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Excited electronic states of MnO_4^-: Challenges for wavefunction and density functional response theories

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ABSTRACT

The lowest excited electronic states of the permanganate ion MnO_4^- are calculated using a hierarchy of coupled cluster response approaches, as well as time-dependent density functional theory. It is shown that while full linear response coupled cluster with singles and doubles (or higher) performs well, that permanganate represents a stern test for approximate coupled cluster response models, and that problems can be traced to very large orbital relaxation effects. TD-DFT is reasonably robust although errors around 0.6 eV are still observed. In order to further investigate the strong correlations prevalent in the electronic ground state large-scale RASSCF calculations were also performed. Again very large orbital relaxation in the correlated wavefunction is observed. Although the system can qualitatively be described by a single configuration, multi-reference diagnostic values show that care must be taken in this and similar metal complexes.

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1. Introduction

The theoretical study of the excited states of transition metal complexes has, over previous years, presented a particular challenge to researchers due to the complex nature of the electronic spectra of many transition metal compounds. A high density of states, of often different chemical character in a narrow energy range, gives rise to broad–featureless experimental spectra [1,2]. We have previously shown how the supposedly simple TiO_2 molecule is challenging to describe [3]. The challenges when trying to accurately study the electronic excited states of transition metal complexes present a hurdle on the path to fully understanding the rich and varied reactive photochemistry that many transition metal complexes display, with more cases being reported regularly, see for example [4–11]. There are also a number of well-known complexes that despite their modest size and simple structure have been classed as 'tough' examples when trying to fully understand the nature of their ground and electronic excited states due to often poor agreement between many theoretical methods and experiment [12]. It is not always clear when such difficulties will be encountered. One such case that is the subject of this study is the permanganate ion, MnO_4^- [13–20]. This d^0 complex is a very well investigated molecule in chemical research, across many different areas, going back as far as the 1930s [21,22]. A number of studies have been published concerning a theoretical treatment of its ground and excited electronic states. A large range of theoretical studies exist in the literature including older studies based in Hartree–Fock [23], post Hartree–Fock [24], and older density functional theory (DFT) methods, [25] and a time-dependent-DFT (TD-DFT) treatment has also been performed [14,26–29]. A study including a combination of coupled cluster theories and perturbation theory, including EOM-CCSD, has also been reported by Nooijen [30].

One of the most recent and comprehensive studies of this system was reported by Jose et al. [31] in which they use a DFT approach in which they analyse the excitation energies and oscillator strengths of the lowest excited bright states and also optimise the structures of these states and study their vibrational modes, generating vibronically resolved spectra via the Frank–Condon approximation. It was found that the optimised structures of the first three excited states were distorted from the tetrahedral ground state structure with the first excited state having C_{3v} symmetry, the second C_{2v} and the third D_{2d} symmetry. The authors believed these states were fluxional with distortions occurring via Jahn–Teller distortions. Indeed Jahn–Teller distortions could be expected for this highly symmetric system as the nature of the excitations involves transitions amongst orbitally degenerate frontier orbitals. The natures of the transitions that make up the second and third experimental bands were found to mix strongly with each other. This feature is rather common to the electronic excited states of many transition metal complexes and it is the

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ability of their excited states to mix in different ways that allows some of the most varied and rich photochemistry to take place, see for example [32–35].

The hierarchy of coupled cluster response methods [36–41] are a group of methods for studying electronic excited states that have a number of beneficial features such as the ability to treat excited states of different chemical character on a equal footing, where unlike methods such as complete active space self-consistent field (CASSCF), and CAS with a second-order perturbation treatment of dynamical correlation (e.g., CASPT2) an active space of orbitals does not need to be specified *a priori*. So far these methods have found much success when applied to organic systems, see for example [42,43], but the performance of the lower cost CC2 method, and to some extent the higher cost CC3 method has been found to be poor when applied to some transition metal systems [3,44].

Given the current ambiguities surrounding the state ordering and nature of the initial excited electronic states of MnO_4^-, and its importance as a paradigm metal oxide complex, we aim to apply the hierarchy of coupled cluster response methods along with large scale CASSCF, and the related restricted active space self-consistent field (RASSCF) method, and TD-DFT using modern Coulomb attenuated functionals (here CAM-B3LYP [45,46]) to this system, most of these for the first time. Secondly we wish to use CASSCF and RASSCF to determine the nature of the electronic structure of the ground electronic state of MnO_4^-, and detail the balance of static and dynamic correlation present, and to understand orbital relaxation in the ground state. The purpose of applying CC2 and CC3 response methods to understand the performance of these popular correlated excited state treatments to a paradigm molecule such as MnO_4^-, where some of the previous preliminary results indicate that transition metal oxides molecules and clusters present significant challenges. We also hope that this detailed set of results for the lowest excitations in MnO_4^- will help to resolve some of the current ambiguities regarding the ordering of the initial excited states of this system. Finally we also look to compare these methods with modern Coulomb attenuated density functionals (CAM-B3LYP) that have been developed to describe charge transfer excitations within TD-DFT, which should be paramount in describing the LMCT states in a d^0 oxide complex.

2. Computational details

MnO_4^- was optimised in its ground electronic state ($^1A_1$) with tetrahedral (T_d) symmetry using a variety of double and triple zeta quality all electron basis sets in conjunction with Hartree–Fock, coupled cluster singles and doubles (CCSD), and Bruckner doubles (BD) wavefunction methods, together with a variety of density functionals. All optimised structures were confirmed as minima via frequency calculations (analytical if available, otherwise numerical).

The optimised structure at the B3LYP/aug-cc-pVTZ level was then used to perform calculations of the lowest electronic singlet excited states with the coupled cluster linear response (LR) coupled cluster hierarchy CCS, CC2, CCSD and CC3, along with perturbative corrected methods CIS(D) and CCSDR(3). The correlated response methods were performed with an all-electron atomic natural orbital (ANO) basis set contracted to 6s5p4d3f1g on manganese, [47] together with the cc-pVTZ basis set on the oxygen atoms. The all-electron correlated calculations invoked a 13 orbital frozen core (O 1s, Mn 1s2s2p3s3p). Trial calculations correlating these orbitals only had a minor effect on excitation energies. For comparison the EOM-CCSD method with the cc-pVTZ basis on all atoms was tested to compare with LR-CCSD. These formally give exactly the same excitation energies, although the transition moments are more accurate for LR-CCSD. Abelian symmetry (D_2) was used in all correlated excited state calculations.

A wide variety of CC methods have been developed over the years in order to retain the overall accuracy of the cluster expansion while reducing the computational scaling. Most of these ideas are inspired by many-body perturbation theory in which terms in the cluster equations are evaluated or discarded depending on the order in which they contribute to the correlation energy. For electronic ground states the most well known approximation is the CCSD(T) approach in which CCSD equations are solved and the resulting singles and doubles amplitudes are used in the triples equations from perturbation theory. This reduces the N^8 scaling of full CCSDT to N^7, allowing triples correlated calculations to be routinely performed for the ground states of small to medium sized molecules. There exist a similarly rich variety of CC approximations for electronically excited states as obtained from response function theory [30,36,37,39–41]. However, a simple correlation contribution analysis is complicated by virtue of the fact that in the absence of the external perturbation of response theory the singles contribute to the correlation energy (via Brillouin's Theorem) at second order and above, but contribute at zeroth order when the external perturbation is present. Thus, for a balanced description of singles the CCn methods have been developed in which singles amplitudes are used to similarity transform all operators, and then this modified order counting (keeping only the lowest non-vanishing order) is performed on the doubles equation of CCSD to give CC2 [40,41], triples equation of CCSDT to give CC3 [39], etc. These have scalings of N^5 and N^7 respectively, and together with the full CC methods generate a systematic hierarchy of CCS, CC2, CCSD, CC3, CCSDT,..., with each one giving response functions correct to the next order in the fluctuation potential [41]. For ground electronic states one can think of CC2 and CC3 as similar to MP2 and CCSD(T) respectively, but with the addition of orbital relaxation. For excited states calculated via response functions the CCn methods provide a balanced systematic series applicable to a wide range of molecules. Indeed, for organic systems this hierarchy has proved exceptionally valuable in benchmarking a plethora of excited state approaches [42,43]. However, for certain inorganic molecules we have shown that the same levels of accuracy may not be obtained and the nature of the electron correlation in the ground (reference) state the Refs. [3,4].

Within time-dependent density functional theory (TD-DFT) the excited states were calculated using the B3LYP and the CAM-B3LYP functionals, also with the cc-pVTZ basis. CAM-B3LYP was designed to more correctly describe charge transfer (CT) states by varying the amount of exact Hartree–Fock exchange with inter-electronic distance to give a better long range potential, known to be important for CT states [45,46].

In order to examine the nature of the electronic ground state in more detail restricted active space self-consistent field (RASSCF) calculations were performed using an overall active space comprising of 40 electrons and 39 orbitals partitioned into a 17 orbital RAS1, 9 orbital RAS2, and 13 orbital RAS3. The RAS1 space consists of those orbitals strongly occupied outside the doubly occupied set and we find that 17 orbitals are required here. The orbital occupancies (diagonal elements of the one electron density matrix) for the RASSCF orbitals are given in Table S1 in supporting information. The RAS2 space includes those orbitals that are partially occupied, the degree of partial occupancy indicating how much multi-configurational character there is in the wavefunction. Finally the RAS3 space contains weakly occupied orbitals. All excitations are allowed in RAS2, while single particle and holes and allowed in RAS3 and RAS1 respectively. This generates 2,984,730 singlet configurations using Slater determinants as the many electron basis functions. Although the orbitals in the respective restricted space partitions are invariant to separate unitary transformations it is

none the less instructive to compare the canonical Hartree–Fock orbitals with converged RAS(40,39,1,1) orbitals (initialised using the RHF guess).

DFT, TD-DFT, CASSCF, RASSCF, ground state CCSD and BD, and excited state EOM-CCSD were performed using the Gaussian 09 program [48], while LR-CC excited state calculations were performed with Dalton 2.0 [49,50].

3. Results and discussion

3.1. Geometry optimisation

The results of the geometry optimisation of MnO_4^- with various methods and one-electron bases are shown in Table 1. The Hartree–Fock Mn–O bond-length is significantly shorter than the experimental value of 1.629 Å. We see that CCSD also underestimates the bond length though by less than Hartree–Fock. Bruckner doubles performs slightly better than CCSD in the same cc-pVTZ basis. This can be explained by a degree of multireference character of the ground state and the large single-particle orbital relaxation as discussed in more detail below. DFT without any exact exchange performs best as the correlation functional and exchange give opposing increased and decreased binding respectively, thus BP86 fortuitously gets close to experiment.

3.2. Wavefunction response theory results

Table 2 presents the computed results for the lowest energy excited states of the permanganate ion for wavefunction response theory.

The lowest cost method CCS (equivalent to CIS for excited state wavefunctions), and its doubles perturbed variant CIS(D) (also know as CC(2)) greatly overestimate the excitation energies of these states, sometimes by several eV. We see here that the underlying single-particle orbital picture struggles with these states due to the strong correlation in the electronic ground state (by strong correlation we mean that the orbital picture from a single-configuration is qualitatively incorrect, and that a multi-configurational picture is required to generate appropriate zeroth order one-particle orbitals). As we discuss below this causes severe problems in methods that use the $\hat{T}_1$ operators to "dress" all operators via a similarity transformation in reduced cost coupled cluster response methods such as CC2 and CC3 [37–41]. The single-particle picture does qualitatively describe the nature of the states, although for the higher excited states the amount of mixing of configurations is rather inaccurate relative to correlated methods (Inc. TD-DFT).

Table 1
Geometrical parameters of the permanganate anion computed with different methods and basis sets. (T_d angles = 109.5°).

Method	Basis set	Mn–O distance (Å)
HF	cc-pVTZ	1.542
BP86	cc-pVTZ	1.621
M062X	cc-pVTZ	1.573
M06HF	cc-pVTZ	1.554
M06L	cc-pVTZ	1.607
B3LYP	cc-pVTZ	1.601
B3LYP	aug-cc-pVTZ	1.602
CCSD	6-31G(d)	1.594
CCSD	6-311G(d)	1.576
CCSD	cc-pVDZ	1.601
CCSD	cc-pVTZ	1.575
BD	cc-pVTZ	1.590
Experimental [51]	–	1.629

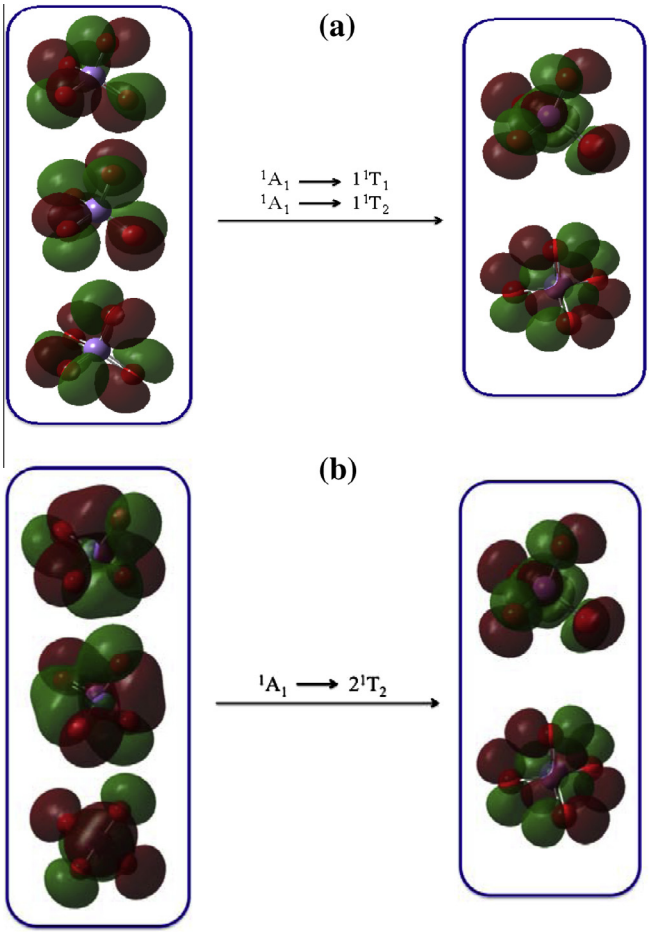

Fig. 1. Hartree–Fock orbitals involved in the dominant configurations of (a) the first two excited states (1^1T1 and 1^1T_2), and (b) the third excited state (2^1T_2) as computed with EOM-CCSD.

The best performance of the correlated response methods is seen to be LR-CCSD or equivalently EOM-CCSD. Deviations from experimental peaks of around 0.2 eV for the first two states, and 0.4 eV for the third state are observed. The intensity pattern is also reproduced regarding the bright second and third excited states. The oscillator strength for the 2^1T_2 state does differ a little comparing LR-CCSD and EOM-CCSD. These differ slightly in calculating transition moments (LR-CCSD being slightly more accurate using relaxed density matrices). The dominant orbitals involved in the response eigenvectors for the first three states are shown in Fig. 1. There are appropriate $T \otimes e$ symmetry adapted combinations of these for each, which are not shown. The LR-CCSD results also qualitatively match the previous DFT calculations. [31]

Table 2
Excitation energies in eV (and oscillator strengths) of the lowest electronic excited states using a range of many-body wavefunction based response theories. ANO (6s3p4d3f1g) for Mn, cc-pVTZ for O with CC response methods, cc-pVTZ for Mn and O with EOM-CCSD.

State	Character	CCS	CIS (D)	CC2	LR-CCSD	EOM-CCSD	CC3	Experiment [24]
1^1T_1	LMCT	3.791 (0.00000)	2.730	0.489 (0.00000)	1.944 (0.00000)	1.926 (0.00000)	1.041	1.71–1.77
1^1T_2	LMCT	3.846 (0.00127)	3.033	0.184 (−0.0342)	2.404 (0.01030)	2.461 (0.01450)	−0.344	2.27 (Strong)
2^1T_2	LMCT	4.588 (0.00224)	3.742	1.861 (−0.02970)	3.871 (0.00253)	3.862 (0.00080)	1.387	3.47 (Weak)

We now turn our attention to approximate coupled cluster (CC) methods. Here we see that MnO_4^- provides an example of a strongly correlated inorganic system, *vide supra,* where both CC2 and CC3 have severe problems with the lowest valence states (Table 2). For the lowest three excited states CC2 excitation energies are too low by several eV, and provide negative unphysical oscillator strengths. Rather counter intuitively though CC3 also gives unphysical results with negative excitation energy for the 1^1T_2 state, and excitations out by 1–2 eV for 1^1T_1 and 2^1T_2. The latter two are methodologically incorrect given the accuracy of the corresponding LR-CCSD (or EOM-CCSD). These results can be traced to the CCn approximations (see computational details). The orbital relaxation, via the T1 amplitudes, is so large here that the singles treatment in CC2 and CC3 give rise to unphysical response functions, despite the underlying qualitatively correct CCS and CCSD amplitudes. The very large difference between LR-CCS and LR-CCSD excitation energies is indicative of problems that may exist in CC2 and CC3 treatments.

One may think of the large T1 amplitudes as being indicative of multi-reference character. This forms the basis of the well-known CC T1 diagnostic of Lee and co-workers [52]. A value above 0.02 is generally taken to be indicative of some multireference character in the ground state. The values for the CCSD T1 diagnostic for MnO_4^- are insensitive to basis set (0.060 for 6-31G(d), 0.058, cc-pVTZ, and 0.059 for aug-cc-pVTZ). We calculate and analyse multi-configurational wavefunctions below. Care must be taken to distinguish the effects of true multi-reference character and orbital relaxation effects. These are not entirely synonymous as the very good performance of LR-CCSD (or EOM-CCSD) and TD-DFT shows. As we discuss below, MnO_4^- is qualitatively described by a single electron configuration but configurations involving electron transfer from O to Mn do have significant combined weight, but not so

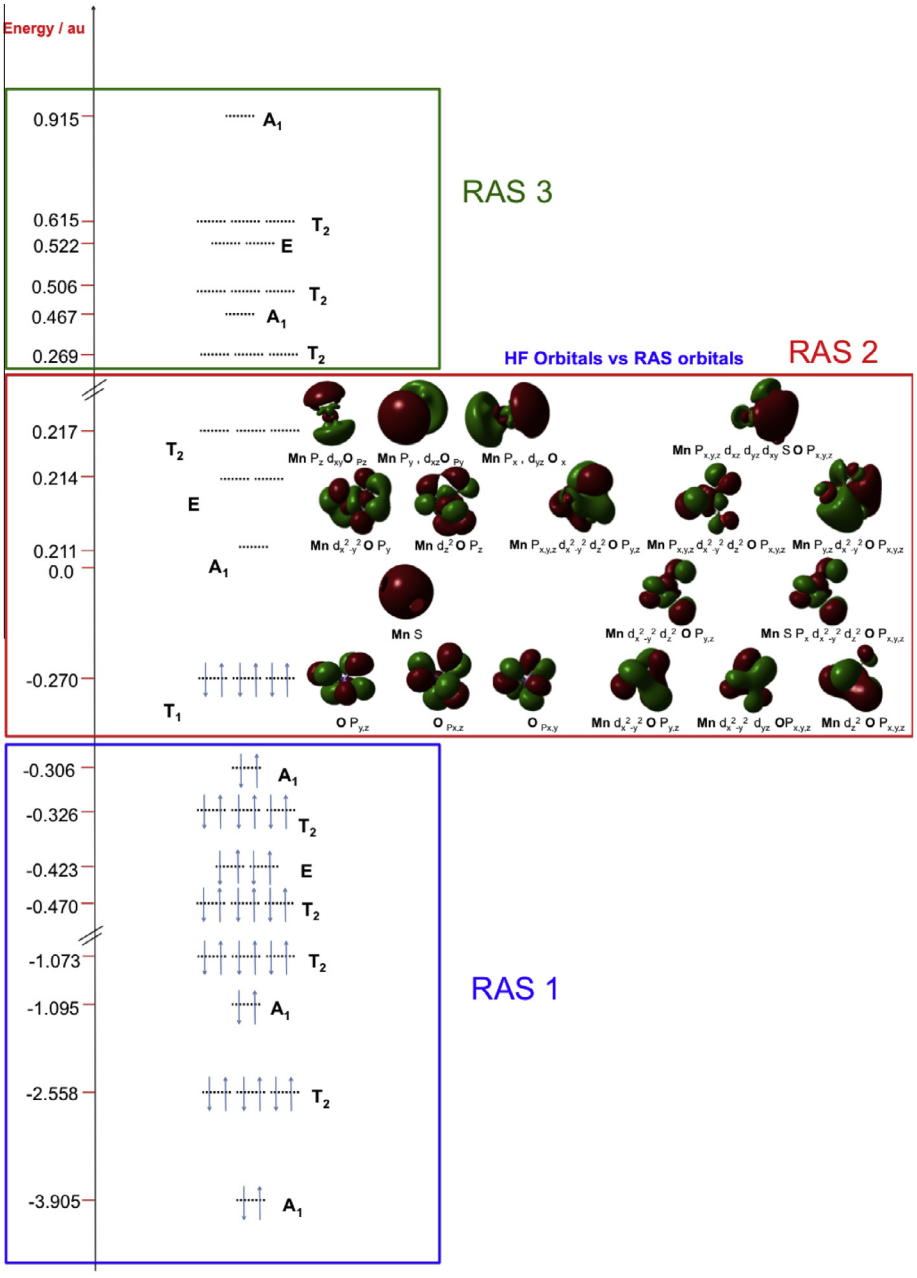

Fig. 2. Quantitative molecular orbital diagram of MnO_4^- showing both canonical Hartree–Fock frontier orbitals, together with schematic RASSCF orbital partitioning.

much as to completely invalidate a single reference treatment. The poor one-electron canonical Hartree–Fock molecular orbitals (in the sense of being very different in shape from MC-SCF ones) are far more important, and can be used in a robust treatment involving the full LR-CC equations, but present massive problems when used as part of an approximate CCn method.

The CIS(D) model [53] is related to the CC2 model. In fact it involves a non-iterative doubles correction from perturbation theory to CCS and is therefore sometimes known as CC(2). This is analogous to the CCSDR(3) non-iterative triples correction to excitation energies relative to the CC3 model [9]. Interestingly the CIS(D) is qualitative and even semi-quantitative for the lowest LMCT excitation energies here. Thus, despite the poor orbital description, and consequent large orbital relaxation the non-iterative variant of CC2 actually performs quite well, and the doubles correction uniformly lowers the excitation energies by ~0.8–1 eV. We also note for completeness that the non-iterative CCSDR(3) approximation [9] to CC3 excitation energies gives 3.491 eV for the highly unphysical CC3 1^1T_2 state.

The assignment of the experimental absorption bands is still somewhat ambiguous. The general consensus regarding the first excited state is qualitatively arising from the t_1 HOMO to the e LUMO transition (see Figs. 1 and 2 below). Different assignments of the second and third bands have been proposed over the years with the most recently reported DFT calculations on this system [31] showing that they are of mixed character with both bands arising principally from t_2 HOMO − 1 to e LUMO and t_1 HOMO to t_2 LUMO + 1 transitions. The former transition was found to be the dominant contribution to the second band, while the latter transition the dominant contribution to the third band. It should also be noted that direct comparison with experiment is entirely straightforward, as the centre of the absorption band may not always relate to the vertical transition as is computed here. With this caveat in mind we will now discuss the excitation energies for the system as computed by LR-CC methods.

Fig. 1a and b show the dominant particle-hole orbitals involved for the lowest three excited states with EOM-CCSD (there are several symmetry equivalent large amplitudes for each excitation among degenerate sets of orbitals). These depict ligand-to-metal charge transfer character for first three excited states.

3.3. CASSCF and RASSCF results

In order to further explore why the approximate LR-CC methods may have problems we have further examined the ground electronic state using large-scale RASSCF. In principle complete active space self-consistent field (CASSCF) calculations for the ground state can detail the importance of orbital optimisation to a the given configuration interaction expansion wavefunction, and can provide insight into the nature of electron correlation as primarily static or dynamic, and what electron configurations are qualitatively important to describe the electronic state. However, while a small frontier orbital based active space is apparent for MnO_4^-, consisting of the highest occupied oxygen p orbitals and the unoccupied manganese d set (partially hybridised), as shown by the RAS2 space in Fig. 2, such a wavefunction poorly describes the system as the correlation treatment is unbalanced between static and dynamic correlation. By selectively expanding the active space from this to include more occupied and virtual sets to increase the amount of correlation included in the wavefunction of the ground state, it is apparent that a RASSCF treatment is appropriate and that the orbital space and be partitioned as shown in Fig. 2. It is clear in Fig. 2 that the optimal RASSCF orbitals are fairly different than the RHF ones, and that a significant amount of mixing between the oxygen and manganese centred orbitals takes place. The RASSCF wavefunction has one dominant configuration accounting for ~73%. However, it is clear that some electron density has been transferred from the oxygens onto the Mn 3d and 4s set through both orbital relaxation and electronic configurations involving occupancy of these orbitals (~0.2 electrons in a pair of orbitals having large amplitude for 3d functions). Such a description of the ground state electronic structure is consistent with other recent theoretical treatments [31]. Interestingly, despite the obvious partitioning suggested by selectively expanding CASSCF wavefunctions into restricted active spaces, upon optimisation of the full RAS (40,39,1,1) wavefunction we observe that certain RAS1 and RAS3 orbitals have occupancies suggestive of importance in multi-configurational wavefunctions (1.986 and 1.974 in RAS1, and 0.034 in RAS3). Such occupancies are borderline between strongly/weakly occupied and partially occupied, and indicate that the orbital relaxation achieved from the single particle/hole excitations in the external restricted active spaces is very important.

Orbital relaxation can also be investigated within coupled cluster theory by transforming to a Bruckner wavefunction, in which the singles amplitudes are rigorously zero. Bruckner variants of coupled cluster theory have been found to be more stable in cases involving symmetry breaking. Here we calculate the ground state wavefunction for MnO_4^-. Unsurprisingly we observe some orbital relaxation; the Bruckner orbitals differing from the canonical Hartree–Fock ones and showing a certain degree of mixing between metal and oxygen orbitals (although less than the RASSCF orbitals discussed above). As discussed above the optimised geometry for BD, compared to CCSD, is slightly better compared to experiment (Table 1).

3.4. TD-DFT results

Our TD-DFT results are listed in Table 3.

Unlike correlated wavefunction methods TD-DFT has been extensively applied to this system so we will limit our discussion here to more recent results. Van Gisbergen et al. performed an extensive study comparing different TD-DFT methods in transition metals for MnO_4^-, $Ni(CO)_4$ and $Mn_2(CO)_{10}$ [29]. They obtained the first four $^1T_2$ excited states at 2.82 eV, 3.89 eV, 4.74 eV and 5.84 eV using the BP functional, and 2.63 eV, 3.60 eV, 4.52 eV and 5.46 eV for LB94. Neugebauer et al. used TD-DFT to calculate the vibronic structure of the permanganate ion with a range of different basis sets [14]. The results for the first four $^1T_2$ states, using a triple zeta basis with two added polarisations (TZ2P) has an error of around 0.7 eV when compared to experiment. When using an even larger basis set, the error changed little (0.6 eV for QZ3P). As discussed above Zeigler et al. used TD-DFT to calculate the electronic transitions in the d^0 tetroxo complexes: MnO_4^-, TcO_4^-, RuO_4 and OsO_4. The calculations were performed using VWN with a TZ2P basis set including scalar relativistic effects with the zeroth order regularised approximation (ZORA). The first three $^1T_2$ vertical and 0–0 excitation energies were calculated. Vertical energies of 3.11 eV, 4.16 eV and 5.12 eV are quite close to our results in Table 3 for both TD-B3LYP and TD-CAM-B3LYP. Our results have an error of 0.6–0.7 eV for both of these functionals. Again we see that they are relatively insensitive to the basis set quality.

Interestingly, although the transitions involved are all formally LMCT from the electron rich oxygens to the d^0 metal (Fig. 1) there

Table 3
Excitation energies in eV (and oscillator strengths) of the lowest electronic excited states using TD-DFT. cc-pVTZ for Mn and O.

State	Character	TD-B3LYP	TD-CAM-B3LYP	Experiment [24]
1^1T_1	LMCT	2.498 (0.00000)	2.393 (0.00000)	1.71–1.77
1^1T_2	LMCT	3.025 (0.00710)	2.986 (0.00770)	2.27 (Strong)
2^1T_2	LMCT	4.179 (0.00140)	4.194 (0.00070)	3.47 (Weak)
3^1T_2	LMCT	4.716 (0.00800)	4.594 (0.00770)	3.99 (Strong)

are only small differences between TD-B3LYP and TD-CAM-B3LYP excitation energies (Table 3). This is probably due to the fact that metal and oxygen orbitals are considerably mixed, and in actual fact only a very small amount of overall charge is transferred, and only over a small distance, thus the differences between the B3LYP and CAM-B3LYP long-range exchange potentials are not really important in describing these states.

4. Conclusions

We have examined the ground and excited state electronic structure of the permanganate anion using a wide variety of electronic structure methods including RASSCF for the ground state, and linear response coupled cluster for the excited states. Many of these methods were applied to this system for the first time in the literature. This paradigm inorganic molecule provides a fascinating test bed of excited state electronic structure methods. When addressing the second aim of this paper of using CASSCF and RASSCF to determine the nature of the electronic structure of the ground electronic state of MnO_4^-, and detail the balance of static and dynamic correlation present, it was found that MnO_4^- can be approximately described by a single electron configuration although the canonical Hartree–Fock orbitals provide a very poor description of the system. This system represents a case where care must be taken to distinguish the (slightly) different notions of static and strong electron correlation, *vide supra*. Multi-reference diagnostics indicate some multi-configurational character in the ground electronic state, although coupled cluster and density functional theories describe the ground state reasonably well. Additionally the low-lying valence excited states are well described via response theory for these full coupled cluster and DFT references. However, the strong ground state correlation (large singles amplitudes and very poor uncorrelated treatment of excited states) causes severe methodological problems for approximate CC response methods. Care therefore must be taken when applying approximate coupled cluster response to such inorganic complexes.

Conflict of interest

There are no conflicts of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemphys.2014.11.011.

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