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Comparison of TDDFT and multireference treatment of ground and excited states of Fe(II) ammonia octahedral complex

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Multireference methods and time dependent density functional theory (TDDFT) is used to compute the ground and excited states at different spin states of a prototype spin crossover complex. It is observed that while density functional theory (DFT) with certain functionals can get the energetics of the ground state accurately, multireference treatment is crucial to the proper depiction of the excited states. We have further used a DFT orbital based complete active space self consistent field method to form a computationally affordable alternative. This approach proves to be quite efficient in accurate depiction of the ground and excited states of such complexes.

Keywords: Spin crossover, multireference, Fe(II) ammonia octahedral complex.

Introduction

Spincrossover (SCO) complexes form a very interesting class of transition metal complexes, where the stable spin state of the complex can change with light irradiation, magnetic field, applied pressure or thermal equilibria[1,2]. This change in spin state is accompanied with change in a plethora of physical properties of the complex or material, such as magnetism, optical absorption etc. Fe(II), i.e. $3d^6$ complexes in a nearly octahedral ligand field is known to exhibit such SCO properties[3–5]. This is governed by the fact that the Fe(II) moiety in the octahedral ligand field, shows a d-orbital splitting that gives access to an array of different spin states with small differences in their energies. The SCO complexes were discovered more than 50 years back, and have fascinated researchers due to its obvious material and technological applications in the fields of spintronics and molecular memory storage devices[6–9].

In spite of its immense technological applications, the accurate understanding, prediction and therefore, engineering of SCO molecules and materials are still extremely challenging problems[10]. Fig. 1 shows the schematics for the different spin states of a typical SCO molecule. The two different scenario can give rise to temperature or light induced spin crossover processes. The most stable spin state and

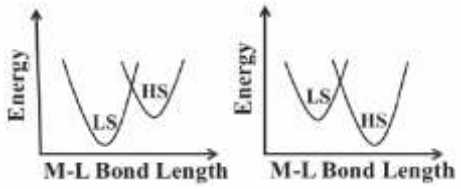

Fig. 1. Schematics of high and low spin state energies at different metal ligand bond lengths. In case of octahedral Fe-N bonded complexes, the high and low spin states are close in energy giving rise to possibility of spin crossover.

the energy differences between the spin states are a combined effect of the central metal ion, ligand field effect as well as other environmental factors, such as counter-ion etc. While experimental techniques such as magnetic susceptibility[11–15] can detect the spin state (or fractional population of the spin states) of the material at a particular temperature, it lacks insight into the electronic structure of the molecule. Ultrafast optical, X-ray or Raman spectroscopies have been used to get a dynamical picture of the structural reorganization[16–20]. Combined with theoretical insights these experimental techniques can indeed prove to be decisive in elucidating the exact mechanism of the spin state changes that are relevant in processes such as light induced excited spin state trapping (LIESST)[21–29].

As mentioned above, the SCO phenomenon relies on the accurate d-orbital splitting of the octahedral complexes. These d-orbital splitting energies are very small in magnitude (< 1.0 eV) and therefore, the accurate estimation of the ligand fields on the splitting is crucial to the prediction of the phenomena[30,31]. Due to the near degeneracies of the d-orbitals at the valence space, computationally these systems are challenging. The wavefunction is multireference in nature and the d-orbitals are strongly correlated with each other. Therefore, state of the art multireference methods need to be applied to understand the electronic structure of the system. Complete active space based methods, such as complete active space self consistent field (CASSCF) have been applied for such systems[23,25]. However, as is well known now, large basis sets and complete information about the large ligands is also crucial which makes these methods quite computationally expensive. Furthermore, it is known that large active space including a few metal-ligand orbitals are required to characterize the ligand field splitting accurately[23]. Dynamic correlation needs to be included either perturbatively or variationally via, complete active space perturbation (CASPT2) or multireference configuration interaction (MRCI). Even for state of the art multireference methods, such as CASPT2, the adiabatic HS-LS gap is overestimated, i.e. it over stabilizes the HS state by about 0.4 eV[27]. This is somewhat higher than the expected chemical accuracy of 0.1 eV. Here, it should be noted that density functional theory (DFT) with several functionals have been used to benchmark the HS-LS gap of these octahedral complexes and it is found and PBE0 and OPBE functionals are best known to reproduce the *ab initio* (wavefunction based) HS-LS gaps[32–36]. Furthermore, there is severe dearth of benchmark experimental results for these quantities due to the difficulty in isolating the moieties. The best theoretical estimates have been developed from a CASPT2 scheme with correction for extra dynamic correlation[23,27].

However, extending this approach to excited states is always fraught with complications. DFT is known to underestimate the charge transfer state energies and therefore, it is expected to overestimate the effect of metal-ligand charge transfer (MLCT) nature of the transitions. This would, therefore, fundamentally change the electronic structure of the states and therefore, use of TDDFT to study the low-lying excited states may indeed give rise to spurious method dependent artefacts.

In this study we have applied active space based methods with increasing active spaces to understand the interplay of the methods and active spaces, to obtain a best estimate value of the ground and excited spin states of Fe(II) octahedral complex. As a prototype nitrogen core based octahedral complex we have chosen $[Fe(NH_3)_6]^{2+}$. The active space methods that are evaluated are CASSCF, CASPT2, *n*-electron valence perturbation (NEVPT2) and MRCI. It is to be noted that MRCI is the most robust of these approaches due to its variational approach of including dynamic correlation as opposed to the perturbative schemes, such as CASPT2 and NEVPT2. However, MRCI is computationally expensive and therefore, in our study we have compared, small active space MRCI to large active space perturbative approaches. We have further developed a computationally efficient DFT orbital based CASCI scheme.

Here, the idea is to include effective dynamic correlation in the DFT orbitals which are then strongly correlated. We compare the accuracy and limitations of this scheme.

Computational details

$[Fe(NH_3)_6]^{2+}$ complex have been optimized at the DFT level with PBE0 functional and TZVP basis set at the singlet, triplet and quintet states. These will be referred to as low spin (LS), intermediate spin (IS) and high spin (HS) states, respectively. Cartesian coordinate of optimized geometries and frequency analysis of all spin states are given in Supporting information.

The linearly interpolated internal coordinate (LIIC) approach is used to generate the structures in between the optimized HS and LS geometries. Here we generate 7 LIIC intermediate structures. These LIIC geometries are used to obtain the potential energy surface (PES) for the ground states at different spin states with PBE0 and B3LYP functionals as well as with active space based methods. Several different active spaces are used to understand its effect. The smallest active space (5o,6e) contains the 6 electrons and the 5d orbitals of the $3d^6$ Fe atom. Next, we include 5 more 4d orbitals that are vacant in the Hartree Fock level, thus making a (10o,6e) active space. It is also reported in the literature that 4s and 3d orbitals are strongly correlated and therefore can lead to significant change in the energetics, therefore an even larger (12o,10e) active space is also investigated. With all these three different active spaces, CASSCF, CASPT2 and NEVPT2 methods are used to cal-

culate the HS-LS energy difference in the ground state. State averaged (SA) CASSCF and multi state (MS) CASPT2 have been used for the ground and excited states, while state specific (SS) NEVPT2 have been used for the ground states. Finally, in order to include more metal ligand correlation at an equal footing a CASSCF of (15o,10e) largest active space is used. We have proposed and tested a DFT orbital based CASCI method for HS-LS energy difference. In this protocol, a PBE0/TZVP level of theory calculation is performed to generate KS orbitals which are then reused for CASCI calculations with appropriate active space.

Excited states with the same levels of theory are compared with the TDDFT (with B3LYP functional) excited states to understand the difference in the energetics and electronic structure of the states as determined by the various theoretical approaches. For the single point ground state and excitation energies quantum chemistry software packages, Q-Chem 5.037 and Molpro 2018[38] were used.

Results and discussion

Structure of the molecule

The optimized HS, LS and IS states of the $[Fe(NH_3)_6]^{2+}$ complex is shown in Fig. 2. As expected, the higher spin states are characterized by longer metal ligand bond lengths (2.28 Å, 2.28 Å and 2.29 Å) as compared to the other spin states. The bond lengths of the IS are 2.07 Å, 2.23 Å and 2.29 Å, and is characterized by maximally different bond lengths with inversion symmetry. The low spin is completely symmetric with 2.09 Å bond length.

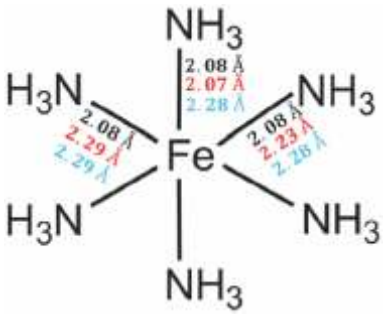

Fig. 2. Optimized structure of $[Fe(NH_3)_6]^{2+}$: black, red and blue colour signify the bond lengths in LS , IS and HS state respectively.

Active space

In complete active space based approaches, the qualitative and quantitative accuracy of the states depend strongly on the choice of the correct active spaces. This is especially true in case of SCO compounds where the different spin states are very close in energy. The orbitals involved in the various active spaces used in our study are shown in Fig. 3.

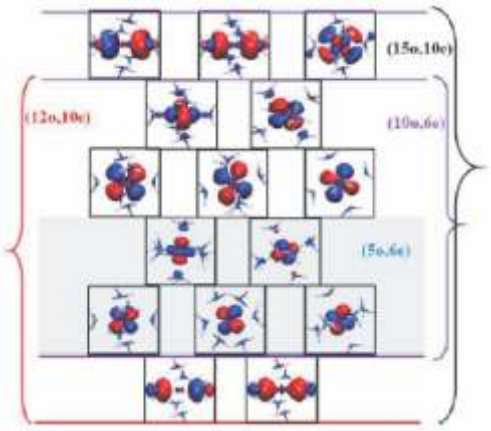

Fig. 3. Orbitals included in different active space.

One would expect naively that the minimal active space containing the most strongly correlated antibonding combination of metal 3d and ligand orbitals would be sufficient to obtain a correct qualitative picture of the spin states. When the metal ligand bonds are considered to be ionic in the limiting case, these orbitals reside completely on the metal. However, these bonds are not completely ionic, they have some covalent contribution and therefore, there are small ligand contributions in these orbitals. Pierloot[23] and co-workers have noted in their studies on 3d and higher transition metal complexes that a double shell effect is important for transition metal ions for those that have more than half filled d shell. They have shown that significant 3d-4s transition is needed to capture the exact energetics of the spin states. In order to include the double shell effect therefore, another 5 vacant 4d orbitals are included in the active space. This double shell effect is included in the (6e,10o) active space. Two e-like σ bonding orbitals are also close energetically to the d-orbitals and can therefore, be strongly correlated, which forms the (10e,12o) active space as shown in Fig. 3. Finally, three ligand virtual orbitals of π^* character are included to capture the correlated metal ligand charge transfer components of the excited states. This forms the largest (10e,15o) active space used in our calculations. This is expected to

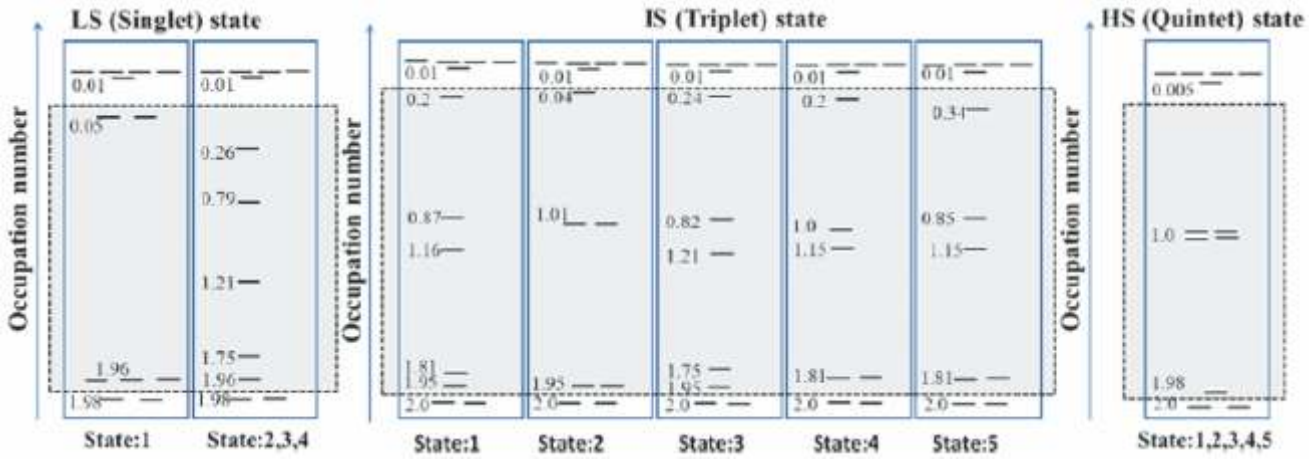

Fig. 4. Natural orbitals occupation number of excited states of HS optimized geometry for different spin states in CASSCF (12o,10e) calculation.

include all strongly correlated orbitals in the full valence space.

One can understand the importance of the different orbitals in the active space from the occupation numbers of the CASSCF natural orbitals. Fig. 4 shows the natural orbital populations of the lowest few excited states. It depicts the relative importance of the orbitals and have been shown only at the high spin optimized geometry.

Ground state

The ground state energy differences between HS and LS states (adiabatic HS-LS energy gap) at different levels of theory are shown in Table 1. It shows that the active spaces (12o,10e) and (15o,10e) are both quite adequate in depicting the energetics of the ground state. This is in accordance with our expectation since the antibonding orbitals on the ligands are not expected to play an important role in the ground state energies as corroborated by the occupation numbers of these orbitals in the ground state. However, these orbitals might well be crucial for higher excited states, especially when these excited states have a mixed MLCT character. Furthermore, we notice that dynamic correlation is important to predict the accurate energy gaps. From earlier work, the best estimate of *ab initio* HS-LS energy gap for the system at the CASPT2 and corrected CASPT2 levels of theory are around 100–131 kJ/mol[23,27]. Our results follow the same observation. As expected from earlier work, PBE0 functional is in reasonable accordance with CASPT2 results with HS-LS gap of 86 kJ/mol[22]. We have also included zero-point energy corrections to get the best estimate of HS-LS gap at 102 kJ/mol, at the DFT level of theory.

Table 1. Energy difference between HS and LS at different levels of theory for various active spaces are shown. The ZPE correction is not included

Active space	Energy differences (LS-HS) (kJ/mol)		
	CASSCF	CASPT2	NEVPT2
(5o,6e)	231	172	133
(10o,6e)	203	162	169
(12o,10e)	134	100	98
(15o,10e)	83	NA	NA

This is compared to the DFT orbital based CASCI protocol. The idea here is to have dynamically correlated orbitals (albeit from DFT) and to include the static correlation from an active space based approach. It should be noted that for large active spaces this method might suffer from double counting of correlation effects. The DFT-CASCI estimate for the adiabatic HS-LS energy difference is 143.80 kJ/mol, as compared to the best estimates of 100–131 kJ/mol. This is indeed quite encouraging, since the DFT-CASCI approach is significantly computationally efficient.

Excited state

While much of the existing literature deals with the comparison of the ground HS-LS states with complete active space based methods and that of DFT based functionals, there is relatively little that is known about the excited states at the different spin states. Table 2 shows the vertical excitation energies (VEEs) at different spin states at the stable HS geometry.

Table 2. VEEs at different spin states in various level of theory at the stable HS geometry are shown

State	Excitation energy (kJ/mol)				
	(12o,10e) CASSCF	(12o,10e) CASPT2	(5o,6e) MRCI	TDDFT	CASCI Using DFT orbitals
$^5T_{2g}$	0.00	0.00	0.00	0.00	0.00
	0.77	1.22	0.26	8.45	0.29
	0.86	1.39	0.56	11.33	11.62
^5E_g	105.97	115.52	104.00	125.86	127.39
	110.40	116.21	104.06	147.84	127.58
$^3T_{1g}/^3T_{2g}$	93.50	101.62	173.51	88.03	170.30
	93.79	104.16	174.11	96.58	180.29
	95.90	106.37	174.22	123.17	180.38
$^3T_{1g}/^3T_{2g}$	149.86	134.61	221.57	126.91	236.93
	159.94	160.79	221.81	147.84	237.12
$^1A_{1g}$	139.01	125.11*	196.69	94.08	148.42
$^1T_{2g}/^1T_{1g}$	274.94	218.58*	289.40	206.21	287.90
	275.14	218.84*	289.51	206.50	296.83
	275.52	221.96*	289.61	206.88	297.89

*In these calculations, occupied orbitals (below active space) are kept as frozen core to facilitate convergence.

The VEEs are compared for TDDFT and CASCI-DFT methods, with benchmark results from CASPT2 and MRCI. The TDDFT methods show qualitatively wrong results with almost no degenerate states and incorrect state orderings. However, since the ligand field is symmetric, certain number of degeneracies are expected and indeed observed in all multireference methods. CASSCF and CASPT2 excitation energies are in good agreement while MRCI and CASCI-DFT excitation energies agree well with each other. We expect MRCI results to be more robust than that of CASPT2. However, it should be noted that the MRCI results are with a small active space, due to its extreme computational cost. We do not expect this to a significant problem since the occupation numbers (Fig. 4), of the natural orbitals vary significantly only for the 3d-orbitals, i.e. those contained in the small active space. Since, the excitation energies from the CASCI-DFT scheme is in good agreement with MRCISD it offers a computationally efficient and accurate method for HS and LS ground and excited states.

Fig. 5a and 5b shows the comparison of the different spin state energies at CASSCF (12o,10e) and TDDFT levels of theory with B3LYP functional. While the qualitative energetic features of the HS and LS states look similar in CASSCF and TDDFT levels of theory, the IS states are quite different. In the HS quintet state, the expected near degeneracy of the ground and 2 excited states is lifted in the TDDFT level of theory possibly due to self-interaction errors. The same is true for the 3rd and 4th excited HS states. In between the lowest 3 HS states and next 2 HS states, there are many IS states that are noticed in the TDDFT calculation as opposed

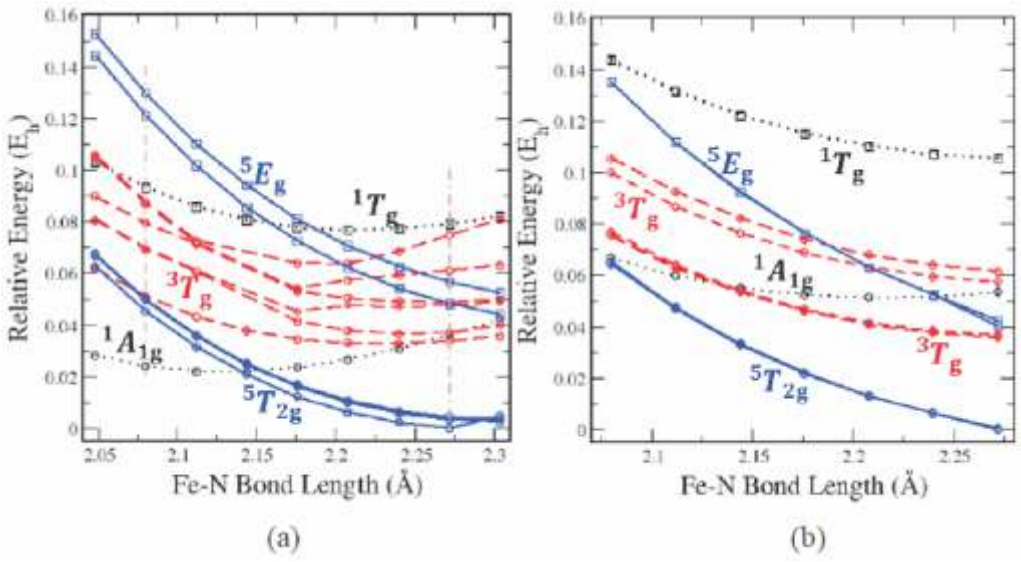

Fig. 5. LIIC-PES of $[Fe(NH_3)_6]^{2+}$: (a) with (12o,10e) SA-CASSCF using TZVP basis, (b) with TDDFT level of theory using B3LYP functional and TZV basis.

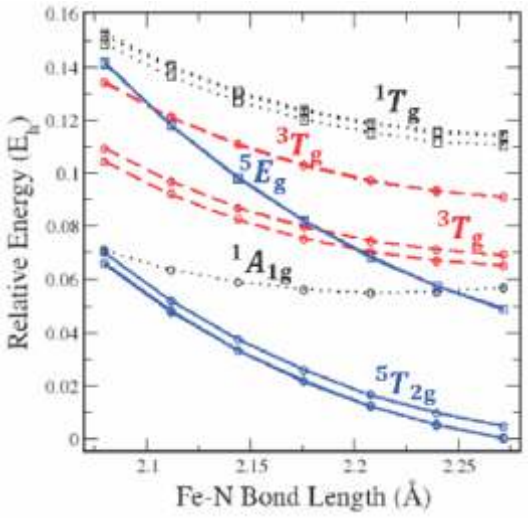

Fig.6. LIIC-PES of $[Fe(NH_3)_6]^{2+}$: (12o,10e) SA-CASSCF/TZVP using PBE0/TZVP orbitals.

to the 6 degenerate IS states in CASSCF. Again, one does expect this degeneracy in a completely symmetric ligand field. Therefore, we inspected these excited states in the TDDFT level of theory more closely. On closer inspection, it seems to include charge transfer (metal ligand) components (as shown in Supporting information). Therefore, the comparison between multireference wavefunction based methods and DFT based approaches shows that while the ground states can be depicted by some functionals, the excited states are more complicated and cannot be captured well with these same functionals. One indeed needs to resort to completely multireference approaches.

We have used the DFT-CASCI scheme to include the dynamic and static correlated excited states across the LIIC generated geometries (shown in Fig. 6). While the qualitative nature of the curves looks reasonable as compared to CASSCF, there is some lifting of degeneracies, possibly due to the use of DFT orbitals. However, much of the severe artefacts of TDDFT, such as presence of many MLCT states in the IS case is not observed for the DFT-CASCI method.

Conclusions

In this work, we have compared multireference methods with both static and dynamic correlation to DFT based approaches for estimating the HS-LS gap at the ground state. We have also used a DFT orbital based DFT-CASCI protocol to calculate these systems and the estimated adiabatic HS-LS energy gap is 143.80 kJ/mol, which is in reasonable accordance with existing theoretical estimates. Furthermore, from the comparison of different active spaces, we have shown that the double shell effect and inclusion of e-like σ bonding orbitals are imperative for qualitative and quantitative accuracy of different spin states.

For the excited states, we have shown that due to the underestimation of charge transfer excitation energies, TDDFT is not a reliable method to understand the qualitative and quantitative electronic structure of the lowest few excited spin states in such SCO molecules. Both static and dynamic correlations are crucial to the accurate estimation of the energetics of the excited states. Finally, the DFT-CASCI approach was shown to be a computationally affordable alternative to the more computationally demanding CASPT2 calculations for ground and excited states. Work is in progress to understand the limitations of the approach and therefore, improve the approach.

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Supporting information

The supporting information is available.

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