Investigation of the *Stuttgart/Dresden* pseudopotential in the G3(MP2,CSSD,rel) theory for compounds containing transition elements

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INTRODUCTION

The Gaussian theory [1,2] has been developed over the last decades with the goal of approaching exact molecular energies using a set of ab initio calculations. These composite methods combine high-level correlated/moderate basis set calculations with lower level correlated/larger basis set calculations to approximate the results of a single high level and much more expensive computational procedure.

Transition metal compounds are one of the challenges in the search for reliable theoretical methods to predict thermochemical properties. In order to combine composite methods and transition metal compounds DeYonker et al. [3] tested a set comprising 17 enthalpies of formation for such class of compounds with a method referred to as the correlation consistent composite approach (ccCA). Their method presented a mean absolute deviation (MAD) of 5.6 kcal mol^{-1}, which is almost twice the average of the experimental uncertainty of 3.1 kcal mol^{-1} for the same set of molecules.

Mayhall et al. [4] collected a test set comprising of 20 enthalpies of formation for transition metal compounds for testing three different methods. One of them is referred to as the G3(MP2,CCSD,rel) theory and provided a mean absolute deviation (MAD) of 4.58 kcal mol^{-1}, which is three times the average experimental uncertainty of 1.5 kcal mol^{-1}.

Recently, the use of the CEP pseudopotential (Compact Effective Potential) along with the G3 theory [5] proved to be possible preserving a high level of accuracy and a considerable gain in the CPU time. The objective of this work is to test the Stuttgart/Dresden pseudopotential in the G3(MP2,CCSD,rel) to be used in transition metal compounds.

METHODS

The G3(MP2,CCSD,rel) composite energy is obtained by combining CCSD(T), MP2, and Douglas-Kroll-Hess (DKH) calculations with progressively larger basis sets, and including first-order spin-orbit corrections for atoms and molecules (ΔE(SO)), zero-point energy corrections (E(ZPE)), and an empirical higher level correction (E(HLC)) that depends on the number of paired and unpaired electrons.

All steps of the original G3(MP2,CCSD,rel) theory were used and adapted to include the Stuttgart/Dresden pseudopotential. The modified method was named as G3(MP2,CCSD,rel,SDD). The general expression for the composite energy is given by the expression:

$$E_o[\text{G3(MP2, CCSD, rel)}]) = \text{CCSD(T)/6-31G(d)} + \Delta E(\text{MP2}) + \Delta E(\text{rel}) + \Delta E(\text{SO}) + E(\text{HLC}) + E(\text{ZPE})$$

Where:

$$\Delta E(\text{MP2})) = E[\text{MP2/G3MP2LargeXP}] - E[\text{MP2/6-31G(d)}]$$

And

$$\Delta E(\text{rel})) = E[\text{DKH-CCSD(T)/6-31G(d)}] - E[\text{CCSD(T)/6-31G(d)}]$$

The scalar relativistic corrections were obtained from DKH-CCSD(T)/6-31G(d) single-point energy calculations using a second-order DKH scalar relativistic Hamiltonian. The ZPE correction was obtained from scaled harmonic approximation and spin-orbit effects were obtained from the literature.

RESULTS AND DISCUSSION

Table 1 contains 20 enthalpies of formation of compounds containing Sc-Zn atoms calculated using the G3(MP2,CCSD,rel) and G3(MP2,CCSD,rel,SDD) methods. The deviations with respect to available experimental data for these molecules are given in this table as well as the mean absolute deviation (MAD). All data are in kcal mol^{-1} and were calculated as experiment minus theoretical data.

G3(MP2,CCSD,rel) presented a MAD of 4.58 data with a maximum deviation of 9.43 data, while G3(MP2,CCSD,rel,SDD) presented a similar MAD of 4.39 kcal mol^{-1}. A general comparison of the data shows that the use of pseudopotential does not follow the same trend of the deviation observed for the all-electron calculations. For example, the G3(MP2,CCSD,rel,SDD) present three outliers deviations of -16.07 kcal mol^{-1}, -10.32 kcal mol^{-1} and 11.50 kcal mol^{-1} for VO, CuH and CuCl, respectively. The same compounds calculated by the all-electron version differ by -1.97 kcal mol^{-1}, -0.53 kcal mol^{-1} and 0.83 kcal mol^{-1} for the same compounds. On the other hand, the all-electron calculations yielded presented deviations of 9.12 kcal mol^{-1} , 8.95 kcal mol^{-1} and 7.71 kcal mol^{-1} for CrO3, FeCl and FeCl2, respectively, while the pseudopotential calculations showed deviations of 2.67 kcal mol^{-1}, 0.46 kcal mol^{-1} and -1.66 kcal mol^{-1}.

TABLE 1: Experimental enthalpies of formation (in kcal mol^{-1}) at 298 K and deviations calculated at the G3(MP2,CCSD,rel) and G3(MP2,CCSD,rel,SDD) levels of theory.

Molecule	Experiment	G3(MP2,CCSD,rel)	G3(MP2,CCSD,rel,SDD)
ScO	-13.0±2.2	-2.4	-6.02
ScCl$_3$	-160,5±2.1	5.97	0.37
TiO	-13.7±2.2	0.68	-4.89
TiF$_4$	-370.8±1	5.48	0.24
VO	-31.8±2	-1.97	-16.07
CrCl	-31.0±0.6	1.13	1.87
CrO$_3$	-77.3±1	9.12	2.67
MnCl	15,8±1.6	9.37	9.21
MnS	63.31±2	1.5	-3.10
FeCl	49.5±1.6	8.95	0.46
FeCl$_2$	-32.8±1	7.71	-1.66
FeCl$_3$	-60.5±1.2	9.43	5.45
CoCl$_2$	-22.6±1	5.56	-0.63
CoCl$_3$	-39.1±2.5	2.94	-5.29
NiCl$_2$	-17.4±1	5.35	-0.17
NiF2	-77.8±1.1	8.9	7.73
CuH	65.9±2	-0.53	-10.32
CuCl	19.3±2	0.83	11.50
ZnH	62.9±0.5	0.31	0.14
Zn(CH$_3$)$_2$	12.86±2	3.52	0.04
MAD		4.58	4.39

It is worth to mention that the average experimental uncertainty for the 20 transition metal molecules is 1.5 kcal mol^{-1}. In addition, some experimental atomic enthalpies of formation, such as for Ti, V, and Ni present uncertainties between 2-4 kcal mol^{-1}. And these atomic data are used in the calculation of the molecular enthalpies and introduce uncertainties in the theoretical results.

CONCLUSIONS

The G3(MP2,CCSD,rel,SDD) method, which includes scalar relativistic effects, presented a mean absolute deviation of 4.39 kcal mol^{-1} for a test set of 20 enthalpies. The method presents an excellent performance when compared with the all-electron version. The outliers observed in both sets of calculations are being analyzed.

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