Ground state of Fe(II)-porphyrin model corresponds to quintet: A DFT and DMRG-based tailored CC study

Andrej Antalík,[1,2] Dana Nachtigallová,[3,4] Rabindranath Lo,[3,4] Mikuláš Matoušek,[1,2]
Jakub Lang,[1] Örs Legeza,[5] Jiří Pittner,[1] Pavel Hobza,[3,4,*] and Libor Veis[1,†]

[1] *J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of
the Czech Republic, v.v.i., Dolejškova 3, 18223 Prague 8, Czech Republic*
[2] *Faculty of Mathematics and Physics, Charles University,
Ke Karlovu 3, 12116, Prague 2, Czech Republic*
[3] *Institute of Organic Chemistry and Biochemistry,
Academy of Sciences of the Czech Republic, v.v.i.,
Flemingovo nám. 2, 16610 Prague 6, Czech Republic*
[4] *Regional Centre of Advanced Technologies and Materials,
Palacký University, 77146 Olomouc, Czech Republic*
[5] *Strongly Correlated Systems "Lendület" Research group,
Wigner Research Centre for Physics, H-1525, Budapest, Hungary*

**Fe(II)-porphyrins play an important role in
many reactions relevant to material science and
biological processes, due to their closely lying spin
states. Although the prevalent opinion is that
these systems posses 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 DFT and DMRG-based
tailored CC study of Fe(II)-porphyrin model,
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
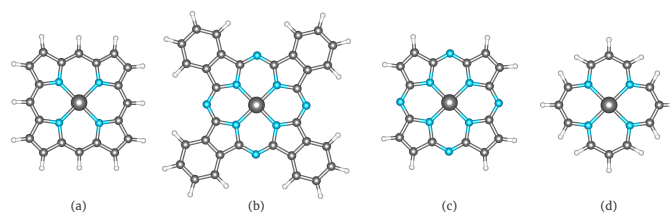possesses the quintet ground state.**

Figure 1: Structures of Fe(II)-porphyrin (a),
Fe(II)-phtalocyanine (b), Fe(II)-porphyrazine (c), and a
model system of Fe(II)-porphyrin (d) studied in this
work and in the text denoted as **1**, or depending on the
geometry, the Fe-N distance in particular, employed **1a**,
1b, and **1c** (see Table I).

Porphyrins are conjugated aromatic systems composed
of four pyrrole rings connected at their C_α atoms by $C_\beta H$
groups (see Fig. 1). Their metal-derivates, in particular
Fe(II)-porphyrins based on Fe(II)-porphyrin (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 (sin-
glet) states. A well-known example is the triplet to sin-
glet spin crossover upon binding of molecular oxygen to
the Fe(II) active site of hemoglobin[1].

Since neither FeP, nor FePz exists in an unsubstituted
state, the direct comparison of theoretical and experi-
mental results is not possible. Although the existing ex-
perimental studies on four-coordinated Fe(II) embedded
in substituted porphyrin systems[2–10] mostly predict the
triplet ground state, they have been performed either in
the crystal phase or polar solvent, which are far from the
gas phase conditions of computational studies.

We have recently investigated the effect of different
environments on the FePc ground state by means of
the Mössbauer spectroscopy and various computational
methods[11]. Our experiments have unambiguously indi-
cated the triplet ground state of FePc in the crystalline
form and dissolved in dimethyl-formamide, and the quin-
tet when dissolved in monochlorobenzene (resemblance
to gas phase conditions of computational studies). The
quintet ground state was also confirmed by the multiref-
erence density matrix renormalization group (DMRG)
calculations. These findings clearly contradict the preva-
lent opinion in the literature.

The experimental observations of Fe(II)-porphyrins
guided several follow-up computational studies on FeP
and FePz with the density functional theory (DFT)[5,11–23]
and multireference methods[24–32]. Nevertheless, due to
the complexity of the problem, an unambiguous answer
to the state ordering has not been found even with the
multireference methods that are able to correlate a rela-
tively large number of electrons[28,29,33,34].

The effects of different contributions to electron
correlation,[25,26,30] have recently been investigated by cal-
culations on model system of Fe(II)-porphyrin in which
the bridging $C_\beta H$ groups are replaced by hydrogen atoms
(model **1**, Fig. 1d). In the recent work of Li Manni et
al.[31], 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. 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-CAS correlation by employing the single reference coupled cluster correction further stabilized the triplet ground state and provided the final estimate of the triplet-quintet energy gap as 5.7 kcal/mol. Comparing these results to the FePc experimental data[11] and our preliminary DFT calculations on the spin state ordering in FeP and FePc (see ESI), we reopen the debate over the character of the Fe(II)-porphyrins and their modelling. Besides discussing the extent of electron correlation in the multireference approach, we explore the role of other parameters which may influence the ground state predictions.

Among such parameters, particular attention should be paid to the geometry of FeP systems. The Fe–N bond distance (R_{FeN}) has been discussed by several authors[35–37], with some proposing that the increase in R_{FeN} stabilizes quintet states via the relaxation of $d_{x^2-y^2}$ orbital[38]. The calculated Fe–N bond distances obtained for the quintet states typically range from 2.0 to 2.1 Å[35,39,40]. In comparison, the value of 1.972 Å taken from the X-ray diffraction of Fe(II)-tetraphenylporphyrin (FeTPP)[8] is closer to the value of 1.989 Å obtained for the FeP triplet state by employing the PBE0 functional in DFT optimization[40]. This result confirms the suggestion discussed in Ref.[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 or quintet optimized distance is used?

To resolve this issue, apart from the DFT calculations with the B97-D3 functional, we investigated the electronic structure of **1** by means of DMRG-based methods. DMRG is a well-established and very powerful approach suitable for treatment of strongly correlated problems that require large active spaces[41,42]. However, despite its favorable scaling, it is still computationally prohibitive to treat the dynamic correlation solely with DMRG. As a possible solution, we have introduced the TCCSD method, in which the CC wave function is externally corrected using the information extracted from the DMRG calculation[43]. We showed that it is able to describe both non-dynamic and dynamic correlation in a balanced way[44], but due to the scaling of the CCSD part, the 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[45], which employs the pair natural orbitals to exploit the locality of electron correlation[46–48]. The electronic structure of parent FeP was recently studied also by means of an alternative post-DMRG method, namely the DMRG-based pair density functional theory

Table I: The Fe–N distance (R_{FeN}, in Å) optimized for each state at the B97-D3/def2-TZVPP level for FeP-based systems with the exception of **1a** which is from Ref.[31]

	Triplet	Quintet
FeP model (**1**)	1.989 (**1a**)	
	2.048 (**1b**)	2.180 (**1c**)
FeP	1.997	2.064
FeTPP	1.995, 1.998	2.063–2.065

(DMRG-PDFT)[34].

The R_{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[40]. Additionally, the R_{FeN} values obtained from the triplet optimizations agree reasonably well with the distance of 1.972 Å found in the X-ray diffraction experiment[8] (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_{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 $C_\beta H$ groups.

Table II lists the relative spin state energies from DFT obtained by employing the B97-D3 functional for various geometries of **1** and their comparison with the previously reported results on **1a** obtained with the Stochastic-CASSCF[30,31]. The B97-D3 adiabatic energy gap is determined as 11.0 kcal/mol with the quintet ground state by using the Fe–N distances from the fully optimized triplet **1b** and quintet **1c** geometries (the difference in R_{FeN} is 0.132 Å). This gap then reduces to 2.8 kcal/mol when R_{FeN} values from the optimized FeP are used (the difference in R_{FeN} is 0.067 Å). The vertical gap at the triplet geometry **1b** results in reversed ordering with the triplet state more stable than quintet by 2.9 kcal/mol and it increases to 8.0 kcal/mol when R_{FeN} optimized for FeP triplet is used. At the similar Fe–N distance **1a**, the Stochastic-CASSCF calculations[30,31] predict the triplet ground state as well, but with the smaller energy gap of 3.1 and 4.4 kcal/mol using the CAS(32,34) and CAS(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, it seems that the value of this structure parameter can dominate the energy balance and thus relative ordering of the spin states. We

Table II: Relative energies in kcal/mol of the triplet and quintet states of **1** based on the DFT calculations and Stochastic-CASSCF calculations from Ref.[31]. Geometry denotes the source of geometry parameters

Method	Excitation	Geometry	Triplet	Quintet
B97-D3/def2-TZVPP	adiab.	**1b**, **1c**	11.0	0.0
	vert.	**1b**	0.0	2.9
	adiab.	FeP (T,Q)	2.8	0.0
	vert.	FeP (T)	0.0	8.0
Stoch.-CASSCF(32,34)	vert.	**1a**	0.0	3.1
(40,38)	vert.	**1a**	0.0	4.4^a

^{a} Involving CCSD(T) correlation treatment increases the gap to 5.7 kcal/mol.

evaluate this effect together with another significant influence which is the level of electron correlation treatment. In the following, we present the main results of (DMRG-)CASSCF and TCC calculations, while the complete set of energies together with Computational Details is provided in the ESI.

Based on the previous discussions on the ground state of FeP systems in literature, only the lowest quintet ($^5A_{1g}$) and triplet states are considered. Unlike in the study of Li Manni et al.[31], the lowest triplet state in all our (DMRG-)CASSCF and TCC calculations corresponds to $^3A_{2g}$ with the occupation $(d_{x^2-y^2})^2(d_{z^2})^2(d_{xz})^1(d_{yz})^1(d_{xy})^0$. Considering a very small energy gap of only about 0.5 kcal/mol between the two lowest triplets ($^3A_{2g}$ and ^3E_g) in the aforementioned study, this discrepancy might be attributed to the difference in basis sets. Nevertheless, we believe that such a small energy gap is below the resolution of the employed methods. Also, the $^3A_{2g}$ state was found to be the lowest triplet state of FeP in Ref.[40].

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 Fig. 2a. This system has already been a subject of previous studies by Li Manni et al.[30,31] 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.[31], 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 π-orbitals[49] in CAS does not change the relative
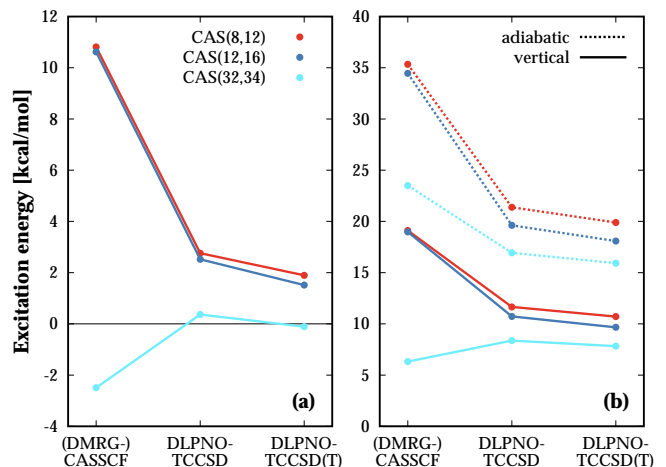

Figure 2: The (DMRG-)CASSCF, DLPNO-TCCSD, and DLPNO-TCCSD(T) (a) vertical $\Delta E^{Q\rightarrow T}$ energy gaps of **1a**[31], (b) vertical $\Delta E^{Q\rightarrow T}$ energy gaps of **1b** and adiabatic energy gaps of fully optimized **1** in kcal/mol in def2-TZVP basis. The keys are shared by both plots.

energies of the lowest quintet and triplet states and virtually no difference in enegy gap between CAS(8,12) and CAS(12,16) at all levels of correlation treatment is observed. 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 π-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 -2.49 kcal/mol, which agrees well with the energy gap of -3.1 kcal/mol of the said study[30]. 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 the majority of important corre-

lations is already captured by the active space containing 34 orbitals as previously discussed[30]. Interestingly, the dynamic correlation stabilizes the quintet state, resulting in $\Delta E^{Q \to T}$ 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[31]. We would like to add that in Ref.[34], the effect of active space on the energetic ordering of the lowest spin states of FeP was studied by means of DMRG-PDFT. The ground state was identified as triplet, the question of the geometry was not discussed in Ref.[34] though.

This inconsistency between our and the previously published results deserves a few comments. In the study[31], the authors investigated the effect of Fe(3s,3p) orbitals, 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.[31] 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 0.6, 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. The semi-core correlation is included directly at the CCSD level and the effect of triplet stabilization is even more prominent than in Li Manni et al.[31] (with respect to calculations with frozen Fe(3s,3p) orbitals, see ESI). Nevertheless, further studies which would employ alternative computational methods of calculation of dynamic correlation on top of CASSCF(32,34) (e.g. adiabatic connection[50]) are necessary to confirm our hypothesis.

Since Radoń showed that CCSD(T) method itself can perform well on FeP[51], we have carried out additional single reference DLPNO-CCSD(T) calculations of the FeP model. The resulting vertical gaps presented in ESI are in qualitative agreement with the DLPNO-TCCSD(T) results, differing by 2.8 and 3.6 kcal/mol in case of **1a** and **1b** geometry respectively.

Next, the results are analyzed in terms of R_{FeN} distance for spin state specific optimized structures of FeP model **1** and presented in Fig. 2b. The solid lines show the values of vertical $\Delta E^{Q \to T}$ 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 dashed lines show the values of adiabatic $\Delta E^{Q \to T}$ calculated for fully optimized **1** i.e. with

the triplet and quintet states in **1b** and **1c** geometries, respectively. Compared to the vertical $\Delta E^{Q \to T}$, these stabilize the quintet even more.

Now, considering the most important geometrical parameter R_{FeN} of the models used in this study, our best estimate of the vertical $\Delta E^{Q \to T}$ of **1a** ($R_{FeN} = 1.989$ 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** ($R_{FeN} = 2.048$ 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 and the conclusions made on these systems will thus be slightly biased towards quintet (just as **1a** reflects their triplet geometry and is biased towards triplet, see Table I). As can be seen from the comparison of the spin state ordering of **1** with FeP and FePc (see Table II and ESI), the former is not a sufficient model to describe the correlation of electrons in Fe(3d,4d) orbitals and pyrrolic π-electron system in Fe(II)-porphyrins. In addition, the changes in triplet and quintet geometries of **1** are overestimated due to the increased flexibility caused by removing the $C_{\beta}H$ groups. Despite this, our results highlight the crucial role of Fe–N distance in the spin-state ordering and shed new light on the experimental data interpretation of Fe(II)-porphyrins.

In this communication, 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[28,30,31,34] – 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 $\Delta E^{Q \to T} = 7.8$ kcal/mol), which is consistent with the previous measurements on an isolated molecule of Fe(II)-phthalocyanine[11].

CONFLICTS OF INTEREST

There are no conflicts to declare.

* pavel.hobza@uochb.cas.cz
† libor.veis@jh-inst.cas.cz

[1] K. P. Kepp, Coord. Chem. Rev. **344**, 363 (2017).

[2] K. Spartalian, G. Lang, and C. A. Reed, J. Chem. Phys. **71**, 1832 (1979).

[3] M. Evangelisti, J. Bartolomé, L. J. de Jongh, and G. Filoti, Phys. Rev. B **66** (2002), 10.1103/physrevb.66.144410.

[4] G. Filoti, M. D. Kuz'min, and J. Bartolomé, Phys. Rev. B **74** (2006), 10.1103/physrevb.74.134420.

[5] J. Bartolomé, F. Bartolomé, L. M. García, G. Filoti, T. Gredig, C. N. Colesniuc, I. K. Schuller, and J. C. Cezar, Phys. Rev. B **81** (2010), 10.1103/physrevb.81.195405.

[6] M. Gruyters, T. Pingel, T. G. Gopakumar, N. Néel, C. Schütt, F. Köhler, R. Herges, and R. Berndt, J. Phys. Chem. C **116**, 20882 (2012).

[7] T. Kitagawa and J. Teraoka, Chem. Phys. Lett. **63**, 443 (1979).

[8] J. P. Collman, J. L. Hoard, N. Kim, G. Lang, and C. A. Reed, J. Am. Chem. Soc. **97**, 2676 (1975).

[9] J. Mispelter, M. Momenteau, and J. M. Lhoste, J. Chem. Phys. **72**, 1003 (1980).

[10] J. R. Sams and T. B. Tsin, Chem. Phys. Lett. **25**, 599 (1974).

[11] D. Nachtigallová, A. Antalík, R. Lo, R. Sedlák, D. Manna, J. Tuček, J. Ugolotti, L. Veis, Örs Legeza, J. Pittner, R. Zbořil, and P. Hobza, Chem. Eur. J. **24**, 13413 (2018).

[12] T. Kroll, R. Kraus, R. Schönfelder, V. Y. Aristov, O. V. Molodtsova, P. Hoffmann, and M. Knupfer, J. Chem. Phys. **137**, 054306 (2012).

[13] M. D. Kuz'min, A. Savoyant, and R. Hayn, J. Chem. Phys. **138**, 244308 (2013).

[14] V. E. J. Berryman, R. J. Boyd, and E. R. Johnson, J. Chem. Theory Comput. **11**, 3022 (2015).

[15] M.-S. Liao, J. D. Watts, and M.-J. Huang, J. Comput. Chem. **27**, 1577 (2006).

[16] A. R. Groenhof, M. Swart, A. W. Ehlers, and K. Lammertsma, J. Phys. Chem. A **109**, 3411 (2005).

[17] V. E. J. Walker, N. Castillo, C. F. Matta, and R. J. Boyd, J. Phys. Chem. A **114**, 10315 (2010).

[18] B. Brena, C. Puglia, M. de Simone, M. Coreno, K. Tarafder, V. Feyer, R. Banerjee, E. Göthelid, B. Sanyal, P. M. Oppeneer, and O. Eriksson, J. Chem. Phys. **134**, 074312 (2011).

[19] N. Marom and L. Kronik, Appl. Phys. A **95**, 165 (2008).

[20] S. Obara and H. Kashiwagi, J. Chem. Phys. **77**, 3155 (1982).

[21] M. D. Kuz'min, R. Hayn, and V. Oison, Phys. Rev. B **79** (2009), 10.1103/physrevb.79.024413.

[22] P. A. Reynolds and B. N. Figgis, Inorg. Chem. **30**, 2294 (1991).

[23] M.-S. Liao and S. Scheiner, J. Chem. Phys. **114**, 9780 (2001).

[24] T. Ichibha, Z. Hou, K. Hongo, and R. Maezono, Sci. Rep. **7** (2017), 10.1038/s41598-017-01668-6.

[25] K. Pierloot, Q. M. Phung, and A. Domingo, J. Chem. Theory Comput. **13**, 537 (2017).

[26] Q. M. Phung, M. Feldt, J. N. Harvey, and K. Pierloot, J. Chem. Theory Comput. **14**, 2446 (2018).

[27] Q. Sun, J. Yang, and G. K.-L. Chan, Chem. Phys. Lett. **683**, 291 (2017).

[28] G. L. Manni, S. D. Smart, and A. Alavi, J. Chem. Theory Comput. **12**, 1245 (2016).

[29] J. E. T. Smith, B. Mussard, A. A. Holmes, and S. Sharma, J. Chem. Theory Comput. **13**, 5468 (2017).

[30] G. L. Manni and A. Alavi, J. Phys. Chem. A **122**, 4935 (2018).

[31] G. L. Manni, D. Kats, D. P. Tew, and A. Alavi, J. Chem. Theory Comput. **15**, 1492 (2019).

[32] M. Radoń and K. Pierloot, J. Phys. Chem. A **112**, 11824 (2008).

[33] R. Olivares-Amaya, W. Hu, N. Nakatani, S. Sharma, J. Yang, and G. K.-L. Chan, J. Chem. Phys. **142**, 034102 (2015).

[34] C. Zhou, L. Gagliardi, and D. G. Truhlar, J. Phys. Chem. A **123**, 3389 (2019).

[35] Y.-K. Choe, T. Nakajima, K. Hirao, and R. Lindh, J. Chem. Phys. **111**, 3837 (1999).

[36] S. F. Sontum, D. A. Case, and M. Karplus, J. Chem. Phys. **79**, 2881 (1983).

[37] U. Nagashima, T. Takada, and K. Ohno, J. Chem. Phys. **85**, 4524 (1986).

[38] Y.-K. Choe, T. Hashimoto, H. Nakano, and K. Hirao, Chem. Phys. Lett. **295**, 380 (1998).

[39] C. Rovira, P. Ballone, and M. Parrinello, Chem. Phys. Lett. **271**, 247 (1997).

[40] S. Vancoillie, H. Zhao, V. T. Tran, M. F. A. Hendrickx, and K. Pierloot, J. Chem. Theory Comput. **7**, 3961 (2011).

[41] S. R. White, Phys. Rev. Lett. **69**, 2863 (1992).

[42] G. K.-L. Chan and S. Sharma, Annu. Rev. Phys. Chem. **62**, 465 (2011).

[43] L. Veis, A. Antalík, J. Brabec, F. Neese, Örs Legeza, and J. Pittner, J. Phys. Chem. Lett. **7**, 4072 (2016).

[44] L. Veis, A. Antalík, Örs Legeza, A. Alavi, and J. Pittner, J. Chem. Theory Comput. **14**, 2439 (2018).

[45] J. Lang, A. Antalík, L. Veis, J. Brabec, O. Legeza, and J. Pittner, arXiv e-prints, arXiv:1907.13466 (2019), arXiv:1907.13466 [physics.chem-ph].

[46] F. Neese, A. Hansen, and D. G. Liakos, J. Chem. Phys. **131**, 064103 (2009).

[47] F. Neese, F. Wennmohs, and A. Hansen, J. Chem. Phys. **130**, 114108 (2009).

[48] C. Riplinger and F. Neese, J. Chem. Phys. **138**, 034106 (2013).

[49] M. Gouterman, J. Mol. Spectrosc. **6**, 138 (1961).

[50] E. Pastorczak and K. Pernal, J. Phys. Chem. Lett. **9**, 5534 (2018).

[51] M. Radoń, J. Chem. Theory Comput. **10**, 2306 (2014).