International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:12, No:5, 2018

Quantum Modelling of $AgHMoO_4$, $CsHMoO_4$ and $AgCsMoO_4$ Chemistry in the Field of Nuclear Power Plant Safety

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Abstract**—**In a major nuclear accident, the released fission products (FPs) and the structural materials are likely to influence the transport of iodine in the reactor coolant system (RCS) of a pressurized water reactor (PWR). So far, the thermodynamic data on cesium and silver species used to estimate the magnitude of FP release show some discrepancies, data are scarce and not reliable. For this reason, it is crucial to review the thermodynamic values related to cesium and silver materials. To this end, we have used state-of-the-art quantum chemical methods to compute the formation enthalpies and entropies of $AgHMoO_4$, $CsHMoO_4$, and $AgCsMoO_4$ in the gas phase. Different quantum chemical methods have been investigated (DFT and CCSD(T)) in order to predict the geometrical parameters and the energetics including the correlation energy. The geometries were optimized with TPSSh-5%HF method, followed by a single point calculation of the total electronic energies using the CCSD(T) wave function method. We thus propose with a final uncertainty of about 2 $kJmol^{-1}$ standard enthalpies of formation of $AgHMoO_4$, $CsHMoO_4$, and $AgCsMoO_4$.

Keywords**—**ASTEC, Accident Source Term Evaluation Code, quantum chemical methods, severe nuclear accident, thermochemical database.

I. INTRODUCTION

SINCE the Fukushima disaster, the possibility of a major accident occurring in a nuclear plant cannot be quantified based on probabilistic arguments. It is therefore necessary to develop means of limiting the consequences of such accidents, especially in terms of contamination of the population and the environment.

During a severe accident (SA) [1], FPs are released from the nuclear fuel and may reach the nuclear containment building [2]. In the short-term, the radioisotopes of iodine are one of the key concerns of post-accident management due to their high radiotoxicity induced by their affinity with the thyroid. Among the FPs, cesium (Cs) [3] is of particular interest due to its ability to form volatile oxide compounds in highly oxidizing conditions combined with its high radiotoxicity in the medium term after the accident, while molybdenum affects Cs chemistry by the formation of molybdates which can have a significant impact on iodine transport in the RCS [4]. FPs can react with Control Rods (CRs) materials consisting of silver-indium-cadmium (SIC) alloys or boron carbide, during the core degradation phase, forming complex compounds which are difficult to predict. Thus, the French Institute de Radioprotection et de Sûreté Nuclèaire (IRSN) has developed over several years the ASTEC software package [5]. This code aims at simulating an entire SA sequence in a nuclear water-cooled reactor from the initiating event up to the release of radioactive elements out of the containment. This code requires reliable input data and accurate sets of thermodynamic properties [$\Delta_f H^0$ (298 K), S^0 (298 K), $C_P = f(T)$]. Usually, for most of the databases used, the reference values are taken from different publications found in the literature. However, the thermodynamic database on Cs and silver species used to estimate the magnitude of FPs releases shows some discrepancies, data are scarce and not reliable, calling for quantum chemical calculations. Thus, ab initio electronic structure calculations at the coupled cluster level with different basis sets have been performed for the estimation of the thermochemical properties of $AgHMoO_4$, $CsHMoO_4$ and $AgCsMoO_4$. The standard enthalpies of formation at 298 K and at constant pressure were evaluated. The calculated standard enthalpies of formation are within the range of uncertainties of the most recent experimental data.

In the second part of this paper, the choice of electronic correlation treatment and a benchmark of basis sets are discussed along with the methodology to evaluate the reaction energies. In the second part, the standard enthalpies of formation of target species in the gas phase are presented and discussed. These data will be implemented in the Material Data Bank (MDB) containing thermodynamic properties of a large variety of compounds. The MDB is currently used by the ASTEC code to predict the chemistry behavior of Cs and silver in severe nuclear accident conditions. Furthermore, this methodology can then be applied in forthcoming studies to explore other Cs and silver species for which very few or no experimental data are available.

II. COMPUTATIONAL DETAILS

A. Chemical Reactions Used to Derive the Standard Enthalpies of $CsHMoO_4$, $AgHMoO_4$, and $AgCsMoO_4$

To derive the standard enthalpies of formation in the gaseous phase of $CsHMoO_4$, $AgHMoO_4$ and $AgCsMoO_4$ molecules, literature values of the enthalpies of formation of several species listed in Table I are used together with the computed

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enthalpies of the following reactions leading to the formation of the targeted molecules:

$$2Cs(g) \rightarrow Cs_2(g) \quad (1)$$

$$2Ag(g) \rightarrow Ag_2(g) \quad (2)$$

$$MoO2 + \frac{1}{2}O_2(g) \rightarrow MoO_3(g) \quad (3)$$

$$\frac{1}{2}Ag_2(g) + \frac{1}{2}O_2(g) + MoO_3(g) + \frac{1}{2}H_2(g) \rightarrow AgHMoO_4(g) \quad (4)$$

$$\frac{1}{2}Ag_2(g) + O_2(g) + MoO_2(g) + \frac{1}{2}H_2(g) \rightarrow AgHMoO_4(g) \quad (5)$$

$$\frac{1}{2}Ag_2(g) + H_2O(g) + MoO_3(g) \rightarrow AgHMoO_4(g) + \frac{1}{2}H_2(g) \quad (6)$$

$$\frac{1}{2}Cs_2(g) + \frac{1}{2}Ag_2(g) + \frac{1}{2}O_2(g) + MoO_3(g) \rightarrow AgCsMoO_4(g) \quad (7)$$

$$\frac{1}{2}Cs_2(g) + \frac{1}{2}Ag_2 + O_2(g) + MoO_2(g) \rightarrow AgCsMoO_4(g) \quad (8)$$

$$\frac{1}{2}Cs_2(g) + \frac{1}{2}Cs_2(g) + H_2O(g) + MoO_3(g) \rightarrow AgCsMoO_4(g) + H_2(g) \quad (9)$$

$$\frac{1}{2}Cs(g) + \frac{1}{2}O_2(g) + MoO_3(g) + \frac{1}{2}H_2(g) \rightarrow CsHMoO_4(g) \quad (10)$$

$$\frac{1}{2}Cs_2(g) + O_2(g) + MoO_2(g) + \frac{1}{2}H_2(g) \rightarrow CsHMoO_4(g) \quad (11)$$

$$\frac{1}{2}Cs_2(g) + H_2O(g) + MoO_3(g) \rightarrow CsHMoO_4(g) + \frac{1}{2}H_2(g) \quad (12)$$

The chosen reactions offer the possibility to obtain accurate reaction enthalpies.

B. Computational Methods

The structures of the various species containing silver, Cs and other compounds that enter in the formation reactions were optimized with Gaussian package [9] without symmetry constrains and with default numerical integration grids. All geometries were optimized in the gas phase using the density functional theory where the electronic correlation is introduced in a comprehensive manner. The TPSSh%5HF functional [10] was used (note that the correlation part of the TPSS functional related to self-interaction is error free [10], [11]). Def2-QZVP basis sets were used for all atoms [12], [13]. Effective core potentials were employed for Cs, cadmium and silver which are ECP46MWB [14], ECP28MWB [15], ECP28MWB [15] respectively. We have used the gas phase geometries for all the further single-point energy calculations, and to calculate the enthalpy contributions to the gas phase energies. Perspective views of the optimal geometries of $CsHMoO_4$, $AgHMoO_4$ and $AgCsMoO_4$ are displayed on Fig. 1.

Correlation effects are treated with correlated wave-function theory (WFT) methods of increasing accuracy, namely the single and double coupled cluster theory with inclusion of a perturbative estimation for triple excitation [CCSD(T)], the latter representing the “gold standard”. All WFT calculations are performed with either the parallel resolution of the identity approximation, [16], [17] or density fitting correlated methods [18], with the appropriate atomic auxiliary basis functions [12], [13], and the frozen-core approximation (chemical core, that is, only the valence electrons were correlated). All the single point calculations were performed with Gaussian package [9] with the spin-unrestricted open-shell coupled cluster theory for open-shell systems where the computed T1 diagnostics for the various species are less than 0.05 [19], [20] for all the studied complexes. For all these single-point energy computations, the aug-cc-pVnZ basis sets were used to describe all light atoms, while for Cs the basis set and pseudopotential are identical to those used for the geometry optimization. For silver, the aug-cc-pVnZ-PP basis sets were used for the valence electrons and the ECP28MDF [21] pseudopotential was used for the core electrons. For the aug-cc-pVnZ basis sets, extrapolation to the CBS limit was carried out according to the two-point extrapolation formula for HF energies E_{HF} [22], [23]:

$$E_{HF}(n) = E_{HF}{}^{CBS} + Bn^{-3},$$

and a two-point extrapolation for the total DFT energies or the WFT correlation energies E_{corr} [24]:

$$E_{corr}(n) = E_{CORR}{}^{CBS} + An^{-3}.$$

TABLE I
KNOWN GAS PHASE STANDARD ENTHALPIES OF FORMATION Δ_fH^0 (298.15 K) IN KJMOL^{-1}

Molecule	Δ_fH^0 (298 K)	Reference
Cs (g)	76.5 ± 1.0	[6]
Ag (g)	284.9 ± 0.8	[6]
Cs_2 (g)	107.39 ± 0.0	[7]
MoO_2 (g)	-8.31 ± 0.0	[7]
MoO_3 (g)	-346.44 ± 0.0	[7]
Ag_2 (g)	410.0 ± 0.0	[8]
H_2O (g)	-241.826 ± 0.04	[6]

The derivation of unknown formation enthalpies requires computing reaction enthalpies, which are composed of reaction energies and enthalpy corrections. The accuracy is mostly determined by the errors in the computed electronic reaction energies with respect to both the basis set (basis-set error) and the treatment of electron correlation (intrinsic error with respect to the exact energy), by considering the reactions leading to the formation of the desired molecule.

III. RESULTS AND DISCUSSION

A. Standard Enthalpy of Formation of Cs_2, Ag_2 and MoO_3

In an attempt to validate our approach in predicting the standard enthalpies of formation, the Δ_fH^0 of well-known species (Cs_2, Ag_2 and MoO_3) were determined in the gaseous state from Reactions 1, 2 and 3 respectively. Electronic energies of involved species are computed with the TPSSh%5HF/CBS and CCSD(T)/CBS approaches, whereas the vibrational contributions are calculated at the TPSSh%5HF/Def2-QZVP level (like geometry optimization) to ultimately derive the enthalpies of reaction. To transform the standard enthalpy of reaction into the standard enthalpy of formation, the standard heats of formation at 298.15K of key species (Table I) are taken into account. The calculated value of standard enthalpies of formation of Cs_2 in the gaseous phase and using the

CCSD(t)/CBS method is 107.4 ± 2.0 kJmol^{-1}, see Table II. The comparison of the results obtained with the CCSD(t)/CBS method to that obtained with TPSSh%5HF/CBS method shows a difference of around 8.7 kJmol^{-1} for Cs$_2$. CCSD(t) method treats well the correlation energy unlike the DFT methods. For this, we will compare our enthalpies computed with CCSD(t)/CBS method to the experimental values found in the literature. The calculated value is in a good agreement with the experimental one found in the literature [7] which is -107.4 kJmol^{-1} for Cs$_2$. The good prediction of the calculated standard enthalpy validates our methodology and gives us confidence to apply it on other complexes.

Using the same methodology, we computed the $\Delta_fH^0$of Ag$_2$ and MoO$_3$ in the gaseous state starting from reactions: 2 and 3.

The $\Delta_fH^0$of Ag$_2$) is 400.1 kJmol^{-1} and 407.8 kJmol^{-1} using the TPSSh-5%HF/CBS method and CCSD(t)/CBS method respectively (see Table II). For MoO$_3$, the Δ_fH^0 computed by the TPSSh-5%HF/CBS method is -342.7 kJmol^{-1} whilst using the CCSD(t)/CBS method is -346.3 kJmol^{-1}.

Again, the calculated values for Ag$_2$ and MoO$_3$ are in a good agreement with the experimental ones found in the literature [7], [8] which are 410.0 kJmol^{-1} for Ag$_2$ and -346.44 kJmol^{-1} for MoO$_3$. The good prediction of calculated standard enthalpies validates our methodology and gives us confidence to apply it on other complexes.

B. Standard Enthalpies of Formation of AgHMoO$_4$ and AgCsMoO$_4$

After the validation of our methodology in predicting the enthalpies of formation in the gaseous state, we have used our methodology to predict the Δ_fH^0 of AgHMoO$_4$ in the gaseous state from Reactions: 4, 5 and 6. The Δ_fH^0 of AgHMoO$_4$ using the TPSSh-5%HF/CBS method and starting from reactions 4 and 5 are -583.1 kJmol^{-1} and -579.3 kJmol^{-1} respectively, see Table III. However, using reaction 6, the Δ_fH^0 value is equal to -623.5 kJmol^{-1}. There are important discrepancies among the computed values using the TPSSh-5%HF functional. Thus, to reduce the discrepancies among the computed values, there is a need to treat well the correlation effects with correlated wave-function methods of increasing accuracy, namely the single-and-double-coupled cluster theory with inclusion of a perturbative estimation for triple excitation CCSD(T), the latter representing the “gold standard”. Thus, we computed the Δ_fH^0 of AgHMoO$_4$ in the gaseous state starting from the same reactions mentioned above (4, 5 and 6). The discrepancy among the three values is less than 3.0 kJmol^{-1} and the average value is equal to -634.3 ±1.6 kJmol^{-1}. Although there are no available experimental data to compare our results with, the low uncertainty among the computed values makes us confident concerning our approach.

Using the same methodology, we computed the $\Delta_fH^0$of AgCsMoO$_4$ in the gaseous state starting from different reactions: 7, 8 and 9 and using the TPSSh-5%HF/CBS method. This gives a value equal to -764.0 ± 24.5 kJ mol^{-1} (see table III). Again, the $\Delta_fH^0$of AgCsMoO$_4$ starting from 8 and 9 are close to each other. However, the Δ_fH^0 value calculated using reaction 7 is 40 kJmol^{-1} higher. Thus, the uncertainty among the three values is around 40 kJmol^{-1}. Again, we computed the $\Delta_fH^0$of AgCsMoO$_4$ using the CCSD(t)/CBS method that treats well the correlation energy. The uncertainty among the three values is less than 3 kJ mol^{-1} and the average value is equal to -721.0 ± 1.6 kJ mol^{-1}. Again, in the literature, there exist no experimental data to compare our results with.

TABLE II
Computed Standard Enthalpy of Formation for Cs$_2$, Ag$_2$ and MoO$_3$ obtained at the DFT and CCSD(T) Levels for the Various Reactions R(n), and with Multireference Correlated Calculations Using TPSSh-5%HF Optimized Geometries. Δ_fH^0 (298 K) ± σ Represents the Average and the Standard Deviation of Computed Standard Enthalpies of Formation

Cs$_2$		
Method	Basis set	Δ_fH^0 (298 K)
TPSSh-5%5HF	Aug-cc-PVTZ	100.1 ± 2.0
TPSSh-5%5HF	Aug-cc-PVQZ	99.3 ± 2 .0
TPSSh-5%5HF	CBS	98.7 ± 2 .0
CCSD(t)	Aug-cc-PVTZ	118.5 ± 2.0
CCSD(t)	Aug-cc-PVQZ	112.1 ± 2.0
CCSD(t)	CBS	107.4 ± 2.0
Ag$_2$		
Method	Basis set	Δ_fH^0 (298 K)
TPSSh-5%5HF	Aug-cc-PVTZ	400.6 ± 0.0
TPSSh-5%5HF	Aug-cc-PVQZ	400.3 ± 0 .0
TPSSh-5%5HF	CBS	400.1± 0 .0
CCSD(t)	Aug-cc-PVTZ	413.1 ± 0.0
CCSD(t)	Aug-cc-PVQZ	410.1 ± 0.0
CCSD(t)	CBS	407.8 ± 0.0
MoO$_3$		
Method	Basis set	Δ_fH^0 (298 K)
TPSSh-5%5HF	Aug-cc-PVTZ	-342.5 ± 0.0
TPSSh-5%5HF	Aug-cc-PVQZ	-342.6 ± 0 .0
TPSSh-5%5HF	CBS	-342.7 ± 0 .0
CCSD(t)	Aug-cc-PVTZ	-339.6 ± 0.0
CCSD(t)	Aug-cc-PVQZ	-343.5 ± 0.0
CCSD(t)	CBS	-346.6 ± 0.0

C. Standard Enthalpy of Formation of CsHMoO$_4$

The calculated values of standard enthalpy of formation for CsHMoO$_4$ in the gaseous state, starting from the reactions 10, 11and 12 are reported in Table III. The $\Delta_fH^0$of CsHMoO$_4$ using the TPSSh-5%HF/CBS method is equal to -1029.2 ±24.5 kJmol^{-1}. Again, the CCSD(t) method is used to treat well the correlation energy and decrease the uncertainty among the computed values. However, for CsHMoO$_4$, we were not able to perform CCSD(t) with aug-cc-pVTZ because there was a mixing between the valence orbitals and the core orbitals. For this, we performed only CCSD(t) with the aug-cc-pVQZ basis set. The uncertainty among the three values is again less than 3.0 kJmol^{-1} and the average value is equal to -865.8±1.6 kJmol^{-1}. Again, there are no available experimental data with which to compare these results.

IV. Conclusion

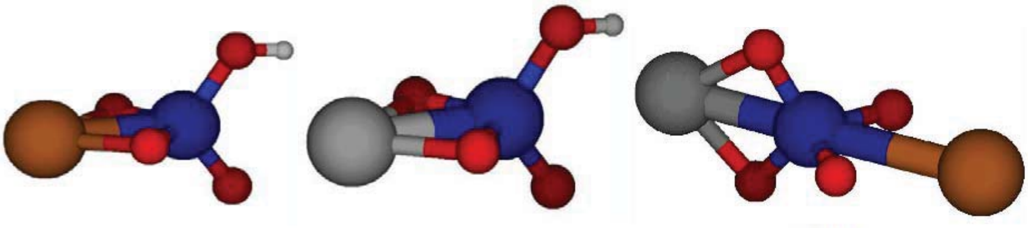
In this paper, we have applied established a methodology to predict the thermodynamic parameters of AgHMoO$_4$, AgCsMoO$_4$ and CsHMoO$_4$ in the gaseous phase. Using geometries and partition functions obtained at the DFT level

(U-TPSSh-5%HF), and CCSD(T) wave function method for calculating accurate reaction enthalpies that are used to determine heats of formations for $AgHMoO_4$, $AgCsMoO_4$ and $CsHMoO_4$ compounds in the gaseous state. The excellent similarities of the derived standard enthalpies of formation irrespective to the chosen formation reaction, makes us propose that the uncertainty in the herewith reported $\Delta_f H^0$ is in the range of 2 kJmol^{-1}. In the absence of experimental data for $AgHMoO_4$, $AgCsMoO_4$ and $CsHMoO_4$, this work predicts their heats of formation in the gaseous phase to be -634.3 ±1.6 kJmol^{-1}, -721.0 ± 1.6 kJmol^{-1}, -865.8 ± 1.6 kJmol^{-1} respectively. These new data will be implemented in the thermodynamical databases that are used by the ASTEC code (accident source term evaluation code) to build models of Cs and silver chemistry behavior in severe nuclear accident conditions.

TABLE III

Computed Standard Enthalpies of Formation for AgHMoO4, AgCsMoO4 and CsHMoO4 Obtained at the DFT and CCSD(T) Levels for the Various Reactions R(N), and with Multireference Correlated Calculations Using TPSSh-5%HF Optimized Geometries. $\Delta_f H^0$ (298 K) ± σ Represents the Average and the Standard Deviation of Computed Standard Enthalpies of Formation

$AgHMoO_4$					
Method	Basis set	R(4)	R(5)	R(6)	$\Delta_f H^0$ (298 K)
TPSSh-5%5HF	Aug-cc-PVTZ	-584.7	-580.7	-625.2	-596.9 ± 24.6
TPSSh-5%5HF	Aug-cc-PVQZ	-583.7	-579.9	-624.2	-596.0 ± 24 .6
TPSSh-5%5HF	CBS	-583.1	-579.3	-623.5	-595.3 ± 24.5
CCSD(t)	Aug-cc-PVTZ	-631.6	-624.7	-633.9	-630.1 ± 4.8
CCSD(t)	Aug-cc-PVQZ	-633.7	-630.8	-633.1	-632.5 ± 1.6
CCSD(t)	CBS	-635.3	-635.2	-632.4	-634.3 ± 1.6
$AgCsMoO_4$					
Method	Basis set	R(7)	R(8)	R(9)	$\Delta_f H^0$ (298 K)
TPSSh-5%5HF	Aug-cc-PVTZ	-751.4	-747.4	-791.9	-763.6 ± 24.6
TPSSh-5%5HF	Aug-cc-PVQZ	-751.6	-747.7	-792.1	-763.8 ± 24 .6
TPSSh-5%5HF	CBS	-751.7	-747.9	-792.2	-764.6 ± 24.5
CCSD(t)	Aug-cc-PVTZ	-723.4	-716.5	-725.7	-721.9 ± 4.8
CCSD(t)	Aug-cc-PVQZ	-722.6	-719.6	-721.9	-721.4 ± 1.6
CCSD(t)	CBS	-722.0	-721.9	-719.1	-721.0 ±1.6
$CsHMoO_4$					
Method	Basis set	R(10)	R(11)	R(12)	
TPSSh-5%5HF	Aug-cc-PVTZ	-1015.8	-1011.9	-1056.3	-1028.0 ± 24.6
TPSSh-5%5HF	Aug-cc-PVQZ	-1016.5	-1012.6	-1057.0	-1028.7 ± 24 .6
TPSSh-5%5HF	CBS	-1017.0	-1013.2	-1057.5	-1029.2 ± 24.5
CCSD(t)	Aug-cc-PVQZ	-867.0	-864.1	-866.4	-865.8 ± 1.6



(a) $CsHMoO_4$ (b) $AgHMoO_4$ (c) $AgCsMoO_4$

Fig 1 Perspective views of $CsHMoO_4$, $AgHMoO_4$ and $AgCsMoO_4$ optimized at the TPSSh%5HF/Def2-QZVP level of theory. **Cs** atoms in brown, oxygen atoms in red, molybdenum atoms in blue, silver atoms in grey, and hydrogen atoms in white

ACKNOWLEDGMENT

The authors express gratitude to the head of the Laboratory (Laboratoire d'étude du corium et du transfert des radioéléments (LETR), Christian MUN, for permitting us to participate in this conference. The authors would like to thank Mirco Di Giuli, Marc Barrachin and Tim Haste for the fruitful conversations and discussions.

REFERENCES

[1] D. Jacquemain et al., "Nuclear power reactor core melt accidents. Current State of Knowledge" (2015).

[2] L. Herranz et al., "In-containment source term: key insights gained from a comparison between the PHEBUS-FP programme and the US-NRC NUREG-1465 revised source term." Progress in Nuclear Energy 52.5 (2010), pp: 481-486.

[3] G. Schumacher et al., "Modeling cesium behavior in nuclear reactor fuels at high temperatures",Journal of Nuclear Materials 130 (1985), pp: 21-35.

[4] A-C Grégoire et al., "Studies on the role of molybdenum on iodine transport in the RCS in nuclear severe accident conditions.", Annals of Nuclear Energy 78 (2015): 117-129.

[5] P. Chatelard, et al. "Main modelling features of the ASTEC V2.1 major version.", Annals of Nuclear Energy 93 (2016), pp: 83-93.

[6] J. Cox, D. Wagman and V. Medvedev, in CODATA Key Values for Thermodynamics, Hemisphere Publishing Corp., 1984, p. 1.

[7] M. W. Chase, "NIST—JANAF Thermochemical Tables (Journal of Physical and Chemical Reference Data Monograph No. 9)." American

Institute of Physics (1998).

[8] D. R. Lide, "CRC Handbook of Chemistry and Physics, 84th Edition", CRC PRESS, Dordrecht, 2003-2004, p. 842.

[9] M. J. E. A. Frisch et al. "Gaussian 09, revision a. 02, gaussian." Inc., Wallingford, CT 200 (2009).

[10] J. Tao et al. "Climbing the density functional ladder: Nonempirical meta–generalized gradient approximation designed for molecules and solids." Physical Review Letters 91.14 (2003), pp: 146401.

[11] O. A. Vydrov et al., "Scaling down the Perdew-Zunger Self-Interaction Correction in Many-Electron Regions", Journal of Chemical Physics, 2006, 124, pp: 094108.

[12] F. Weigend et al., "RI-MP2: optimized auxiliary basis sets and demonstration of efficiency.", Chemical Physics Letters 294.1-3 (1998), pp: 143-152.

[13] F. Weigend et al., "Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy.", Physical Chemistry Chemical Physics 7.18 (2005), pp: 3297-3305.

[14] T. Leininger et al., "The accuracy of the pseudopotential approximation: Non-frozen-core effects for spectroscopic constants of alkali fluorides XF (X= K, Rb, Cs)." Chemical physics letters 255.4-6 (1996): 274-280.

[15] D. Andrae et al., "Energy-adjusted ab initio pseudopotentials for the second and third row transition elements". Theoretica Chimica Acta, 77(2), ((1990), pp: 123-141.

[16] C. Hättig and F. Weigend,. "CC2 excitation energy calculations on large molecules using the resolution of the identity approximation.", The Journal of Chemical Physics 113.13 (2000), pp: 5154-5161.

[17] C. Hättig et al., "Distributed memory parallel implementation of energies and gradients for second-order Møller–Plesset perturbation theory with the resolution-of-the-identity approximation." Physical Chemistry Chemical Physics 8.10 (2006), pp: 1159-1169.

[18] H.-J. Werner and M. Schütz, "An efficient local coupled cluster method for accurate thermochemistry of large systems." The Journal of Chemical Physics 135.14 (2011), pp: 144116.

[19] P. J. Knowles et al., "Coupled cluster theory for high spin, open shell reference wave functions." The Journal of Chemical Physics 99.7 (1993), pp: 5219-5227.

[20] P. J. Knowles et al.,"Erratum: "Coupled cluster theory for high spin, open shell reference wave functions" (J. Chem. Phys. 99, 5219 (1993))." The Journal of Chemical Physics 112.6 (2000), pp: 3106-3107.

[21] D. Figgen et al. "Energy-consistent pseudopotentials for group 11 and 12 atoms: adjustment to multi-configuration Dirac–Hartree–Fock data." Chemical Physics 311.1-2 (2005), pp: 227-244.

[22] D. Feller, "Application of systematic sequences of wave functions to the water dimer." The Journal of Chemical Physics 96.8 (1992), pp: 6104-6114.

[23] D. Feller, "The use of systematic sequences of wave functions for estimating the complete basis set, full configuration interaction limit in water." The Journal of Chemical Physics 98.9 (1993), pp: 7059-7071.

[24] T. Helgaker et al., "Basis-set convergence of correlated calculations on water." The Journal of Chemical Physics 106.23 (1997), pp: 9639-9646.