Quantum Calculations to Estimate the Heat of Hydrogenation Theoretically

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Abstract

Standard enthalpies of hydrogenation of 29 unsaturated hydrocarbon compounds were calculated in the gas phase by CCSD(T) theory with complete basis set cc-pVXZ, where X = DZ, TZ, as well as by complete basis set limit extrapolation. Geometries of reactants and products were optimized at the M06-2X/6-31g(d) level. This M06-2X geometries were used in the CCSD(T)/cc-pVXZ//M06-2X/6-31g(d) and cc-pV(DTZ) extrapolation calculations. (MAD) the mean absolute deviations of the enthalpies of hydrogenation between the calculated and experimental results that range from 8.8 to 3.4 kJ mol\(^{-1}\) based on the Comparison between the calculation at CCSD(T) and experimental results. The MAD value has improved and decreased to 1.5 kJ mol\(^{-1}\) after using complete basis set limit extrapolation. The deviations of the experimental values are located inside the “chemical accuracy” (±1 kcal mol\(^{-1}\)≈±4.2 kJ mol\(^{-1}\)) as some results showed. A very good linear correlations between experimental and calculated enthalpies of hydrogenation have been obtained at CCSD(T)/cc-pVTZ//M06-2X/6-31g(d) level and CCSD(T)/cc-pV(DTZ) extrapolation levels (SD =2.11 and 2.12 kJ mol\(^{-1}\), respectively).

Keywords: complete basis set (CBS), density functional theory (DFT), CCSD (T), extrapolated method, molecules, energy, enthalpy, hydrocarbons

1. Introduction

The calculation of enthalpies of formation for the large unsaturated molecules, some of which are not included in the practical range of combustion thermochemistry, based on quantum mechanical first principles which have been possible basing on the recent important advances in computational chemistry. Necessary, Quantum mechanical calculations of molecular thermochemical properties are approximate. Approximations may be employed by the Composite quantum mechanical procedures at each of several computational steps and in the same time it may have an empirical factor to correct the cumulative error. When the error of the various approximations is known within narrow limits, but the question about the accuracy of the “known” value is noticed immediately because the uncertainty of the comparison between the approximate quantum mechanical result and the standard to which it is compared.

The most correct quantum mechanical procedure is been established after its ability to reproduce various accurate experimental results to calculate unknown
thermochemical values of explosive compounds or unstable, unsuited to classical thermochemical methods, or to calculate thermochemical properties of radicals, molecules, or ions of fleeting existence [1-15]. Here where a major advantage to create the accuracy of inherent hydrogen thermochemical results lies, and it works for encouraging and renewing interest in the diverse literature devoted to hydrogen thermochemistry.

The main part of the quantum chemistry is contend in the total electronic energy of a molecule. And this total electronic energy is a function of the nuclear geometric configuration after Born-Oppenheimer separation of electronic and nuclear motion, therefore generating hyper surfaces of potential energy— for electronically excited states as well as for the ground state.

At the end of this work a very important fact is clear now which clarify that wave function-based quantum-chemical methods can produce molecular electronic energies with an accuracy that surpasses that of experimental measurements of molecular energies (in terms of enthalpies of formation).

An important feature of the wavefunction-based quantum-chemical methodology is the ability to access the exact characterizing of the molecular electronic structure in a systematic manner. To achieve systematic approach two basic steps have been taken, the first step using advanced hierarchy of wavefunction models and the second step using systematic sequence of basis sets – or a nearly complete basis set – of atomic orbitals.

2. Basis-set convergence

It is noted that the type of wavefunction model used, or density functional, plays an important role in determining accuracy of computed molecular electronic energies. In addition to the important role played by the flexibility of the one electron basis set of atomic orbitals (AOs) by which the molecular orbitals (MOs) are expanded. It is worth noting that Slater’s determinants are constructed using MOs for use in Kohn - Sham theory or to expand the n-electron wavefunction.

Different ways can be chosen from basis sets of AOs (the literature [16–18]). As for the approach followed in study of molecular electronic-structure based on wavefunction methods, a well-defined procedure must have been used in order to generating sequences of the basis sets in order to increase flexibility. This way is very useful by generating hierarchies for basis sets, Each next higher level describes an improved systematically of the molecular electronic structure compared to the next lower level. Within the hierarchy the calculated results converge within a prescribed accuracy, and then the basis-set hierarchy ends up effectively complete basis [16]. Therein lies the problem where approaches of wavefunction that depend on the electron-correlation effects of the convergence to an effectively complete basis are very slow. When increasing the number N of AOs in the basis according to an optimal manner, it reduces the basis-set error as \( \propto N^{-1} \), thus obtaining a good approximation. It is often noticed that the accuracy of the electronic correlation calculations is limited by computational technical constraints. This is due to computing times growing at least as N4 and the computational effort grows more quickly compared to gain in accuracy.

2.1 Correlation-consistent basis sets

The correlation-consistent basis sets from Dunning and his co-workers [19, 20] represent a popular hierarchy of basis sets. When the valence orbitals are
correlated in a calculations only then can the expansion mainly in the Limit extrapolation, until it ends to an effectively complete basis [21–26]. The term X-tuple zeta basis sets represents to correlation-consistent polarized valence, denoted by cc-pVXZ, and is used in the calculations of this work, where $X = D, T, (double, triple zeta)$. It should be noted that when all the electrons are correlated (core as well as valence orbitals), the cc-pCVXZ basis sets must be used provided $2 \leq X \leq 5$.

| Reactions                                      | $\Delta_{\text{calc}}H^0_{\text{H}_{\text{exp}}}$ (exp. ) |
|------------------------------------------------|---------------------------------------------------------|
| Ethyne + 2 H$_2$ → ethane                      | $-312.0 \pm 0.63$                                       |
| Ethene + H$_2$ → ethane                        | $-136.3 \pm 0.3$                                       |
| Propadiene + 2 H$_2$ → propane                 | $-295.1 \pm 0.1$                                       |
| Prop-1-yne + 2 H$_2$ → propane                 | $-289.6 \pm 0.63$                                      |
| Prop-1-ene + H$_2$ → propane                   | $-125.0 \pm 0.42$                                      |
| But-2-yne + 2 H$_2$ → butane                   | $-272.4 \pm 1.3$                                       |
| Isobutene + H$_2$ → isobutane                 | $-117.8 \pm 0.42$                                      |
| (2E)-but-2-ene + H$_2$ → butane                | $-118.5 \pm 0.42$                                      |
| (2Z)-but-2-ene + 2 H$_2$ → butane              | $-114.6 \pm 0.42$                                      |
| (2E)-pent-2-ene + H$_2$ → pentane              | $-113.8 \pm 0.8$                                       |
| (2Z)-pent-2-ene + H$_2$ → pentane              | $-117.7 \pm 0.8$                                       |
| 2-Methylbut-1-ene + H$_2$ → 2-methylbutane     | $-118.2 \pm 0.42$                                      |
| 2-Methylbut-2-ene + H$_2$ → 2-methylbutane     | $-111.6 \pm 0.3$                                       |
| 3-Methylbut-1-ene + H$_2$ → 2-methylbutane     | $-126.3 \pm 0.3$                                       |
| Cyclopenta-1,3-diene + 2 H$_2$ → cyclopentane  | $-210.8 \pm 0.84$                                      |
| Hex-1,5-diene + 2 H$_2$ → hexane               | $-251.2 \pm 0.42$                                      |
| Hex-1-ene + H$_2$ → hexane                     | $-126.0 \pm 2.0$                                       |
| 2,3-Dimethylbuta-1,3-diene + 2 H$_2$ → 2,3-dimethylbutane | $-223.4 \pm 0.63$                                      |
| 2,3-Dimethylbuta-1-ene + H$_2$ → 2,3-dimethylbutane | $-116.1 \pm 0.4$                                      |
| 2,3-Dimethylbuta-2-ene + H$_2$ → 2,3-dimethylbutane | $-110.4 \pm 0.42$                                      |
| 3,3-Dimethylbuta-1-ene + H$_2$ → 2,2-dimethylbutane | $-125.9 \pm 0.63$                                      |
| Benzene + 3 H$_2$ → cyclohexane                | $-205.3 \pm 0.6$                                       |
| Cyclohexa-1,3-diene + 2 H$_2$ → cyclohexane    | $-229.6 \pm 0.42$                                      |
| Cyclohexene + H$_2$ → cyclohexane              | $-118.6 \pm 0.42$                                      |
| Hept-1-ene + H$_2$ → heptane                   | $-125.1 \pm 0.3$                                       |
| 4,4-Dimethylpent-1-ene + H$_2$ → 2,2-dimethylpentane | $-122.5 \pm 0.42$                                      |
| Cyclohepta-1,3,5-triene + 3 H$_2$ → cycloheptane | $-301.7 \pm 1.3$                                      |
| Cyclohepta-1,3-diene + 2 H$_2$ → cycloheptane  | $-212.4 \pm 0.63$                                      |
| Cycloheptene + H$_2$ → cycloheptane            | $-108.9 \pm 0.63$                                      |

NIST - JANAF thermochemical tables, Ref. [33]

Table 1. Experimental values of hydrogenation enthalpy of some unsaturated hydrocarbons in the gas phase (in kJ Mol$^{-1}$).
2.2 Basis-set extrapolation

The correlation-consistent basis sets form a basis-set hierarchy well suited for complete basis-set limit extrapolations of the correlation-energy. Then the correlation energy can have been determined depending on $X$ when $X \to \infty$.

In 1977, 27 formulas for two-point linear extrapolation were introduced by Helgaker et al. [27] via the basis sets cc-pCVXZ and cc-pCVYZ, the electron-correlation energies and are computed $E_X$ and $E_Y$, and the $C_{XY} = X^3/(X^3 Y^3)$ coefficient is determined in Eq. (1),

$$E_{XY} = (E_X X^3 - E_Y Y^3) / (X^3 - Y^3) = C_{XY}E_X + (1 - C_{XY})E_Y \quad (1)$$

The EX correlation energy can be recovered in correlation-consistent basis of cc-pVXZ via the Eq. (2), When performing calculations according to the basis sets, cc-pVXZ and cc-pVYZ, two equations with two unknowns are obtained, $a$ and $E$,

$$E_X = E_{\infty} + aX^3 \quad (2)$$

Note that through experience [28–32] that the best estimate of complete basis set limit extrapolation is by using two consecutive basis set when $X = Y - 1$, for example the pair cc-pCVDZ/cc-pCVTZ, and so on).

The level at which the results were obtained by extrapolation is denoted by cc-pCV(XY)Z, where XY = DT, TQ, and so forth. It is only at this level that the correlation energy is extrapolated.

The CCSD(T)/cc-pV(XY)Z extrapolation will be applied to obtain estimates of the basis-set limit of corrections for M06-2X/6-31g(d) level of theory by calculations of hydrogenation enthalpies of some unsaturated hydrocarbon compounds (Table 1).

In Section 3, we shall describe the methods used, the molecular equilibrium geometries, and the basis sets. Results will be shown in Section 3.2, including molecular electronic energies, enthalpies of hydrogenation, and statistical analysis of the computational results.

3. Computational details

3.1 Computational methods

Electronic energies were computed by the density-functional (M06-2X) [34] approach with 6-31g(d) basis set. The M06-2X/6-31g(d) equilibrium geometries of the reactants and products was optimized with the Gaussian 09 program [35]. All CCSD(T)/cc-pV(DT)Z calculations were performed at fixed molecular equilibrium geometries that were optimized at the M06-2X/6-31g(d) level can be found in supporting information.

3.2 Results and discussion

3.2.1 Nonrelativistic electronic energies

The total electronic M06-2X/6-31g(d) energies, $H_{\text{corr}}$, $G_{\text{corr}}$, and the zero-point vibrational energies (ZPE) are reported in Table 2, while Table 3 shows CCSD...
| Compounds          | M06-2X/6-3g(d) |        |        |        |
|--------------------|----------------|--------|--------|--------|
|                    | \(E_o\) & H\(_{corr}\) & G\(_{corr}\) & ZPE   |
| H\(_2\)           | -1.1635655    | 0.013609 | -0.001167 | 0.010304 |
| Ethane             | -79.771814    | 0.080116 | 0.054255 | 0.075684 |
| Ethyne             | -77.287772    | 0.031118 | 0.008428 | 0.027383 |
| Ethene             | -78.536836    | 0.055732 | 0.030890 | 0.051757 |
| Propane            | -119.064602   | 0.110657 | 0.080306 | 0.105246 |
| Propadiene         | -116.591917   | 0.060782 | 0.033335 | 0.056103 |
| Prop-1-yne         | -116.591781   | 0.061355 | 0.03375  | 0.056509 |
| Prop-1-ene         | -117.834775   | 0.085736 | 0.055653 | 0.080695 |
| Cis-butane         | -158.357373   | 0.140439 | 0.106229 | 0.133684 |
| But-2-yne          | -155.894141   | 0.091157 | 0.060488 | 0.085379 |
| Isobutene          | -158.359492   | 0.139891 | 0.10558 | 0.132229 |
| (2E)-but-2-ene     | -157.132136   | 0.116000 | 0.083013 | 0.109658 |
| (2Z)-but-2-ene     | -157.130271   | 0.115947 | 0.081911 | 0.109398 |
| pentane            | -197.650150   | 0.171137 | 0.133095 | 0.163224 |
| (2E)-pent-2-ene    | -196.424444   | 0.146203 | 0.108344 | 0.138462 |
| (2Z)-pent-2-ene    | -196.422473   | 0.146538 | 0.108366 | 0.138911 |
| 2-Methylbutane     | -197.650616   | 0.170492 | 0.132540 | 0.162599 |
| 2-Methylbut-1-ene  | -196.425399   | 0.145953 | 0.108348 | 0.138377 |
| 2-Methylbut-2-ene  | -196.428427   | 0.145977 | 0.108516 | 0.138233 |
| 3-Methylbut-1-ene  | -196.421594   | 0.146029 | 0.109827 | 0.138805 |
| Cyclopentane       | -196.447999   | 0.148834 | 0.115170 | 0.142836 |
| Cyclopenta-1,3-diene| -194.004693   | 0.099092 | 0.067447 | 0.094033 |
| Hexane             | -236.942859   | 0.201129 | 0.159944 | 0.191831 |
| Hex-1,2-diene      | -234.482131   | 0.151996 | 0.111965 | 0.143762 |
| Hex-1-ene          | -235.712709   | 0.176575 | 0.135740 | 0.167804 |
| 2,3-Dimethylbutane | -236.944627   | 0.200377 | 0.160337 | 0.191276 |
| 2,3-Dimethylbuta-1,3-diene| -234.499027| 0.152102 | 0.114663 | 0.144198 |
| 2,3-Dimethylbuta-1-ene | -235.719209| 0.176092 | 0.136350 | 0.167500 |
| 2,3-Dimethylbuta-2-ene | -235.721700| 0.175800 | 0.134436 | 0.166165 |
| 2,2-Dimethylbutane | -236.946825   | 0.199906 | 0.159467 | 0.190810 |
| 3,3-Dimethylbuta-1-ene | -235.717309| 0.175580 | 0.136683 | 0.167108 |
| Cyclohexane        | -235.752287   | 0.179349 | 0.145101 | 0.172770 |
| Benzenes           | -232.136474   | 0.107012 | 0.07593 | 0.101699 |
| Cyclohexa-1,3-diene| -233.301453   | 0.130219 | 0.096574 | 0.124132 |
| Cyclohexene        | -234.525715   | 0.154825 | 0.119853 | 0.148434 |
| Heptane            | -276.235598   | 0.231328 | 0.186546 | 0.226693 |
| Hept-1-ene         | -275.005449   | 0.206749 | 0.162214 | 0.196621 |
| Compounds                  | E<sub>a</sub> | H<sub>corr</sub> | G<sub>corr</sub> | ZPE   |
|----------------------------|---------------|-----------------|-----------------|-------|
| 2,2-Dimethylpentane        | −276.239366   | 0.230120        | 0.186120        | 0.219693 |
| 4,4-Dimethylpent-1-ene     | −275.010862   | 0.205633        | 0.163043        | 0.195795 |
| Cycloheptane               | −275.035841   | 0.209838        | 0.171462        | 0.201976 |
| Cyclohepta-1,3,5-triene     | −271.377165   | 0.136474        | 0.100791        | 0.129851 |
| Cyclohepta-1,3-diene        | −272.592107   | 0.161000        | 0.123047        | 0.153676 |
| Cycloheptene               | −273.812872   | 0.185183        | 0.147448        | 0.177646 |

**Table 2.**
Calculated total electronic energy (E<sub>a</sub>), H<sub>corr</sub>, G<sub>corr</sub>, and the zero-point vibrational energies (ZPE) at the M06-2X/6-31g(d) level (in hartree).

| Compounds                  | E<sub>D</sub><sup>a</sup> | E<sub>T</sub><sup>b</sup> | E<sub>m</sub><sup>c</sup> |
|----------------------------|---------------------------|---------------------------|---------------------------|
| H<sub>2</sub>              | −1.1723118                | −1.1737775                | −1.17439464               |
| Ethane                     | −79.582513                | −79.674425                | −79.713125                |
| Ethyne                     | −77.109286                | −77.187516                | −77.220455                |
| Ethene                     | −78.354614                | −78.438673                | −78.474067                |
| Propane                    | −118.780810               | −118.914036               | −118.970132               |
| Propadiene                 | −116.314867               | −116.433424               | −116.483343               |
| Prop-1-ynie                | −116.315794               | −116.435339               | −116.485674               |
| Isobutene                  | −157.978111               | −158.152797               | −158.226349               |
| Isobutane                  | −156.760003               | −156.927219               | −156.997626               |
| Trans-butane               | −157.979256               | −158.153758               | −158.22733                |
| (2E)-but-2-ene             | −156.758622               | −156.925479               | −156.995734               |
| (2Z)-but-2-ene             | −156.756385               | −156.923701               | −156.994150               |
| Pentane                    | −197.176630               | −197.392504               | −197.483398               |
| (2E)-pent-2-ene            | −195.956786               | −196.164955               | −196.252605               |
| (2Z)-pent-2-ene            | −195.954467               | −196.163063               | −196.250893               |
| 2-Methylbutane             | −197.177674               | −197.393756               | −197.484738               |
| 2-Methylbut-1-ene          | −195.957367               | −196.165990               | −196.253832               |
| 2-Methylbut-2-ene          | −195.959915               | −196.167943               | −196.255837               |
| 3-Methylbut-1-ene          | −195.954457               | −196.163021               | −196.250837               |
| Cyclopentane               | −195.977809               | −196.185015               | −196.272260               |
| Cycloptena-1,3-diene       | −193.544249               | −193.735901               | −193.816596               |
| Hexane                     | −236.376059               | −236.633206               | −236.741478               |
| 1,5-Hexdiene               | −233.926959               | −234.168762               | −234.270574               |
| Hex-1-ene                  | −235.151737               | −235.401337               | −235.506432               |
| 2,3-Dimethylbutane         | −236.377394               | −236.635041               | −236.743524               |
Table 3. Computed CCSD(T)/cc-pVXZ energies at the M06-2X/6-31g(d) geometries, where X = D, T, as well as extrapolated values by the Eq. (2) (in hartree).

| Compounds                  | $E_D^a$ | $E_T^b$ | $E_{\infty}^c$ |
|----------------------------|---------|---------|----------------|
| 2,3-Dimethylbuta-1,3-diene | −233.940431 | −234.183237 | −234.285471 |
| 2,3-Dimethylbuta-1-ene     | −235.156478 | −235.406736 | −235.512108 |
| 2,3-Dimethylbuta-2-ene     | −235.157255 | −235.407711 | −235.513167 |
| 2,2-Dimethylbutane         | −236.380072 | −236.637444 | −236.745811 |
| 3,3-Dimethylbuta-1-ene     | −235.156438 | −235.406113 | −235.51240 |
| Cyclohexane                | −235.187080 | −235.434840 | −235.539160 |
| Benzene                    | −231.580490 | −231.805751 | −231.900598 |
| Cyclohexa-1,3-diene        | −232.746205 | −232.978902 | −233.076879 |
| Cyclohexene                | −233.965459 | −234.205764 | −234.306946 |
| Heptane                    | −275.574466 | −275.872952 | −275.998630 |
| Hept-1-ene                 | −274.350163 | −274.641090 | −274.763585 |
| 2,2-Dimethylpentane        | −275.578608 | −275.877182 | −276.002897 |
| 4,4-Dimethylpent-1-ene     | −274.355543 | −274.646391 | −274.768853 |
| Cycloheptane               | −274.375461 | −274.664943 | −274.786830 |
| Cyclohepta-1,3,5-triene    | −270.731145 | −270.997511 | −271.109665 |
| Cyclohepta-1,3-diene       | −271.941636 | −272.215680 | −272.331066 |
| Cycloheptene               | −273.157974 | −273.439442 | −273.557955 |

Limit energies were obtained using the web page http://sf.anu.edu.au/~vve900/cbs/sref_3 [36].

$^a$M06-2X/cc-pVDZ//M06-2X/6-31g(d) level.

$^b$M06-2X/cc-pVTZ//M06-2X/6-31g(d) level.

$^c$cc-pV(TD)Z extrapolated level.

3.2.2 Enthalpies of hydrogenation at 298.15 K in gas phase

The usual way to calculate enthalpies of reaction is to calculate heats of formation, and take the appropriate sums and difference (Eq. (3)).

$$\Delta_{\text{hyd}}H^o(298) = \sum_{\text{products}} \Delta_fH^o(298) - \sum_{\text{reactants}} \Delta_fH^o(298)$$ (3)

However, since Gaussian program provides the sum of electronic and thermal enthalpies, there is a short cut: namely, to simply take the difference of the sums of these values for the reactants and the products. This works since the number of atoms of each element is the same on both sides of the reaction, therefore all the atomic information cancels out, and you need only the molecular data. For example,
using the information in Table 2 (or Table 3 for energies), the enthalpy of reaction can be calculated simply by Eq. (4):

\[
\Delta_{\text{hyd}} H_{298}^0 = \sum (E_0 + H_{\text{corr}})_{\text{products}} - \sum (E_0 + H_{\text{corr}})_{\text{reactants}}
\]  

\(E_0\) can represent either \(E_{\text{DZ}}, E_{\text{TZ}}, E_{\text{QZ}}\) or \(E_{\infty}\) keeping the calculated \(H_{\text{corr}}\) value at M06-2X/6-31g(d) level is fixed. The calculated enthalpies of hydrogenation are

| Reactions | X = Da | X = Tb | \(E_0^a\) | \(\Delta_{\text{hyd}} H^{a,\text{exp}}\) |
|-----------|--------|--------|---------|-----------------|
| Ethyne + 2 H2 → ethane | 16.0   | 4.4    | -0.5    | -312.0 ± 0.63   |
| Ethene + H2 → ethane | 5.1    | 2.0    | 0.7     | -136.3 ± 0.3    |
| Propadiene + 2 H2 → propane | 11.4   | 4.1    | -1.3    | -295.1 ± 0.1    |
| Prop-1-yne + 2 H2 → propane | 16.0   | 6.1    | -0.5    | -289.6 ± 0.63   |
| Prop-1-ene + H2 → propane | 4.9    | 2.0    | -0.4    | -125.0 ± 0.42   |
| But-2-yne + 2 H2 → butane | 15.2   | 4.1    | -0.6    | -272.4 ± 1.3    |
| Isobutene + H2 isobutane | 7.6    | 3.0    | 1.1     | -117.8 ± 0.42   |
| (2E)-but-2-ene + H2 → butane | 6.1    | 1.7    | -0.2    | -118.5 ± 0.42   |
| (2Z)-but-2-ene + H2 → butane | 7.6    | 3.9    | 2.4     | -114.6 ± 0.42   |
| (2E)-pent-2-ene + H2 → pentane | 5.8    | 2.3    | 0.8     | -113.8 ± 0.8    |
| (2Z)-pent-2-ene + H2 → pentane | -1.7   | -5.3   | -6.7    | -117.7 ± 0.8    |
| 2-Methylbut-1-ene + H2 → 2-methylbutane | 2.9    | -1.3   | -3.1    | -118.2 ± 0.42   |
| 2-Methylbut-2-ene + H2 → 2-methylbutane | 4.7    | 0.2    | -1.7    | -111.6 ± 0.3    |
| 3-Methylbut-1-ene + H2 → 2-methylbutane | 2.6    | -1.4   | -3.1    | -126.3 ± 0.3    |
| Cyclopenta-1,3-diene + 2 H2 → cyclopentane | 11.1   | 4.4    | 1.6     | -210.8 ± 0.84   |
| Hex-1,5-diene + 2 H2 → hexane | 13.1   | 5.8    | 2.8     | -251.2 ± 0.42   |
| Hex-1-ene + H2 → hexane | 5.6    | 1.6    | 0.0     | -126.0 ± 2.0    |
| 2,3-Dimethylbuta-1,3-diene + 2 H2 → 2,3-dimethylbutane | 11.3   | 2.7    | -0.9    | -223.4 ± 0.63   |
| 2,3-Dimethylbuta-1-ene + H2 → 2,3-dimethylbutane | 7.2    | 2.9    | 1.0     | -116.1 ± 0.4    |
| 2,3-Dimethylbuta-2-ene + H2 → 2,3-dimethylbutane | 10.1   | 2.7    | -0.9    | -110.4 ± 0.42   |
| 3,3-Dimethylbuta-1-ene + H2 → 2,2-dimethylbutane | 4.5    | 0.9    | -0.6    | -125.9 ± 0.63   |
| Benzene + 3 H2 → cyclohexane | 18.6   | 6.4    | 1.3     | -205.3 ± 0.6    |
| Cyclohexa-1,3-diene + 2 H2 → cyclohexane | 13.1   | 5.1    | 1.8     | -229.6 ± 0.42   |
| Cyclohexene + H2 → cyclohexane | 6.0    | 1.8    | 0.0     | -118.6 ± 0.42   |
| Hept-1-ene + H2 → heptane | 6.4    | 2.4    | 0.8     | -125.1 ± 0.3    |
| 4,4-Dimethylpent-1-ene + H2 → 2,2-dimethylpentane | 5.9    | 2.5    | 1.0     | -122.5 ± 0.42   |
| Cyclohepta-1,3,5-triene + 3 H2 → cycloheptane | 18.6   | 8.0    | 3.5     | -301.7 ± 1.3    |
| Cyclohepta-1,3-diene + 2 H2 → cycloheptane | 12.5   | 5.6    | 2.6     | -212.4 ± 0.63   |
| Cycloheptene + H2 → cycloheptane | 4.5    | 1.7    | 0.6     | -108.9 ± 0.63   |

\(a\) CCSD(T)/cc-pVDZ//M06-2X/6-31g(d) level.

\(b\) CCSD(T)/cc-pVTZ//M06-2X/6-31g(d) level.

\(c\) cc-pVTZ extrapolated level.

\(d\) NIST-JANAF thermo-chemical tables.

Table 4.
Difference between experimental and calculation values of standard enthalpies of hydrogenation of some unsaturated hydrocarbons in the gas phase at 298.15 K (in kJ Mol\(^{-1}\)).
reported in Table 4, along with the experimental values. Table 5 shows statistical parameters for all used computational methods. Figure 1 shows a linear analysis of the best calculated results in terms of experimental results.

Our best theoretical estimates of the enthalpies of hydrogenation are based on basis set limit extrapolation calculations, when the pair cc-pVDZ and cc-pVTZ are used, and the mean absolute deviation (MAD) between experimental and calculated values is 1.5 kJ mol\(^{-1}\) (Table 5). The enthalpies of hydrogenation of some alkenes (12 compounds) have been calculated at the HF, B3LYP, M06, MP2, G3, G4, CBS-QB3, CBS-APNO, and W1BD levels and, in the case of the first four methods, using a variety of basis sets up to aug-ccpVTZ [37], and it is found that the MAD decreases gradually from the first to the last method (18.4–4.2 kJ mol\(^{-1}\)). Moreover, Rogers et al. [38–40] calculated the hydrogenation enthalpy at 298.15 K for reactions involving cyclic and acyclic C4 (20 reactions), cyclic C5 (23 reactions) and C6 (24 reactions) hydrocarbons using the G2 and G2(MP2) ab initio methods, and it is found that the MAD is about 3.3, 3.7 and 5.0 kJ \(^{-1}\), respectively.

| Level | MAD  | RMS  | Error% | SD   | R\(^2\) |
|-------|------|------|--------|------|---------|
| CCSD(T)/cc-pVDZ//M06-2X/6-31g(d) | 8.8  | 10.0 | 5.0%   | 2.78 | 0.9987  |
| CCSD(T)//cc-pVTZ//M06-2X/6-31g(d) | 3.4  | 3.9  | 2.0%   | 2.11 | 0.9992  |
| cc-pV(DT)Z extrapolated level   | 1.5  | 2.1  | 1.0%   | 2.12 | 0.9992  |

Table 5. Statistical parameters for all used methods to calculate hydrogenation enthalpies. (in kJ Mol\(^{-1}\)).

Figure 1. Calculated versus experimental hydrogenation enthalpy \(\Delta H_{\text{hyd}}(298, 15 K), \text{kJ mol}^{-1}\) of 29 hydrocarbons.

4. Conclusion

Enthalpies of hydrogenation are relatively easy to calculate with CCSD(T)/cc-pVXZ/M06-31g(d)/6-31g(d) level, where X = D, T, giving fairly good agreement...
with experiment, especially when cc-pVTZ basis set are used, and basis set extrapolation techniques by Eq. (2) seem to represent an easy-to-use alternative, especially when the pair cc-pVDZ and cc-pVTZ are used.

**Appendix: supporting information** (All computed molecule Cartesian coordinates (XYZ)) were optimized at the M06-2X/6-31g(d) level

|   | Hydrogen (H2) |   | Ethane (C2H6) |   | Ethene (C2H4) |   | Ethyne (C2H2) |   | Propadiene |
|---|---------------|--|---------------|--|---------------|--|---------------|--|------------|
| 1 | H 0.000000000 0.000000000 0.368263000 | 2 | C 0.000000000 0.000000000 0.762978000 | 3 | C 0.000000000 0.000000000 0.663573000 | 4 | C 0.000000000 0.000000000 0.600962000 | 5 | C 0.000000000 0.000000000 0.000000000 |
|   | H 0.000000000 0.000000000 -0.368263000 | | C 0.000000000 0.000000000 -0.762978000 | | C 0.000000000 0.000000000 -0.663573000 | | H 0.000000000 0.000000000 -1.668037000 | | C 0.000000000 0.000000000 -1.304952000 |
|   | | | H 0.000000000 1.019590000 1.159421000 | | H 0.000000000 0.000000000 1.234547000 | | C 0.000000000 0.000000000 1.304952000 | | H 0.000000000 0.000000000 1.868109000 |
|   | | | H -0.882991000 -0.509795000 1.159421000 | | H 0.000000000 -1.019590000 -1.159421000 | | C 0.000000000 -0.000000000 1.304952000 | | H 0.882991000 0.509795000 -1.159421000 |
|   | | | H -0.882991000 -1.019590000 -1.159421000 | | H 0.000000000 -0.000000000 -1.304952000 | | H 0.882991000 0.000000000 -1.868109000 | | H 0.000000000 0.000000000 0.000000000 |
| 2 | | | H 0.882991000 -0.509795000 1.159421000 | | H 0.000000000 -1.019590000 -1.159421000 | | H 0.882991000 1.019590000 -1.868109000 | | C 0.000000000 0.000000000 0.000000000 |
|   | | | H 0.000000000 0.509795000 1.159421000 | | H 0.000000000 0.000000000 0.600962000 | | H 0.000000000 0.000000000 0.000000000 | | H 0.000000000 0.000000000 0.000000000 |
|   | | | H 1.159421000 0.000000000 0.762978000 | | H 1.234547000 0.000000000 0.663573000 | | H 1.868109000 0.000000000 0.600962000 | | H 1.868109000 0.000000000 0.000000000 |
### Propane

|       | x       | y       | z       |
|-------|---------|---------|---------|
| H     | -0.928749000 | 0.000000000 | -1.868109000 |
| H     | 0.928749000   | 0.000000000 | -1.868109000 |

### Propene

|       | x       | y       | z       |
|-------|---------|---------|---------|
| C     | -1.286905000 | 0.145875000 | 0.000000000 |
| C     | 0.000000000   | 0.478432000 | 0.000000000 |
| H     | -1.601612000  | -0.895181000 | 0.000000000 |
| H     | -2.072231000  | 0.895120000  | 0.000000000 |
| H     | 0.274287000   | 1.533078000  | 0.000000000 |
| C     | 1.134779000   | -0.502407000 | 0.000000000 |
| H     | 1.773172000  | -0.366223000 | 0.880442000 |
| H     | 0.765971000   | -1.531971000 | 0.000000000 |
| H     | 1.773172000   | -0.366223000 | -0.880442000 |

### Propyne

|       | x       | y       | z       |
|-------|---------|---------|---------|
| C     | 0.000000000   | 0.000000000 | 1.423679000 |
| C     | 0.000000000   | 0.000000000 | 0.219688000 |
| H     | 0.000000000   | 0.000000000 | 2.490285000 |
| C     | 0.000000000   | 0.000000000 | -1.242799000 |
| H     | 0.000000000   | 1.022382000 | -1.631230000 |
| H     | 0.885409000   | -0.511191000 | -1.631230000 |
| H     | -0.885409000  | -0.511191000 | -1.631230000 |

### But-2-yne

|       | x       | y       | z       |
|-------|---------|---------|---------|
| C     | 0.000000000   | 0.000000000 | 2.066654000 |
| H     | 0.000000000   | 1.021413000 | 2.458673000 |
| H     | 0.884570000   | -0.510706000 | 2.458673000 |
| H     | -0.884570000  | -0.510706000 | 2.458673000 |
(Z)-but-2-ane

10

(Z)-but-2-ene

11

Isobutene2-methylprop-1-ene

12
Quantum Calculations to Estimate the Heat of Hydrogenation Theoretically
DOI: http://dx.doi.org/10.5772/intechopen.93955

| 13 | Methylpropane |
|----|---------------|
| C  | -0.878102000 | 1.160442000 | 0.000000000 |
| C  | 0.318200000 | 0.209420000 | 0.000000000 |
| C  | 0.318200000 | -0.659704000 | 1.256954000 |
| C  | 0.318200000 | -0.659704000 | -1.256954000 |
| H  | -1.816717000 | 0.592600000 | 0.000000000 |
| H  | -0.876505000 | 1.803417000 | 0.886375000 |
| H  | -0.876505000 | 1.803417000 | -0.886375000 |
| H  | 1.236570000 | 0.812776000 | 0.000000000 |
| H  | -0.585386000 | -1.280771000 | 1.290810000 |
| H  | 1.184708000 | -1.328777000 | 1.278998000 |
| H  | 0.337765000 | -0.047918000 | 2.164877000 |
| H  | -0.585386000 | -1.280771000 | -1.290810000 |
| H  | 0.337765000 | -0.047918000 | -2.164877000 |
| H  | 1.184708000 | -1.328777000 | -1.278998000 |

| 14 | (E)-but-2-ane |
|----|---------------|
| C  | 0.704814000 | 1.820298000 | 0.000000000 |
| C  | 0.704814000 | 0.294113000 | 0.000000000 |
| C  | -0.704814000 | -0.294113000 | 0.000000000 |
| C  | -0.704814000 | -1.820298000 | 0.000000000 |
| H  | 0.188158000 | 2.209779000 | 0.883837000 |
| H  | 0.188158000 | 2.209779000 | -0.883837000 |
| H  | 1.721212000 | 2.224575000 | 0.000000000 |
| H  | 1.249565000 | -0.076964000 | 0.878126000 |
| H  | 1.249565000 | -0.076964000 | -0.878126000 |
| H  | -1.249565000 | 0.076964000 | -0.878126000 |
| H  | -1.249565000 | -0.076964000 | 0.878126000 |
| H  | -1.721212000 | -2.224575000 | 0.000000000 |
| H  | -0.188158000 | -2.209779000 | 0.883837000 |
| H  | -0.188158000 | -2.209779000 | -0.883837000 |
|    | (E)-but-2-ene                                      |       |       |       |
|----|--------------------------------------------------|-------|-------|-------|
|    | C                                               | -0.326383000 | 0.580069000 | 0.000000000 |
|    | C                                               | 0.326383000  | -0.580069000 | 0.000000000 |
|    | H                                               | -1.417413000 | 0.566444000 | 0.000000000 |
|    | H                                               | 1.417413000  | -0.566444000 | 0.000000000 |
|    | C                                               | 0.326383000  | 1.930669000 | 0.000000000 |
|    | C                                               | -0.326383000 | 1.930669000 | 0.000000000 |
|    | H                                               | -0.032478000 | -2.513587000 | 0.880427000 |
|    | H                                               | -1.416586000 | -1.840628000 | 0.000000000 |
|    | H                                               | -0.032478000 | -2.513587000 | -0.880427000 |
|    | H                                               | 1.416586000  | 1.840628000 | 0.000000000 |
|    | H                                               | 0.032478000  | 2.513587000 | -0.880427000 |
|    | H                                               | 0.032478000  | 2.513587000 | 0.880427000 |

|    | (2E)-pent-2-ene                                 |       |       |       |
|----|--------------------------------------------------|-------|-------|-------|
|    | C                                               | 2.314095000  | -0.475261000 | 0.268047000 |
|    | C                                               | 1.301568000  | 0.569988000 | -0.210535000 |
|    | C                                               | -0.062964000 | -0.022508000 | -0.417562000 |
|    | C                                               | -1.160170000 | 0.335620000 | 0.246048000 |
|    | C                                               | -2.517862000 | -0.272036000 | 0.051547000 |
|    | H                                               | -0.132949000 | -0.822240000 | -1.158725000 |
|    | H                                               | -1.084442000 | 1.130940000 | 0.989387000 |
|    | H                                               | 2.000934000  | -0.903693000 | 1.224639000 |
|    | H                                               | 2.397884000  | -1.295127000 | -0.453050000 |
|    | H                                               | 3.308026000  | -0.036515000 | 0.395980000 |
|    | H                                               | 1.236711000  | 1.388220000 | 0.516039000 |
|    | H                                               | 1.659489000  | 1.009665000 | -1.150825000 |
|    | H                                               | -3.247227000 | 0.481088000 | -0.268021000 |
|    | H                                               | -2.490794000 | -1.061858000 | -0.704665000 |
|    | H                                               | -2.895632000 | -0.705300000 | 0.984558000 |

|    | (2B)-pentane                                    |       |       |       |
|----|--------------------------------------------------|-------|-------|-------|
|    | C                                               | -2.087737000 | -0.682010000 | 0.167473000 |
|    | C                                               | -1.397858000 | 0.612858000 | -0.246114000 |
|    | H                                               | -1.623234000 | -1.556933000 | -0.305129000 |
|    | H                                               | -2.032398000 | -0.827405000 | 1.252942000 |
|    | H                                               | -3.144187000 | -0.681110000 | -0.116273000 |
|    | H                                               | -1.418421000 | 0.705421000 | -1.339990000 |
|    | H                                               | -1.966593000 | 1.464569000 | 0.145544000 |
|    | C                                               | 0.049630000  | 0.716811000 | 0.239083000 |
## Quantum Calculations to Estimate the Heat of Hydrogenation Theoretically

DOI: [http://dx.doi.org/10.5772/intechopen.93955](http://dx.doi.org/10.5772/intechopen.93955)

| Atom | x       | y       | z       | Energy (kcal/mol) |
|------|---------|---------|---------|------------------|
| H    | 0.06761 | 0.68675 | 1.338   | -0.04847         |
| H    | 0.45641 | 1.69552 | 0.094   | -0.40113         |
| C    | 0.96894 | -0.37702 | 0.051   | -1.39776         |
| H    | 0.62978 | -1.35757 | 0.043   | 0.05073          |
| C    | 2.42414 | 0.16694 | 0.063   | 0.10633          |
| H    | 2.80276 | 0.78870 | -0.213  | -0.27130         |
| H    | 2.52245 | -0.15360 | 0.197   | 1.19723          |
| H    | 3.07129 | -0.96039 | -0.278  | -0.27866         |

### (2Z)-pent-2-ene

| Atom | x       | y       | z       | Energy (kcal/mol) |
|------|---------|---------|---------|------------------|
| C    | -2.15766| 0.30650 | 0.032   | 0.42174          |
| C    | -1.01566| -0.16283 | 0.126   | 0.59013          |
| C    | 0.01032 | 0.83274 | 0.165   | 0.12652          |
| C    | 1.29436 | 0.61266 | -0.304  | -0.16057         |
| C    | 0.43151 | -0.85516 | -0.278  | -0.07087         |
| H    | -0.36928 | 1.84698 | 0.004   | 0.00479          |
| H    | 1.88616 | 1.46289 | -0.492   | 0.49228          |
| H    | -1.77991 | 0.68106 | -1.377   | 1.37733          |
| H    | -2.92434 | -0.99752 | -0.059   | 0.05931          |
| H    | -2.63589 | 0.66061 | -0.608   | 0.60873          |
| H    | -1.42949 | 0.17224 | 1.550   | 1.55022          |
| H    | -0.56002 | -1.14019 | 0.773   | 0.77356          |
| H    | 2.86855 | -0.60733 | 0.645   | 0.64595          |
| H    | 1.40913 | -1.51904 | 0.237   | 0.23737          |
| H    | 2.48801 | -0.94092 | -1.039   | -1.03928         |

### (2Z)-pentane

| Atom | x       | y       | z       | Energy (kcal/mol) |
|------|---------|---------|---------|------------------|
| C    | -1.81849 | 0.75353 | 0.174   | 0.17432          |
| C    | -1.14734 | -0.47073 | -0.450   | -0.45017         |
| H    | -1.11321 | 1.57715 | 0.316   | 0.31694          |
| H    | -2.63998 | 1.11834 | -0.450   | -0.45001         |
| H    | -2.23202 | 0.50181 | 1.156   | 1.15692          |
| H    | -1.90397 | -1.25486 | -0.566   | -0.56621         |
| H    | -0.80547 | -0.23053 | -1.466   | -1.46630         |
| C    | 0.03645 | -1.01580 | 0.368   | 0.36837          |
| H    | -0.11550 | -0.77114 | 1.429   | 1.42918          |
| H    | 0.05183 | -2.11018 | 0.308   | 0.30806          |
| C    | 1.40727 | -0.49883 | -0.079   | -0.07938         |
| H    | 2.18029 | -0.95690 | 0.549   | 0.54943          |
| H    | 1.59795 | -0.84640 | -1.103   | -1.10321         |
## Advanced Applications of Hydrogen and Engineering Systems in the Automotive Industry

| 20 | 1,2 Di metgyl cyclo propane |
|----|-----------------------------|
|    | C  | 1.555115000 | 1.020482000 | -0.032216000 |
| H  | 2.574480000 | 1.324615000 | -0.288218000 |
| H  | 0.878078000 | 1.509222000 | -0.740322000 |
| H  | 1.329769000 | 1.407174000 | 0.968220000 |

| 21 | 1,2 Di metgyl cyclo propene |
|----|-----------------------------|
|    | C  | -0.983015000 | 0.923486000 | 0.000000000 |
| C  | 0.245532000 | 0.490166000 | 0.753182000 |
| C  | 0.245532000 | 0.490166000 | -0.753182000 |
| H  | -1.826999000 | 0.237791000 | 0.000000000 |
| H  | -1.259771000 | 1.972523000 | 0.000000000 |
| H  | 0.818353000 | 1.295146000 | 1.208149000 |
| H  | 0.818353000 | 1.295146000 | -1.208149000 |
| C  | 0.245532000 | -0.790236000 | -1.556100000 |
| C  | 0.245532000 | -0.790236000 | 1.556100000 |
| H  | -0.406160000 | -1.546084000 | -1.108730000 |
| H  | -0.117937000 | -0.607772000 | -2.572546000 |
| H  | 1.251787000 | -1.216486000 | -1.629081000 |
| H  | 1.251787000 | -1.216486000 | 1.629081000 |
| H  | -0.117937000 | -0.607772000 | 2.572546000 |
| H  | -0.406160000 | -1.546084000 | 1.108730000 |

| 22 | 1,3-Pentadiene(Z) |
|----|-----------------------------|
|    | C  | 2.386185000 | 0.144512000 | 0.000000000 |
| C  | 1.101237000 | -0.219798000 | 0.000000000 |
| C  | 0.000000000 | 0.740650000 | 0.000000000 |
C \(-1.309264000\) 0.457570000 0.000000000
C \(-1.947457000\) \(-0.899208000\) 0.000000000
H 2.674974000 1.192770000 0.000000000
H 3.188346000 \(-0.585678000\) 0.000000000
H 0.854201000 \(-1.278983000\) 0.000000000
H 0.299494000 1.788083000 0.000000000
H \(-2.003506000\) \(-1.278983000\) \(-0.879756000\)
H \(-2.003506000\) \(-1.278983000\) \(0.879756000\)

2-Methylbut-1-ene
C \(-1.897352000\) 0.069688000 \(-0.379011000\)
C \(-0.803183000\) \(-0.497117000\) 0.532182000
C 0.590454000 \(-0.115154000\) 0.094446000
C 0.898099000 1.358700000 0.048952000
C 1.496741000 \(-1.039110000\) \(-0.237691000\)
H \(-1.735338000\) 1.163502000 \(-0.353795000\)
H \(-1.735338000\) \(-0.242153000\) \(-1.415566000\)
H \(-0.969559000\) \(-0.131539000\) 1.555187000
H \(-0.883921000\) \(-1.588740000\) 0.568655000
H 0.309642000 1.863055000 \(-0.726222000\)
H 0.646334000 1.839248000 1.002285000
H 1.955247000 1.539160000 \(-0.160321000\)
H 2.500315000 \(-0.757627000\) \(-0.549409000\)
H 1.266234000 \(-2.095358000\) \(-0.207945000\)

2-Methylbut-2-ene
C \(-1.739392000\) \(-0.815690000\) 0.000068000
C \(-0.445666000\) \(-0.042781000\) \(-0.000040000\)
C 0.731454000 \(-0.676023000\) 0.000031000
C 2.107037000 \(-0.076409000\) \(-0.000012000\)
C \(-0.622934000\) 1.452321000 \(-0.000085000\)
H \(-2.344490000\) \(-0.563945000\) \(-0.879881000\)
H \(-1.567257000\) \(-1.895111000\) 0.000185000
H \(-2.344512000\) \(-0.563761000\) 0.879948000
H 0.707982000 \(-1.766396000\) 0.000137000
H 2.672750000 \(-0.405010000\) \(-0.879551000\)
H 2.095891000 1.015122000 \(-0.000370000\)
H 2.672570000 \(-0.404435000\) 0.879859000
|  |  |  |  |  |
|---|---|---|---|---|
| H | -1.19812000 | 1.767121000 | -0.879475000 |  |
| H | -1.197796000 | 1.767263000 | 0.879516000 |  |
| H | 0.320061000 | 2.000645000 | -0.000338000 |  |
| 25 |  |  |  |  |
| 25-Methylbutane |  |  |  |  |
| C | 1.780516000 | -0.000029000 | -0.519793000 |  |
| C | 0.912273000 | -0.000063000 | 0.738834000 |  |
| C | -0.603203000 | 0.000030000 | 0.481637000 |  |
| C | -1.060235000 | 1.257557000 | -0.259637000 |  |
| H | 2.841975000 | 0.000039000 | -0.255438000 |  |
| H | 1.595066000 | -0.884813000 | -1.136689000 |  |
| H | 1.595016000 | 0.884859000 | -1.136563000 |  |
| H | 1.163734000 | -0.878612000 | 1.346829000 |  |
| 26 |  |  |  |  |
| 3-Methylbut-1-ene |  |  |  |  |
| C | 1.517055000 | -0.862537000 | 0.318229000 |  |
| C | 0.477587000 | -0.019857000 | -0.432825000 |  |
| C | -0.887587000 | -0.639452000 | -0.271180000 |  |
| C | -1.965772000 | -0.056795000 | 0.245400000 |  |
| C | 0.538897000 | 1.437769000 | 0.013736000 |  |
| H | 1.307767000 | -0.848847000 | 1.393325000 |  |
| H | 1.502760000 | -1.905424000 | -0.014449000 |  |
| H | 2.526055000 | -0.468418000 | 0.160305000 |  |
| H | 0.729278000 | -0.062673000 | -1.503161000 |  |
| H | -0.960847000 | -1.676811000 | -0.601961000 |  |
| H | -2.905847000 | -0.597111000 | 0.336269000 |  |
| H | -1.956820000 | 0.971942000 | 0.593763000 |  |
| H | 0.312097000 | 1.523918000 | 1.082556000 |  |
| H | 1.540556000 | 1.846234000 | -0.150203000 |  |
| H | -0.176082000 | 2.057026000 | -0.536608000 |  |
| 27 |  |  |  |  |
| Cyclopenta |  |  |  |  |
Quantum Calculations to Estimate the Heat of Hydrogenation Theoretically
DOI: http://dx.doi.org/10.5772/intechopen.93955

|   | C     | H     | H     | H     | H     | H     | H     | H     | H     | H     | H     | H     | H     | H     |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 28| Cyclopenta-1,3-diene |       |       |       |       |       |       |       |       |       |       |       |       |       |
|   | C     | H     | H     | C     | H     | H     | H     | C     | H     | H     | H     | H     | H     | H     |
|   | -1.177268000 | -0.280759000 | -0.000082000 | -0.735260000 | 0.988357000 | 0.000143000 | 0.735254000 | 0.988361000 | -0.000114000 | 1.177270000 | -0.280752000 | 0.000041000 | 2.209216000 | -0.610008000 | -0.000131000 |
|   | -1.348626000 | 1.882297000 | 0.000233000 | 1.348614000 | 1.882306000 | -0.000183000 | 2.209219000 | -0.609995000 | 0.000059000 | 0.000004000 | -1.214780000 | 0.000009000 | 0.000033000 | -1.873598000 | -0.879427000 |
|   | -0.000021000 | -1.873571000 | 0.879466000 | 1.275667000 | -0.527113000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 | 0.000000000 |
| 29| Pentane |       |       | C     | C     | H     | H     | C     | H     | H     | H     | H     | H     | H     | H     |
|   | C     | H     | H     | C     | H     | H     | H     | C     | H     | H     | H     | H     | H     | H     | H     |
|   | 1.275667000 | -0.527113000 | 0.000000000 | 0.000000000 | 0.312488000 | 0.000000000 | 1.274183000 | -1.185569000 | 0.878212000 | 1.274183000 | -1.185569000 | -0.878212000 | -1.275794000 | -0.527541000 | 0.000000000 |
|   | -0.000023500 | 0.973329000 | 0.878523000 | -0.000235000 | 0.973329000 | -0.878523000 | -2.540546000 | 0.327170000 | 0.000000000 | -1.273566000 | -1.186150000 | -0.878131000 | -1.273566000 | -1.186150000 | 0.878131000 |
|   | -3.444413000 | -0.288920000 | 0.000000000 | -0.000235000 | 0.973329000 | -0.878523000 | -2.540546000 | 0.327170000 | 0.000000000 | -1.273566000 | -1.186150000 | -0.878131000 | -1.273566000 | -1.186150000 | 0.878131000 |
| 20 | Advanced Applications of Hydrogen and Engineering Systems in the Automotive Industry |
|----|-----------------------------------------------------------------------------------|
| 30 | Hexane                                                                            |
|    | H        | -2.573779000 | 0.973295000 | 0.883728000 |
|    | H        | -2.573779000 | 0.973295000 | -0.883728000 |
|    | C        | 2.540652000  | 0.328153000 | 0.000000000  |
|    | H        | 3.444340000  | -0.288153000 | 0.000000000  |
|    | H        | 2.573497000  | 0.974161000  | -0.883830000  |
|    | H        | 2.573497000  | 0.974161000  | 0.883830000   |
| 31 | Hex1-ene                                         |
|    | C        | 0.429918000  | 1.910882000  | 0.000000000   |
|    | C        | -0.416794000 | 0.639666000  | 0.000000000   |
|    | H        | 1.088648000  | 1.905049000  | 0.878012000   |
|    | H        | 1.088648000  | 1.905049000  | -0.878012000  |
|    | C        | 0.416794000  | -0.639666000 | 0.000000000   |
|    | H        | -1.077316000 | 0.643829000  | 0.878621000   |
|    | H        | -1.077316000 | 0.643829000  | -0.878621000  |
|    | C        | -0.429918000 | -1.910882000 | 0.000000000   |
|    | H        | 1.077316000  | -0.643829000 | -0.878621000  |
|    | H        | 1.077316000  | -0.643829000 | 0.878621000   |
|    | H        | -1.088648000 | -1.905049000 | 0.878012000   |
|    | H        | -1.088648000 | -1.905049000 | -0.878012000  |
|    | C        | 0.416794000  | -3.181079000 | 0.000000000   |
|    | C        | -0.416794000 | 3.181079000  | 0.000000000   |
|    | H        | 1.062641000  | -3.219144000 | 0.883682000   |
|    | H        | -0.205277000 | 4.080748000  | 0.000000000   |
|    | H        | 1.062641000  | -3.219144000 | -0.883682000  |
|    | H        | -1.062641000 | 3.219144000  | 0.883682000   |
|    | H        | 0.205277000  | 4.080748000  | 0.000000000   |
|    | H        | -1.062641000 | 3.219144000  | -0.883682000  |
| 31 | Hex1-ene                                         |
|    | C        | 3.059992000  | -0.191825000 | 0.443719000   |
|    | C        | 2.031872000  | -0.193363000 | -0.399121000  |
|    | C        | 0.770381000  | 0.599545000  | -0.216038000  |
|    | C        | -0.469432000 | -0.294413000 | -0.100878000  |
|    | C        | -1.763936000 | 0.502583000  | 0.045414000   |
|    | C        | -2.993402000 | -0.394630000 | 0.161583000   |
|    | H        | 3.053025000  | 0.421594000  | 1.341658000   |
|    | H        | 3.944231000  | -0.796826000 | 0.270109000   |
|    | H        | 2.072945000  | -0.824722000 | -1.287818000  |
|    | H        | 0.634999000  | 1.279548000  | -1.069067000  |
|    | H        | 0.857556000  | 1.227717000  | 0.679261000   |
|      |      |      |      |
|------|------|------|------|
| H    | -0.348838000 | -0.965753000 | 0.759219000 |
| H    | -0.537335000 | -0.939318000 | -0.988075000 |
| H    | -1.874101000 | 1.172797000 | -0.816907000 |
| H    | -1.691686000 | 1.148473000 | 0.929906000 |
| H    | -2.913980000 | -1.053717000 | 1.032463000 |
| H    | -3.098725000 | -1.028497000 | -0.725217000 |
| H    | -3.910937000 | 0.191320000 | 0.266394000 |

1,5-Hexadiene
|      |      |      |      |
|------|------|------|------|
| C    | 0.758365000 | 1.082281000 | 0.132388000 |
| C    | -0.758365000 | 1.082282000 | -0.132388000 |
| C    | 1.443512000 | -0.106603000 | -0.476857000 |
| C    | -1.443512000 | -0.106603000 | 0.476857000 |
| C    | 2.164328000 | -0.995960000 | 0.198166000 |
| C    | -2.164328000 | -0.995960000 | -0.198166000 |
| H    | 1.184567000 | 2.006667000 | -0.278514000 |
| H    | -0.944891000 | 1.097752000 | -1.213365000 |
| H    | -1.184567000 | 2.006667000 | 0.278517000 |
| H    | 1.309651000 | -0.233049000 | -1.552214000 |
| H    | -1.309647000 | -0.233051000 | 1.552213000 |
| H    | 2.634034000 | -1.842946000 | -0.291621000 |
| H    | 2.310076000 | -0.906735000 | 1.272141000 |
| H    | -2.634031000 | -1.842948000 | 0.291621000 |
| H    | -2.310079000 | -0.906734000 | -1.272140000 |

Cyclohexane
|      |      |      |      |
|------|------|------|------|
| C    | 1.262524000 | 0.728918000 | 0.234036000 |
| C    | 0.000000000 | 1.457837000 | -0.234036000 |
| C    | 1.262524000 | -0.728918000 | -0.234036000 |
| C    | -1.262524000 | 0.728918000 | 0.234036000 |
| C    | 0.000000000 | -1.457837000 | 0.234036000 |
| C    | -1.262524000 | -0.728918000 | -0.234036000 |
| H    | 2.158102000 | 1.246032000 | -0.127892000 |
| H    | 1.303908000 | 0.752778000 | 1.332235000 |
| H    | -0.000044000 | 2.491987000 | 0.127892000 |
| H    | 0.000029000 | 1.505607000 | -1.332235000 |
| H    | 1.303879000 | -0.752829000 | -1.332235000 |
| H    | 2.158146000 | -1.245955000 | 0.127892000 |
| H    | -1.303879000 | 0.752829000 | 1.332235000 |
| H    | -2.158146000 | 1.245955000 | -0.127892000 |
|     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|
| H   | 0.000044000 | -2.491987000 | -0.127892000 |     |     |
| H   | -0.000029000 | -1.505607000 | 1.332235000  |     |     |
| H   | -2.158102000 | -1.246032000 | 0.127892000  |     |     |
| H   | -1.303908000 | -0.752778000 | -1.332235000 |     |     |
|     | 34   |     |     |     |     |
| Cyclohexene |     |     |     |     |     |
| C   | 1.493515000 | 0.041995000 | 0.112710000 |     |     |
| C   | 0.663935000 | 1.299645000 | 0.060049000 |     |     |
| C   | 0.689634000 | -1.182733000 | -0.330220000 |     |     |
| C   | -0.663940000 | 1.299643000 | -0.060038000 |     |     |
| C   | -0.689633000 | -1.182730000 | 0.330228000 |     |     |
| C   | -1.493513000 | 0.041991000 | -0.112723000 |     |     |
| H   | 2.383076000 | 0.161360000 | -0.517404000 |     |     |
| H   | 1.868656000 | -0.105470000 | 1.135883000 |     |     |
| H   | 1.195274000 | 2.247684000 | 0.118372000 |     |     |
| H   | 0.563006000 | -1.155757000 | -1.420384000 |     |     |
| H   | 1.236070000 | -2.101254000 | 0.092430000 |     |     |
| H   | -1.195279000 | 2.247680000 | -0.118380000 |     |     |
| H   | -1.236069000 | -2.101254000 | 0.092447000 |     |     |
| H   | -0.563007000 | -1.155740000 | 1.420392000 |     |     |
| H   | -2.383086000 | 0.161354000 | 0.517372000 |     |     |
| H   | -1.868631000 | -0.105470000 | -1.135904000 |     |     |
|     | 35   |     |     |     |     |
| 1,3-Cyclohexadiene |     |     |     |     |     |
| C   | 0.053086000 | 1.420006000 | 0.110022000 |     |     |
| C   | -0.053086000 | 0.732806000 | 1.253379000 |     |     |
| C   | 0.317632000 | 0.696571000 | -1.188121000 |     |     |
| C   | 0.053086000 | -0.732806000 | 1.253379000 |     |     |
| C   | -0.317632000 | -0.696571000 | -1.188121000 |     |     |
| C   | -0.053086000 | -1.420006000 | 0.110022000 |     |     |
| H   | 0.009378000 | 2.505852000 | 0.107322000 |     |     |
| H   | -0.199118000 | 1.245544000 | 2.199955000 |     |     |
| H   | -0.048864000 | 1.277555000 | -2.039930000 |     |     |
| H   | 1.407129000 | 0.603229000 | -1.319023000 |     |     |
| H   | 0.199118000 | -1.245544000 | 2.199955000 |     |     |
| H   | -1.407129000 | -0.603229000 | -1.319023000 |     |     |
| H   | 0.048864000 | -1.277555000 | -2.039930000 |     |     |
| H   | -0.009378000 | -2.505852000 | 0.107322000 |     |     |
|     | 36   |     |     |     |     |
| Benzene |     |     |     |     |     |
| C   | 0.000000000 | 1.392899000 | 0.000000000 |     |     |
|   |          |          |          |
|---|----------|----------|----------|
| C | -1.206286000 | 0.696449000 | 0.000000000 |
| C | -1.206286000 | -0.696449000 | 0.000000000 |
| C | 0.000000000 | -1.392899000 | 0.000000000 |
| C | 1.206286000 | -0.696449000 | 0.000000000 |
| C | 1.206286000 | 0.696449000 | 0.000000000 |
| H | 0.000000000 | 2.478737000 | 0.000000000 |
| H | -2.146649000 | 1.239368000 | 0.000000000 |
| H | -2.146649000 | -1.239368000 | 0.000000000 |
| H | 0.000000000 | -2.478737000 | 0.000000000 |
| H | 2.146649000 | -1.239368000 | 0.000000000 |
| H | 2.146649000 | 1.239368000 | 0.000000000 |

**2,2-Dimethylbutane**

|   |          |          |          |
|---|----------|----------|----------|
| C | -0.891138000 | -0.493307000 | 1.251301000 |
| C | -0.370919000 | 0.222873000 | 0.000000000 |
| C | 1.169743000 | 0.270629000 | 0.000000000 |
| C | 1.881540000 | -1.081438000 | 0.000000000 |
| C | -0.891138000 | -0.493307000 | -1.251301000 |
| C | -0.891138000 | 1.664786000 | 0.000000000 |
| H | -0.501945000 | -0.023609000 | 2.162317000 |
| H | -0.601978000 | -1.549129000 | 1.262973000 |
| H | -1.985360000 | -0.450049000 | 1.291227000 |
| H | 1.493610000 | 0.845543000 | 0.878474000 |
| H | 1.493610000 | 0.845543000 | -0.878474000 |
| H | 2.966509000 | -0.941691000 | 0.000000000 |
| H | 1.627577000 | -1.672866000 | -0.884945000 |
| H | 1.627577000 | -1.672866000 | 0.884945000 |
| H | -0.501945000 | -0.023609000 | -2.162317000 |
| H | -1.985360000 | -0.450049000 | -1.291227000 |
| H | -0.601978000 | -1.549129000 | -1.262973000 |
| H | -0.542658000 | 2.207179000 | 0.886401000 |
| H | -1.986701000 | 1.686130000 | 0.000000000 |
| H | -0.542658000 | 2.207179000 | -0.886401000 |

**2,3-Dimethylbut-1-ene**

|   |          |          |          |
|---|----------|----------|----------|
| C | 0.659232000 | -0.195091000 | -0.376320000 |
| C | -0.758257000 | 0.238013000 | -0.048663000 |
| C | 1.076755000 | -1.392899000 | 0.489680000 |
| C | -1.068744000 | 1.449914000 | 0.412114000 |
| C | -1.827608000 | -0.802948000 | -0.270301000 |
| C | 1.691496000 | 0.922771000 | -0.254484000 |
### 2,3-Dimethylbut-2-ene

|  |  |  |  |
|---|---|---|---|
| H | 0.649873000 | -0.535486000 | -1.423394000 |
| H | 1.040697000 | -1.122393000 | 1.550654000 |
| H | 2.099986000 | -1.700065000 | 0.250914000 |
| H | 0.425460000 | -2.258481000 | 0.336733000 |
| H | -2.098779000 | 1.715751000 | 0.632887000 |
| H | -0.322860000 | 2.217576000 | 0.588034000 |
| H | -1.756161000 | -1.611912000 | 0.465518000 |
| H | -1.728065000 | -1.263127000 | -1.260728000 |
| H | -2.826508000 | -0.367173000 | -0.192154000 |
| H | 1.774495000 | 1.264263000 | 0.783396000 |
| H | 1.428232000 | 1.782970000 | -0.876827000 |
| H | 2.676389000 | 0.563342000 | -0.567120000 |

### 2,3-Dimethylbuta-1,3-diene

|  |  |  |  |
|---|---|---|---|
| C | 0.000000000 | 0.000000000 | 0.671173000 |
| C | 0.000000000 | 0.000000000 | -0.671173000 |
| C | -0.023373000 | 1.248611000 | 1.520147000 |
| C | -0.023373000 | -1.248611000 | -1.520147000 |
| C | 0.023373000 | 1.248611000 | -1.520147000 |
| C | 0.023373000 | -1.248611000 | 1.520147000 |
| H | 0.927460000 | 1.370741000 | 2.054393000 |
| H | -0.801416000 | 1.159365000 | 2.288220000 |
| H | -0.218303000 | 2.163384000 | 0.961223000 |
| H | 0.927460000 | -1.370741000 | -2.054393000 |
| H | -0.801416000 | -1.159365000 | -2.288220000 |
| H | -0.218303000 | -2.163384000 | -0.961223000 |
| H | 0.218303000 | 2.163384000 | -0.961223000 |
| H | -0.927460000 | 1.370741000 | -2.054393000 |
| H | 0.801416000 | 1.159365000 | 2.288220000 |
| H | 0.218303000 | -2.163384000 | 0.961223000 |
| H | -0.218303000 | 2.163384000 | 0.961223000 |
| H | -0.927460000 | -1.370741000 | 2.054393000 |
| H | 0.801416000 | -1.159365000 | 2.288220000 |

### Additional table content

|  |  |  |  |
|---|---|---|---|
| C | -0.048431000 | 0.739804000 | 0.000000000 |
| C | 0.048431000 | -0.739804000 | 0.000000000 |
| C | 1.232834000 | -1.362556000 | 0.000000000 |
| C | -1.232834000 | 1.362556000 | 0.000000000 |
| C | -1.232834000 | -1.534469000 | 0.000000000 |
| C | 1.232834000 | 1.534469000 | 0.000000000 |
| H | 1.292502000 | -2.446623000 | 0.000000000 |
### 2,3-Dimethylbutane

| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| H    | 2.175776000  | -0.826780000 | 0.000000000  |
| H    | -1.292502000 | 2.446623000  | 0.000000000  |
| H    | -2.175776000 | 0.826780000  | 0.000000000  |
| H    | -1.840021000 | -1.303373000 | 0.881915000  |
| H    | -1.840021000 | -1.303373000 | -0.881915000 |
| H    | -1.023657000 | 2.606232000  | 0.000000000  |
| H    | 1.840021000  | 1.303373000  | 0.881915000  |
| H    | 1.840021000  | 1.303373000  | -0.881915000 |
| H    | 1.023657000  | 2.606232000  | 0.000000000  |

### 3,3-Dimethylbut-1-ene

| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| H    | -0.234895000 | 0.734238000  | 0.000000000  |
| H    | 0.234895000  | -0.734238000 | 0.000000000  |
| H    | -1.336373000 | 0.723893000  | 0.000000000  |
| H    | 1.336373000  | -0.723893000 | 0.000000000  |
| C    | 0.234895000  | 1.483701000  | 1.249947000  |
| C    | 0.234895000  | 1.483701000  | -1.249947000 |
| C    | -0.234895000 | -1.483701000 | 1.249947000  |
| C    | -0.234895000 | -1.483701000 | -1.249947000 |
| H    | 1.327318000  | 1.431574000  | 1.339772000  |
| H    | 1.327318000  | 1.431574000  | -1.339772000 |
| H    | -1.327318000 | -1.431574000 | 1.339772000  |
| H    | -1.327318000 | -1.431574000 | -1.339772000 |
| H    | -0.043497000 | 2.540861000  | 1.194199000  |
| H    | -0.199022000 | 1.076299000  | 2.166612000  |
| H    | -0.043497000 | 2.540861000  | -1.194199000 |
| H    | -0.199022000 | 1.076299000  | -2.166612000 |
| H    | 0.043497000  | -2.540861000 | 1.194199000  |
| H    | 0.199022000  | -1.076299000 | 2.166612000  |
| H    | 0.043497000  | -2.540861000 | -1.194199000 |
| H    | 0.199022000  | -1.076299000 | -2.166612000 |
|        |        |        |        |
|--------|--------|--------|--------|
|        | -2.305984000 | 0.993632000 | -0.000028000 |
| H      | 1.218068000 | -1.545397000 | -1.277328000 |
| H      | 2.127783000 | -0.024058000 | -1.261702000 |
| H      | 0.600398000 | -0.138891000 | 2.162255000  |
| H      | 1.219797000 | -1.546319000 | 1.275015000  |
| H      | 2.127460000 | -0.023762000 | 1.262103000  |
| H      | -0.296827000 | 1.880611000 | 0.888408000  |
| H      | -0.297058000 | 1.881397000 | -0.886724000 |
| H      | 1.233616000 | 1.977959000 | 0.000725000  |
| 43     |        |        |        |
| Heptane|        |        |        |
| C      | 0.000000000 | 3.816380000 | -0.355934000 |
| C      | 0.000000000 | 2.550538000 | 0.497249000  |
| C      | 0.000000000 | 1.275049000 | -0.343162000 |
| C      | 0.000000000 | 0.000000000 | 0.497153000  |
| C      | 0.000000000 | -1.275049000 | -0.343162000 |
| C      | 0.000000000 | -2.550538000 | 0.497249000  |
| C      | 0.000000000 | -3.816380000 | -0.355934000 |
| H      | 0.883668000 | 3.851044000 | -1.001985000 |
| H      | -0.883668000 | 3.851044000 | -1.001985000 |
| H      | 0.000000000 | 4.719247000 | 0.261473000  |
| H      | 0.877995000 | 2.547991000 | 1.156034000  |
| H      | -0.877995000 | 2.547991000 | 1.156034000  |
| H      | -0.878586000 | 1.275903000 | -1.003697000 |
| H      | 0.878586000 | 1.275903000 | -1.003697000 |
| H      | 0.878658000 | 0.000000000 | 1.157453000  |
| H      | -0.878658000 | 0.000000000 | 1.157453000  |
| H      | -0.878586000 | -1.275903000 | -1.003697000 |
| H      | 0.878586000 | -1.275903000 | -1.003697000 |
| H      | 0.877995000 | -2.547991000 | 1.156034000  |
| H      | -0.877995000 | -2.547991000 | 1.156034000  |
| H      | 0.883668000 | -3.851044000 | -1.001985000 |
| H      | -0.883668000 | -3.851044000 | -1.001985000 |
| 44     |        |        |        |

| Hept-1-ene|        |        |        |
| C        | 3.692297000 | 0.028549000 | 0.511847000 |
| C        | 2.690421000 | 0.199010000 | -0.345267000 |
| C        | 1.389176000 | -0.548470000 | -0.304483000 |
| C        | 0.188884000 | 0.381040000 | -0.091386000 |
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| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | -1.143889000 | -0.363761000 | -0.086599000 |
| C       | -2.344382000 | 0.555634000  | 0.129274000  |
| C       | -3.670073000 | -0.201302000 | 0.131598000  |
| H       | 3.631048000  | -0.703658000 | 1.313598000  |
| H       | 4.608215000  | 0.607152000  | 0.445302000  |
| H       | 2.786275000  | 0.945692000  | -1.134834000 |
| H       | 1.247545000  | -1.094471000 | -1.247969000 |
| H       | 1.421289000  | -1.299699000 | 0.494489000  |
| H       | 0.316660000  | 0.918774000  | 0.856942000  |
| H       | 0.176568000  | 1.145757000  | -0.880365000 |
| H       | -1.264338000 | -0.901542000 | -1.037704000 |
| H       | -1.129179000 | -1.131904000 | 0.699428000  |
| H       | -2.221584000 | 1.091322000  | 1.079300000  |
| H       | -2.357131000 | 1.322114000  | -0.656300000 |
| H       | -3.687483000 | -0.954244000 | 0.927060000  |
| H       | -4.518051000 | 0.471536000  | 0.288407000  |
| H       | -3.824438000 | -0.720975000 | -0.819598000 |

Cycloheptane

| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 1.540218000 | -0.757590000 | 0.103863000 |
| C       | 1.539673000 | 0.758424000  | -0.103985000 |
| C       | 0.303129000 | -1.503353000 | -0.411665000 |
| C       | 0.302232000 | 1.503480000  | 0.411742000  |
| C       | -0.956989000 | -1.229545000 | 0.422263000  |
| C       | -1.774812000 | -0.000626000 | -0.000180000 |
| C       | -0.957879000 | 1.229151000  | -0.421999000 |
| H       | 2.436806000  | -1.169628000 | -0.374998000 |
| H       | 1.640684000  | -0.971628000 | 1.177230000  |
| H       | 2.436076000  | 1.171097000  | 0.374675000  |
| H       | 1.639780000  | 0.972488000  | -1.177384000 |
| H       | 0.123246000  | -1.256849000 | -1.467568000 |
| H       | 0.520383000  | -2.577146000 | -0.382375000 |
| H       | 0.122666000  | 1.256978000  | 1.467695000  |
| H       | 0.518925000  | 2.577387000  | 0.382331000  |
| H       | -1.617911000 | -2.103210000 | 0.393286000  |
| H       | -0.651897000 | -1.123453000 | 1.471726000  |
| H       | -2.434456000 | -0.274800000 | -0.832574000 |
| H       | -2.435441000 | 0.272841000  | 0.831661000  |
| H       | -1.619386000 | 2.102348000  | -0.392348000 |
| H       | -0.652910000 | 1.123927000  | -1.471587000 |
### Cycloheptene

| C     | 0.939356000 | -1.298189000 | -0.289022000 |
|-------|-------------|--------------|--------------|
| C     | -0.427770000 | -1.524953000 | 0.375080000  |
| C     | 1.639039000  | -0.002500000 | 0.128026000  |
| C     | -1.537590000 | -0.664007000 | -0.178750000 |
| C     | 0.943343000  | 1.295358000  | -0.289111000 |
| C     | -0.423032000 | 1.526208000  | 0.375150000  |
| C     | -1.535477000 | 0.668765000  | -0.178758000 |
| H     | 1.595075000  | -2.138227000 | -0.030196000 |
| H     | 0.816195000  | -1.317336000 | -1.379279000 |
| H     | -0.705382000 | -2.578162000 | 0.268292000  |
| H     | -0.324350000 | -1.344353000 | 1.455986000  |
| H     | 1.756342000  | -0.002621000 | 1.221614000  |
| H     | 2.653590000  | -0.004169000 | -0.288485000 |
| H     | -2.393544000 | -1.180120000 | -0.609202000 |
| H     | 1.601747000  | 2.133339000  | -0.030454000 |
| H     | 0.820180000  | 1.314701000  | -1.379352000 |
| H     | -0.320020000 | 1.344939000  | 1.455997000  |
| H     | -0.697460000 | 2.580291000  | 0.268765000  |
| H     | -2.389773000 | 1.187633000  | -0.609248000 |

### Cyclohepta-1,3-diene

| C     | 0.626434000  | -1.333437000 | -0.444722000 |
|-------|---------------|--------------|--------------|
| C     | -0.687971000  | -1.403822000 | 0.344298000  |
| C     | 1.630982000   | -0.320385000 | 0.096587000  |
| C     | -1.648946000  | -0.291034000 | 0.029133000  |
| C     | 1.200146000   | 1.118461000  | 0.116506000  |
| C     | -0.025181000  | 1.648909000  | -0.008730000 |
| C     | -1.334932000  | 0.999430000  | -0.140935000 |
| H     | 1.102963000   | -2.320040000 | -0.433508000 |
| H     | 0.400314000   | -1.100768000 | -1.491392000 |
| H     | -1.180706000  | -2.359727000 | 0.138085000  |
| H     | -0.464456000  | -1.405737000 | 1.421161000  |
| H     | 1.933505000   | -0.610052000 | 1.113718000  |
| H     | 2.548954000   | -0.385960000 | -0.502840000 |
| H     | -2.694995000  | -0.570273000 | -0.079947000 |
| H     | 2.019096000   | 1.825928000  | 0.241881000  |
| H     | -0.075849000  | 2.736268000  | 0.007137000  |
| H     | -2.152030000  | 1.681646000  | -0.367001000 |

### Cyclohepta-1,3,5-triene
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| C       | 0.964691000  | 1.217230000  | -0.203092000 |
|---------|--------------|--------------|--------------|
| C       | 1.433199000  | 0.000827000  | 0.549650000  |
| C       | -0.341603000 | 1.525117000  | -0.283706000 |
| C       | 0.966111000  | -1.216127000 | -0.203079000 |
| C       | -1.419861000 | 0.678036000  | 0.190540000  |
| C       | -1.419069000 | -0.679659000 | 0.190528000  |
| C       | -0.339831000 | -1.525505000 | -0.283710000 |
| H       | 1.702040000  | 1.858591000  | -0.679737000 |
| H       | 2.518483000  | 0.000146000  | 0.668971000  |
| H       | 0.977725000  | 0.000561000  | 1.549688000  |
| H       | -0.633152000 | 2.462759000  | -0.752945000 |
| H       | 1.704202000  | -1.856672000 | -0.679679000 |
| H       | -2.351095000 | 1.176801000  | 0.451907000  |
| H       | -2.349726000 | -1.179516000 | 0.451856000  |
| H       | -0.630301000 | -2.463496000 | -0.752921000 |

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2,2-Dimethylpentane

| C       | -2.154402000 | -0.685199000 | 0.000000000 |
|---------|--------------|--------------|--------------|
| C       | -0.621362000 | -0.698299000 | 0.000000000 |
| C       | -0.131793000 | 0.762807000  | 0.000000000 |
| C       | 1.381503000  | 0.980454000  | 0.000000000 |
| C       | 1.737571000  | 2.466132000  | 0.000000000 |
| C       | -0.131793000 | -1.435877000 | 1.251552000 |
| C       | -0.131793000 | -1.435877000 | -1.251552000 |
| H       | -2.541975000 | -0.17012000  | 0.886403000 |
| H       | -2.541975000 | -0.17012000  | -0.886403000 |
| H       | -2.554471000 | -1.705369000 | 0.000000000 |
| H       | -0.557966000 | 1.269257000  | -0.878932000 |
| H       | -0.557966000 | 1.269257000  | 0.878932000  |
| H       | 1.829251000  | 0.501703000  | 0.879010000 |
| H       | 1.829251000  | 0.501703000  | -0.879010000 |
| H       | 1.326566000  | 2.965874000  | 0.883635000 |
| H       | 2.820398000  | 2.620465000  | 0.000000000 |
| H       | 1.326566000  | 2.965874000  | -0.883635000 |
| H       | -0.433818000 | -0.905544000 | 2.162348000 |
| H       | -0.557085000 | -2.444993000 | 1.292827000 |
| H       | 0.958268000  | -1.536168000 | 1.262279000 |
| H       | -0.557085000 | -2.444993000 | -1.292827000 |
| H       | -0.433818000 | -0.905544000 | -2.162348000 |
| H       | 0.958268000  | -1.536168000 | -1.262279000 |
4,4-Dimethylpent-1-ene

|   |   |   |
|---|---|---|
| C | -1.066700000 | 1.348704000 | 0.637920000 |
| C | -0.793507000 | -0.024821000 | 0.015959000 |
| C | 0.454353000 | 0.031139000 | -0.897384000 |
| C | 1.710994000 | 0.497945000 | -0.219693000 |
| C | 2.755100000 | -0.281174000 | 0.049890000 |
| C | -0.580273000 | -1.058089000 | 1.125718000 |
| C | -1.994208000 | -0.437624000 | -0.840752000 |
| H | -0.263309000 | 1.646746000 | 1.319596000 |
| H | -1.163915000 | 2.120188000 | -0.135275000 |
| H | -1.999959000 | 1.329650000 | 1.212801000 |
| H | 0.621989000 | -0.968812000 | -1.319260000 |
| H | 0.229350000 | 0.699988000 | -1.740856000 |
| H | 1.749439000 | 1.549144000 | 0.066591000 |
| H | 3.642689000 | 0.989919000 | 0.546189000 |
| H | 2.757930000 | -1.334164000 | -0.223691000 |
| H | 0.284819000 | -0.799812000 | 1.744369000 |
| H | -1.462190000 | -1.114986000 | 1.773679000 |
| H | -0.406820000 | -2.054409000 | 0.701931000 |
| H | -2.900236000 | -0.514094000 | -0.229161000 |
| H | -2.182008000 | 0.296370000 | -1.632836000 |
| H | -1.822997000 | -1.411237000 | -1.314032000 |

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References

[1] Schleyer, P. v. R., Encyclopedia of computational chemistry. John Wiley & Sons: 1998.

[2] Feller, D.; Peterson, K. A., An examination of intrinsic errors in electronic structure methods using the Environmental Molecular Sciences Laboratory computational results database and the Gaussian-2 set. The Journal of chemical physics 1998, 108 (1), 154–176.

[3] Klopper, W.; Bak, K. L.; Jørgensen, P.; Olsen, J.; Helgaker, T., Highly accurate calculations of molecular electronic structure. Journal of Physics B: Atomic, Molecular and Optical Physics 1999, 32 (13), R103.

[4] Dunning, T. H., A road map for the calculation of molecular binding energies. The Journal of Physical Chemistry A 2000, 104 (40), 9062–9080.

[5] Feller, D.; Sordo, J. A., A CCSDT study of the effects of higher order correlation on spectroscopic constants. I. First row diatomic hydrides. The Journal of Chemical Physics 2000, 112 (13), 5604–5610.

[6] Feller, D.; Sordo, J. A., Performance of CCSDT for diatomic dissociation energies. The Journal of Chemical Physics 2000, 113 (2), 485–493.

[7] Helgaker, T.; Jorgensen, P.; Olsen, J., Molecular electronic-structure theory. John Wiley & Sons: 2000.

[8] Feller, D.; Dixon, D. A., Extended benchmark studies of coupled cluster theory through triple excitations. The Journal of Chemical Physics 2001, 115 (8), 3484–3496.

[9] Helgaker, T.; Klopper, W.; Halkier, H.; Bak, K.; Jørgensen, P.; Olsen, J., In Highly Accurate Ab Initio Computation of Thermochemical Data, Gioslowski J. Kluwer: Dordrecht: 2001.

[10] Dixon, D. A.; De Jong, W. A.; Peterson, K. A.; Francisco, J. S., Heats of formation of CBr, CHBr, and CBr2 from ab initio quantum chemistry. The Journal of Physical Chemistry A 2002, 106 (18), 4725–4728.

[11] Martin, J. M.; de Oliveira, G., Towards standard methods for benchmark quality ab initio thermochemistry—W1 and W2 theory. The Journal of chemical physics 1999, 111 (5), 1843–1856.

[12] Parthiban, S.; Martin, J. M., Fully ab initio atomization energy of benzene via Weizmann-2 theory. The Journal of chemical physics 2001, 115 (5), 2051–2054.

[13] de Oliveira, G.; Martin, J. M.; Silwal, I. K.; Liebman, J. F., Definitive heat of formation of methylenimine, CH2NH, and of methyleniminium ion, CH2NH2+, by means of W2 theory. Journal of Computational Chemistry 2001, 22 (13), 1297–1305.

[14] Parthiban, S.; Martin, J. M.; Liebman, J. F., The heats of formation of the haloacetylenes XCCY [X, Y = H, F, Cl]: basis set limit ab initio results and thermochemical analysis. Molecular Physics 2002, 100 (4), 453–464.

[15] Martin, J. M.; Parthiban, S., W1 and W2 theories, and their variants: thermochemistry in the kJ/mol accuracy range. In Quantum-Mechanical Prediction of Thermochemical Data, Springer: 2001; pp 31–65.

[16] Feller, D.; Davidson, E. R., Basis sets for ab initio molecular orbital calculations and intermolecular interactions. Reviews in computational chemistry 1990, 1–43.
[17] Helgaker, T.; Taylor, P. R., Gaussian basis sets and molecular integrals. In Modern Electronic Structure Theory: Part II, 1995; pp 725–856.

[18] Dunning Jr, T.; Peterson, K.; Woon, D., Schleyer PvR, Allinger NL, Clark T, Gesteiger J, Kolman PA, Schaefer HF III (eds) In: Encyclopedia of computational chemistry. Wiley, Chichester: 1998, 88–115.

[19] Dunning Jr, T., Rates of convergence and error estimation formulas for the Rayleigh–Ritz variational method. J. Chem. Phys 1989, 90, 1007–1023.

[20] Woon, D. E.; Dunning Jr, T. H., Gaussian basis sets for use in correlated molecular calculations. V. Core-valence basis sets for boron through neon. The Journal of chemical physics 1995, 103 (11), 4572–4585.

[21] Feller, D., Application of systematic sequences of wave functions to the water dimer. The Journal of chemical physics 1992, 96 (8), 6104–6114.

[22] Feller, D., 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 1993, 98 (9), 7059–7071.

[23] Martin, J. M., Ab initio total atomization energies of small molecules —towards the basis set limit. Chemical physics letters 1996, 259 (5–6), 669–678.

[24] Martin, J. M., Benchmark ab initio calculations of the total atomization energies of the first-row hydrides AHn (A= Li–F). Chemical physics letters 1997, 273 (1–2), 98–106.

[25] Martin, J. M., Coupling between the convergence behavior of basis set and electron correlation: a quantitative study. Theoretical Chemistry Accounts 1997, 97 (1–4), 227–231.

[26] Martin, J. M., Very accurate ab initio binding energies—a comparison between empirical corrections and extrapolation methods. Journal of Molecular Structure: THEOCHEM 1997, 398, 135–144.

[27] Helgaker, T.; Klopper, W.; Koch, H.; Noga, J., Basis-set convergence of correlated calculations on water. The Journal of chemical physics 1997, 106 (23), 9639–9646.

[28] Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K., Basis-set convergence in correlated calculations on Ne, N2, and H2O. Chemical Physics Letters 1998, 286 (3–4), 243–252.

[29] Klopper, W.; Helgaker, T., Extrapolation to the limit of a complete basis set for electronic structure calculations on the N2 molecule. Theoretical Chemistry Accounts 1998, 99 (4), 265–271.

[30] Halkier, A.; Helgaker, T.; Klopper, W.; Jørgensen, P.; Csaszar, A. G., Comment on “Geometry optimization with an infinite basis set” w 2/≥ J. Phys. Chem. A 103 1999 651 and “Basis-set extrapolation” w 2/≥ Chem. Phys. Lett. 294 1998 45. Chemical physics letters 1999, 310, 385–389.

[31] Bak, K.; Halkier, A.; Jørgensen, P.; Olsen, J.; Helgaker, T.; Klopper, W., Chemical accuracy from ‘Coulomb hole’extrapolated molecular quantum-mechanical calculations. Journal of Molecular Structure 2001, 567, 375–384.

[32] Bak, K. L.; Jørgensen, P.; Olsen, J.; Helgaker, T.; Klopper, W., Accuracy of atomization energies and reaction enthalpies in standard and extrapolated electronic wave function/basis set calculations. The Journal of Chemical Physics 2000, 112 (21), 9229–9242.

[33] 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/.

[34] 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. *Theoretical Chemistry Accounts* 2008, 120 (1–3), 215–241.

[35] Frisch, M.; Trucks, G.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G., gaussian 09, Revision d. 01, Gaussian. *Inc., Wallingford CT* 2009, 201.

[36] Vasilyev, V., Online complete basis set limit extrapolation calculator. *Computational and Theoretical Chemistry* 2017, 1115, 1–3. http://sf.anu.edu.au/~vvv900/cbs/#ref_3.

[37] Wiberg, K. B., Accuracy of calculations of heats of reduction/hydrogenation: Application to some small ring systems. *The Journal of organic chemistry* 2012, 77 (22), 10393–10398.

[38] Rogers, D. W.; McLafferty, F. J.; Podosenin, A. V., Ab Initio Calculations of Enthalpies of Hydrogenation and Isomerization of Cyclic C4 Hydrocarbons. *The Journal of Physical Chemistry* 1996, 100 (43), 17148–17151.

[39] Rogers, D. W.; McLafferty, F. 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. *The Journal of Physical Chemistry A* 1998, 102 (7), 1209–1213.

[40] Li, Z.; Rogers, D. W.; McLafferty, F. J.; Mandziuk, M.; Podosenin, A. V., Ab initio calculations of enthalpies of hydrogenation, isomerization, and formation of cyclic C6 hydrocarbons. Benzene isomers. *The Journal of Physical Chemistry A* 1999, 103 (3), 426–430.