD methodology quickly becomes unfeasible for larger systems. To remove this bottleneck, we have recently developed its domain-based local pair natural orbital (DLPNO) version\textsuperscript{52} which exploits the locality of electron correlation and employs the pair natural orbitals. These are natural orbitals specific for each pair of localized occupied orbitals and which are known to provide compact parametrization of the virtual orbital space.\textsuperscript{46,47} Compared to the other nearly linear scaling methods, the main advantage of the DLPNO formalism\textsuperscript{53} is that it is controlled only by a limited number of cut-off parameters which do not explicitly involve distances in real space.

The \( R_{\text{FeN}} \) values resulting from spin separate triplet and quintet optimizations of model 1, performed at the B97-D3/def2-TZVPP level, are given in Table I. For comparison, we also report the distances for FeP and FeTPP, which are in very good agreement with the PBE0 values of 1.989 Å and 2.053 Å optimized for the FeP triplet and quintet states, respectively.\textsuperscript{32} Additionally, the \( R_{\text{FeN}} \) values obtained from the triplet optimizations agree reasonably well with the distance of 1.972 Å found in the X-ray diffraction experiment\textsuperscript{9} (where FeTPP is predicted to possess the triplet state), thus confirming the reliability of B97-D3 functional. In agreement with the discussion above, the quintet-optimized \( R_{\text{FeN}} \) values of FeP, FeTPP and 1 are larger compared to the triplet state, with the differences 0.060 Å, 0.067 Å and 0.132 Å, respectively. The significant increase in elongation for 1 compared to FeP and FeTPP stems from the larger flexibility of the surrounding ring because of the missing bridging C\(_3\)H groups.

Table I lists the relative spin state energies from DFT obtained by employing the B97-D3 functional for various \( R_{\text{FeN}} \) distances of 1 and their comparison with the previously reported results on 1a obtained with the Stochastic-CASSCF\textsuperscript{32,33}. The B97-D3 adiabatic energy gap is determined as 11.0 kcal/mol with the quintet ground state by using the \( R_{\text{FeN}} \) distances from the fully optimized 1 triplet and quintet geometries (the difference in \( R_{\text{FeN}} \) is 0.132 Å). This gap then reduces to 2.8 kcal/mol when \( R_{\text{FeN}} \) values from the optimized FeP are used (the difference in \( R_{\text{FeN}} \) is 0.067 Å). The ordering reverses and the triplet state becomes more stable than quintet by 2.9 kcal/mol at the triplet geometry \textsuperscript{1b}. This vertical gap increases to 8.0 kcal/mol when \( R_{\text{FeN}} \) optimized for FeP triplet is used. At the similar Fe–N distance 1a, the Stochastic-CASSCF calculation\textsuperscript{32,33} predict the triplet ground state as well, but with the smaller energy gap of 3.1 and 4.4 kcal/mol using the CAS\textsuperscript{(32,34)} and CAS\textsuperscript{(40,38)}, respectively.

These results indicate that the Fe–N bond distances play a significant role in the spin state ordering of FeP systems, but the extent of its influence has not yet been evaluated in detail. In fact, our DFT results indicate that the effect of this structure parameter can dominate energy balance and thus relative ordering of the spin states. We evaluate this effect together with another significant influence which is the level of electron correlation treatment.

In the following text, the results of (DMRG-)CASSCF and DMRG-TCC calculations are evaluated. Below only the final data are presented; the complete set of results is provided in the Supplementary Information. The details on the employed methods and their settings are given in Computational Details. Based on the previous discussions on the ground state of FeP systems in the literature, only the lowest quintet (\( ^5\text{A}_1g \)) and triplet states are considered. Unlike in the study of Li Manni et al.\textsuperscript{33}, the lowest triplet state in all our (DMRG-)CASSCF and TCC calculations corresponds to \( ^3\text{A}_2g \) with the occu-
In order to assess the accuracy of the DLPNO approximation, we first performed a series of benchmark calculations. In these, we calculated the energy differences of the studied quintet to triplet energy gaps \( \Delta E^{Q\rightarrow T} = E^T - E^Q \) between the canonical TCC methods and its DLPNO counterparts in the smaller SVP basis set. The resulting errors coming from the DLPNO approximation are well below 0.5 kcal/mol, except those obtained for 1a with CAS(8,12), where the errors are about 0.6 kcal/mol.

We first discuss the results for vertical \( \Delta E^{Q\rightarrow T} \) in the 1a geometry which are presented in the left plot of Figure 2. This system has already been a subject of previous studies by Li Manni et al. and it therefore offers an opportunity to compare our approach with a different method. Starting with the smaller CAS(8,12) and CAS(12,16), CASSCF results show an initial stabilization of the quintet state. Similarly to Ref. 33, the additional dynamic correlation on top of the CASSCF reference wave functions by means of the DLPNO-TCCSD stabilizes the triplet, i.e. decreases \( \Delta E^{Q\rightarrow T} \). Its further, yet less prominent stabilization is observed when perturbative triples are employed. At this point, it is obvious that the inclusion of four Gouterman’s \( \pi \)-orbitals in CAS does not change the relative energies of the lowest quintet and triplet states and there is virtually no difference in energy gap between CAS(8,12) and CAS(12,16) at all levels of correlation treatment. However, the situation is different when the largest active space is used.

While for the smaller active spaces each method assigns the quintet ground state, the addition of all \( \pi \)-orbitals stabilizes the triplet state with respect to quintet at the DMRG-CASSCF(32,34) level. Thus, the triplet becomes the ground state with \( \Delta E^{Q\rightarrow T} \) gap corresponding to -3.1 kcal/mol of the said study. The difference between these two values might originate in the use of different basis sets and/or slightly differently optimized CASSCF orbitals, since the bond dimension in DMRG-CASSCF is not in full accordance with the given number of walkers in Stochastic-CASSCF. When the dynamic correlation is added on top of DMRG-CASSCF, the change in \( \Delta E^{Q\rightarrow T} \) is less prominent compared to the smaller active spaces. This means that most of the important correlations are already captured by the active space containing 34 orbitals as has been previously discussed. Interestingly, the dynamic correlation stabilizes the quintet state, resulting in \( \Delta E^{Q\rightarrow T} \) of \(-0.11\) kcal/mol at our highest level of theory DLPNO-TCCSD(T)(32,34), which contrasts with the previous observations \(-5.7\) kcal/mol.

This inconsistency between our and the previously published results deserves a few comments. In the study, the authors investigated the effect of so-called semi-core orbitals Fe(3s,3p), as well as the virtual orbitals not included in CAS(32,34). Both groups of orbitals have a different stabilization effect: semi-core orbitals stabilize the triplet state, whereas the dynamic...
correlation of the full virtual space stabilizes the quintet state. In our opinion, the observed discrepancy stems from the fact that in the article by Li Manni et al. the correlation effects have been studied at a different level of theory. The semi-core orbitals have been eventually included into the active space, and thus described at the multireference level, while the effect of full virtual space has been studied by means of single-reference CC. Taking into account that in our TCC calculations the HF determinants contribute to the total wave function with the weight of about 0.60, the single-reference level of theory might be inadequate. Even though we employ the single-reference CC formalism (using one-determinant Fermi vacuum), our TCC approach systematically accounts for the strong-correlation effects via the CC amplitudes extracted from the DMRG wave function with semi-core correlation included directly at the CCSD level. Nevertheless, further studies which would employ alternative computational methods of calculation of dynamic correlation on top of CASSCF(32,34) (e.g. adiabatic connection[61,62]) are necessary to confirm our hypothesis.

Next, the results are analyzed in terms of \( R_{\text{FeN}} \) distance for spin state specific optimized structures of FeP model 1 and presented in Figure 3. The left plot shows the values of vertical \( \Delta E^{Q\rightarrow T} \) calculated for the 1b geometry, which with improving treatment of electronic correlation exhibit very similar trends as for 1a, but shifted by about 8 kcal/mol towards the more stable quintet. The right plot shows the values of adiabatic \( \Delta E^{Q\rightarrow T} \) calculated for fully optimized 1 i.e. with the triplet and quintet states in 1b and 1c geometries, respectively. Compared to the vertical \( \Delta E^{Q\rightarrow T} \), these stabilize the quintet even more.

The flexibility of the basis sets is demonstrated in Figure 4 in which the results of vertical \( \Delta E^{Q\rightarrow T} \) of 1a and 1b calculated with CAS(32,34) and def2-TZVP basis set are compared with those obtained with def2-SVP basis set. The larger basis systematically stabilizes triplet with respect to the quintet state, the effect which is more prominent for 1a. Even though the differences in \( \Delta E^{Q\rightarrow T} \) values are small, ranging from 1.2 to 2.6 kcal/mol, they can change the ordering of spin states as observed for 1a.

Now, considering the most important geometrical parameter \( R_{\text{FeN}} \) of the models used in this study, our best estimate of the vertical \( \Delta E^{Q\rightarrow T} \) of 1a (\( R_{\text{FeN}} = 1.989 \) Å) obtained at the DLPNO-TCCSD(T)(32,34)/def2-TZVP level of theory puts the triplet state below quintet with the negligible gap of \(-0.11 \) kcal/mol. On the other hand, the same calculations of 1b (\( R_{\text{FeN}} = 2.048 \) Å), which is optimized for the triplet state, result in quintet being
more stable by 7.83 kcal/mol. Note that although the 1b model comes from the triplet optimized geometry, its Fe–N distance closely reflects the quintet state geometry of FeP and its derivatives (just as 1a reflects their triplet geometry, see Table I). Therefore, we consider it to be a sensible model for ground state predictions of FeP systems. Based on this, the presented results support the conclusions of a combined experimental and computational study on Fe(II)-phthalocyanine, according to which isolated FePc systems possess the quintet ground state. The values of adiabatic \( \Delta E^{Q \rightarrow T} \) of fully optimized \( 1 \) further emphasize the importance of \( R_{\text{Fe-N}} \) for correct predictions of the FeP spin state ordering, although the changes in geometry are overestimated in this system, due to the increased flexibility caused by removing the \( C_\beta \) groups.

In this letter, we presented a thorough study of Fe(II) porphyrin model, which explored various effects influencing the spin state ordering of FeP systems. We included all previously discussed correlation effects, – non-dynamic valence correlation via DMRG-CASSCF(32,34), and beyond-active-space and semi-core dynamic correlation via DMRG-based DLPNO-TCCSD(T). The use of the latter method allowed us to employ basis sets flexible enough to capture subtle changes in the spin state ordering. On top of that, we stress the crucial importance of geometrical parameters, the Fe–N distances in particular, which is an aspect that has not been previously addressed and has a substantial impact on the ground state character. By exploring different geometries, we conclude that by using the model structure with Fe–N distances close to the quintet optimized geometry of FeP and its derivatives, the ground state is found to be a quintet (vertical \( \Delta E^{Q \rightarrow T} = 7.8 \) kcal/mol), which is consistent with the previous measurements on an isolated molecule of Fe(II)-phthalocyanine.

### COMPUTATIONAL DETAILS

All CASSCF, TCCSD, and TCCSD(T) calculations were performed with the ORCA program package. The DMRG calculations for the purposes of DMRG-CASSCF were performed with the Budapest QC-DMRG code and the DMRG calculations for TCCSD and TCCSD(T) by means of the parallel MOLMPS program. The DFT calculations were performed with the Gaussian program.

The calculations have been performed with the following geometries: 1a – \( R_{\text{Fe-N}} \) match the distances from triplet geometry optimization of FeP; 1b and 1c – fully optimized \( 1 \) in the triplet and quintet states, respectively. B97-D3 functional and def2-TZVPP basis set has been used for the geometry optimizations and following DFT calculations. For the DMRG-TCCSD and DMRG-TCCSD(T) calculations def2-SVP and def2-TZVPP basis sets were used with the auxiliary def2-TZVPP/6-31G(d) basis set. In def2-SVP basis, the canonical DMRG-TCC calculations of 1 are feasible were therefore used to assess the accuracy of the DLPNO approximation, for which we applied the TightPNO settings in ORCA.

Following the works of Li Manni et al. three active spaces were selected: CAS(8,12) constructed from 3d, 4s and 4d orbitals of Fe center and \( \sigma_{\text{Fe-N}} \), CAS(12,16) containing additional four ring \( \pi \)-orbitals selected according to their single orbital entropies and CAS(32,34) containing the complete \( \pi \)-space. The molecular orbitals have been optimized by means of the standard CASSCF for CAS(8,12) and CAS(12,16) or the DMRG-CASSCF method for CAS(32,34). For the latter, the bond dimension, which is a parameter influencing the accuracy of DMRG, was fixed to 1024.

The acquired orbitals were then split-localized and accurate DMRG calculations employing the dynamical block state selection were performed with the truncation error criterion set to \( 10^{-6} \) and the maximum bond dimension set to 8200. These final DMRG energies are presented in the following text as DMRG-CASSCF. In case of the triplet state calculations, which turned out to be more correlated, the maximum bond dimension was reached by DBSS and the actual truncation error was slightly higher, corresponding roughly to \( 10^{-5} \). The active space single and double CC amplitudes have been generated from the aforementioned accurate DMRG calculations and subsequently used in the TCCSD and TCCSD(T) runs. In the following, we denote the DMRG-TCCSD/DMRG-TCCSD(T) methods by the abbreviations TCCSD(e,o)/TCCSD(T)(e,o), where the numbers inside the brackets specify the DMRG active space.

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### SUPPORTING INFORMATION

DMRG-CASSCF(32,34) natural orbitals for FeP model 1, geometries of FeP models 1a, 1b and 1c, one-orbital entropies from DMRG-CASSCF(32,34), energies for accuracy assessment of DLPNO approximation in TCCSD, complete DMRG and DLPNO-TCC results.
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