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magnesium-containing systems.

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## CONTENTS

Introduction.....	3
Electrical Properties of Magnesium Compounds.....	3
Higher Level Calculations and Heats of Formation.....	10
Acknowledgements.....	12
References.....	13

## INTRODUCTION

The principal scientific objectives for this contract, that is, the determination of energetic and structural properties for about forty magnesium compounds, were achieved at the planned termination date for the contract, 31st May 1991. These results were presented in the second interim report[1] to the AFOSR in July 1991. At this time, some unspent funds were available and a no-cost extension was negotiated until 31st May 1992. This extension was to permit the further study of two specialized aspects of the main contract. These aspects are:

- (i) the difficulty in reproducing realistic electric dipole moments for many species and,
- (ii) the effect on the energies of performing higher level computation.

These two topics are divorced from the main objectives of the contract but seemed worthy of further examination.

This final report presents some results on these aspects.

## ELECTRICAL PROPERTIES OF MAGNESIUM-COMPOUNDS

Although the calculation of molecular structure by ab initio calculations is now at a stage that structures may be routinely calculated to desired accuracy, the same cannot be claimed for electrical properties. Hinchcliffe[2], writing in 1988, compared dipoles calculated from extended polarized basis sets with corresponding experimental values for 30

species with dipoles ranging from 1.3 to 13.0 D, and found a mean absolute deviation of 1.2 D (alternatively expressed, the proportional error was about 30% with the calculated value nearly always high). Considerable attention has been devoted to the computation of dipole moments, polarisabilities, absorption intensities and scattering cross sections. The sensitivity of these properties to the electron distribution remote from the internuclear axes leads to a strong dependence on the basis set and on configuration interaction. Unfortunately there is no equivalent to the *Variation Principle* which might be used to direct results towards an asymptotic limit. It is commonly believed that at the Hartree Fock limit dipole moments are reliable to significantly better than 1 Debye.

This study arose from the observation, during calculations of properties of magnesium compounds, that Møller-Plesset corrections in some cases were several Debyes. As reliable electric dipole moments of such compounds were required for the parameterisation of MOPAC it was decided to explore their sensitivity to the choice of basis set and to the level of CI correction.

Molecular structure is generally given in the HF limit to an accuracy of  $\pm 0.02$  Å and  $\pm 1^\circ$ , at least for structures based on first row elements plus hydrogen. Even relatively simple split valence basis sets approach this accuracy. First order properties are predicted much less satisfactorily at this level. For instance, n-31G basis sets yield dipole moments about 50% too large[3]. Numerous studies have been made to

explore how reliable values might be obtained [see for instance ref.4 for a reasonably extensive bibliography]. Configuration interaction applied to organic systems and small hydrides generally produce corrections of less than 0.5 D [5]. Such errors are far from insignificant however when transition moments are to be calculated. Errors in infrared absorption intensities of even strong bands are regularly 100% in error at the SCF level with basis sets of moderate complexity [6,7]. Polarisability and its derivatives are second order properties and their calculation is consequently even more demanding.

Møller-Plesset perturbational approximations to configuration interaction produces a substantial improvement in dipole moments and infrared intensities, though there generally appears to be a tendency for MP2 to overshoot substantially the full CI correction. Thus for formaldehyde [3] the calculated dipole at HF/6-311G(2d,2p), its MP2 corrected value and the experimental value are 2.796 D, 2.172 D and 2.332 D respectively. The CISD result with the same basis is 2.404D.

CI evaluations do not compensate for inadequacy in the basis set. The chosen basis must be adequate to describe the electron density variations in the molecular space. It has been established that energy optimised basis sets fail to describe the space remote from the nuclei, which may result in substantial inadequacies in the charge distributions [4,8]. It is necessary to supplement the basis set with polarisation functions with exponents of the order of double the largest energy optimised value. This is increasingly important in the

case of Raman polarisability tensors, for which energy optimised functions may yield very poor values of the polarisability gradients perpendicular to the molecular framework.

The interim report[1] referred in the introduction contained dipole moments at the 6-311G\*\*/MP2 level for most of the compounds studied - these were shown on the individual data sheets for each compound. Initially it was expected that the dipole moments at this level would might be reliable to  $\pm 0.2D$ . Experimental values are not known for any gaseous magnesium compounds, so it is very important to establish some measure of reliability. As several studies with  $H_2O$  have established, extension of the basis set does not lead to asymptotic convergence on the true value [3,5]. Nor is it possible to establish bounds on the values. Nevertheless some measure of reliability may be estimated by suitable expansions of the basis set with addition of polarisation functions.

Initial tests were made on  $MgO$  ( $^1 \Sigma$  state). MP2 corrections applied to the 6-311G\*\* basis set resulted in a reduction of the dipole from 8.01 D to 6.24 D. The magnitude of this change exceeded our expectations, but on evaluating the CISD dipole an even larger additional decrease to 4.14 D was found. As this basis is essentially energy optimised the effect of additional polarisation functions was evaluated. As seen in table 1 the changes at MP2 and CISD levels are confirmed, though it is noted that the lowest energy with the 6-311G(2d,pd) basis has a slightly smaller dipole change to 5.00D. The results for  $MgO$  are collected in table 1.



Table 1: Dipole Moments for MgO( $^1\Sigma$ )

<u>Basis Set</u>	<u><math>\mu/D</math></u>
6-311G**/SCF	8.0
6-311G**/MP2	6.2
6-311G**/CISD	4.1
6-311G(2p, pd)/SCF	8.7
6-311G(2d, pd)/CISD	5.0
6-311G(df, pd)/CISD	4.2

It is apparent from the results in table 1 that failure to make a correlation correction i.e. the two SCF values, yields high dipoles, even with polarized basis sets.

It is clearly pertinent at this stage to examine how these computational procedures behave with a system for which a reliable experimental dipole moment exists. Unfortunately, there are no values for gas phase magnesium compounds so water was chosen as a test substance - the results are collected in table 2.

Table 2: Dipole Moments for H<sub>2</sub>O, gas

<u>Basis Set</u>	<u><math>\mu/D</math></u>
6-311G**/SCF	2.17
6-311G**/MP2	2.05
6-311G**/CISD	2.02
6-311G(df, pd)/CISD	2.04
Experimental[9]	1.84±0.01

For water the range of values is much smaller than for MgO - a second decimal place is necessary to resolve the differences - and again the SCF result is the largest. Inclusion of CI and polarization functions produces only modest improvement but no obvious convergence to the experimental value. The only

general conclusion is that computations with CISD probably produce moments to within  $\pm 0.2$  D. In passing it may be noted that there was no correlation between the energies and the dipoles for the water calculations so decreasing energy cannot be used as a criterion for improving accuracy in the moment calculation. Results for another test system,  $\text{CH}_2\text{F}$  - see table 3 - confirm these conclusions.

Table 3: Dipole Moments for  $\text{CH}_2\text{F}$

Basis Set	$\mu/D$
6-311G**/SCF	1.98
6-311G**/CISD	1.74
Experimental[9]	$1.83 \pm 0.02$

Three further magnesium-containing systems were studied,  $\text{HMgF}$ ,  $\text{MgF}$ ,  $\text{MgH}$  and the results for these are given in tables 4 and 5.

Table 4: Dipole Moments and Structures for  $\text{HMgF}$

Basis set	$r(\text{MgH})/\text{\AA}$	$r(\text{MgF})/\text{\AA}$	$\mu/D$
6-311G**SCF <sup>a</sup>   SCF	1.691	1.756	1.47
6-311G**/MP2 <sup>b</sup>   MP2	1.687	1.775	-
6-311G**/CISD <sup>b</sup>   MP2			1.39
6-311G(2d, pd)/SCF <sup>b</sup>   CISD	1.682	1.753	1.35
6-311G(2d, pd)/MP2 <sup>b</sup>   CISD			1.16
6-311G(2d, pd)/CISD <sup>b</sup>   CISD			1.27
6-311G**/cbasp <sup>a</sup> (0.3, 0.6)	1.695	1.725	1.09

<sup>a</sup>cbasp means inclusion of centre bond functions with sp character and with exponents of 0.3 and 0.6

<sup>b</sup>| means 'at the geometry of'

The results for  $\text{HMgF}$  are more detailed than for previous examples in that different geometries are considered. As an

example of the notation in the table, 6-311G\*\*/CISD|MP2 means that the geometry was optimized at the 6-311G\*\*/MP2 level and a single point energy and dipole calculation was then performed at the 6-311G\*\*/CISD level using this MP2 geometry. For the three optimized geometries studied (SCF, MP2, and CISD) the structural constants for HMgF(linear) vary within 0.05A and so it is unsurprising that the geometry has little effect on the dipole. Again, the SCF result appears high and the MP2 value 'overshoots' the CISD value yielding the pattern,  $\mu(\text{SCF}) > \mu(\text{CISD}) > \mu(\text{MP2})$ .

The centre bond functions (or floating orbitals) may be used in place of additional polarization functions; they are placed between bonding atoms on the internuclear axis and there is no mass associated with them. They give enhanced flexibility to the basis set with only a modest increase in cpu time. Their efficacy depends markedly on the choice of exponent and this is only gained by experience through working with a series of molecules of similar structure and preferably, including some with known experimental values.

Table 5: Dipole Moments for MgF and MgH

Basis set	$\mu(\text{MgH})/\text{D}$	$\mu(\text{MgF})/\text{D}$
6-311G**/SCF	1.41	3.38
6-311G*/MP2	1.33	2.95
6-311G*/CISD	1.21	3.09
6-311G**/cbasp/SCF	1.45	3.04
literature[10]	1.48 <sup>b</sup> , 1.24 <sup>c</sup>	

<sup>a</sup> \*\* for MgH, \* for MgF      N.B. \*\* means (d,p)  
<sup>b</sup> SCF                              <sup>c</sup> CEPA (coupled electron pair approach)

Calculated values for open shell species are much less satisfactory than corresponding calculations for closed shell

systems. The reason is that Brillouin's theorem (single excited states constructed from HF orbitals do not interact with the electronic ground state) does not apply to open shell systems so there is a first order correction to be made to the dipole when using CI.

#### HIGHER LEVEL CALCULATIONS AND HEATS OF FORMATION

The results for the magnesium compounds presented in the preceding interim report[1] were computed at the 6-311G\*\*/MP2 level, including the optimization. This choice was a compromise between computational rigour and available computational resource. The results presented in this section seek to explore whether using more sophisticated basis sets, eg. more polarization functions and/or more precise methods of estimating electron correlation, significant improvement in the derived heats of formation could be obtained. Full optimisation at, for example the 6-311G(2d,pd)/CISD level is very time-consuming for a medium-sized molecule so the geometries of selected compounds were optimised at the 6-311G\*\*/CISD level and single point calculations were then performed at higher levels.

The following species were selected for this exercise: MgO, MgF, MgH, MgH<sub>2</sub>, and HMgF. Three of this subset are validation species[1]. Corresponding results for O<sub>2</sub>, H<sub>2</sub>, HF, and Mg<sub>2</sub> were also required so as to complete isogyric (or near-isogyric) reactions for the test subset. The energies at three different higher levels of computation are collected in table 7.

Table 7: Total electronic energies at 0 K for the test subset at different levels of computation

ELECTRONIC ENERGIES/H			
Species	6-311G**/CISD	6-311G(2d,pd)/CISD	6-311G(df,pd)/CISD
Mg <sub>2</sub>	-399.28808	-399.28055	-399.28056
MgH <sub>2</sub>	-200.79466	-200.79804	-200.80104
MgO	-274.62959	-274.65408	-274.65339
HMgF	-299.95565	-299.98993	-299.98705
MgH	-200.18500	-200.18690	-200.18838
MgF	-299.34759	-299.38115	-299.37636
H <sub>2</sub>	-1.16827 <sub>5</sub>	-1.17001	-1.17001
O <sub>2</sub>	-150.02691	-150.05916	-150.04005
HF	-100.26986	-100.29587	-100.29963

The ancillary data required to correct these results to heats of formation are collected in table 8.

Table 8: Ancillary data

Species	(H <sub>298</sub> <sup>0</sup> -H <sub>0</sub> <sup>0</sup> )/kJ mol <sup>-1</sup>	ZPE/kJ mol <sup>-1</sup>
Mg <sub>2</sub>	10.88	0.304
MgH <sub>2</sub>	10.2*	23.1*
MgO	8.9	4.68
HMgF	11.3*	16.6*
MgH	8.67	8.94
H <sub>2</sub>	8.43	26.32
O <sub>2</sub>	8.98	4.24
HF	8.59	24.75
MgF	8.97	4.24

\* these values are slightly different to those given in the earlier interim report as the vibrational frequencies used to calculate them are scaled by 0.9, as recommended by Pople[11].

The results in table 9 compare the derived heat of

formation with those reported earlier and literature results, if available.

Table 9: Standard enthalpies of formation at 298.15 K  
calculated at different levels

Level #1 = 6-311G\*\*/MP2    Level #2 = 6-311G\*\*/CISD  
Level #3 = 6-311G(2d,pd)/CISD    Level #4 = 6-311G(df,pd)/CISD

Species	Standard enthalpies of formation/kJ mol <sup>-1</sup>				
	Level # 1	Level# 2	Level#3	Level#4	lit.[1]
MgH <sub>2</sub>	168	174	170	162	-
MgO	157	210	187	164	146±21
HMgF	-275	-257	-279	-261	-
MgF	-217	-191	-214	-191	-236±8
MgH	232	243	240	236	233±5

These results show the following:

- (i) there is no clear convergence to a limiting value,
- (ii) and there is no improvement in accuracy

when moving to higher level basis sets. Hence, it appears that the original choice of 6-311G\*\*/MP2 was justified.

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