



Multilevel Quantum Chemical Calculation of Hydrogenation Enthalpies of Some Unsaturated Organic Compounds in the Gas Phase

Ali Amir Khairbek¹, Mohammad Abed Al-Hakim Badawi²

¹Master Student in Physical Chemistry, Faculty of Science, Tishreen university, Lattakia

²Professor, Department of Chemistry, Faculty of Science, Tishreen university, Lattakia

Abstract The standard enthalpies of hydrogenation of 29 unsaturated hydrocarbon compounds were calculated in the gas phase by the M06-2X theory of level with the 6-31g(d) and cc-pVXZ, where X =D, T, Q, as well as by complete basis set limit extrapolation using two different formulas. Geometries of compounds were optimized at the M06-2X/6-31g(d) level. This M06-2X geometries were used in the M06-2X and extrapolation calculations with cc-pVXZ basis sets. Comparison of calculation and experimental results shows that the median absolute deviations (MAD) between the calculated and experimental enthalpies of hydrogenation range from 25.1 to 5.1 kJ mol⁻¹ at M06-2X calculations, and for calculations, where using complete basis set limit extrapolation, the MAD have decreased to 2.7 kJ mol⁻¹. The results of some calculations showed that the deviations from experimental values are located inside the "chemical accuracy" (± 1 kcal mol⁻¹ \approx ± 4.2 kJ mol⁻¹). Very good linear correlations between experimental and calculated enthalpies of hydrogenation have been obtained at M06-2X/TZ method.

Keywords Complete basis set (CBS), density functional theory (DFT), extrapolation method

Introduction

Recent developments in computational chemistry have enabled the calculation of the enthalpies of large molecules that are not saturated with the elementary principles of quantum mechanics. Some of these molecules lie outside the practical scope of the thermal chemistry of combustion. Quantum mechanical calculations of molecular thermochemical properties are approximate, and complex quantum mechanical procedures are used at almost every step of the multiple computation, and may have a trial factor to correct the cumulative error. Approximate methods are useful in that the error resulting from different approximations is known within narrow limits. The error of approximation is determined by comparison with the "known" value, but the question of the accuracy of the "known" value arises immediately, because the uncertainty in comparison is determined by the common uncertainty of the approximate quantum mechanical result and the benchmark being compared.

After validation of the quantum mechanical procedure of its ability to recalculate many accurate experimental results, we can Calculation of unknown thermal chemical values for unstable or explosive compounds, which is not appropriate for classical chemical thermodynamics or the calculation of the thermal chemical properties of molecules, free radicals or transient ions [1], here lies the importance of quantum mechanical calculations in providing accurate results for hydrogenation. Many hydrogenation experiments are not performed which may be interesting and useful because they are impractical due to polymerization of reactive or undesirable substances because they are dangerous, as in the case of poly alkenes, some of which explode spontaneously.



Many works have been calculated $\Delta_{\text{hyd}}H_{298}^0$ For some small unsaturated cyclohydrocarbon compounds [2], ketones and cycloaldehydes [3] And many cyclo and non-cyclo hydrocarbons [4-10] Using different theoretical methods (Ab initio), such as Gn, MP2, and M06-2X. In this work we will calculate the $\Delta_{\text{hyd}}H_{298}^0$ of 29 unsaturated hydrocarbons by M06-2X [11], compare our results with available experimental results, and interpret them linearly. In addition, we will use induction schemes for the Complete basis set Group (CBS) Based on two formulas proposed in the two studies [12-13] to calculate the hydrogenation temperature.

Research Methods and Materials

The molecular orbital calculations (Ab initio) [14] were performed by the Gaussian09- Gaussian16 program [15]. The geometric shapes of the studied compounds were obtained using the theoretical level M06-2X / 6-31g (d). These best geometric shapes were used to recalculate their improved energies through M06-2X with the cc-pVXZ [16]; X = D, T, Q.

Research Objectives and Importance

This research aims to:

1. Calculation of hydrogenation of 29 unsaturated carbonyl compounds by Theory M06-2X in different methods.
2. Comparison of theoretical and experimental results, and determination of statistical coefficients for each method used.
3. Know the effect of using the complete basis set group in the results of Theoretical level M06-2X/6-31g (d).
4. Use of the complete basis set group (CBS) extrapolation schemes to calculate the hydrogenation of the studied vehicles.
5. Obtain linear correlation between theoretical and experimental results.

The importance of this research is to know how best to deflect from experimental values within the chemical accuracy ($\pm 1 \text{ kcal mol}^{-1} \approx 4.2 \text{ kJ mol}^{-1}$) and to use it later to calculate other hydrogenation of compounds or to be used as a standard method for determining some physical properties of molecules or reactions Chemical calculation details:

If the enthalpies of Formation of unsaturated compounds and hydrogenation products are known in the gaseous state at 298 K, we can calculate the hydrogenation equation from the following equation:

$$\Delta_{\text{hyd}}H^0(298) = \sum_{\text{products}} \Delta_f H^0(298) - \sum_{\text{reactans}} \Delta_f H^0(298) \quad (1)$$

Or from the following equation:

$$\Delta_{\text{hyd}}H_{298}^0 = \sum (E_0 + H^0)_{\text{products}} - \sum (E_0 + H^0)_{\text{reactants}} \quad (2)$$

E_0 and H^0 represent the energy and the standard enthalpy of the molecule calculated at the theoretical level M06-2X / 6-31g (d), respectively. The calculated value can be represented by M06-2X, but with a base set Integrated cc-pVXZ. To obtain a better estimate of the "real" energy of the molecule.

The limit extrapolation scheme of the CBS group are used; the calculations are organized for infinite basis group by extrapolation to the CBS boundary by two expressions: a Gaussian-Exponential mixed expression with three coefficients [12] and an expression of force 3 with two coefficients [13]:

$$E(X) = E_{\text{CBS}} + Ae^{-(X-1)} + Be^{-(X-1)^2} \quad (3)$$

$$E(X) = E_{\infty} + \frac{A}{X^3} \quad (4)$$



X represents the complete basis set number (2, 3 and 4 for the DZ, TZ and QZ groups respectively), and E_{CBS} and E_{∞} are the energy of limit, A and B are the configuration coefficients. These energies are used to calculate the enthalpies of Hydrogenation for studied compounds based on the equation (2). We performed a process extrapolation of limit of CBS group by using the web page mentioned in the search [17].

The data are analyzed by the square root of the median error (RMS), the absolute mean deviations (MAD), and by linear correlation. In the latter case, we plotted the linear relationship between the calculated values $\Delta_{\text{hyd}}H^{\circ}$ (cal.) and the experimental values $\Delta_{\text{hyd}}H^{\circ}$ (exp.) to obtain the standard deviations (SD) and R^2 .

Results and Discussion

Enthalpies of Hydrogenation

Enthalpies of Hydrogenation were calculated at point 298 K using the equation (2) through the data of the theory M06-2X with different basic groups. Table (2) show calculated enthalpies and experimental enthalpies in the gaseous state. The experimental data were obtained from the book [18], as shown in Table (1).

Calculations at theoretical level M06-2X / XZ:

Note from Table 2 that the three theoretical levels M06-2X / XZ; X represents either D, T or Q, a deviation of MAD from the experimental values is equal to 9.5 kJ mol⁻¹ or 3.8 kJ mol⁻¹ or 5.0 kJ mol⁻¹, respectively; the use of a larger core group (QZ) does not improve the result, meaning that the calculated energy value of this group is far from the real value. In the research [2] the same theoretical level was used M06-2X, but with the AUG-cc-pVTZ group in order to calculate the hydrogenation of 13 Unsaturated compounds (Alkenes) and found that the RMS value was about 10.0 kJ mol⁻¹, which is larger than the value specified in this research, Which is about 4.6 kJ mol⁻¹, which is because the AUG-cc-pVTZ group presents different results than the cc-pVTZ group used in this research.

The limit extrapolation scheme of the CBS group by equation (3) or (4) require three energy points (X = D, T, Q) or two energy points (X = D, T or X = T, Q) respectively [Figure (1)], It is expected from the results of the calculations at the three theoretical levels that the value of MAD when using The limit extrapolation scheme of the two CBS groups X = D, T is less than that for the two CBS groups X = T, Q by the equation (4); in the first case it is about 2.7 kJ mol⁻¹, and in the second case it is 4.8 kJ mol⁻¹, which is why the CBS group extrapolation scheme by equation (4) provides better accuracy than when using equation (3); the deviation is about 4.5 kJ mol⁻¹ when using the group X = D, T.

It is also noticed from Table (2) that the percentage of absolute mean error presented by the limit extrapolation scheme of the group X = D, T is about 1.6%, It is less than the percentage error of the theoretical level M06-2X / TZ, at about 2.3%.

Table 1: Experimental values of enthalpy reactions of hydrogenation of some unsaturated hydrocarbons in the gaseous state (kJ mol⁻¹)

| Reaction | $\Delta_{\text{hyd}}H^{\circ}_{298}$ (exp.) |
|--|---|
| ethyne + 2 H ₂ → ethane | -312.0 ± 0.63 |
| ethene + H ₂ → ethane | -136.3 ± 0.3 |
| propadiene + 2 H ₂ → propane | -295.1 ± 0.1 |
| prop-1-yne + 2 H ₂ → propane | -289.6 ± 0.63 |
| prop-1-ene + H ₂ → propane | -125.0 ± 0.42 |
| but-2-yne + 2 H ₂ → butane | -272.4 ± 1.3 |
| 2-methylprop-1-ene + H ₂ → 2-methylprop-1-ane | -117.8 ± 0.42 |
| (2E)-but-2-ene + H ₂ → butane | -118.5 ± 0.42 |
| (2Z)-but-2-ene + H ₂ → butane | -114.6 ± 0.42 |
| (2E)-pent-2-ene + H ₂ → pentane | -113.8±0.8 |



| | |
|--|---------------|
| (2Z)-pent-2-ene + H ₂ → pentane | -117.7 ± 0.8 |
| 2-methylbut-1-ene + H ₂ → 2-methylbutane | -118.2 ± 0.42 |
| 2-methylbut-2-ene + H ₂ → 2-methylbutane | -111.6 ± 0.3 |
| 3-methylbut-1-ene + H ₂ → 2-methylbutane | -126.3 ± 0.3 |
| cyclopenta-1,3-diene + 2 H ₂ → cyclopentane | -210.8 ± 0.84 |
| hex-1,5-diene + 2 H ₂ → hexane | -251.2 ± 0.42 |
| hex-1-ene + H ₂ → hexane | -126.0 ± 2.0 |
| 2,3-dimethylbuta-1,3-diene + 2 H ₂ → 2,3-dimethylbutane | -223.4 ± 0.63 |
| 2,3-dimethylbuta-1-ene + H ₂ → 2,3-dimethylbutane | -116.1 ± 0.4 |
| 2,3-dimethylbuta-2-ene + H ₂ → 2,3-dimethylbutane | -110.4 ± 0.42 |
| 3,3-dimethylbuta-1-ene + H ₂ → 2,2-dimethylbutane | -125.9 ± 0.63 |
| benzene + 3 H ₂ → cyclohexane | -205.3 ± 0.6 |
| cyclohexa-1,3-diene + 2 H ₂ → cyclohexane | -229.6 ± 0.42 |
| cyclohexene + H ₂ → cyclohexane | -118.6 ± 0.42 |
| hept-1-ene + H ₂ → heptane | -125.1 ± 0.3 |
| 4,4-dimethylpent-1-ene + H ₂ → 2,2-dimethylpentane | -122.5 ± 0.42 |
| cyclohepta-1,3,5-triene + 3 H ₂ → cycloheptane | -301.7 ± 1.3 |
| cyclohepta-1,3-diene + 2 H ₂ → cycloheptane | -212.4 ± 0.63 |
| cycloheptene + H ₂ → cycloheptane | -108.9 ± 0.63 |

Table 2: Experimental deviations of enthalpies of hydrogenation ($\Delta_{\text{hyd}}H_{298}^0$) (kJ. mol⁻¹) from the calculated values using the theoretical level M06-2X in various methods

| Compounds | M06-2X | | | | | | Exp. |
|----------------------------|----------|------|------|------|-------|-------|-------------|
| | 6-31g(d) | D | T | Q | Eq. 3 | Eq. 4 | |
| ethyne | 42.7 | 20.6 | 8.0 | 8.3 | 8.9 | 2.7 | -312.0±0.63 |
| ethene | 22.9 | 9.5 | 5.3 | 5.8 | 6.2 | 3.6 | -136.3±0.3 |
| propadiene | 27.1 | 7.6 | -2.2 | -1.4 | -0.4 | -6.3 | -295.1±0.1 |
| propene | 28.4 | 6.7 | 2.7 | 2.9 | 3.2 | 1.0 | -125.0±0.42 |
| propyne | 32.9 | 16.2 | 2.7 | 3.1 | 3.8 | -2.9 | -289.6±0.63 |
| but-2-yne | 27.3 | 11.4 | -2.3 | 27.0 | -0.6 | -8.2 | -272.4±1.3 |
| 2-methylprop-1-ene | 18.8 | 6.8 | 2.8 | 3.0 | 3.3 | 1.1 | -117.8±0.42 |
| 2E-but-2-ene | 17.6 | 5.3 | 1.8 | 2.1 | 2.3 | 0.4 | -118.5±0.42 |
| 2Z-but-2-ene | 18.7 | 7.5 | 3.7 | 4.1 | 4.5 | 2.1 | -114.6±0.42 |
| 2E-pent-2-ene | 17.1 | 7.2 | 3.0 | 3.3 | 3.6 | 1.2 | -113.8±0.8 |
| 2Z-pent-2-ene | 10.2 | -0.1 | -3.8 | -3.6 | -3.3 | -5.4 | -117.7±0.8 |
| 2-methylbut-1-ene | 15.8 | 3.7 | -0.5 | -0.3 | 0.0 | -2.3 | -118.2±0.42 |
| 2-methylbut-2-ene | 14.1 | 3.0 | -0.4 | -0.3 | -0.2 | -1.9 | -111.6±0.3 |
| 3-methylbut-1-ene | 17.3 | 4.1 | 0.0 | 0.3 | 0.7 | -1.7 | -126.3±0.3 |
| cyclopenta-1,3-diene | 30.8 | 12.0 | 5.4 | 6.0 | 6.6 | 2.7 | -210.8±0.84 |
| 1,3-Cyclohexadiene | 45.4 | 16.2 | 7.9 | 8.4 | 9.1 | 4.3 | -229.6±0.42 |
| 1,5-hexadiene | 40.9 | 17.8 | 9.3 | 10.3 | 11.2 | 5.8 | -251.2±0.42 |
| 2,3-dimethylbut-1-ene | 18.1 | 6.9 | 2.7 | 3.0 | 3.4 | 1.0 | -116.1±0.4 |
| 2,3-dimethylbut-2-ene | 18.4 | 7.6 | 4.1 | 4.1 | 4.3 | 2.6 | -110.4±0.42 |
| 2,3-dimethylbuta-1,3-diene | 13.7 | 10.7 | 3.3 | 3.8 | 4.5 | 0.1 | -223.4±0.63 |
| 3,3-dimethylbut-1-ene | 19.2 | 6.5 | 2.5 | 2.9 | 3.4 | 0.8 | -125.9±0.63 |
| benzene | 43.4 | 11.4 | 1.2 | 3.0 | 4.5 | -3.0 | -205.3±0.6 |
| cyclohexene | 19.6 | 7.1 | 2.6 | 2.9 | 3.2 | 0.7 | -118.6±0.42 |
| hex-1-ene | 19.4 | 8.1 | 3.5 | 3.9 | 4.3 | 1.6 | -126.0±2.0 |
| 4,4-dimethylpent-1-ene | 19.3 | 7.7 | 3.8 | 4.3 | 4.8 | 2.2 | -122.5±0.42 |
| cyclohepta-1,3,5-triene | 51.0 | 22.8 | 10.9 | 12.2 | 13.5 | 5.8 | -301.7±1.3 |
| cyclohepta-1,3-diene | 40.5 | 15.2 | 7.6 | 8.4 | 9.2 | 4.4 | -212.4±0.63 |
| cycloheptene | 16.5 | 6.7 | 2.8 | 3.0 | 3.4 | 1.1 | -108.9±0.63 |



| | | | | | | | |
|----------------|-------|-------|-------|-------|-------|-------|------------|
| hept-1-ene | 20.8 | 8.9 | 4.3 | 4.7 | 5.2 | 2.4 | -125.1±0.3 |
| MAD | 25.1 | 9.5 | 3.8 | 5.0 | 4.5 | 2.7 | |
| RMS | 27.4 | 10.8 | 4.6 | 7.1 | 5.5 | 3.4 | |
| Error% | 15.0% | 5.5% | 2.3% | 2.8% | 2.7% | 1.6% | |
| SD | 7.55 | 5.50 | 3.18 | 3.32 | 3.35 | 3.44 | |
| R ² | 0.992 | 0.995 | 0.998 | 0.998 | 0.998 | 0.998 | |

Linear Analysis of Results

A very good linear correlation relationship was obtained between experimental enthalpies of Hydrogenation and calculations of method M06-2X / TZ , as well as when using the limit extrapolation schemes of the CBS group by equation (4) [Figures (2)].

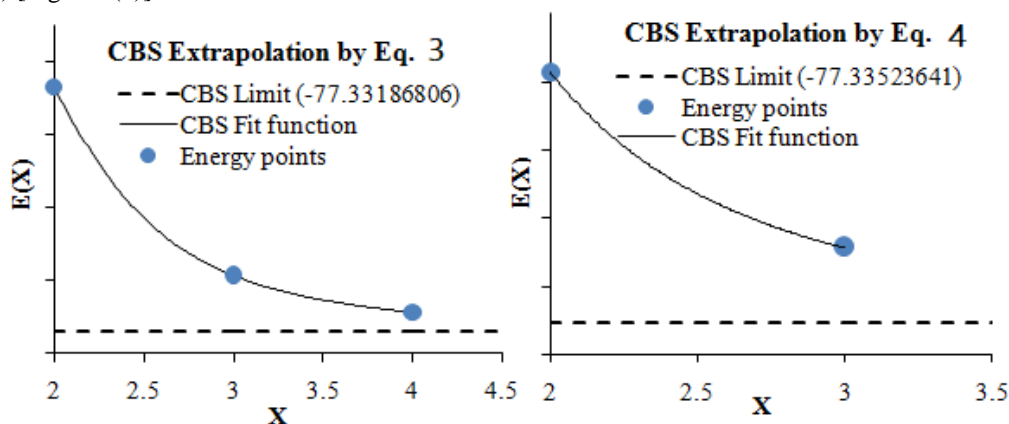


Figure 1: The limit extrapolation schemes of the CBS group based on equation (3) and (4) for the Acetylene molecule C_2H_2 according to the results of the theory M06-2X, the Integer coordinates 2, 3, and 4 refer to DZ, TZ, and QZ

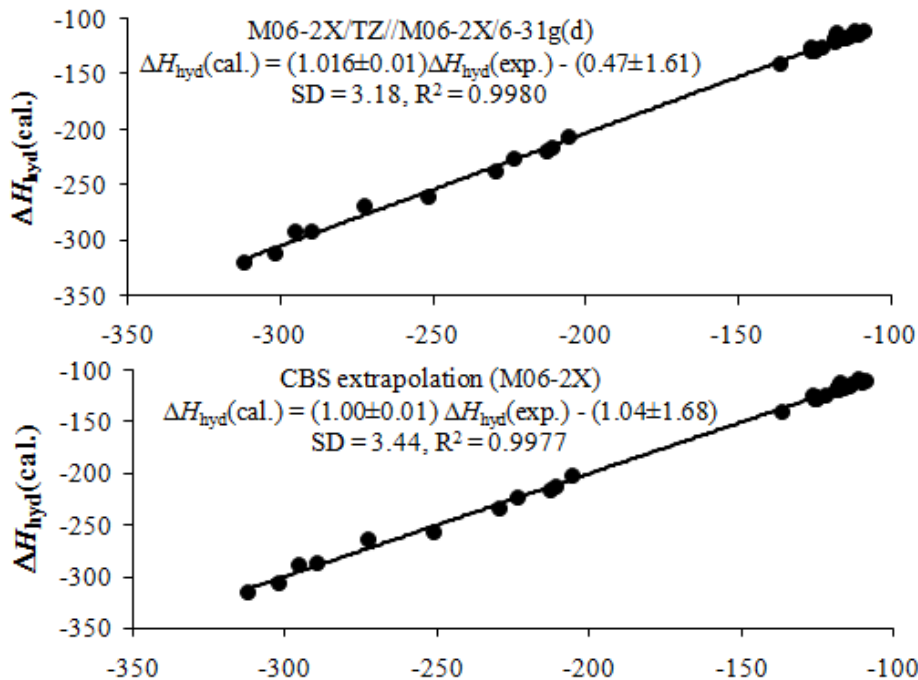


Figure 2: Linear correlation relationships between experimental enthalpies values (in kJ mol^{-1}) and calculated by the theoretical level M06-2X / TZ, as well as according to the limit extrapolation schemes of the CBS group by equation (4)

We note, in general, that the value of the standard deviation (SD) is about 3.18 kJ mol^{-1} and 3.44 kJ mol^{-1} for the theoretical level M06-2X / TZ, and the method for the limit extrapolation schemes of the group X = D, T by the equation (4) at Respectively, The value of R^2 is approximately 1.

Conclusions and Recommendations

We conclude from the above that the absolute mean deviations of the M06-2X / TZ method, as well as the approval limit extrapolation schemes of the CBS group by equation (4), fall within “chemical accuracy” ($1 \text{ kcal mol}^{-1} \approx 4.2 \text{ kJ mol}^{-1}$), It can be adopted in order to determine the physical and chemical properties of relatively large particles, since the related calculations do not require a long time for the calculation.

References

- [1]. Matsunaga; D. W., Mc Lafferty; F. J., Zavitsas; A. A., Liebman; J. F. “On the lack of conjugation stabilization in polyynes (polyacetylenes)”. *J. Org.Chem.*, 2004, 69, pp. 7143-7147.
- [2]. Wiberg; K. B. “Accuracy of Calculations of Heats of Reduction/Hydrogenation: Application to Some Small Ring Systems”. *J. Org. Chem.* 2012, 77, pp. 10393–10398.
- [3]. Rogers; D. W., Mc Lafferty; F. J., Podosenin; A. V. “G2 *ab Initio* Calculations of Enthalpies of Hydrogenation, Isomerization, and Formation of C3 Cyclic and Acyclic Ketones and Alcohols”. *J. Org. Chem.* 1998, 63, pp. 7319-7321.
- [4]. Rogers; D. W., Mc Lafferty. J., Podosenin A. V. “Ab Initio Calculations of Enthalpies of Hydrogenation and Isomerization of Cyclic C4 Hydrocarbons”. *J. Phys. Chem.* 1996, 100, pp. 17148-17151.
- [5]. Rogers; D. W., Mc Lafferty. J., Podosenin A. V.”G2(MP2) and G2 (MP2,SVP) Calculations of Enthalpies of Hydrogenation, Isomerization, and Formation of C5 Hydrocarbons. 2. Substituted Cyclobutenes, Vinylcyclopropene, Spiropentane, and Methyltetrahedrane”. *J. Phys. Chem.* 1998, 102, pp. 1209-1213.
- [6]. LI; Z., Rogers; D. W., Mc Lafferty F. J., Mandziuk M., Podosenin; A. V. “Ab Initio Calculations of Enthalpies of Hydrogenation, Isomerization, and Formation of Cyclic C6 Hydrocarbons. Benzene Isomers”. *J. Phys. Chem.*, 1999, 103, pp. 426-430.
- [7]. Rogers; D. W., Mc Lafferty. J. “G3(MP2) Calculations of Enthalpies of Hydrogenation, Isomerization, and Formation of Biand Tricyclic C8 and C10 Hydrocarbons. The Bicyclo[3.3.0]octenes and Triquinacenes”. *J. Phys. Chem.* 2000, 104, pp. 9356-9361.
- [8]. Pan; J.W., Rogers; D. W., Mc Lafferty; F. J. “Density functional calculations of enthalpies of hydrogenation, isomerization, and formation of small cyclic hydrocarbons”. *J. Mol. Struc. (Theochem)*, 1999, 468, pp. 59-66.
- [9]. Rogers; D. W., Mc Lafferty. J. “G3(MP2) Calculations of Enthalpies of Hydrogenation, Isomerization, and Formation of [3]-Radialene and Related Compounds”. *J. Phys. Chem. A* 2002, 106, pp. 1054-1059.
- [10]. Rogers; D. W., Matsunaga; N., Zavitsas; A. A. “G3(MP2) enthalpies of hydrogenation isomerization, and formation of extended linear polyacetylenes”. *J. Phys. Chem. A*, 2005, 109, pp. 9169-9173
- [11]. Zhao; Y., Truhlar; D. G. “The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals”. *Theo. Chem. Acc.*, 2008, 120, 215–241.
- [12]. Halkier; A. and et. al. “Basis-set convergence of the energy in molecular Hartree–Fock calculations”, *Chem. Phys. Lett.*, 1999, 302, pp. 437–446.
- [13]. Halkier; A. and et. al. “Basis-set convergence of correlated calculations on water”. *J. Chem. Phys.* 1997, 106, pp. 9639-9646.
- [14]. Hehre; W. J. and et. al. “Ab Initio Molecular Orbital Theory”. Wiley, New York, 1986.
- [15]. Frisch; M. J. and et. al. Gaussian 09, Revision A.02. Gaussian, nc., Wallingford, CT, 2009.



- [16]. Dunning Jr; T. H., “*Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen*”. J. Chem. Phys. 1989, 90, pp. 1007-1027.
- [17]. Vasilyev; V. “Online complete basis set limit extrapolation calculator. Compu. Theo. Chem., 2017, 1115, pp. 1–3. http://sf.anu.edu.au/~vvv900/cbs/#ref_3.
- [18]. Rogers; D. W. “*Heats of hydrogenation: experimental and computational hydrogen thermochemistry of organic compounds*”. World Scientific, 2006. Or from website <https://webbook.nist.gov/chemistry/formser/>