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MnO$^+$: a challenge for density functional theory methods

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Abstract. The $^5\Sigma^+$ and $^5\Pi$ states of MnO$^+$ are studied using density functional theory (DFT) and the complete-active-space self-consistent-field (CASSCF)/multireference configuration interaction (MRCI) and CASSCF/average coupled pair functional (ACPF) levels of theory. All the DFT methods give a reasonable description of the $^5\Sigma^+$ state, but only the hybrid functionals give $^5\Pi$ spectroscopic constants that agree with those obtained using the MRCI and ACPF approaches. The origin of the difference between the pure and hybrid functionals is discussed.

Key words: Density functional theory – Complete-active-space self-consistent-field – Multireference configuration interaction – MnO$^+$

1 Introduction

Density functional theory (DFT) has become one of the most commonly used techniques in computational chemistry. In general, the hybrid [1] functionals yield the most reliable results for molecules containing first- and second-row atoms. For transition-metal-containing systems, the functional of choice is not as obvious. For example, Barden et al. [2] found that the functional of choice varied with the metal for the 3*d* transition-metal dimers. Another example is the MCO species. For MnCO and MnCO$^-$, the hybrid B3LYP [3] functional predicts Π ground states with vibrational frequencies that agree with experimental observations [4], while the BP86 [5, 6] functional predicts Σ^- ground states with vibrational frequencies that do not agree well with experiment. This is in contrast to many other MCO species where the BP86 vibrational frequencies agree better with experiment than do the B3LYP values [7]. We found several other examples where the hybrid functionals favor a Π state, while the pure functionals favor a Σ state, and here we discuss one of these cases, MnO$^+$, where hybrid functionals predict a $^5\Pi$ ground state with spectroscopic constants that agree well with those obtained by the configuration interaction (CI) approach, while the pure functionals yield virtually degenerate $^5\Pi$ and $^5\Sigma^+$ states, with $^5\Pi$ spectroscopic constants that do not agree well with CI results. MnO$^+$ is sufficiently simple that it is possible to perform accurate calculations and analyze the bonding. Finally, we should note that in their study of the metal monoxide cations, Nakao et al. [8] noted that the DFT r_e values for MnO$^+$ did not agree well with those obtained by CI methods.

2 Methods

Our highest levels of theory include the internally contracted [9, 10] multireference configuration interaction (IC-MRCI) approach and the IC averaged coupled pair functional [11] (IC-ACPF) method. In the IC-MRCI approach, the effect of higher excitations is estimated using a MR analog of the Davidson correction, and is denoted IC-MRCI + Q. In the MRCI and ACPF calculations, the orbitals are determined using the complete-active-space self-consistent-field (CASSCF) approach, with the manganese 3*d* and 4*s* and oxygen 2*p* orbitals in the active space. In addition to the active orbitals, the oxygen 2*s* orbital is also correlated in the IC-MRCI and IC-ACPF treatments; however, only the CASSCF configurations are used as references, i.e., the oxygen 2*s* orbital is in the inactive space.

In the DFT calculations, we consider several different functionals as implemented in Gaussian98 [12]: hybrid [1] B3LYP [3], hybrid PBE1PBE [13, 14, 15], BP86 [5, 6], BLYP [5, 16], BPW91[5, 17], and PBEPBE [15].

In the MRCI and ACPF calculations, we used the Mn (20s15p10d6f4g)/[7s6p4d3f2g] averaged atomic natural orbital (AANO) basis set [18] and the oxygen augmented correlation consistent polarized valence triple zeta (aug-cc-pVTZ) set [19, 20], while in the DFT calculations, we used the 6-311 + G* basis sets [21, 22, 23, 24]. Using the same basis set for both the MRCI and DFT approaches would eliminate any questions of differences arising from the use of different basis sets. Since the basis set requirements are much more severe for the MRCI approaches than for the DFT approaches, this would require using the AANO/aug-cc-pVTZ set in the DFT calculations. This change in the basis set leads to very much longer calculations. For example, the B3LYP calculation on the $^5\Pi$ state increases from about 20 min using the 6-311 + G* set to 2.5 days using the AANO/aug-cc-pVTZ set, but

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with only a small change in results; the bond length is unchanged and the vibrational frequency is increased by 13 cm^{-1}. In addition, the 6-311+G* set is more representative of sets used in DFT calculations. For these reasons, we used different sets for the MRCI-based and DFT-based approaches.

We analyze the bonding using Mulliken populations, which are dependent on the basis set used; however, we are interested in changes between the two states and changes between the different methods, and the Mulliken populations should be sufficient for this purpose.

The CASSCF/IC-MRCI and CASSCF/IC-ACPF calculations were performed using Molpro [25], while the DFT calculations were performed using the Gaussian 98 program [12].

3 Results and discussion

We summarize our computed results in Table 1. We first note that the IC-MRCI + Q and IC-ACPF values are very similar. The $^5\Pi$ state is computed to be about 2000 cm^{-1} below the $^5\Sigma^+$ state. This separation is somewhat smaller than that reported by Nakao et al. [8] at the MRCI level using a smaller basis set. The $^5\Pi$ IC-MRCI + Q and IC-ACPF bond lengths are longer and the harmonic frequencies lower than those found for the $^5\Sigma^+$ state. We note that the $^5\Pi$ vibrational frequency of Nakao et al. is significantly higher than our value. Our computed D_0 value is about 15 kcal mol^{-1} smaller than that obtained by experiment [26]. This is somewhat larger than expected, but higher levels of theory would be expected to increase the computed value, reducing the disagreement with experiment.

The two hybrid approaches are in reasonable agreement with the IC-MRCI + Q and IC-ACPF approaches. While the B3LYP T_0 value agrees better with the traditional approaches than does the PBE1PBE value, the PBE1PBE dissociation energy agrees better with the traditional approaches. We note that the B3LYP D_0 value is in reasonable agreement with that obtained by experiment. The B3LYP frequencies are both too large, while the PBE1PBE functional yields a $^5\Sigma^+$ value that is smaller but a $^5\Pi$ value that is larger than the IC-MRCI + Q or IC-ACPF values.

An inspection of the results obtained using the pure functionals shows that the $^5\Sigma^+$ r_e values agree well with the hybrid functionals and traditional methods, but the pure functionals yield ω_e values that are a bit larger. Unlike the $^5\Sigma^+$ state, the $^5\Pi$ results do not agree well with the traditional methods; the ω_e values are too large and the r_e values are too small. The pure functionals yield much larger D_0 values and much smaller T_0 values. Note that the BLYP approach actually places the $^5\Sigma^+$ state below $^5\Pi$; it is only after the inclusion of zero-point energy that the ground state is $^5\Pi$. The D_0 values are significantly larger than those obtained by experiment, but the error is no larger than that found at the IC-MRCI + Q and IC-ACPF levels.

We now consider the origin of the difference in the description of the two states between the pure and hybrid functionals. The $^5\Sigma^+$ state cannot be formed from Mn$^+$ and O if both are in their ground states, and therefore this state is probably best viewed as arising from Mn^{2+} $3d^5$ and O$^-$ $p\sigma^1 p\pi^4$ with σ and π bonds forming, which leads to a valence orbital occupation of $\sigma^2\pi^4\pi^{*2}\delta^2$. The $^5\Pi$ state can be viewed as arising from Mn$^+$ $3d^5 4s^1$ + O $p\sigma^1 p\pi^3$ with σ and π bonds forming, leading to a valence occupation of $\sigma^2\sigma^1\pi^4\pi^{*1}\delta^2$. The $^5\Pi$ state can also be viewed as arising from Mn^{2+} and O$^-$ $p\sigma^2 p\pi^3$, but the Mn net and 4*s* populations appear more consistent with the Mn$^+$ + O$^-$ view (Table 2).

The B3LYP and BPW91 $\alpha + \beta$ populations are similar for both the $^5\Pi$ and $^5\Sigma^+$ states. The $^5\Sigma^+$ state has more charge transfer from the manganese to the oxygen and a higher Mn 3*d* population than the $^5\Pi$ state. The larger charge transfer is consistent with the view that the $^5\Sigma^+$ state is best viewed as arising from Mn^{2+} + O$^-$. In addition to these differences in the $\alpha + \beta$ populations, the $\alpha - \beta$ populations show that the Mn 3*d* open-shell character is greater for the $^5\Pi$ state. The larger α population on the Mn is compensated by a β population in the oxygen 2$p\pi$ orbital, i.e., a good bonding orbital with similar α and β components does not form, but owing to the small overlap, a weak bond is formed, with one component mostly on the Mn and the other mostly on the O. Another way to view this is that the $^5\Pi$ state has some antiferromagnetic coupling of the 3$d\pi$ and 2$p\pi$ orbitals. In the CASSCF wave functions this weak bonding shows up as some MR character, with the occupations $\pi^4\pi^{*1}$, $\pi^3\pi^{*2}$, and $\pi^2\pi^{*3}$ all having significant weight. We should note that spin polarization occurs for the σ orbital of the $^5\Sigma^+$ state, but the magnitude is smaller than for the π orbitals in the $^5\Pi$ state.

The question "does the difference between the pure and hybrid functionals arise from the extra ionic character or larger 3*d* population in the $^5\Sigma^+$ state or from the larger α

Table 1. Summary of computed results for MnO$^+$

	r_e (Å)		ω_e (cm^{-1})		D_0 (kcal/mol)	T_0 (cm^{-1})
	$^5\Pi$	$^5\Sigma^+$	$^5\Pi$	$^5\Sigma^+$	$^5\Pi$	$^5\Sigma^+ - {}^5\Pi$
IC-MRCI + Q	1.753	1.618	599	901	53.81	1955
IC-ACPF	1.755	1.618	594	896	53.90	2018
B3LYP	1.730	1.587	639	922	61.03	2044
PBE1PBE	1.741	1.587	649	856	54.18	3184
BPW91	1.638	1.587	724	983	76.82	210
BP86	1.629	1.587	758	986	83.42	114
BLYP	1.644	1.599	732	962	82.49	61
PBEPBE	1.633	1.585	738	987	81.17	151
Previous work						
MRCI [8]	1.812	1.637	801	890	44.9	3733
Experiment [26]					68.0 ± 3.0	

Table 2. Mulliken populations; the molecule is along the z-axis

	$^5\Sigma^+$				$^5\Pi$			
	B3LYP		BPW91		B3LYP		BPW91	
	$\alpha+\beta$	$\alpha-\beta$	$\alpha+\beta$	$\alpha-\beta$	$\alpha+\beta$	$\alpha-\beta$	$\alpha+\beta$	$\alpha-\beta$
Mn								
s	6.10	−0.04	6.11	−0.02	6.47	0.31	6.53	0.40
p_x	4.09	0.03	4.09	0.04	4.02	−0.02	4.02	−0.01
p_y	4.09	0.03	4.09	0.04	4.07	0.03	4.08	0.04
p_z	4.04	−0.02	4.04	−0.01	4.06	0.02	4.05	0.01
p total	12.21	0.05	12.22	0.08	12.16	0.03	12.15	0.04
$d0$	0.88	0.39	0.83	0.22	1.10	0.75	1.14	0.61
$d-1$	1.29	0.71	1.34	0.66	1.17	0.85	1.26	0.75
$d+1$	1.29	0.71	1.34	0.66	1.02	0.85	0.92	0.55
$d-2$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$d+2$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
d total	5.46	3.80	5.51	3.54	5.29	4.45	5.32	3.91
Total	23.79	3.81	23.85	3.59	23.92	4.78	24.00	4.35
O								
s	3.93	0.04	3.93	0.02	3.91	−0.04	3.91	−0.05
p_x	1.61	0.26	1.57	0.30	0.95	−0.83	1.05	−0.54
p_y	1.61	0.26	1.57	0.30	1.76	0.13	1.66	0.21
p_z	1.04	−0.37	1.09	−0.21	1.46	−0.03	1.37	0.03
p total	4.27	0.15	4.22	0.39	4.17	−0.74	4.08	−0.30
Total	8.21	0.19	8.15	0.41	8.08	−0.78	8.00	−0.35

population on the Mn in the $^5\Pi$ state?" arises. This is not easy to answer, but some insight can be obtained from certain atomic properties, namely the s to d excitation energy in Mn^+, the ionization potential of Mn^+, and the electron affinity of oxygen, which are summarized in Table 3 along with experimental results [27, 28] [note, the Mn^+ $^7S(3d^5 4s^1)$ $-^5D(3d^6)$ separation is computed by imposing D_{2h} symmetry in the calculations to avoid the ^5D state from collapsing to a solution that is best described as $^5S(3d^5 4s^1)$ or a mixture of ^5S and ^5D]. We note that the B3LYP and BPW91 approaches yield similar results for these quantities. Thus, it does not appear that the pure functionals favor the $^5\Sigma^+$ state because they favor the ^5D state of Mn^+ or because they favor the ionic component of the bonding. This is probably not too surprising considering that all the functionals yield similar r_e and ω_e values for the $^5\Sigma^+$ state. Thus it appears that the hybrid functionals, with their inclusion of some Hartree–Fock exchange, can describe the bonding in the $^5\Pi$ state better than the pure functionals. This is consistent with the poor r_e and ω_e values for the pure functionals.

Since we are unable to find an atomic property that explains the different results obtained for the $^5\Pi$ state, we return to the differences in the bonding between the $^5\Pi$ and $^5\Sigma^+$ states. For the $^5\Sigma^+$ state, all bonds are Mn 3d–O 2p in character, while for the $^5\Pi$ state the σ bond contains significant Mn 4s character. This σ bond with 4s character prefers a longer bond than the π bonds, which are Mn 3d–O 2p in character. Apparently, the hybrid functionals can describe this compromise bonding situation better than the pure functionals.

Table 3. Mn^+ ionization potential (IP) and excitation energy and O electron affinity (*EA*)

	B3LYP	BPW91	Experiment
Mn^+ $^7S(3d^5 4s^1) - {}^5D(3d^6)$	1.21	1.19	1.81 [27]
Mn^+ IP	15.90	16.07	15.64 [27]
O EA	1.61	1.63	1.46 [28]

4 Conclusions

The computed spectroscopic constants obtained using the hybrid functionals are in reasonable agreement with the results obtained using CI-based techniques. The Mn 4s involvement in the σ bond of the $^5\Pi$ state results in a longer bond for the $^5\Pi$ state than for the $^5\Sigma^+$ state. The populations suggest that the hybrid functionals are better able to describe the longer Π bond that occurs in the $^5\Pi$ state.

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