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An *ab initio* Study of the Ground and Low-Lying Excited States of the Permanganate Ion

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The results of *ab-initio* self-consistent field calculations for the ground state and configuration interaction calculations for the excited states of the permanganate ion are presented and discussed. The calculations were performed using two large basis sets of contracted gaussian functions, and singly excited configurations were used in the calculations of the excited states. Fair agreement is obtained between these results and the experimental absorption spectra.

Key word: Permanganate ion

1. Introduction

The ground and excited states of the permanganate ion (MnO_4^-) have been the subject of increasingly intensive experimental and theoretical study since the first visible-UV absorption spectra of the ion was published in 1938 by Teltow [1]. More recent experimental work [2–10] has resulted in the almost definite assignments of all the bands occuring with excitation energies up to ~7 eV.

The first molecular orbital (MO) study undertaken to investigate the nature of the ground and excited states of the ion was by Wolfsberg and Helmholz in 1952 [11], and they assigned the first two low-lying intense bands of the absorption spectra to $t_1 \rightarrow t_2$ and $t_2 \rightarrow t_2$ electronic transitions. During the years following this early calculation many other semi-empirical calculations were performed [12–22], including studies of the CNDO type, resulting in many different assignments of the bands of the absorption spectra. A review of much of the early work has been given by Ballhausen and Gray [23].

The first reported *ab initio* self-consistent field (SCF) calculation of the ground state of MnO_4^- was that due to Hillier and Saunders [24] who used a minimal basis set of Slater type orbitals (STO), each STO being expanded in terms of only three gaussian type functions (GTF). They also calculated the excited states using a configuration interaction (CI) procedure. These workers subsequently improved their agreement with the experimental absorption spectra by using a double zeta basis of 3*d* STO's and by describing the oxygen 2*p* STO's in terms of four instead of three GTF's [25]. Dacre and Elder [26] also obtained a minimal basis set description of the ground state of MnO_4^- using a larger basis of primitive GTF's. They noted that the form of the MO's of *e* symmetry was quite sensitive

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to the basis set used and suggested that this fact could account for the difficulties encountered in providing a satisfactory interpretation of the observed absorption spectra. Recently, two more extensive *ab initio* studies of the ground states of MnO_4^- have been published. In the first of these Mortola *et al.* [27] employed a (15, 11, 5/8, 5) basis of GTF's contracted to (4, 3, 2/2, 2), that is to say a minimal basis except for double zeta manganese 3*d* and oxygen 2*p* representations. These workers also calculated the excited states by virtual orbital theory. In the second extensive study Johansen [28] used a (16, 13, 6/10, 6) basis of GTF's contracted to (10, 7, 3/5, 3). A calculation of the ground state and the optical properties of MnO_4^- using the scattered-wave model has also been reported [29]. This calculation gives a reasonable description of the experimental results.

After so much computational effort it is disappointing that the elucidation of the experimental absorption spectra has not been obtained from theoretical studies. It is, therefore, desirable to extend these theoretical efforts. In this study we have attempted to pursue the direction of Hillier and Saunders [24, 25] by removing some of the limitations imposed upon their early work.

2. Computational Approach

We have used the *ab initio* SCF procedure in order to determine the ground state of MnO_4^-. The excited states have been described by a CI wavefunction obtained by using the occupied and virtual SCF MO's to construct singly excited configurations of the ion (only excitations from the valence to some virtual MO's were considered) which were then allowed to interact, in an analogous manner to that described previously [24].

Two basis sets were employed for our calculations, both based upon the published (12, 6, 4) atomic GTF basis of manganese [30] and (8, 4) atomic GTF basis of oxygen [31]. Basis I, chosen to represent the ground state, was (11, 7, 5/8, 4) contracted to (4, 3, 2/3, 2), and Basis II was (12, 8, 6/8, 5) contracted to (5, 4, 3/3, 2). The additional primitive functions in Basis II were more diffuse than any present in Basis I, since it was thought that such functions might be important for a description of the excited states. Details of the two basis sets are given in Table 1.

Three calculations were performed for the excited states, the first two (Calculations I and II) both employed Basis I and Calculation III used Basis II. In these calculations excitations were considered from all the 12 valence MO's to the first 5, 15, and 19 virtual orbitals for Calculations I, II, and III respectively. Hillier and Saunders [24, 25] used the 12 valence and first 9 virtual MO's in their small basis set calculations. It was hoped that our three calculations would yield information concerning the importance of the basis set and the length of the CI expansion on the calculation of the excited states of MnO_4^- and other transition metal complexes.

All of the calculations were performed using a computer program written by us in FORTRAN for the Univac 1108 computer. The program has been optimised in order to perform large scale CI calculations with the particular facilities available to us. As a result of this optimisation it was possible, for example, to obtain all of the excited states in calculation I for approximately the same cost as the corresponding ground state wavefunction.

Table 1. Basis sets

Atom	Type	Exponent	Contraction coefficient[a]	
Mn	*s*	60370.5	0.001664	
		8910.51	0.013141	
		2008.93	0.064526	
		579.251	0.216181	
		192.434	0.449749	
		69.069	0.391899	
		17.7053	0.391110	
		7.39915	0.640779	
		1.94442	0.468130	
		0.791057	0.567508	
		0.15	1.000000	
		0.03		(1.000000)
Mn	*p*	383.732	0.025900	
		90.5004	0.166234	
		28.2205	0.469064	
		9.82707	0.502968	
		2.64911	0.524436	
		0.839238	0.567884	
		0.19	1.000000	
		0.04		(1.000000)
Mn	*d*	21.088	0.064304	
		5.51882	0.286621	
		1.66192	0.531032	
		0.461264	0.425642	
		0.14	1.000000	
		0.03		(1.000000)
O	*s*	4909.0	0.002115	
		729.7	0.016462	
		162.9	0.082121	
		45.05	0.271899	
		14.37	0.488472	
		5.052	0.287640	
		1.106	1.000000	
		0.329	1.000000	
O	*p*	23.79	0.046078	(0.028925)
		4.941	0.291806	(0.183177)
		1.285	0.786971	(0.494008)
		0.3186	1.000000	(0.527536)
		0.05		(1.000000)

[a] The values given are for Basis I, and are the same for Basis II except when indicated in parenthesis. Different contracted functions are separated by horizontal lines.

3. Results and Discussion

3.1. Ground State

The total energies obtained for the ground state with Bases I and II were -1446.140 and -1446.206 a.u. respectively.

All of the previous *ab initio* calculations of MnO_4^- [24–28] have been mainly concerned with a description of the form of the valence and low-lying virtual

Table 2. Calculated orbital energies (in a.u.)

Orbital	Basis I	Basis II	Previous calculations[a]		
			A	B	C
$3e$	0.800	0.199		1.000	
$8t_2$	0.680	0.213	0.477	0.571	0.488
$7a_1$	0.483	0.159	0.475	0.421	0.318
$7t_2$	0.214	0.183	0.289	0.185	0.200
$2e$	+0.193	+0.164	+0.227	+0.199	+0.202
$1t_1$	−0.264	−0.283	−0.211	−0.294	−0.280
$6a_1$	−0.290	−0.305	−0.244	−0.276	−0.295
$6t_2$	−0.319	−0.339	−0.267	−0.336	−0.333
$1e$	−0.420	−0.441	−0.418	−0.432	−0.422
$5t_2$	−0.456	−0.475	−0.438	−0.487	−0.471
$4t_2$	−1.042	−1.060		−1.068	−1.082
$5a_1$	−1.063	−1.080		−1.087	−1.103

[a] Column A, see Ref. [25]; Column B, see Ref. [27]; Column C, see Ref. [28].

MO's obtained from the ground state SCF calculation, and the general description of these orbitals from such calculations is therefore well documented and, we feel, need not be elaborated on in further detail.

Of particular interest from the point of view of the calculation of the excited states using the CI method are calculated orbital energies. We compare in Table 2 our results from Bases I and II with the results of three previous such calculations [25, 27, 28]. It can be seen that our calculated valence MO's are in close agreement with the extensive basis set calculations of Johansen [28], especially for our Basis II. The virtual orbitals calculated using Basis I are also in reasonable agreement with those of Johansen. However, the addition of diffuse functions to the basis, as in our Basis II, results in a considerable energy lowering of the low-lying virtual orbitals. This might be expected to result in a substantially different description of the excited states.

3.2. *Excited States*

In Table 3 we give the symmetry designation and excitation energies for all the excited singlet states calculated to lie within the range of experimental measurements. A large number of states are calculated within 7 eV of the ground state. However, only transitions to excited $^1T_2$ states are dipole allowed from the $^1A_1$ ground state. The three calculations are seen to produce very nearly identical results, for all the states given in the table, with calculated excitation energies for any particular state being within 0.2 eV from all three calculations. Thus, it appears that only the $2e$ and $7t_2$ virtual MO's are important in describing the low-lying excited states of MnO_4^- and that diffuse functions are not important for a description of such states, unlike for the low-lying excited states of small first-row molecules [32]. It is worthwhile noting the effect of performing the CI calculations, which can be seen by comparing our results with those presented in table 13 Ref. [27]. In agreement with the conclusions of Demuynck and Veillard

Table 3. Calculated excitation energies (eV)

State	Calculation		
	I	II	III
^1E	3.48	3.30	3.44
$^1T_2$	3.62	3.43	3.57
$^1T_1$	3.83	3.78	3.82
$^1T_1$	3.95	3.90	3.94
^1E	4.21	4.18	4.11
$^1T_2$	4.26	4.22	4.28
$^1T_2$	4.37	4.27	4.30
$^1T_1$	4.43	4.25	4.43
$^1A_1$	4.94	4.85	4.99
$^1A_2$	5.02	4.94	5.02
$^1T_1$	5.49	5.38	5.55
$^1T_2$	5.59	5.48	5.67
^1E	5.90	5.83	5.96
$^1A_2$	6.49	6.46	6.51
$^1T_2$	6.62	6.58	6.58
$^1T_1$	6.63	6.60	6.67
^1E	6.64	6.61	6.66

for Ni(CN)$_4^{2-}$ [33] we see that the effect of going beyond the simple virtual orbital approach can be appreciable.

The details of the experimentally determined excited states are given in Table 4 together with the corresponding details from our calculations and the previous calculations of Hillier and Saunders. The agreement between experiment and theory is poor for the first two excited states observed experimentally, of $^1T_1$ and $^1T_2$ symmetry. We predict these two states to lie very close together with the $^1T_2$ state slightly below the $^1T_1$ state which is in disagreement with experiment. This latter state is calculated at ~2 eV higher energy than expected. Also, the oscillator strength, computed using the dipole length formula is very much smaller than is observed. Hillier and Saunders, perhaps suprisingly, obtained

Table 4. Experimental and calculated spectrum of MnO$_4^-$

	Experiment[a]			Calculation[b]					
State[c]	Excitation energy (eV)	Oscillator strength	State and predominant orbital transition	Excitation energy (eV)		Oscillator strength		% of predominant orbital transition	
				A	B	A	B	A	B
$^1T_1$	1.8	v. weak	$^1T_1(1t_1 \rightarrow 2e)$	3.9	3.1	0	0	75	95
$^1T_2$	2.3	0.032	$^1T_2(1t_1 \rightarrow 7t_2)$	3.6	3.4	0.000066	0.0019	69	64
$^1T_1$	3.0 – 3.7	0.021	$^1T_2(1t_1 \rightarrow 2e)$	4.4	3.8	0.0015	0.0085	70	66
$^1T_2$	4.0	0.035	$^1T_2(6t_2 \rightarrow 2e)$	4.3	4.2	0.022	0.0084	50	52
$^1T_2$	5.5	0.04 – 0.07	$^1T_2(5t_2 \rightarrow 2e)$	5.6	6.3	0.029	0.0041	43	64
$^1T_2$	6.6		$^1T_2(6a_1 \rightarrow 7t_2)$	6.6	7.4	0.032	0.035	45	48

[a] References [1–10], see also Table 7 of Ref. [27].

[b] A refers to our work with Basis I (Calculation I). B refers to Hillier and Saunders [25].

[c] The assignment given for the optical spectrum of MnO$_4^-$ is due to Johnson and McGlynn [8].

slightly better agreement with experiment for these two states with the $^1T_1$ state predicted to lie just below the $^1T_2$ state. The second $^1T_1$ state, calculated at 3.8 eV above the ground state, is due to $5t_2 \rightarrow 2e$ and $6t_2 \rightarrow 2e$ electronic excitation. Experimental results indicate that it is this state which gives rise to the next, fairly intense, absorption band. However, our results, in agreement with those of Hillier and Saunders, would predict this latter band to be due to a second $^1T_2$ state, as indicated in Table 4. Our results for the remaining three, intense, bands are in good agreement with experiment. The calculated excitation energies are all within 0.3 eV of experiment and the calculated oscillator strengths for the third and fourth $^1T_2$ states are also in good agreement with those measured. The computed value of this latter quantity for the fifth $^1T_2$ state is difficult to compare with experiment since the corresponding band is known to be medium dependant [34], being greatly enhanced in solution. Our results for the two latter $^1T_2$ states are substantially in better agreement with experiment than those due to Hillier and Saunders. The orbital electronic transitions giving rise to the various states obtained in our study are in agreement with those obtained by these workers.

4. Conclusions

Although the calculations of this study are the most extensive performed for the excited states of MnO_4^-, the results obtained are only in fair agreement with results from the experimental spectra. It appears from our results that the number of virtual orbitals included in the CI is not important, provided that the $2e$ and $7t_2$ levels are present, and that the addition of diffuse functions to the basis set does not significantly alter the results obtained for the low-lying states. Although the contracted bases used in this study, especially basis II, were probably adequate (metal $4s$, $4p$, and oxygen $2s$, $2p$ in double zeta, metal $3d$ in triple zeta), it is likely that our uncontracted bases are rather inadequate, particularly in the inner valence description. In this context it should perhaps be noted that the diffuse d-orbital of Basis II has its maximum at about two and a half times the Mn–O bond distance which is probably a rather inefficient use of an extra orbital. Now that we have demonstrated the feasibility of performing large scale CI calculations with extensive contracted bases, an extension of the uncontracted basis set presents no obstacle to enlarging upon the present studies.

Of course, it may be that the method we have chosen to describe the excited states is itself not adequate and that it is necessary to obtain these states through separate SCF calculations followed, perhaps, by a CI calculation amongst these SCF states. Studies are at present underway in the laboratory to calculate the excited states of ferrocene using both the SCF and singly excited CI approaches. On the other hand, it is possible that no adequate theoretical description of the experimental absorption spectra can be obtained without the inclusion of correlation effects. The doubts presented above on the theoretical methods employed must remain until further work is done.

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