On the Limits of Coupled Cluster Calculations for Non-Heme Iron Complexes

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Abstract

In a large variety of studies, the coupled-cluster method with singles, doubles and perturbative triples (CCSD(T)) is used as a reference for benchmarking the performance of density functional theory (DFT) functionals. In the case of open-shell species this theory can be applied in different forms depending on the restricted or unrestricted treatment of spin. In this study, we show that these different approaches can produce results which deviate by ~ 5 kcal/mol for different species on the potential energy surfaces. This was demonstrated for a simple model of the C–H activation carried out by non-heme iron enzymes. Assessing the limits of CCSD(T) prior to its use as a general benchmark tool is warranted. This was done using higher-order coupled cluster calculations as well as multiconfigurational second-order perturbation theory (CASPT2), since iron-oxo species present some multireference character. Furthermore, we tested two different implementations of the local coupled cluster method and compared them to

the CCSD(T) results, showing that even though these novel approaches are promising, without further developments they appear not to be suitable for describing two-state reactivity of the system investigated in the current study. Additionally, we implemented and assessed the performance of the *hotspot* approach for local unrestricted CCSD(T) scheme which aims at reducing the pair error for systems containing transition metals.

1 Introduction

Heme and non-heme mononuclear iron oxygenases and their synthetic analogues are known to perform a wide range of catalytic oxidative transformations in chemistry and biochemistry.¹⁻⁵ In many enzymes such as Cytochrome P450 and Taurine dioxygenase an iron-oxo active intermediate has been proposed to perform C-H hydroxylation and the activation of unreactive C-H bonds in general.⁶ The rate-limiting step in these reactions was found to be the hydrogen atom abstraction process.⁷⁻⁹ Due to the importance of the C-H bond activation process, a lot of effort has been put into the development of synthetic catalysts such as $[(\text{N}_4\text{Py})\text{Fe}^{\text{IV}}(\text{O})]^{2+}$.¹⁰⁻¹² These synthetic non-heme systems are known for their two-state reactivity. In most of these systems, the triplet state is experimentally found to be the ground state, with theoretical calculations predicting a low-lying quintet state.¹³ The transition state on the quintet surface often has a lower barrier and modulates the reaction.

The importance of these reactions for the challenging C-H bond activation attracted also theoretical studies. These reactions involving non-heme iron complexes were investigated mostly using density functional theory (DFT) methods,¹⁴⁻¹⁸ while canonical coupled cluster (CC) methods were applied only for small model complexes.^{19,20} Unfortunately, the results obtained from DFT methods sometimes are not of sufficient accuracy and therefore these reactions cannot be fully understood. Since these reactions have been shown to follow two-state reactivity, accurate calculations for both transition state energies and triplet-quintet gaps are needed. However, it was seen earlier that DFT methods struggle to accurately compute spin state energetics of transition metal complexes.²¹⁻²⁶

For more accurate calculations, one usually turns to CCSD(T) which is viewed as the “gold standard” within computational chemistry and is therefore used to benchmark DFT functionals.²⁷ One such study by Chen et al. focuses on a small non-heme iron oxo complex which performs C–H activations.¹⁹ The ground state of the complex was found to be a triplet with a low lying quintet state. However, the reaction occurs preferentially through the quintet transition state. The transition states and the associated orbital occupation changes for both spin states for the C–H activation process are shown in Figure 1. In another previous study, a detailed analysis of possible paths for each spin state of iron oxo complexes was carried out.²⁰ The authors used the same model complex $[\text{Fe}(\text{NH}_3)_5\text{O}]^{2+}$ with ethane as a substrate. In that study it was found that in the triplet state the substrate follows a π approach path, while in the quintet state it follows a σ approach path. Therefore, only these two paths will be investigated in the present study.

In the study by Chen et al., restricted open-shell Kohn-Sham (ROKS) with B3LYP was used to generate orbitals to serve as a basis for restricted CCSD(T) (RCCSD(T)) calculations.¹⁹ However, as will be discussed below, in this case ROKS-RCCSD(T) might not be a reliable “gold standard”. The reason for this is that quintet abstraction leads to a sextet iron complex antiferromagnetically coupled to a doublet radical, and this low-spin coupling – which is already partially present at the corresponding TS – is not well described in the ROKS ansatz.

Figure 1: Transition states on triplet and quintet surfaces and orbital occupation changes in hydrogen atom transfer processes.

In the present study we will use high-level correlated methods for the example of $[\text{Fe}(\text{NH}_3)_5\text{O}]^{2+}$ performing C–H activation of methane to study these reactions. This is itself not a trivial endeavour, since a smooth method convergence pattern for such systems is hard to establish, and a careful comparison of the different approaches is needed. The core method that we wish to consider here is coupled cluster theory with single and double excitations and perturbative triples, CCSD(T). This method is efficient enough to be applied to medium-sized models of iron-oxo species and to describe their reactivity. However, CCSD(T) applied to this type of compound comes in many different flavors, depending on the unrestricted or restricted treatment (RO-RCCSD(T), RO-UCCSD(T) or U-UCCSD(T)), as well as on the type of reference orbitals used in the coupled cluster expansion. These can be either Hartree–Fock orbitals, Kohn–Sham orbitals, or various types of multi-configuration SCF orbitals. All three types will be considered here.

As will be seen, these different CCSD(T) approaches yield rather different results. Two other types of method were then used to assess which of these CCSD(T) approaches is most reliable. On the one hand, the higher-order coupled cluster methods CCSDT and

CCSDT(Q) were considered. These methods are computationally expensive, and hence can only be applied to a small model $[\text{FeHe}_5\text{O}]^{2+}$. The other approach is multireference perturbation theory using a very large active space and the density matrix renormalization group approach (DMRG-CASPT2).

In a third phase, we explore the prospect of applying coupled cluster methods to larger iron-oxo species. In order to do this, we base our conclusions on calculations performed with two available versions of *local* coupled cluster theory, LUCCSD(T0) and DLPNO-CCSD(T0), which we benchmarked against canonical results. Finally, we propose a variation of the LUCCSD(T0) pair selection procedure, targeting specific atoms for greater accuracy, which we will refer to as *hotspot* calculations (*hs*(X)-LUCCSD(T0), X stands for the targeted atoms). We report benchmark calculations using the *hotspot* approach and compare it to canonical coupled cluster.

2 Method

2.1 Canonical Coupled Cluster Theory

The coupled cluster method with singles, doubles and perturbative triples (CCSD(T))^{28–30} is often used to benchmark more affordable computational approaches, but for open-shell species, one must first choose which variety of CCSD(T) to use. First of all one has the option to use either a spin-unrestricted (UHF) or spin-restricted open-shell (ROHF) Hartree–Fock wavefunction as a reference.²⁸ Furthermore, there is the possibility to use Kohn–Sham (KS) orbitals instead of Hartree–Fock (HF) ones. Indeed, other types of orbitals, including those optimized using multireference methods, can be used. Finally, one must choose the type of excitation operator used in the coupled cluster treatment. This can be either in the form of spin-unrestricted coupled cluster ansatz (UCCSD)²⁹ or in the form of partially restricted coupled cluster theory (RCCSD).²⁹ In the following we will describe the main differences between these approaches.

When one thinks of the choice between the UHF or ROHF wavefunction, one should know that in the case of UHF, α and β spin orbitals are optimized independently. This leads to a wavefunction which is not an eigenfunction of $\hat{S}^2$, causing various problems such as convergence issues and lower accuracy of post-HF methods.²⁸ This effect is more pronounced in the case of Møller–Plesset (MP) theory, but it can be also present in CC theory.²⁹ However, for many systems using a ROHF reference can remove this problem and is often preferred. The caveat is that the restricted description of the doubly occupied orbitals is qualitatively correct. On the other hand, the lack of spin polarization in the ROHF reference may be a drawback.

Another question is the choice between Hartree–Fock and Kohn–Sham orbitals. In the case of HF orbitals, electron correlation effects are not included at the orbital level, while they are included to some extent in the case of KS orbitals.^{31–34} This can lead to decreased orbital relaxation effects in the coupled cluster expansion, and hence to a reduced T_1 diagnostic, mimicking to some extent the behavior observed with Brueckner orbitals.^{31,35–38}

The last difference is in the treatment of the spin in these methods. In the case of UCCSD, $|\Psi\rangle = \exp(\hat{T}_1 + \hat{T}_2)|\Psi_0\rangle$ is not an eigenfunction of $\hat{S}^2$ and this leads to spin contamination of the CC wave function. To reduce spin contamination, in the case of RCCSD theory, the linearized coupled cluster wave function is required to be a spin eigenfunction. This is achieved by introducing certain restrictions among the amplitudes in the RCCSD theory. Some spin contamination can nevertheless still arise, but only via products of cluster amplitudes. Since the residual equations are simpler in the case of UCCSD, in the Molpro program UCCSD and RCCSD use exactly the same code, except that in the RCCSD case, the residuals and amplitudes are projected in each iteration such that the linear terms become spin-adapted.²⁹

Furthermore, in the case of UCCSD theory, α and β spins are treated separately, so that separate amplitudes for single excitations as well as for α - α , α - β and β - β excitations are obtained. This can lead to the situation that amplitudes from the same orbital can have a

different magnitude for different spins. Additionally, more excitations are calculated which can also include semi-internal excitations, such that upon a double excitation a singly excited determinant is obtained.

In this work we use spin unrestricted (ROKS-UCCSD(T))^{29,30} and partially spin restricted (ROKS-RCCSD(T))^{29,30} open-shell coupled cluster theories as implemented in the Molpro program package. The latter makes use of spin restricted KS orbitals. Furthermore, the UKS-UCCSD(T) method as implemented in ORCA with spin-unrestricted KS orbitals is also applied. For comparison, HF orbitals were also used as a reference in both spin-restricted and spin-unrestricted forms.

2.2 Local Coupled Cluster Theory

In this study two different versions of local coupled cluster methods have been applied. The first one is local unrestricted coupled cluster with singles, doubles and non-iterative triples (LUCCSD(T0))³⁹⁻⁴² as implemented in Molpro. This method is based on using projected atomic orbitals (PAOs). The second version is the domain-based pair natural orbitals DLPNO-CCSD(T) method⁴³⁻⁴⁸ as implemented in ORCA. In the following, we shortly summarize these two methods and discuss the similarities and differences between them.

The LUCCSD(T0) method is based on two approximations. The first one is the domain approximation. In the first step, the occupied orbitals are localized usually through Pipek-Mezey localization.⁴⁹ They are then projected out of the atomic orbital (AO) space to generate PAOs. These orbitals are used as a local virtual space while being assigned to the same atoms as the original AOs and grouped together in orbital domains specific to each occupied orbital ($[i]$). In the case of pairs and triples, the domains are constructed as unions of the orbital domains ($[ij]=[i]\cup[j]$). The orbital domains can be defined using different criteria, such as Boughton-Pulay⁵⁰ or Natural Population Analysis (NPA).^{51,52} In the domain approximation, the excitations are restricted to specific domains thereby truncating the number of configurations. The second approximation is a pair approximation. It is

known that the correlation energy decreases quickly with the distance between two localized orbitals. Therefore, distant orbital pairs can be either neglected, or treated at a lower level of theory. In this scheme five different pair classes can be defined based on the distance criteria. These pairs are strong pairs (treated at the CC level), close pairs (treated at the MP2 level, but amplitudes can be included in the strong pairs), weak and distant pairs (treated at the MP2 level) and at the end very distant pairs which are neglected. A minor approximation made is the use of non-iterative triples (T0), but the latter has always lead to much smaller errors compared with the aforementioned approximations.³⁹

The DLPNO-CCSD(T) scheme is based on the combination of the concepts of PAOs and pair natural orbitals (PNOs). DLPNO-CCSD(T) starts similarly to LUCCSD(T0) with the localization of orbitals usually using the Foster–Boys criterion.⁵³ For the virtual space a large PAO space is constructed. Based on a semi-canonical RI-MP2 calculation the PNOs are computed and expanded from the PAO set that in turn belongs to a given electron pair specific domain.⁴⁴ Two types of domains are used, initial orbital domains and extended domains. The initial orbital domains are constructed according to a threshold T_{CutMKN} and the pair domains according to a fixed delocalization parameter. The extended domains for each pair [ij] consist of the union of the orbital domains [i] and [j] and also include all atoms of the domains of all orbitals [k] that fulfill the condition that none of the pairs [ij], [ik] and [jk] has been excluded from the calculation. These domains are used as a buffer space for the calculation of pair-pair interactions. Furthermore, the accuracy of the local PNO approach is controlled by two cut-off parameters, $T_{CutPairs}$ and T_{CutPNO} . The first parameter $T_{CutPairs}$ determines below which estimated pair correlation energy a given electron pair is neglected. The second parameter T_{CutPNO} represents the occupation number at which the PNO expansion of a given pair is terminated. At the end, non-iterative triples (T0) are used, as is also the case for LUCCSD(T0).

2.3 *hotspot* Local Coupled Cluster

The LUCCSD(T0) scheme, as explained above, is based on two main approximations, the domain and pair approximations, each of which is associated with a certain error. In previous studies different ways of reducing the error due to the domain approximation have been suggested.^{54–56} In this work we implemented the so-called *hotspot* approach whereby the error in the pair approximation is reduced within a selected subspace. In the LUCCSD(T0) calculations, depending on the distance between atoms, pairs are separated into five classes where only strong pairs are fully treated at the coupled cluster level. For systems which contain metal centers it can be necessary to treat all pairs at those centers at the coupled cluster level. In a *hs*(X)-LUCCSD(T0) calculation with a selected list of atoms X, the strong pairs are expanded by including extra pairs with orbitals at those centers, irrespective of the distance criteria. The number of strong pairs is increased which also leads to higher computational costs, but it offers the possibility of selectively converging the calculations with respect to the pair approximations.

2.4 Computational Details

Two different octahedral model systems were used in this study: $[\text{Fe}(\text{NH}_3)_5\text{O}]^{2+}$ and $[\text{FeHe}_5\text{O}]^{2+}$ with methane as a coreactant in each case. The reaction path for H atom abstraction includes the following stationary points: separate reactants (SR), reactant complex (RC), transition state (TS) and product intermediate state (IM). All energies are expressed relative to that of the triplet state of the separated reactants, except where stated otherwise.

Geometry optimizations were performed using the B3LYP functional^{57,58} and the def2-SVP basis set using Gaussian 09.⁵⁹ Harmonic vibrational frequencies were computed for the optimized geometries so as to ensure that all local minima display only real frequencies and that the transition states have only one imaginary frequency.

The basis sets used in the correlated calculations are summarized in Table 1. In the case of the CCSD(T) calculations, a basis set of triple- ζ quality⁶⁰ was used for the O atom

Table 1: Summary of Different Basis Sets Used in This Study.

	cc-TZ	cc-TZ-DK	acc-TZ-DK	acc-QZ-DK	cc-TZ-F12
Fe	cc-pwCVTZ	cc-pwCVTZ-DK	aug-cc-pwCVTZ-DK	aug-cc-pwCVQZ-DK	cc-pwCVTZ
O	cc-pVTZ	cc-pVTZ-DK	aug-cc-pVTZ-DK	aug-cc-pVTZ-DK	cc-pVTZ-F12
CH ₄	cc-pVTZ	cc-pVTZ-DK	aug-cc-pVTZ-DK	aug-cc-pVTZ-DK	cc-pVTZ-F12
NH ₃	cc-pVDZ	cc-pVDZ-DK	aug-cc-pVDZ-DK	aug-cc-pVDZ-DK	cc-pVDZ-F12

and for the C and H atoms in methane. The N and H atoms of the ammonia ligands were described using the cc-pVDZ⁶⁰ basis set, while Fe was described using the core weighted basis set cc-pwCVTZ.^{61,62} This basis set combination will be referred to as the cc-TZ basis.

Relativistic effects were included by using the standard second order Douglas–Kroll–Hess Hamiltonian with appropriate basis sets. Basis sets of three different sizes were used. The smallest was of triple- ζ quality on CH₄ and O (cc-pVTZ-DK⁶⁰), of double- ζ quality on N and all other H atoms (cc-pVDZ-DK⁶⁰) and cc-pwCVTZ-DK^{61,62} on Fe. This basis set will be referred to as cc-TZ-DK. The medium-sized basis set was also of triple- ζ quality with augmented functions, using the standard aug-cc-pVTZ-DK⁶³ basis on all atoms except Fe and H. Fe used the aug-cc-pwCVTZ-DK^{61,62} basis set and augmented functions on H atoms were omitted except on H1 (the H atom on methane which undergoes transfer). This basis set will be denoted as acc-TZ-DK. A larger basis set was also employed, where the aug-cc-pwCVQZ-DK^{61,62} basis set was applied on Fe, while for all other atoms the same basis sets as in acc-TZ-DK were used. This basis set will be denoted as acc-QZ-DK. Two of these basis sets (cc-TZ-DK and acc-QZ-DK) were also used in the case of DMRG-CASPT2 calculations. Furthermore, acc-TZ-DK and acc-QZ-DK basis sets were used for the extrapolations to the complete basis set (CBS) limit.

Extrapolation to the CBS limit was accomplished separately for the reference (ROKS) energy and the CC correlation energy, as described in the work of Wilson et al.⁶⁴ The ROKS reference energies were extrapolated using the following two-point extrapolation equation:⁶⁵

$$E_{\text{ref}}(\text{CBS}) = \frac{e^{1.63m_1} E_{\text{ref}}(m_2) - e^{1.63m_2} E_{\text{ref}}(m_1)}{e^{1.63m_1} - e^{1.63m_2}} \quad (1)$$

while the CC correlation energies were extrapolated using the two-point extrapolation formula of Helgaker et al.⁶⁶:

$$E_{\text{corr}}(\text{CBS}) = \frac{m_2^3 E_{\text{corr}}(m_2) - m_1^3 E_{\text{corr}}(m_1)}{m_2^3 - m_1^3} \quad (2)$$

In these equations, m_1 and m_2 denote the cardinal numbers of the correlation consistent basis sets used, in our case $m_1 = 3$ and $m_2 = 4$. Extrapolations were only performed with respect to the Fe basis set, while keeping the ligand basis set fixed. This means that the extrapolation was performed using the acc-TZ-DK and acc-QZ-DK basis sets. The final total energy is the sum of the extrapolated energies:

$$E(\text{CBS}) = E_{\text{ref}}(\text{CBS}) + E_{\text{corr}}(\text{CBS}) \quad (3)$$

The extrapolated results are denoted as CBS[T:Q]/T.

Finally, CCSD(T)-F12 calculations^{67–70} were also carried out using the F12 family of basis sets. In this case the cc-pVDZ-F12 basis set⁷¹ was used for NH_3 , with the cc-pwCVTZ basis set^{61,62} for Fe and the cc-pVTZ-F12 basis set⁷¹ for O and CH_4 . This basis set will be referred to as cc-TZ-F12. Furthermore, auxiliary basis sets were used in these calculations. In the case of Coulomb and exchange fitting, the cc-pVTZ/JKFIT⁷² basis set was used for all atoms except for Fe for which the def2-QZVP/JKFIT⁷³ basis set was applied. For the correlation fitting the cc-pVTZ/MP2FIT⁷⁴ basis set was used for all atoms except for Fe for which the cc-pwCVTZ/MP2FIT⁷⁵ auxiliary basis set was used. The same auxiliary basis set was used for Fe for the OptRI approximation. For all other atoms the cc-pVTZ-F12/OptRi basis set⁷⁶ was used.

Higher-order coupled cluster calculations were carried out, coupled cluster with singles, doubles and triples (CCSDT)⁷⁷ as well as CCSDT with perturbative quadruples (CCSDT(Q)),⁷⁸ using the MRCC module of Kállay⁷⁹ interfaced to Molpro. Since these calculations are very expensive, a smaller basis set was employed. The cc-pVDZ basis set was used on all atoms

except on Fe, for which cc-pVTZ was used. This basis set was used for all calculations on the helium model system and it will be denoted as cc-DZ. In all calculations with the helium model system 3s3p electrons were not correlated.

In the case of higher-order coupled cluster calculations only two structures were included in the calculations: the separated reactants (SR), where the triplet state was taken as a reference, and the transition states (TS). In the case of all other coupled cluster calculations, as well as these two structures, the reactant complex (RC) and the intermediate (IM) formed after the transition state were considered.

In the CASPT2 calculations,^{80,81} the active spaces were constructed based on our previous work.⁸² The active spaces include one $\sigma_{\text{Fe-N}}$ orbital to describe the covalent interaction between Fe and the NH_3 ligands, five Fe 3d orbitals, and three O 2p orbitals. Furthermore, in order to describe the so-called ‘double-shell’ effect, three oxygen 3p orbitals, as well as five Fe 4d orbitals were included. In the triplet state only three 4d orbitals ($4d_{xz}$, $4d_{yz}$ and $4d_{xy}$) that can correlate with the corresponding occupied 3d orbitals were included, as when using all five such orbitals, the low-occupancy fourth and fifth orbitals optimize to adopt different characters, thereby yielding an unbalanced reference wavefunction. Finally, to correctly describe the transition states, the sigma bonding and anti-bonding orbitals of the methane C–H bond were included. The notation $\text{CAS}(n_e, n_o)$ is used, where n_e denotes the number of electrons and n_o the number of orbitals. In the quintet state we employed a $\text{CAS}(14,19)$ reference while $\text{CAS}(14,17)$ was used in the triplet state. In the case of SR, these large active spaces were split into a (2,2) active space on methane and (12,16) and (12,15) active spaces respectively for the quintet and triplet states of the iron oxo complex. Such large active spaces were computationally expensive for conventional CASSCF-CASPT2 calculations. Therefore, we employed a novel multireference technique, known as perturbation theory based on density matrix renormalization group (DMRG-CASPT2).^{83–95} The DMRG calculations were carried out with a spin-adapted DMRG algorithm, implemented in the CHEMPS2–MOLCAS interface.^{96,97} The number of renormalized states used was $m = 2000$. The orbital order-

ing was automated by minimizing the quantum entanglement using Fiedler ordering.⁹⁸ All PT2 calculations were done with the standard ionization potential electron affinity (IPEA) shift⁹⁹ of 0.25 au and an imaginary shift¹⁰⁰ of 0.1 au. As it was recently shown, the semicore correlation (3s3p) for the iron centre is not well described by CASPT2,^{82,101} therefore, only valence electrons were included in the PT2 treatment. The missing 3s3p correlation energy was obtained using UKS-UCCSD(T) calculations with the cc-TZ-DK basis set. In these calculations the two previously described basis sets were employed, cc-TZ-DK and acc-QZ-DK. The results shown in the main text use the smaller of these; results with the larger basis are discussed in the SI.

In the case of local coupled cluster calculations, the cc-TZ basis set was employed. Density fitting approximations^{102,103} were used throughout in LUCCSD(T0). In the case of Coulomb and exchange fitting the cc-pVTZ/JKFIT⁷² auxiliary basis set was used for all atoms except Fe where the def2-QZVP/JKFIT⁷³ basis set was applied. For the correlation fitting the cc-pVTZ/MP2FIT⁷⁴ basis set was used for all atoms except for Fe in which case the cc-pwCVTZ/MP2FIT⁷⁵ was applied. In the DLPNO-CCSD(T) calculations the RIJCOSX approximation^{104,105} was used. The RI-J auxiliary basis was automatically constructed from the orbitals basis set using the AutoAux keyword.¹⁰⁶ For the correlation fitting the same basis set as in the case of the LUCCSD(T0) calculations was used. DLPNO-CCSD(T) calculations were performed with NormalPNO parameters as well as TightPNO parameters. LUCCSD(T) calculations were carried out using the Pipek-Mezey localization scheme⁴⁹ using Natural Population Analysis (NPA)⁵² with threshold $T_{\text{NPA}} = 0.03$ *e*. Furthermore, the strong and close pairs were assigned using the criteria rclose=3 and rweak=5. Also, the MP2 amplitudes of close pairs were included in the calculations for strong pairs (keepcl=1). In the *hotspot* calculations the number of strong pairs was increased by characterizing all pairs which contain Fe orbitals as strong pairs.

Single point DFT calculations were performed using the cc-TZ-DK basis set. Ten different functionals were tested: B3LYP,^{57,58} BP86,¹⁰⁷ TPSS,¹⁰⁸ B97-D,¹⁰⁹ O3LYP,¹¹⁰ OPBE,

OLYP,¹¹¹ M06,¹¹² M06-L¹¹³ and MN15.¹¹⁴ B3LYP calculations were performed with and without the D3 dispersion correction with Becke-Johnson damping, which was obtained using the dftd3 program by Grimme.^{115,116}

The ORCA program package¹¹⁷ was used in the case of UKS-UCCSD(T) and DLPNO-CCSD(T) calculations. Molpro 2015¹¹⁸ was used for ROKS-UCCSD(T) and ROKS-RCCSD(T) and some of the DFT (TPSS, BP86, M06, M06-L and B3LYP) calculations, while all LUCCSD(T0) calculations were carried out using a development version of Molpro. The rest of the DFT (O3LYP, OLYP, OPBE, B97-D and MN15) calculations were performed using Gaussian 16,¹¹⁹ since those functionals were not available in Molpro.

3 Results and discussion

3.1 Canonical Coupled Cluster Calculations

3.1.1 Initial CCSD(T) Results

We start by describing the results of the CCSD(T) calculations obtained with the cc-TZ-DK basis set, see Table 2. All results unless mentioned otherwise are based on using this basis set combination. We have carried out exhaustive checks with larger basis sets that demonstrate that basis set incompleteness effects are smaller than 1 kcal/mol in most cases and smaller than 1.5 kcal/mol in all cases. These test results, as well as a discussion of relativistic effects and of contributions from correlation of the outer core Fe 3s3p electrons, are included in the Supporting Information.

The results obtained with ROKS reference orbitals and with RCCSD(T) are rather similar to those reported previously by others,¹⁹ unsurprisingly given that the same code and method, and similar basis sets, were used. However, it is striking that the two alternative approaches, using an unrestricted excitation ansatz in combination with either ROKS or UKS reference orbitals, yield similar results for most of the structures in agreement with

results described in a previous study by Radon,³⁴ but yield rather different results for ^5TS (this state is significantly lower with an unrestricted ansatz) and the ^5IM system could not be treated using ROKS. This difference in the case of ^5TS was expected given the fact that the quintet abstraction leads to the formation of an antiferromagnetically coupled pair of open-shell species. Furthermore, the $\langle S^2 \rangle$ expectation value for ^5TS from the ROKS-UCCSD calculation is 6.566 (for all $\langle S^2 \rangle$ values see SI) which shows some spin contamination. The disagreement between different CCSD(T) variants despite the relatively modest spin contamination calls into question the accuracy of CCSD(T) methods for this type of system, and thereby motivates the present study.

Table 2: UKS-UCCSD(T), ROKS-UCCSD(T) and ROKS-RCCSD(T) Results^a

	UKS-UCCSD(T)	ROKS-UCCSD(T)	ROKS-RCCSD(T)
^3SR	0.0	0.0	0.0
^5SR	0.6	1.2	2.5
^3RC	-5.0	-4.9	-4.9
^5RC	-2.9	-2.2	-0.8
^3TS	24.6	26.0	26.5
^5TS	14.3	16.0	20.7
^3IM	13.6	15.2	15.4
^5IM	2.5	-	-

^aThe cc-TZ-DK basis set was used. All energies are in kcal/mol.

3.1.2 The Effect of Orbital Type on CCSD(T)

The results just presented show that different CCSD(T) approaches yield different results. The focus there was on the effect of restricted vs. unrestricted treatment of the reference orbitals and excitations. However, it may also be important to consider the level of theory used to generate the reference orbitals. Hence we here look more carefully at the effect of using Kohn–Sham, Hartree–Fock or CASSCF orbitals for the reference, using the UCCSD(T) approach in all cases. In the case of Kohn–Sham orbitals, the B3LYP functional was used in the following discussion, however, in the Supporting information are shown ROKS/UCCSD(T) results with the cc-TZ-DK basis set with orbitals obtained using three additional functionals:

BP86, TPSS, M06. It can be seen there that relative energies do not differ by more than 1 kcal/mol from the results with B3LYP. Therefore, we decided to restrict our discussion only to the results obtained with B3LYP orbitals.

As can be seen in Table 3, the use of ROKS vs. ROHF orbitals, or of UKS vs. UHF orbitals makes a change to some of the calculated relative energies, by up to 4 kcal/mol. As will be discussed below, this is a signature of the onset of multireference character in this system, with KS orbitals perhaps providing a better description. However, all four sets of orbitals return energies for the ^5TS that are more similar to one another than to the ROKS-RCCSD(T) energy in Table 2. Indeed, we also tested coupled cluster expansions based on pseudo-canonical and natural orbitals from CASSCF calculations. As described in the Supporting Information, many different active spaces and orbital types can be obtained and used for expressing the reference wavefunction. Tests showed that natural orbitals derived using an active space of size equal to or larger than 12-electrons-in-12-orbitals yielded stable results that did not change upon further enlarging the active space. These are the results shown in Table 3, and here too it can be seen that they agree quite well with the results obtained with the UHF reference. In summary, while the choice of reference orbitals does impact upon calculated energies, it cannot alone explain the large discrepancies previously noted in Table 2.

Table 3: UCCSD(T) Results Based on Different Reference Orbitals^a

Reference orbitals	ROKS	ROHF	UKS	UHF	CASSCF(12e,12o) ^b
^3SR	0.0	0.0	0.0	0.0	0.0
^5SR	1.2	-1.4	0.6	-2.0	-0.5
^3RC	-4.9	-4.9	-5.0	-4.9	-5.5
^5RC	-2.2	-4.8	-2.9	-5.3	-4.3
^3TS	26.0	22.6	24.6	22.7	21.9
^5TS	16.0	15.4	14.3	11.7	12.4
^3IM	15.2	11.2	13.6	11.3	10.7
^5IM	-	-	2.5	-1.1	-

^aThe cc-TZ-DK basis set was used. All energies are in kcal/mol. ^b Natural CASSCF orbitals have been used.

3.2 Multireference Calculations

3.2.1 Multireference Character of the System

Before discussing the performance of coupled cluster and DMRG-CASPT2, we first analyze various measures of the multireference character of $[\text{Fe}(\text{NH}_3)_5\text{O}]^{2+}$ in order to evaluate to what extent one can rely on the coupled cluster results. The most straightforward way is to analyze the natural orbital occupation numbers (NOONs) calculated with DMRG. Provided the NOONs deviate by less than 0.05 from their formal Hartree–Fock values, the system should probably be considered to be single-reference, but even larger deviations of up to about 0.15 still yield acceptable results in some cases.¹⁰¹ Furthermore, we employed some diagnostics based on the ROKS-UCCSD wave functions such as T_1 (the Frobenius norm), D_1 (the matrix 2-norm of the coupled cluster amplitudes for single excitations), and $|t_{2,max}|$ (the largest doubles excitation amplitude) as well as %TAE[T] (the percent of the atomization energy due to triples). For transition metal complexes, it has been argued that coupled cluster results which have T_1 larger than 0.05, D_1 exceeding 0.15, $|t_{2,max}|$ above 0.1 and $|\text{\%TAE[T]}| > 10$ may have larger errors and suffer from unpredictable behaviour due to the substantial nondynamical correlation.¹²⁰

The NOONs of the most important MOs are shown in Table 4. The results clearly show that in all triplet states, the multireference character is moderate with deviations of NOONs from their formal HF value of less than 0.15. These moderate deviations suggest that the CCSD(T) results for the triplet states could be reliable. All quintet states, in contrast to the triplet states, exhibit a larger multireference character. In particular in the ^5TS state, the two orbitals $\sigma_{\text{C-H-O}}$ and $\sigma_{z^2}^*$ are strongly correlated with large NOONs deviations from the formal value. In the ^5IM state, these two orbitals each hold one electron which are antiferromagnetically coupled. As already noted, care should therefore be taken when discussing CCSD(T) results for these quintet states.

As can be seen in Table 4, the NOONs indicate substantial multireference character for

Table 4: Multireference Character of Systems: DMRG Occupation Numbers of Some Important Natural Orbitals, and ROKS-UCCSD Diagnostics T_1 , D_1 , and $|t_2, max|$ as well as %TAE[T]

State	σ_{C-H-O}	σ_{z^2}	d_{xy}	π_{xz}^*	π_{yz}^*	$d_{x^2-y^2}$	$\sigma_{z^2}^*$	T_1	D_1	[%TAE[T]]	$ t_2, max $
³ SR	-	1.88	1.97	1.06	1.06	0.12	0.04	0.013	0.046	4.72	0.092
⁵ SR	-	1.82	1.00	1.05	1.05	1.00	0.18	0.014	0.071	4.04	0.061
³ RC	1.98	1.88	1.97	1.06	1.06	0.12	0.04	0.014	0.051	3.73	0.086
⁵ RC	1.98	1.80	1.00	1.05	1.05	1.00	0.19	0.014	0.075	3.22	0.061
³ TS	1.93	1.91	1.96	1.01	1.04	0.05	0.11	0.011	0.037	3.26	-
⁵ TS	1.59 ^a	1.96 ^a	1.00	1.03	1.03	1.00	0.42	0.015	0.080	2.99	0.096
³ IM	1.00	1.93	1.96	1.96	1.02	0.05	0.08	0.011	0.035	2.81	-
⁵ IM	1.15	1.97	1.00	1.01	1.01	1.00	0.86	-	-	-	-

^aThe σ_{C-H-O} and σ_{z^2} orbitals mix with each other and cannot be firmly distinguished.

⁵IM and especially ⁵TS, whereas the coupled cluster diagnostics are less informative. This is because NOONs provide information on the extent to which the system has multireference character, while coupled cluster diagnostics serve more as a guide to the quality of the CC wave function. For all states, T_1 is always smaller than 0.015 and D_1 produces values in a range of 0.04–0.08 and %TAE in a range of 2.5–5.0. Similar T_1 values were obtained with the UKS-UCCSD calculations (see Table S7). All diagnostic values are well-below the ‘critical’ thresholds proposed by Jiang et al.¹²⁰ Furthermore, looking into the double amplitudes we can see that even though the largest amplitudes are non-negligible and denote some multireference character, $|t_2, max|$ never exceeds 0.1. One reason for such low T_1 and D_1 values comes from the fact that the KS reference wave function, i.e. the B3LYP wave function, already captures some electron correlation effects, unlike the HF reference wave function.³⁶ Indeed, by employing either an ROHF or UHF reference, the T_1 diagnostic increases by a factor of two to three, from ~ 0.015 to ~ 0.035 (see Table S4). Limited T_1 and D_1 values in calculations based on KS reference orbitals suggest that, even though multireference character is not negligible, CCSD(T) could perhaps produce reasonable results. This is also supported by the relatively small $|t_2, max|$ values, which are not heavily dependent on the orbitals used.

3.2.2 DMRG-CASPT2 Results

The reaction path going from SR to IM was calculated using a composite approach proposed in our recent work⁸² (denoted as CASPT2/CC). In this approach, we combined DMRG-CASPT2 for valence correlation and UKS-UCCSD(T) for semicore correlation. The CASPT2/CC results are shown in Figure 2, in comparison with the CCSD(T) results based on different references.

Since both CASPT2/CC and CCSD(T) have their own limitations, without a reliable absolute benchmark, it is not trivial to assess whether CASPT2/CC or CCSD(T) gives better results for these reaction pathways involving moderately correlated systems with different metal oxidation states. CASPT2/CC typically overstabilizes high-spin states (or those with large numbers of unpaired electrons) as compared to low-spin states (or those with low numbers of unpaired electrons) by a few kcal/mol.⁸² Restricted coupled cluster based on the restricted reference may have difficulties describing states with moderate multireference character and moreover, is not applicable for characterizing the antiferromagnetic coupling in the ⁵IM state. In contrast, an unrestricted-reference such as UKS, which allows breaking spin-symmetry and gives a better variational solution, can qualitatively describe the antiferromagnetic coupling. Thus, UCCSD(T) based on this reference is expected to reasonably describe the ⁵IM state. However, UCCSD(T) results with high spin-contamination should be interpreted with care (even though it has been shown that CCSD and higher-order CC approaches are capable of reducing spin-contamination considerably^{121,122}). Furthermore, it was shown previously^{28,123} that CCSD(T) based on an unrestricted reference outperforms CCSD(T) based on a restricted reference compared to full CI in the case of bond breaking, even for difficult cases like N₂ dissociation. Here, we will discuss in detail CASPT2/CC as compared to coupled cluster results for (i) the triplet-quintet gaps, (ii) the reaction barriers, and (iii) the reaction energies.

For the triplet-quintet gaps, we only compare similar states with similar Fe oxidation state (i.e. ³SR–⁵SR, ³RC–⁵RC, ³TS–⁵TS, and ³IM–⁵IM) since we expect that the performance of

both CASPT2/CC and coupled cluster is better with a fixed Fe oxidation state. The results reconfirm our observation from a previous work.⁸² The general trend is that as compared to coupled-cluster, CASPT2/CC always favours the quintet over the triplet state. The difference between CASPT2/CC and UKS-UCCSD(T) is ~ 1 kcal/mol (in ^3SR – ^5SR and ^3RC – ^5RC), and up to ~ 6 kcal/mol (in ^3TS – ^5TS). The large difference in the latter case might be related to the fact that the ^5TS state has a much larger multireference character (see Table 4), thus it should be less well described by UKS-UCCSD(T). Using ROKS-RCCSD(T) with higher restrictions on single excitations (*vide infra*), the difference is significantly larger (more than 10 kcal/mol), indicating that ROKS-RCCSD(T) is inferior to UKS-UCCSD(T) in describing states with strong multireference character. We finally note that for the ^3SR – ^5SR spin gap, CASPT2/CC predicts a quintet ground state and a near degenerate triplet excited state, in contradiction to coupled-cluster. This disagreement is connected with the size of the basis set. By using larger basis sets and extrapolation to the complete basis set limit, CASPT2/CC correctly predicts the triplet ground state (see also Table S11).⁸²

As ^3SR , ^3RC , ^3IM , and ^3TS have very similar multireference character, the triplet pathway is expected to be well described by the coupled cluster approach. Indeed, all CCSD(T) methods give similar results to within 2 kcal/mol and predict a value of 25–26 kcal/mol for the triplet reaction barrier, and 14–15 kcal/mol for the ^3IM – ^3SR relative energy, whereas CASPT2/CC predicts slightly larger values, 28 and 18 kcal/mol, respectively.

For the quintet reaction pathway, the four structures ^5SR , ^5RC , ^5TS , and ^5IM have substantially different multireference character; hence, we believe that coupled cluster might give results of different quality for these different points. Indeed, the reaction barrier ^5SR – ^5TS predicted by CCSD(T) is 14–18 kcal/mol, *larger* than the value calculated with CASPT2/CC (~ 12 kcal/mol). Perhaps surprisingly, for the completely antiferromagnetically coupled state ^5IM , there is actually reasonable agreement between UKS-CCSD(T) (energy of 2.5 kcal/mol relative to ^5SR) and CASPT2/CC, where the relative energy is 4.4 kcal/mol.

Finally, because this hydrogen abstraction reaction involves a crossing between the triplet

and quintet potential energy surfaces (it is known-as a ‘spin forbidden’ reaction), it is interesting to estimate the ^3SR – ^5TS barrier. Distinctive results were obtained: 11.8, 14.3, 16.0, and 20.8 kcal/mol by CASPT2/CC, UKS-UCCSD(T), ROKS-UCCSD(T), and ROKS-RCCSD(T), respectively. We consider that the ROKS-RCCSD(T) barrier is unreliable here, and note that CASPT2/CC is in fairly good agreement with both UCCSD(T) protocols.

Figure 2: Comparison Among CASPT2/CC, UKS-UCCSD(T), ROKS-UCCSD(T), and ROKS-RCCSD(T) Results.

3.3 Higher-Order Coupled Cluster Calculations

As a separate check of the accuracy of the UKS-UCCSD(T) approach which we argue is the most reliable CCSD(T) ansatz for these systems, we wanted to move to higher-order coupled cluster expansions, namely coupled cluster calculations with singles, doubles and triples (CCSDT) and also with perturbative quadruples (CCSDT(Q)). The CCSDT(Q) re-

sults especially should approach the full CI limit³⁸ even considering the partial multireference character present. However, such calculations remain too challenging with our model $[\text{Fe}(\text{NH}_3)_5\text{O}]^{2+}$ and we had to switch to a smaller $[\text{FeHe}_5\text{O}]^{2+}$ system.

At first sight, helium atoms are very different as ligands compared to ammonia molecules. However, the structures used for this model system were constructed in such a way that the electronic structure (and especially the spin density) was very similar to that of the corresponding ammonia-containing complex. This was achieved by using a decreased Fe–He distance compared to the equilibrium value, so that the helium atoms become stronger electron pair donors, more similar to ammonia ligands, while all other distances were kept as in the ammonia system (Tables S2 and S3). It should be noted that these geometries are not stationary points. Therefore, the overall relative energies are not very similar to those in the ammonia-containing system, but the *difference* between the relative energies computed using CCSD(T) and CCSDT(Q) can be used to assess the accuracy of CCSD(T). In Figure 3 we present the spin density of the oxidant in the reactant triplet state and at the quintet transition state as examples. It can be seen that the density obtained for the helium-containing model is similar to that of the full system. The same observation was obtained for the two other structures. For these systems, the calculations were run on separate reactants and on transition states only.

Figure 3: Upper figures show spin densities of oxidant in triplet state for full system (left) and helium model system (right). Lower figures show spin densities of transition state on quintet surface for full system (left) and helium model system (right). All spin densities have a contour value of 0.001.

As for the larger model, we observe a large 6 kcal/mol change in relative energy from ROKS-UCCSD(T) to UKS-UCCSD(T) (Table 5). The ROKS-RCCSD(T) result is even more different. Including full triples treatment in ROKS-UCCSDT brings us closer to UKS-UCCSD(T), but a difference remains. All UKS-based methods give similar energies for this TS, suggesting that UKS-UCCSD(T) is a good approximation to UKS-UCCSDT(Q). In contrast, the ROKS-based values are likely rather inaccurate, especially ROKS-RCCSD(T).

It should be noted however that the good agreement between all of the UKS-based coupled cluster values obtained for the ^5TS state does not carry over to the ^3TS , where UKS-UCCSDT(Q) gives a relative energy that is 4.4 kcal/mol higher than UKS-UCCSD(T). On the other hand, in this case UKS and ROKS references give similar values, as expected given that both the ROKS and UKS method are able to give a reasonable zeroth-order

Table 5: CCSD(T), CCSDT and CCSDT(Q) Results Using ROKS and UKS Orbitals as a Reference on the Helium Model System^a

Reference	ROKS			UKS		
	UCCSD(T)	RCCSD(T)	UCCSDT	UCCSD(T)	UCCSDT	UCCSDT(Q)
³ SR	0.0	0.0	0.0	0.0	0.0	0.0
⁵ SR	-7.6	-7.3	-7.4	-8.6	-8.3	-10.2
³ TS	42.1	42.2	41.8	41.6	42.2	46.0
⁵ TS	-37.4	-32.7	-39.2	-43.3	-43.8	-42.4

^aAll energies are in kcal/mol. The 3s,3p electrons of Fe were not correlated.

description of the electronic structure in this case. Our suggestion here is that UCCSDT(Q) improves the description of ³SR, ⁵SR and ⁵TS but that the triplet TS is already fairly well described by CCSD(T). This can be seen from the changes in the *absolute* energies of each state (Figure 4) using the UKS reference. First it should be mentioned that the perturbative triples contribution $\Delta(T)$ is the dominant contribution to the correlation energy after CCSD. By going from UCCSD(T) to UCCSDT, a modest change in the total energy of between 1 and 2.5 kcal/mol is observed for all species. However, upon changing from UCCSDT to UCCSDT(Q) the energy changes by between 4 kcal/mol and 7.3 kcal/mol, with the exception in the case of ³TS where the change is only 1.8 kcal/mol. All of this leaves a slightly larger uncertainty concerning the correct relative energy for the ³TS state. We note however that in the case of the ammonia model, DMRG-CASPT2 calculations also suggest that the UKS-UCCSD(T) energy for ³TS is slightly too low.

Figure 4: Method convergence of the absolute energies of each state.

3.4 Correlation Energy in Restricted and Unrestricted Coupled Cluster Calculations

Based on the comparison between CCSD(T), CASPT2 and CCSDT(Q), we have argued here that ROKS-RCCSD(T) results are less reliable than ROKS-UCCSD(T) results, especially for ⁵TS. Now we would like to understand this discrepancy. In order to do that we examined the difference between the correlation energies from these calculations:

$$\Delta\text{Total} = E_{corr}^{\text{RCCSD(T)}} - E_{corr}^{\text{UCCSD(T)}} \quad (4)$$

where E_{corr} is the correlation energy with the superscript denoting the level of theory. This convention applies as well to the following equations. Furthermore, we looked also at the separate contributions to ΔTotal from the CCSD correlations energy:

$$\Delta\text{CCSD}_{\text{Total}} = E_{corr}^{\text{RCCSD}} - E_{corr}^{\text{UCCSD}} \quad (5)$$

and the perturbative triples correction (T):

$$\Delta(\text{T}) = E_{corr}^{\text{R}(\text{T})} - E_{corr}^{\text{U}(\text{T})}. \quad (6)$$

The CCSD correlation energy can be further divided into the singles ($\Delta\text{CCSD}_{\text{singles}}$) and doubles ($\Delta\text{CCSD}_{\text{doubles}}$) contributions. All these contributions are given in Table 6.

One can see that in the triplet state the difference in the total correlation energy is small and does not exceed 1 kcal/mol. In the case of the quintet state, this difference is larger, but in most cases it is not more than 2 kcal/mol. However, in the case of the ^5TS state, this difference is 5 kcal/mol.

Table 6: Difference between Electron Correlation Energy Obtained with ROKS-RCCSD(T) and ROKS-UCCSD(T) as well as the Difference at the CCSD Level (Including Singles and Connected Doubles Energy) and in the (T) Contribution.^a

	ΔCCSD			$\Delta(\text{T})$	ΔTotal
	singles	doubles	total		
^3SR	1.0	0.4	1.5	-1.2	0.3
^5SR	2.8	0.5	3.3	-1.6	1.6
^3RC	1.0	0.4	1.5	-1.2	0.3
^5RC	2.8	0.5	3.3	-1.6	1.7
^3TS	2.0	-0.2	1.8	-0.9	0.8
^5TS	11.0	2.5	13.5	-8.4	5.1
^3IM	0.9	0.0	0.9	-0.4	0.5

^aAll energies are in kcal/mol.

As can be seen from Table 6, $\Delta\text{CCSD}_{\text{Total}}$ for the quintet states is twice as large as for the triplet states, which can be correlated with the fact that quintet states have more unpaired electrons, hence the difference between restricted and unrestricted wavefunctions is larger. The difference in the (T) contribution is also larger for quintets, but not to the same extent. The case of the ^5TS state is an outlier with respect to these trends: $\Delta\text{CCSD}_{\text{Total}}$ is here *much* larger, at 13.5 kcal/mol, compared to the situation for the ^3TS state (1.8 kcal/mol). There is also a big difference between $\Delta(\text{T})$, which are respectively -8.4 kcal/mol for the ^5TS state and -0.9 kcal/mol for the ^3TS state.

Furthermore, as noted above, $\Delta\text{CCSD}_{\text{Total}}$ can be broken down into singles and connected doubles contributions, and these energy differences are also shown in Table 6. It can be seen that $\Delta\text{CCSD}_{\text{double}}$ does not exceed 0.5 kcal/mol except in the case of ^5TS where this difference is 2.5 kcal/mol. This means that the missing 11 kcal/mol in $\Delta\text{CCSD}_{\text{Total}}$ is due to the singles energy. Also, in the case of all states $\Delta\text{CCSD}_{\text{singles}}$ is larger than the difference in $\Delta\text{CCSD}_{\text{doubles}}$. This is very surprising if we take into the account that the absolute singles contribution is two orders of magnitude smaller than the doubles contribution.

These results show that the large difference between RCCSD(T) and UCCSD(T) is due to the significantly large contribution to the CCSD correlation energy at the UCCSD level, more precisely due to the single excitations. Therefore, we can conclude that the difference is due to the restrictions which are imposed on single excitation amplitudes in the construction of the RCCSD(T) scheme. Indeed, upon inspecting the UCCSD and RCCSD amplitudes, it can be seen that they are much larger for some orbital pairs with UCCSD . The associated excitations are those that would be expected based on the DMRG NOONs, i.e. those from the σ_{z^2} orbital to the $\sigma_{z^2}^*$ orbital, which have almost four times larger amplitude in the case of UCCSD(T) than in the case of RCCSD(T) (-0.374 compared to -0.101 in the case of α - α excitation and 0.310 compared to 0.074 in the case of β - β excitation). This is followed by the excitation from $\sigma_{\text{C-H-O}}$ to $\sigma_{z^2}^*$ where this difference is also present, but not that significant.

3.5 DFT Calculations

DFT calculations using the B3LYP functional including both dispersion D3^{115,116} and relativistic effects corrections (using Douglas-Kroll-Hess Hamiltonian) were carried out. All calculations were done with the cc-TZ-DK basis set (see Table 1). These results were then compared to different variants of the CC method as well as to DFT results from Ref. 19. DFT results without dispersion and relativistic effects corrections can be found in the Supporting Information.

First of all, we want to compare ROKS and UKS results. From Table 7 it can be seen

Table 7: Spin-Restricted Open-Shell and Spin Unrestricted DFT-D3 Results Using the B3LYP Functional Compared to Different Variants of the CC Method (ROKS-RCCSD(T), ROKS-UCCSD(T) and UKS-UCCSD(T))^a

	ROKS	UKS	ROKS-RCCSD(T)	ROKS-UCCSD(T)	UKS-UCCSD(T)
³ SR	0.0	0.0	0.0	0.0	0.0
⁵ SR	5.6	3.1	2.5	1.2	0.6
³ RC	-5.8	-5.7	-4.9	-4.9	-5.0
⁵ RC	1.5	-1.0	-0.8	-2.2	-2.9
³ TS	16.6	16.5	26.5 (26.3) ^b	26.0	24.6
⁵ TS	23.9	10.9	20.8 (19.0) ^b	16.0	14.3
³ IM	7.2	8.2	15.4	15.2	13.6
⁵ IM	-	4.1	-	-	2.5

^aThe cc-TZ-DK basis set was used. All energies are in kcal/mol. ^bThe values in brackets represent the ROKS-RCCSD(T) values from 19.

that the results for the triplet state are very similar. On the other hand, the quintet results differ more, always giving lower UKS relative energies, with the largest difference in the ⁵TS state, showing that ROKS cannot properly describe this state. While most of the structures have a spin contamination of about 0.05, the ⁵TS and ⁵IM states have spin contamination of 0.566 and 0.953, respectively. This can explain why ROKS fails to describe these states. Comparing DFT to CC results, we can see that the UKS values are in better agreement with the CC results independent of the variant of CC. However, both transition states calculated with UB3LYP-D3 are significantly lower than with CC, with the triplet transition state being more stabilized than the quintet.

In ref. 19 a large variety of DFT functionals, GGA (general gradient approximation), hybrid-GGA, meta-GGA, and double-hybrid functionals, were benchmarked against ROKS-RCCSD(T) results. Different model systems were used; oxidant **3** from ref. 19 is used in this study. Our ROKS-RCCSD(T) reaction barriers are in good agreement with results from ref. 19, 26.3 kcal/mol compared to our 26.5 kcal/mol for the triplet state and 19.0 kcal/mol compared to our 20.8 kcal/mol for the quintet state, even though different basis sets were used and relativistic effects were not taken into account in the earlier study. It was concluded in ref. 19 that “all tested functionals underestimated the quintet barrier heights compared

with RCCSD(T) results, while most of the functionals also underestimate the triplet barrier heights”. However, as noted above, the ROKS-RCCSD(T) results give a barrier for the quintet state (18.2 kcal/mol) that is too high as compared to both ROKS-UCCSD(T) and UKS-UCCSD(T) (14.8 and 13.7 kcal/mol, respectively). Our detailed analysis of CC results show that problem is not that DFT functionals give a too low quintet barrier, but rather that ROKS-RCCSD(T) produces a too high barrier on this surface. Therefore, we wanted to look into the three values from DFT calculations using different functionals: triplet-quintet gap of the separate reactants ($\Delta E_{\text{gap}} = E_{5\text{SR}} - E_{3\text{SR}}$), triplet reaction barrier ($\Delta E_3^{\text{TS}} = E_{3\text{TS}} - E_{3\text{SR}}$) and quintet reaction barrier ($\Delta E_5^{\text{TS}} = E_{5\text{TS}} - E_{5\text{SR}}$).

Comparing our UB3LYP reaction barriers (see Table 8) with those in the previous work¹⁹ we can see that they are in excellent agreement, differing by less than 0.5 kcal/mol due to the different basis set (see SI). Including D3 dispersion correction with Becke-Johnson damping this difference in the case of the ^5TS state is a bit large (1.7 kcal/mol) because a different dispersion correction was used. Overall reaction barriers are lowered by about 2-3 kcal/mol by inclusion of D3. By including the relativistic effects correction, the barriers became slightly larger by about 1 kcal/mol. We can conclude that the D3 and relativistic corrections change results slightly, but not by more than 2 kcal/mol.

Therefore, we decided that we can compare directly the previously reported DFT results with different functionals with our DFT including relativistic effects correction and UKS-UCCSD(T) results with cc-TZ-DK. All functionals reported in the previous study¹⁹ give lower energies for the quintet state compared to ROKS-RCCSD(T), but the difference is significantly smaller in the case of UKS-UCCSD(T), with the GGA functional OPBE and the meta-GGA functional TPSS closest to the UKS-UCCSD(T) values. In the case of the triplet reaction barriers energies were both underestimated and overestimated; the hybrid O3LYP functional is very close to UKS-UCCSD(T). Finally, we have also calculated triplet-quintet gaps for these species, so that we can evaluate the accuracy of the investigated functionals for processes involved in two-state reactivity. The results shown in Table 8 are

consistent with what has been reported in the literature, see for example ref. 26. GGAs (such as BP86) and meta-GGAs (such as TPSS) functionals tend to strongly overestimate the gap by more than 10 kcal/mol due to errors in their exchange part. By using either a ‘better’ exchange functional such as the semiempirical OPTX (in OLYP and OPBE) or training the functional based on large data sets (in M06-L) the errors are significantly decreased to less than 4 kcal/mol. Except for M06, functionals incorporating a fraction of Hartree-Fock exact exchange such as B3LYP, O3LYP, or MN15 tend to perform slightly better, with absolute errors of around 2 kcal/mol. Of all functionals, OPBE and OLYP are the most promising functionals for the investigation of these kinds of systems since they not only predict the correct ground state but also yield quite accurate spin gap as compared to UKS-UCCSD(T).

Table 8: The Calculated Triplet-Quintet Gap (ΔE_{gap}) and Triplet (ΔE_3^{TS}) and Quintet (ΔE_5^{TS}) Reaction Barriers Using Different Spin Unrestricted DFT Functionals as well as UKS-UCCSD(T)^a

	ΔE_{gap}	ΔE_3^{TS}		ΔE_5^{TS}	
UKS-UCCSD(T)	0.6	24.6		13.7	
B3LYP	3.6	19.0	(17.8)	9.2	(7.4)
B3LYP-D3	3.1	16.5	(13.9)	7.8	(6.5)
BP86	12.2	20.9	(20.2)	12.1	(11.5)
TPSS	14.6	21.7	(21.0)	13.4	(12.5)
TPSSKCIS	-	-	(20.9)	-	(12.4)
M06	-10.1	18.6	(19.8)	4.8	(4.1)
M06-L	-3.4	22.9	(23.0)	7.9	(8.1)
OLYP	2.0	26.8	(26.8)	12.4	(11.6)
OPBE	1.8	27.3	(27.1)	12.9	(12.4)
O3LYP	-1.6	25.6	(25.2)	10.6	(9.4)
B97-D	2.9	19.4	(19.3)	8.5	(7.5)
MN15	2.7	16.3		12.6	

^aThe cc-TZ-DK basis set was used. All energies are in kcal/mol. ^bThe values in brackets represent the values from ref. 19.

3.6 Local Coupled Cluster Calculations

Finally, we want to compare two different version of local coupled cluster with UCCSD(T) (Figure 5). The first one is LUCCSD(T0) based on ROKS orbitals and the second one is

DLPNO-CCSD(T) based on UKS orbitals. It should be pointed out that all results presented in this section have been obtained without relativistic corrections and using the cc-TZ basis set.

We will start by looking into LUCCSD(T0) results. The program used for these calculations requires ROKS (or ROHF) orbitals to be used as a reference, hence to ensure a like-for-like comparison, we compare the results obtained to those obtained with the most similar canonical approach, ROKS-UCCSD(T). It can be seen that the LUCCSD(T0) results deviate strongly from the canonical ones. The errors in the relative energies are for almost all structures between 4 and 6 kcal/mol, which is in agreement with the original study, where it was shown that for more challenging systems the error can go up to 5 kcal/mol.⁴² However, in the case of ⁵RC the error becomes very large indeed, at 13 kcal/mol.

To improve these results we implemented the so-called *hotspot* feature which should reduce errors due to the pair approximation in LUCCSD(T0), as discussed earlier. Two different *hotspot* selections were used (Table 9), including orbitals with strong Fe character or including all orbitals with Fe character. By including different orbitals in the *hotspot* selection, it can be seen that the results improve. Including only orbitals which have a dominant Fe character already improves the results especially in the case of transition states (*hs-small* selection) where the error compared to canonical coupled cluster results is now 1.3 and 2.3 kcal/mol compared to previously being 4.3 and 6.1 kcal/mol for ³TS and ⁵TS, respectively. However, the energy of the ⁵RC state does not change significantly and the error remains around 13 kcal/mol. Furthermore, the error in the ³IM state becomes larger. In case all orbitals which contain any Fe character are included in the *hotspot* selection, most errors are further reduced (*hs-big* selection) with the triplet transition state being almost on the spot (25.3 kcal/mol from *hotspot* calculation vs 25.1 kcal/mol from canonical CC calculation). Furthermore, the error in the calculated triplet-quintet gap is reduced from 4.9 kcal/mol to 2.6 kcal/mol with *hs-big* selection. Both of these improvements are very important for the calculations of spin-state energetics as well as accurate calculations of

transition states of different mechanisms. However, the errors in the ^5RC and ^3IM states are still present and amount to 10.7 kcal/mol and -7.8 kcal/mol, and in the case of the ^3IM states the error is larger compared to results without *hotspot*.

Table 9: Comparison between Different Local Coupled Cluster Methods with Canonical Coupled Cluster. *hs-small* Has Fe Orbitals with Dominant Fe Character Included in *hotspot*. *hs-big* Includes All Orbitals Which Contain Fe in *hotspot*. AllStrong Has All Pairs Treated at the Coupled Cluster Level. Number of strong pairs (n_{str}) in all local calculations was also listed^a

	UCCSD(T)	LUCCSD(T0)		<i>hs-small</i>		<i>hs-big</i>		AllStrong	
		ΔE	n_{str}	ΔE	n_{str}	ΔE	n_{str}	ΔE	n_{str}
^3SR	0.0	0.0	171	0.0	326	0.0	391	0.0	496
^5SR	0.6	5.5	199	4.5	358	3.2	423	3.6	528
^3RC	-4.9	-2.5	181	-2.5	376	-2.4	461	-3.7	630
^5RC	-2.8	10.0	209	9.2	412	7.9	497	7.5	666
^3TS	25.1	29.4	193	26.4	377	25.3	462	23.8	630
^5TS	14.5	20.6	229	16.8	436	16.1	516	16.5	666
^3IM	14.3	9.3	174	6.6	372	6.5	444	4.6	630
^3SP	21.2	13.6	159	12.0	306	11.0	376	10.1	496
^5SP	9.7	4.4	234	8.0	366	4.4	471	5.0	561

^aAll energies are in kcal/mol.

To further understand these results, we ran LUCCSD(T0) calculations where all pairs were treated as strong pairs, therefore, calculated at the full coupled cluster level (Table 9), leaving us only with domain approximations. When the results were compared with canonical coupled cluster results we obtained significant errors in the case of the ^5RC and ^3IM states. These errors must be due to the domain approximation and cannot be overcome by increasing the number of strong pairs; this provides an explanation for the errors from both LUCCSD(T0) and *hs*(Fe)-LUCCSD(T0) calculations. As can be seen in Figure 6 the domain errors are significant in these systems and much larger than the pair errors. Also, the pair errors are more constant along the reaction path. Furthermore, errors due to the pair approximation are almost completely reduced in *hotspot* calculations and as can be seen, the *hs*(Fe)-LUCCSD(T0) errors are now only due to the domain errors. These results also explain why in the case of the ^5RC state the results are higher and in case of the ^3IM state the results are lower than the CCSD(T) results.

Figure 5: Local coupled-cluster results compared with canonical coupled-cluster results. The results in the upper graph used UCCSD(T) and LUCCSD(T) based on ROKS orbitals, while those in the lower graph used UCCSD(T) and DLPNO-CCSD(T) based on UKS orbitals.

Figure 6: Total error in LUCCSD(T0) and *hotspot* calculations, as well as errors due to the domain and pair approximations in these calculations.

To reduce the domain error, different approaches can be applied. In the first step, one can opt for using extended domains.⁵⁴ Domains can be extended either by using the connectivity or distance criteria. However, in this case that did not help (see SI Figure S4). Even though the domain error was reduced for specific states, it was not reduced in such a way that a near-constant domain error was obtained, therefore large errors remain for the relative energies. The other option would be to use the LUCCSD(T0)-F12 method instead of LUCCSD(T0), which reduces the domain error.⁵⁶ However, we were unable to converge the latter calculations.

DLPNO-CCSD(T) calculations were also carried out. The results obtained deviate from canonical calculations by roughly the same amount as do those obtained with LUCCSD(T0). A larger deviation of up to 8 kcal/mol is observed on the quintet surface and in the case of transition states. IM states on both surfaces were obtained in excellent agreement with CCSD(T) results. By changing from NormalPNO to TightPNO this difference is reduced but is still around 5 kcal/mol on the quintet surface. Even though this method was previously applied to systems containing Fe^{124,125} it does not appear to be suitable for describing two state reactivity of the system of the current study, at least not in a 'black-box' sense.

Qualitatively, the DLPNO-CCSD(T) calculations provide a misleading picture in that they predict the quintet state to be the ground state, and therefore do not reproduce the known two-state reactivity of these complexes.

4 Conclusion

In this work the accuracy of the different flavors of CCSD(T) method was investigated in the application to non-heme iron complexes. This was done by comparing CCSD(T) results to higher order CC schemes on a smaller helium model and to DMRG-CASPT2 results on the ammonia system. The ammonia system was checked for the multireference character. It was seen that while in the triplet state the multireference character is small, some states on the quintet surface have larger multireference character. This can be concluded based on occupation numbers from the CASSCF wavefunctions, though most of the diagnostics from CCSD(T) calculations pointed towards single reference states. Furthermore, the impact of different reference orbitals on the energetics was also investigated.

From comparing different CCSD(T) schemes to CCSDT(Q) we concluded that ROKS-RCCSD(T) results were in the worst agreement with CCSDT(Q). However, using unrestricted CC improved the agreement, while going one step further and using also an unrestricted reference led to yet further improvement. Thus, we can conclude that ROKS-RCCSD(T) is the least reliable scheme of those tested in this work for this type of system. The same conclusion was obtained by comparing to DMRG-CASPT2 results. Therefore, we cannot recommend the use of the the fully restricted protocol for the calibration of DFT functionals in the case of systems which exhibit two state reactivity, but we would rather recommend the UCCSD(T) scheme. The latter could be carried out with a restricted open-shell or unrestricted reference. As the new UKS-UCCSD(T) benchmark energies differ quite significantly from earlier benchmark values, the predicted reactivity patterns may also need to be reassessed. Even though the energetic ordering of ^5TS and ^3TS was correctly predicted

in an earlier study, the energy gap between these two states was found to be almost two times larger than previously calculated.¹⁹ Finally, we should emphasize that even though we find the UKS-UCCSD(T) method to be the most accurate among the different flavors of coupled cluster theory with singles, doubles and perturbative triples, errors of up to 5 kcal/mol compared to UCCSDT(Q) were observed here.

In the end local coupled cluster calculations were performed. It was seen that both versions of this method have significant errors when compared to their canonical counterparts. Even though the LUCCSD(T0) method predicted a triplet ground state and described the transition states with appropriate accuracy, this scheme had problems with correctly describing some states along the reaction path. On the other hand, the DLPNO-CCSD(T) scheme underestimated the structures on the quintet surface, predicting the quintet to be the ground state and thus avoiding a two state reactivity altogether. Therefore, we can conclude that despite these methods being promising new approaches, the approximations used are not yet robust enough to enable applications in such demanding systems.

The LUCCSD(T0) results were analyzed in more detail and the error is traced back to two main approximations: the domain and pair approximation. In this work we proposed the *hotspot* approach which aims at reducing the pair error for transition metal systems by selectively including the relevant pairs at the coupled cluster level. This allows to reduce the pair error almost completely. However, the domain error remained in some of the investigated structures. A combination of the latter scheme with explicit correlation could be the key to a robust and cost-effective CC model.

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Supporting Information Available

Important bond distances. Relativistic effects and basis set convergence. Active space used in DMRG-CASPT2 calculations. Extended domains. Cartesian coordinates of all structures used in this work.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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