Fully ab initio atomization energy of benzene via W2 theory

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Abstract

The total atomization energy at absolute zero, \( \text{TAE}_0 \) of benzene, \( \text{C}_6\text{H}_6 \), was computed fully \textit{ab initio} by means of W2\( \text{h} \) theory as 1306.6 kcal/mol, to be compared with the experimentally derived value 1305.7±0.7 kcal/mol. The computed result includes contributions from inner-shell correlation (7.1 kcal/mol), scalar relativistic effects (-1.0 kcal/mol), atomic spin-orbit splitting (-0.5 kcal/mol), and the anharmonic zero-point vibrational energy (62.1 kcal/mol). The largest-scale calculations involved are CCSD/cc-pV5Z and CCSD(T)/cc-pVQZ; basis set extrapolations account for 6.3 kcal/mol of the final result. Performance of more approximate methods has been analyzed. Our results suggest that, even for systems the size of benzene, chemically accurate molecular atomization energies can be obtained from fully first-principles calculations, without resorting to corrections or parameters derived from experiment.
Computational thermochemistry is coming of age as part of the chemist’s toolbox. Popular approaches (such as G3 theory and CBS-QB3) that can lay claim to ‘chemical accuracy’ (1 kcal/mol) on average for small systems, invariably rely on a combination of relatively low-level \textit{ab initio} calculations and sophisticated empirical correction schemes, which have been parametrized against experimental data.

In recent years, a number of groups have focused on obtaining accurate thermodynamic data of small molecules by means of fully \textit{ab initio} approaches (i.e. devoid of parameters derived from experiment); the reader is referred to studies by e.g. Dixon, Klopper, Bauschlicher, and Martin. Very recently, we developed two near-black box methods of this type, known as W1 and W2 theory (for Weizmann-1 and -2, respectively); in the original paper and a subsequent validation study for most of the G2/97 data set, we have shown that these methods yield thermochemical data in the kJ/mol accuracy range for small systems that are well described by a single reference configuration.

The question arises as to how well such methods would ‘scale up’ to larger systems. For this purpose, the ubiquitous benzene molecule would appear to offer an excellent ‘stress test’. It has six heavy atoms, yet its heat of formation is known precisely from experiment, and its high symmetry makes it amenable to fairly large-scale treatments with modern high-performance computing hardware. In the present note, we shall discuss the performance the total atomization energy (TAE\textsubscript{z}, if zero-point exclusive, TAE\textsubscript{0} at 0 K) of benzene of the more rigorous W2h theory, of the more widely applicable W1 and W1h theories, and of a variety of more approximate approaches.

All calculations involved in W1, W1h, and W2h theory were carried out using MOLPRO 98.1 running on a Compaq ES40 minisupercomputer in our laboratory. (For the open-shell calculations on carbon, the definition of the CCSD(T) energy according to Ref. has been used.) Detailed descriptions and justifications of the various steps involved can be found in Refs. We merely note here that, for the system under study, the final result at the highest level of theory (W2h) consists of the following components: (a) an SCF limit extrapolated from SCF/cc-pV\textit{n}Z (correlation consistent polarized valence \textit{n}-tuple
zeta $^{10}$, with $n=$T,Q,5 energies using the formulas $E(n) = E_\infty + B/C^n$ (old style $^{10}$) or $E(n) = E_\infty + A/n^5$ (new style $^{10}$); (b) a CCSD valence correlation limit extrapolated from CCSD/cc-pV$n$Z ($n=$Q,5) results using $E(n) = E_\infty + A/n^3$; (c) a limit for the effect of connected triple excitations extrapolated from [CCSD(T)/cc-pV$n$Z–CCSD/cc-pV$n$Z ($n=$T,Q) using $E(n) = E_\infty + A/n^3$; (d) an inner-shell correlation contribution obtained at the CCSD(T)/MTsmall level; (e) a scalar relativistic (1st-order Darwin and mass-velocity $^{17,18}$) contribution obtained as an expectation value from the ACPF/MTsmall $^{19}$ wave function; (f) a first-order spin-orbit correction derived from the fine structure of the constituent atoms; and (g) the anharmonic zero-point energy (vide infra). The computationally most intensive step was the CCSD/cc-pV5Z calculation. At 876 basis functions, with 30 electrons correlated, this could not be carried out using a conventional algorithm even while exploiting the $D_{2h}$ subgroup of $D_{6h}$; using the direct CCSD algorithm of Lindh, Schütz, and Werner $^{20}$ as implemented in MOLPRO, it took 14 days of CPU time on a 667 MHz Alpha EV67 CPU with 768 MB of memory allocated. (The CCSD(T)/cc-pVQZ optimum geometry required for the W2h calculations was taken from Ref. $^{21}$.)

The W1h calculations primarily differ in that the extrapolations are carried out with smaller cc-pV$n$Z ($n=$D,T,Q) basis sets (and $E(n) = E_\infty + A/n^3$ for the correlation steps, see $^{10}$ for its derivation), while in W1 theory, the carbon basis set is in addition augmented with diffuse functions $^{22}$. All relevant data for the W2h calculation are collected in Table I. Calculations using more approximate methods such as G3 theory $^2$ and CBS-QB3 $^3$ were carried out using their respective implementations in Gaussian 98 $^{23}$.

For a molecule this size, the zero-point vibrational energy (ZPVE) is large enough that even fairly small relative errors may compromise the quality of the final TAE. Handy and coworkers $^{24}$ computed a quartic force field at the B3LYP/TZ2P $^{25,26}$ level; from their published anharmonicity constants (in particular the set deperturbed for Fermi resonances closer than 100 cm$^{-1}$), we obtain an anharmonic ZPVE of 62.04 kcal/mol. At the same level of theory, one-half the sum of the harmonics, $\sum_i \omega_i d_i/2$ (with $d_i$ the degeneracy of mode $i$) comes out 0.9 kcal/mol too high at 62.96 kcal/mol, while one-half the sum of the
fundamentals, $\sum_i \nu_i d_i/2$, comes out 1 kcal/mol too low at 60.98 kcal/mol. The average of both estimates, $\sum_i (\omega_i + \nu_i) d_i/4 = 61.97$ kcal/mol, is only 0.07 kcal/mol below the true anharmonic value. From the best available computed harmonic frequencies, CCSD(T)/ANO4321[27] and the best available experimental fundamentals[24], we obtain ZPVE=62.01 kcal/mol, or, after correction for the difference at the B3LYP/TZ2P level between $\sum_i (\omega_i + \nu_i) d_i/4$ and the true anharmonic ZPVE, we find a best-estimate ZPVE=62.08 kcal/mol.

Of the more approximate approaches used in various computational thermochemistry methods, HF/6-31G* harmonic frequencies scaled by 0.8929 (as used in G2 and G3 theory[2]) yield 60.33 kcal/mol, or about 1.7 kcal/mol too low. The procedure used in the very recent G3X and G3SX theories[28], B3LYP/6-31G(2df,p) scaled by 0.9854, however reproduces the best estimate to within 0.1 kcal/mol. B3LYP/6-311G** harmonic frequencies scaled by 0.99, as used in CBS-QB3[3], yields 62.23 kcal/mol, in very good agreement with the best estimate; the HF/6-31G(d) scaled by 0.9184 estimate in CBS-Q yields 61.69 kcal/mol, slightly too low. Finally, B3LYP/cc-pVTZ harmonics scaled by 0.985 (as used in W1 and W1h theory[9]) yield 62.04 kcal/mol, in near-perfect agreement with the best estimate.

Relevant data for the W2h calculation are collected in Table I. At first sight, the disagreement between the W2h $\Delta H^\circ_{f,0K}=23.1$ kcal/mol and the experimental value of 24.0±0.2 kcal/mol seems disheartening for such a CPU-intensive calculation. (Note that it ‘errs’ on the far side of the most recent previous benchmark calculation[3], 24.7±0.3 kcal/mol, which used similar-sized basis sets as W1 theory.) However, the comparison with experiment is not entirely ‘fair’ since it neglects the experimental uncertainties in the atomic heats of formation required to convert an atomization energy into a heat of formation (or vice versa). Combining these with the experimental $\Delta H^\circ_{f,0K}$ leads to an experimentally derived TAE₀=1305.7±0.7 kcal/mol, where the uncertainty is dominated by six times that in the heat of vaporization of graphite. In other words, our calculated TAE₀=1306.8 kcal/mol is only 0.2 kcal/mol removed from the upper end of the experimental uncertainty interval. (After all, an error of 0.02% seems to be a bit much to ask for.)

Alternatively and equivalently, one could affix an uncertainty of ±0.7 kcal/mol to the
computed W2h $\Delta H^\circ_{f,0K} = 23.1 \pm 0.7$ kcal/mol, where the error bar only reflects the uncertainties in the auxiliary experimental data (i.e., the heats of atomization of the elements), but does not include the uncertainty in the theoretical calculation itself which is harder to quantify. While most chemists would prefer the heat of formation, an analysis in terms of atomization energies is somewhat more elegant since it avoids mixing computed and observed data. (Unfortunately, a benchmark *ab initio* heat of vaporization of graphite does not appear to be feasible at this point in time.)

Secondly, let us consider the ‘gaps’ bridged by the extrapolations. For the SCF component, that is a very reasonable 0.3 kcal/mol (0.03 %), but for the CCSD valence correlation component this rises to 5 kcal/mol (1.7 %) while for the connected triple excitations contribution it amounts to 1 kcal/mol (3.7 % — note however that a smaller basis set is being used than for CCSD). It is clear that the extrapolations are indispensable to obtain even a *useful* result, let alone an accurate one, even with such large basis sets.

Inner-shell correlation, at 7 kcal/mol, is of quite nontrivial importance, but even scalar relativistic effects (at $-1.0$ kcal/mol) cannot be ignored. (The discrepancy between our scalar relativistic correction and the previous SCF-level calculation of Kedziora et al. [29], $-1.27$ kcal/mol, is consistent with the known tendency [30,31] of SCF-level scalar relativistic corrections to be overestimated by 20–25%.) And manifestly, even a 2% error in a 62 kcal/mol zero-point vibrational energy would be unacceptable.

Let us now consider the more approximate results. While W1h coincidentally agrees to better than 0.2 kcal/mol with the W2h result, W1 deviates from the latter by 0.6 kcal/mol. Note however that in W1h theory, the extrapolations bridge gaps of 0.8 (SCF), 10.1 (CCSD), and 2.1 (T) kcal/mol, the corresponding amounts for W1 theory being 0.7, 9.1, and 1.9 kcal/mol, respectively. Common sense suggests that if extrapolations account for 13.0 (W1h) and 11.7 (W1) kcal/mol, then a discrepancy of 1 kcal/mol should not come as a surprise — in fact, the relatively good agreement between the two sets of numbers and the more rigorous W2h result (total extrapolation: 6.3 kcal/mol) testifies, if anything, to the robustness of the method.
As for the difference of about 0.4 kcal/mol between the old-style \[9\] and new-style \[10\] SCF extrapolations in W1h and W1 theories, comparison with the W2h SCF limits clearly confirms the new-style extrapolation to be the more reliable one. (The two extrapolations yield basically the same result in W2h.) This should not be seen as an indication that the $E_\infty + A/L^5$ formula is somehow better founded theoretically, but rather as an example of why reliance on (aug-)cc-pVDZ data should be avoided if at all possible.

Our best TAE$_0$ value (W2h) differs by 1.6 kcal/mol from the previous benchmark calculation of Feller and Dixon \[5\]. In fact, since their largest basis set is of AVQZ quality, the appropriate comparison would be with our W1 atomization energy, which is 2.3 kcal/mol larger than their result using RCCSD(T) atomic energies. The zero-point energy and the corrections for core correlation, scalar relativistic effects, and atomic spin-orbit splitting are all very similar in the two studies. Their extrapolation approach is very different from ours, but in the event this difference nearly cancels out with that caused by the different definitions of the RCCSD(T) energy used in the atomic calculations. (Feller and Dixon followed Ref. \[32\], as opposed to Ref. \[15\] in the present paper: we find the difference for six carbon atoms to be 0.52 kcal/mol at the CCSD(T)/AVQZ level.) The difference is in fact mostly due to a $-2.1$ kcal/mol correction for ‘higher-order correlation effects’ applied in Ref. \[5\], which is an estimate of the CCSDT – CCSD(T) difference from small basis set calculations. However, the generally excellent quality of CCSD(T) computed bond energies rests to a large extent on an error compensation between neglect of higher-order connected triple excitations (which tend to reduce the binding energy) and complete neglect of quadruple excitations (which tend to increase it) \[33\]. It has been known for some time (e.g. \[34\]) that CCSDT energies are not necessarily closer to full CI than CCSD(T). Consequently, an accurate treatment should either include both $T_4$ and higher-order $T_3$ effects where it is possible to do so, or neglect both: including only the higher-order $T_3$ of necessity leads to an underestimate of TAE. We do note that our respective best estimates bracket the experimental value, which may indicate that the ‘true’ (full CI) TAE lies in between. However, in view of the uncertainty on the experimental TAE and the impossibility to carry out even a highly approximate
CCSDTQ calculation on benzene, it is hard to make a definite statement about this.

Turning finally to the more approximate approaches, G2 theory clearly underestimates TAE$_0$: G3 represents a major improvement, but the better than 1 kcal/mol agreement between the G3 TAE$_0$ and the experimentally derived value in fact benefits from an error compensation with the underestimated ZPVE: a rather more pronounced difference is seen for TAE$_e$. This problem is remedied in the very recent G3X and G3SX theories, which predict both TAE$_e$ and TAE$_0$ to within 1 kcal/mol of experiment, as does CBS-QB3. CBS-Q is slightly too low; the fairly elaborate CBS-APNO method find results that nearly coincide with W1 theory. (We note that none of the G$_n$ and CBS methods considered explicitly includes scalar relativistic effects; they instead rely on them being absorbed into the parametrization.)

Summarizing the above, we may state the following:

The total atomization energy of benzene, C$_6$H$_6$, was computed fully ab initio by means of W2h theory as 1306.6 kcal/mol, to be compared with the experimentally derived value 1305.7±0.7 kcal/mol. The computed result includes contributions from inner-shell correlation (7.1 kcal/mol), scalar relativistic effects (-1.0 kcal/mol), atomic spin-orbit splitting (-0.5 kcal/mol), and the anharmonic zero-point vibrational energy (62.1 kcal/mol). The largest-scale calculations involved are CCSD/cc-pV5Z and CCSD(T)/cc-pVQZ; basis set extrapolations account for 6.3 kcal/mol of the final result. Performance of more approximate methods has been analyzed. Our results suggest that, even for systems the size of benzene, chemically accurate molecular atomization energies can be obtained from fully first-principles calculations, without resorting to corrections or parameters derived from experiment.

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TABLE I. Individual components in W1h, W1, and W2h total atomization energy cum heat of formation of benzene. All data in kcal/mol.

| Ref. geom. | B3LYP/cc-pVTZ | CCSD(T)/cc-pVQZ |
|------------|---------------|-----------------|
| W1h        |               |                 |
| SCF        | VDZ 1044.19   | VTZ 1042.19     |
| VTZ        | 1042.59       | 1044.62         |
| VQZ        | 1044.84       | 1045.30         |
| (T)        | VTZ 1042.16   | VTZ 1045.15     |
| VQZ        | 1044.62       | 1045.30         |
| old-style  | E∞ + A/B^a    | V∞Z 1044.95     |
| new-style  | E∞ + A/n^b    | V∞Z 1045.33     |
| CCSD       | VTZ 268.44    | VQZ 280.91      |
| VTZ        | 255.55        | 268.44          |
| VQZ        | 280.97        | 282.39          |
| (T)        | VTZ 265.55    | VQZ 285.72      |
| VQZ        | 291.08        | VQZ 290.77      |
| Inner-shell correlation | 7.09 | 7.08 |
| Darwin and mass-velocity | -0.99 | -0.99 |
| Spin-orbit coupling | -0.51 | -0.51 |
| | | |
| | TAE_e | ZPVE | TAE_0 | AH_{f,0} | H_{298} - H_0 | AH_{f,0}^{298K} |
| Expt. | 1367.8±0.7^b | 62.08^a | 1305.7±0.7^b | 24.0±0.12 | 3.43 | 19.82±0.12 |
| W2h | 1368.71 | 62.08^a | 1306.63 | 25.01 | 3.34 | 18.78 |
| W1 | 1369.33 | 62.04 | 1307.29 | 22.39 | 3.34 | 18.15 |
| W1h | 1368.54 | 62.04 | 1306.49 | 23.18 | 3.34 | 18.95 |
| G3X | 1367.13 | 61.93 | 1305.20 | 24.5 | 3.42 | 20.3 |
| G3SX | 1366.92 | 61.93 | 1304.99 | 24.7 | 3.42 | 20.5 |
| G3 | 1365.48 | 60.33 | 1305.15 | 24.5 | 3.39 | 20.4 |
| G2^c | 1362.24 | 60.33 | 1301.91 | 27.8 | 3.39 | 23.7 |
| CBS-QB3 | 1365.94 | 62.23 | 1303.71 | 25.95 | 3.72 | 22.11 |
| CBS-Q | 1365.45 | 61.69 | 1303.76 | 25.90 | 3.53 | 21.87 |
| CBS-APNO | 1369.34 | 61.88 | 1307.46 | 22.20 | 3.53 | 18.17 |

(a) best estimate (see text).
(b) From ΔH_{f,0}^{298K}[C_6H_6(g)]=24.0±0.12 kcal/mol [36,37], ΔH_{f,0}^{298K}[C(g)]=169.98±0.11 kcal/mol [38], and ΔH_{f,0}^{298K}[H(g)]=51.634 kcal/mol [38]. (The uncertainty in ΔH_{f,0}^{298K}[H(g)] is negligible.)
(c) All values except G2 include corrections for atomic spin-orbit splitting.