

# Benchmark atomization energy of ethane: Importance of accurate zero-point vibrational energies and diagonal Born–Oppenheimer corrections for a ‘simple’ organic molecule

Amir Karton <sup>a</sup>, Branko Ruscic <sup>b</sup>, Jan M.L. Martin <sup>a,\*</sup>

<sup>a</sup> Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, Israel

<sup>b</sup> Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA

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## Abstract

A benchmark calculation of the atomization energy of the ‘simple’ organic molecule C<sub>2</sub>H<sub>6</sub> (ethane) has been carried out by means of W4 theory. While the molecule is straightforward in terms of one-particle and *n*-particle basis set convergence, its large zero-point vibrational energy (and anharmonic correction thereto) and nontrivial diagonal Born–Oppenheimer correction (DBOC) represent interesting challenges. For the W4 set of molecules and C<sub>2</sub>H<sub>6</sub>, we show that DBOCs to the total atomization energy are systematically overestimated at the SCF level, and that the correlation correction converges very rapidly with the basis set. Thus, even at the CISD/cc-pVDZ level, useful correlation corrections to the DBOC are obtained. When applying such a correction, overall agreement with experiment was only marginally improved, but a more significant improvement is seen when hydrogen-containing systems are considered in isolation. We conclude that for closed-shell organic molecules, the greatest obstacles to highly accurate computational thermochemistry may not lie in the solution of the clamped-nuclei Schrödinger equation, but rather in the zero-point vibrational energy and the diagonal Born–Oppenheimer correction.

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## 1. Introduction

As summarized in a 2001 book [1] and a more recent review [2], computational thermochemistry has come a long way in the past decade. For small molecules, at least two families of computational protocols exist that allow sub-kcal/mol accuracy levels to be reached on a semi-routine basis, namely the ‘W<sub>n</sub> theory’ family developed at Weizmann on the one hand [3–7], and the HEAT (Highly accurate Extrapolated Ab initio Thermochemistry) project by a multinational group of researchers [8,9]. (The ‘W<sub>n</sub> theory’ naming scheme was introduced by analogy to the ‘G<sub>n</sub> theory’ family of methods of the late lamented People and coworkers [10].)

Progress beyond the levels of accuracy achieved in W3 theory was impeded somewhat by the accuracy of the available experimental reference data. On this front, relief was afforded by the Active Thermochemical Tables (ATcT) approach of Ruscic and coworkers [11–16]. As opposed to the traditional sequential approach, ATcT derives its results from a Thermochemical Network (TN). Where available, the thermochemical values used in the present work for the purpose of benchmarking the W4 method have been obtained from the latest version of the Core (Argonne) Thermochemical Network, C(A)TN, that is currently under development and encompasses ~700 chemical species containing H, O, C, N, and halogens, which are interlinked by >7000 thermochemically relevant determinations [15].

By comparison to ATcT data for a rather small, but diverse, set of small molecules, we were able to show that the latest member in the W<sub>n</sub> family, W4 theory [7], affords

\* Corresponding author. Tel.: +972 8 9342533; fax: +972 8 9344142.  
E-mail address: comartin@weizmann.ac.il (J.M.L. Martin).

unprecedented accuracy. For the W4 species (see also Table 1), the RMS deviation between theory and experiment is only 0.08 kcal/mol, with a 95% uncertainty band of only 0.16 kcal/mol. Our longtime goal of confident sub-kJ/mol predictions thus finally appears to be in reach – even for such notoriously difficult systems as ozone.

One would therefore imagine that an application to a simple organic molecule like ethane should be trivial. We were thus rather surprised when precisely for ethane it took considerable efforts to achieve a converged result compatible with the ATcT and earlier experimental values. We will show that these difficulties do not derive from the solution of the relativistic clamped-nuclei Schrödinger equation (indeed, ethane is computationally straightforward in this regard), but from the zero-point vibrational energy and the diagonal Born–Oppenheimer correction.

## 2. Computational methods

All quantum mechanical calculations were carried out on quadruple-processor AMD Opteron 846 and quadruple dual-core AMD Opteron 870 machines at the Weizmann Institute, all custom-built by Access Technologies of Rehovot, Israel. Each machine is fitted with 8-way striped scratch disk arrays, a total of 500 gigabytes (Ultra320 SCSI) in the former case, and of 2 TB (Serial ATA) in the latter case. The largest calculations reported in the present paper required about half a terabyte of scratch disk space. The high sustained I/O throughputs of these machines [17] proved essential to handle the daunting I/O requirements for many of the calculations reported.

The DFT (density functional theory) anharmonic force field calculations reported in this paper have all been car-

Table 1  
W4 and experimental total atomization energies at 0 K, diagonal Born–Oppenheimer corrections at the HF/AVTZ level (W4 default) and CISD/VDZ level correlation correction to the DBOC

	DBOC HF/ AVTZ Ref. [7]	$\Delta$ DBOC CISD/ VDZ–HF/AVTZ <sup>d</sup>	ZPVE <sup>a</sup>	TAE0 W4 <sup>b</sup>	TAE W4* <sup>c</sup>	ATcT <sup>e</sup>	uncert.	Earlier expt. <sup>f</sup>	uncert.
H <sub>2</sub> O	0.13	–0.03	13.29	219.36	219.33	219.36	0.01	219.35	0.12
C <sub>2</sub> H <sub>2</sub>	0.12	–0.03	16.46	388.72	388.68	388.62	0.07	388.90	0.24
CH <sub>3</sub>	0.05	–0.03	18.55	289.14	289.11	289.11	0.03	289.00	0.10
CH <sub>4</sub>	0.10	–0.04	27.74	392.52	392.47	392.50	0.03	392.51	0.14
CH	–0.08	–0.02	4.04	80.02	79.99	79.98	0.05	79.90	0.23
CO <sub>2</sub>	0.05	–0.01	7.24	381.94	381.93	382.01	0.03	381.91	0.06
CO	0.02	–0.01	3.11	256.19	256.18	256.25	0.03	256.16	0.12
F <sub>2</sub>	0.00	0.00	1.30	36.84	36.84	36.91	0.07	36.94	0.10
HF	0.08	–0.02	5.85	135.33	135.31	135.27	0.00	135.33	0.17
N <sub>2</sub>	0.02	–0.01	3.36	225.01	224.99	224.94	0.01	225.06	0.04
NH <sub>3</sub>	0.14	–0.04	21.33	276.60	276.56	276.59	0.01	276.73	0.13
N <sub>2</sub> O	0.04	–0.01	6.81	263.39	263.39	263.38	0.03	263.79	
NO	0.01	–0.01	2.71	149.81	149.80	149.82	0.02	149.82	0.03
O <sub>2</sub>	0.01	0.00	2.25	117.90	117.87	117.99	0.00	117.97	0.04
O <sub>3</sub>	–0.03	0.01	4.15	142.24	142.25	142.48	0.01	142.51	
NO <sub>2</sub>	0.00	–0.03	5.40	221.59	221.57	221.67	0.02	221.70	
Cl <sub>2</sub>	0.00	0.00	0.80	57.03	57.03	57.18	0.00	57.18	0.00
ClF	0.00	0.00	1.12	60.23	60.23			60.36	0.01
CS	0.01	0.00	1.83	169.55	169.54			169.41	0.23
H <sub>2</sub> S	0.05	–0.02	9.40	173.60	173.58	173.55	0.07	173.15	0.12
HCl	0.04	–0.01	4.24	102.23	102.21	102.21	0.00	102.24	0.02
HOCl	0.07	–0.02	8.18	156.72	156.71	156.64	0.43	156.61	0.12
PH <sub>3</sub>	0.03 <sup>g</sup>	–0.04	14.44	227.32 <sup>g</sup>	227.28			227.13	0.41
SO	0.01	–0.01	1.64	123.66	123.66	123.72	0.02	123.58	0.04
SO <sub>2</sub>	0.02	–0.01	4.38	254.42	254.42	254.46	0.02	253.92	0.08
OCS	0.03	–0.01	5.72	328.65	328.65			328.53	0.48
CiCN	0.04	–0.01	5.33	278.79	278.78	279.42	0.26	279.20	0.48
C <sub>2</sub> H <sub>4</sub>	0.12	–0.05	31.60	532.11	532.06	532.00	0.06	531.91	0.17
H <sub>2</sub> CO	0.03	–0.04	16.53	357.51	357.47	357.43	0.06	357.25	0.12
HNO	–0.05	–0.03	8.56	196.78	196.74	196.86	0.03	196.85	0.06
H <sub>2</sub>	0.05	–0.04	6.23	103.30	103.26	103.27	0.00	103.27	0.00
C <sub>2</sub> H <sub>6</sub>	0.14 <sup>d</sup>	–0.07	46.39 <sup>d</sup>	666.27 <sup>d</sup>	666.19	666.18 <sup>d</sup>	0.06		See text

All values in kcal/mol.

<sup>a</sup> Zero-point vibrational energies taken from the compilation in Ref. [7], except for H<sub>2</sub> (taken from Huber and Herzberg [56]) and C<sub>2</sub>H<sub>6</sub> (best calculated value, this work). ATcT data are likewise from Ref. [7], except C<sub>2</sub>H<sub>6</sub> (this work). The adjunct uncertainties correspond to 95% confidence intervals, as customary in experimental thermochemistry, which were obtained by utilizing the full covariance matrix computed by ATcT; see also Refs. [11–14].

<sup>b</sup> Ref. [7], DBOC at HF/AVTZ level of theory, as per standard W4 protocol.

<sup>c</sup> Present work, W4+DBOC[CISD/VDZ]–DBOC[HF/VDZ].

<sup>d</sup> Present work.

<sup>e</sup> Ref. [15].

<sup>f</sup> Ref. [6] and references therein.

<sup>g</sup> The DBOC reported for phosphine in Ref. [7] was in error. The correct values for DBOC and TAE0 are given here.

ried out using a locally modified version of Gaussian 03 Revision C.01 [18]. All CCSD(T) and lower level energy calculations were performed using MOLPRO 2006.1 [19], while for post-CCSD(T) calculations we employed the MRCC [20–22] general coupled cluster package developed by Kállay. (The integrals and molecular orbitals required for MRCC were generated using the Austin–Mainz–Budapest version of Aces II [23].) Diagonal Born–Oppenheimer corrections were computed using ACES II at the SCF level, and using PSI 3 [24] at the CISD (configuration interaction with all single and double excitations) level.

With one exception, the basis sets used in the ab initio calculation are all of the correlation consistent family of Dunning and coworkers [25–27]. For the large-scale CCSD(T) calculation, we combined regular cc-pVnZ basis sets ( $n = D, T, Q, 5, 6$ ) on hydrogen with aug-cc-pVnZ ([diffuse-function] augmented polarization consistent) basis sets [26] on carbon. The combination is denoted AVnZ for short throughout the paper. For post-CCSD(T) calculations, regular cc-pVnZ basis sets (PVnZ for short) were employed unless indicated otherwise. In core-valence correlation calculations, we employed Peterson’s core-valence weighted correlation consistent basis sets [28], both regular (cc-pwCVnZ) and augmented (aug-cc-pwCVnZ). Finally, the scalar relativistic calculations were carried out using the PNNL (Pacific Northwest National Laboratory) relativistically contracted correlation consistent basis sets [29].

The W4 computational protocol is documented in great detail elsewhere [7]; for the sake of making the paper self-contained, we will briefly summarize the various steps:

- The reference geometry is obtained at the CCSD(T)/cc-pVQZ level (frozen core).
- The ROHF-SCF contribution is extrapolated from AV5Z and AV6Z basis sets using the recently proposed Martin–Karton modification [30] of Jensen’s extrapolation formula [31]:

$$E_{\text{HF},L} = E_{\text{HF},\infty} + A(L+1) \exp(-9\sqrt{L}) \quad (1)$$

- The RCCSD valence correlation energy is calculated using AV5Z and AV6Z basis set, using the Watts–Gauss–Bartlett definition [32] for open-shell systems. Following the suggestion of Klopper [33], it is partitioned in singlet-coupled pair energies, triplet-coupled pair energies, and  $\hat{T}_1$  terms. (The term linear in the single excitations  $\hat{T}_1$  in the CCSD equations is nonzero for open-shell CCSD calculations using semicanonical orbitals, see, e.g., Ref. [34].) The  $\hat{T}_1$  term (which exhibits very weak basis set dependence) is simply set equal to that in the largest basis set, while the singlet-coupled and triplet-coupled pair energies are extrapolated by the expression

$$E_{\infty} = E(L) + \frac{E(L) - E(L-1)}{(L/L-1)^{\alpha} - 1} \quad (2)$$

with  $\alpha_S = 3$  and  $\alpha_T = 5$ , and  $L$  set equal to the maximum angular momentum present in each basis set (i.e., 5 for AV5Z and 6 for AV6Z). These expressions are physically motivated by the partial-wave expansion of pair correlation energies in helium-like atoms [35–37] as well as by empirical observation [3,38].

- The  $(T)$  [39] valence correlation energy was extrapolated using the same expression with  $\alpha = 3$ , from AVQZ and AV5Z calculations. Note that only a CCSD calculation is required in the largest (AV6Z) basis set. For open-shell systems, the Werner–Knowles–Hampel (a.k.a. MOLPRO) definition [40] of the restricted open-shell CCSD(T) energy is employed throughout, rather than the original Watts–Gauss–Bartlett [32] (a.k.a. ACES II) definition, unless indicated otherwise;
- The CCSDT – CCSD(T) difference is extrapolated, using Eq. (2) and  $\alpha = 3$ , from CCSDT – CCSD(T) differences with PVDZ and PVTZ basis sets
- The  $\hat{T}_4$  difference was estimated from the following equation [7]:

$$\begin{aligned} \Delta E(\hat{T}_4) \approx & 1.10(E[\text{CCSDT}(Q)/\text{cc-pVTZ}] \\ & - E[\text{CCSDT}/\text{cc-pVTZ}] \\ & + E[\text{CCSDTQ}/\text{cc-pVDZ}] \\ & - E[\text{CCSDT}(Q)/\text{cc-pVDZ}]) \quad (3) \end{aligned}$$

where for open-shell systems, UHF references are used throughout except for the full CCSDTQ (coupled cluster with all single, double, triple, and quadruple excitations) calculation, where a restricted open-shell reference is used.

- The  $\hat{T}_5$  (connected quintuple excitations) contribution was estimated from CCSDTQ5 and CCSDTQ calculations using the simple Dunning–Hay valence double zeta (DZ) [41] basis set.
- The difference between ACES II and MOLPRO definitions of the valence ROCCSD(T) definition is computed at the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ levels and extrapolated using Eq. (2) (with  $\alpha = 3$ ). One-half of this contribution is added to the final result.
- The inner-shell correlation contribution was extrapolated using Eq. (2) (with  $\alpha = 3$ ) from CCSD(T)/aug-cc-pwCVTZ and CCSD(T)/aug-cc-pwCVQZ calculations.
- The scalar relativistic contribution is obtained from the difference between nonrelativistic CCSD(T)/aug-cc-pV(Q+d)Z and second-order Douglas–Kroll CCSD(T)/DK-aug-cc-pV(Q+d)Z calculations. The publicly available PNNL Douglas–Kroll–Hess contracted correlation consistent basis sets [29] were used in this step.
- Atomic spin–orbit coupling terms are taken from the experimental fine structure.
- Finally, diagonal Born–Oppenheimer corrections are obtained from ROHF/AVTZ calculations.

We will also consider the post-W4 methods, W4.2 and W4.3, defined in Ref. [7]. W4.2 theory adds a  $T_3 - (T)$

correction to the core-valence contribution computed using the cc-pwCVTZ basis set. In W4.3 theory, all valence post-CCSD(T) corrections are additionally upgraded:  $T_3$ -(T) is extrapolated from cc-pV{T,Q}Z basis sets; (Q) gets extrapolated, using Eq. (2) and  $\alpha = 3$ , from cc-pV{T,Q}Z basis sets;  $T_4$ -(Q) and  $T_5$  are obtained with the cc-pVTZ basis and cc-pVDZ basis sets, respectively; finally, a correction for  $T_6$  (connected sextuple excitations) is calculated using the simple DZ basis.

### 3. Results and discussion

#### 3.1. Bottom-of-the-well atomization energy

For comparison, we will also consider the molecules  $H_2$ ,  $C_2H_2$  and  $C_2H_4$ , as well as the disproportionation reaction  $2C_2H_4 \rightarrow C_2H_2 + C_2H_6$  and the successive hydrogenation reactions from acetylene to ethylene to ethane. All relevant results can be found in Table 2.

The percentage of the total atomization energy (TAE) deriving from connected triple excitations in the CCSD(T) approximation, %TAE[(T)], was shown in Ref. [7] to be a reliable indicator for the importance of post-CCSD(T) correlation effects. For  $C_2H_6$ , we find %TAE[(T)] = 0.9%, which suggests their importance should be negligible. In fact, we do find almost, but not quite, perfect cancellation between higher-order connected triple excitations,  $T_3 - (T)$  effects (−0.35 kcal/mol) and connected quadruple excitations,  $T_4$  (0.23 kcal/mol). Connected quintuple excitations,  $T_5$ , account for 0.01 kcal/mol or less. Near-perfect cancellation likewise holds for ethylene and acetylene, although the mutually opposite  $T_3 - (T)$  and  $T_4$  terms increase systematically from ethane to ethylene to acetylene. The latter goes in lockstep with the increasing %TAE[(T)] – from 0.9% to 1.3% to 2.1%.

The inner-shell correlation contribution is sizable (2.43 kcal/mol), but not dissimilar from those for ethylene and acetylene. Scalar relativistic effects and atomic first-order spin–orbit coupling account for quite non-negligible amounts of −0.39 and −0.17 kcal/mol, respectively. Possibly somewhat surprising is the relatively large diagonal Born–Oppenheimer correction of +0.14 kcal/mol (at the HF/AVTZ level).

#### 3.2. Initial comparison with experiment

Accurate zero-point vibrational energies for  $C_2H_2$  and  $C_2H_4$  are available from the literature (see Ref. [7] for details). No such data are available for  $C_2H_6$ . We initially tried a shortcut, namely to use one-quarter the sum of calculated CCSD(T)/cc-pVTZ harmonic frequencies plus the corresponding observed fundamentals. Both sets of data were taken from the work of Puzzarini and Taylor [42]. As shown in, e.g. Ref. [4], the difference between this and the true anharmonic ZPVE consists of two small terms, the first being one-quarter the sum of the diagonal anharmonicity constants, the second being the  $G_0$  shift.

Table 2  
Component breakdown of the final W4 total atomization energies (kcal/mol). Post-W4 correction to DBOC (kcal/mol)

	SCF	Valence CCSD	Valence (T)	$\hat{T}_3 - (T)$	$\hat{T}_4$	$\hat{T}_5$	Inner shell	Relativ.	Spin-orbit	DBOC	(a)	TAE <sub>e</sub>	ZPVE	TAE <sub>0</sub>	ΔBOC CISSD-HF
$H_2$	83.85	25.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	109.53	6.23	103.30	−0.036
$C_2H_2$	299.87	94.73	8.35	−0.72	0.70	0.07	2.49	−0.28	−0.17	0.12	0.04	405.18	16.46	388.72	−0.035
$CH_4$	331.55	84.72	2.89	−0.08	0.08	0.00	1.27	−0.19	−0.08	0.10	0.02	420.26	27.74	392.52	−0.045
$C_3H_4$	434.97	119.32	7.40	−0.46	0.43	0.03	2.38	−0.33	−0.17	0.12	0.04	563.71	31.60	532.11	−0.053
$C_2H_6$	558.01	146.34	6.37	−0.35	0.23	0.01	2.43	−0.39	−0.17	0.14	0.04	712.66	46.39	666.27	−0.065
<i>Reaction energies</i>															
(A)	−39.19	−1.40	+1.03	−0.11	+0.20	+0.02	−0.05	+0.06	0.00	+0.03	0.00	−39.42	8.56	−30.87	−0.023
(B)	−51.26	+1.04	+0.94	−0.26	+0.27	+0.04	+0.11	+0.05	0.00	+0.06	0.00	−49.01	8.91	−40.10	−0.018
(C)	+12.07	−2.43	+0.09	+0.15	−0.08	−0.02	−0.16	+0.01	0.00	−0.03	0.00	+9.58	−0.35	+9.23	−0.005

(A)  $C_2H_4 + H_2 \rightarrow C_2H_6$ , ATcT  $\Delta H_{r,0}^0 = -30.91 \pm 0.04$  kcal/mol.

(B)  $C_2H_2 + H_2 \rightarrow C_2H_4$ , ATcT  $\Delta H_{r,0}^0 = -40.11 \pm 0.07$  kcal/mol.

(C)  $2C_2H_4 \rightarrow C_2H_2 + C_2H_6$ , ATcT  $\Delta H_{r,0}^0 = 9.20 \pm 0.08$  kcal/mol.

(a) Difference between the ACES II and MOLPRO definitions of the valence ROCCSD(T) atomic energies.

However, in a molecule with six C–H stretches, the ZPVE is quite hefty: 46.10 kcal/mol using the approximation discussed above. (The corresponding one-half-harmonics and one-half-fundamentals values are 46.91 and 45.29 kcal/mol, respectively.) So the validity of this approximation cannot be taken for granted, at least in the accuracy range we are interested in.

We thus obtain a W4 TAE<sub>0</sub> = 666.56 kcal/mol. This is considerably higher than the established experimental value from Gurvich[43] of 666.1 ± 0.2 kcal/mol. The latter derives from ΔH<sub>f,0</sub><sup>o</sup>[C<sub>2</sub>H<sub>6</sub>(g)] = −16.34 ± 0.10 kcal/mol, three times the very well-established dissociation energy of H<sub>2</sub>, and the CODATA [44] heat of sublimation of graphite, 169.98 ± 0.11 kcal/mol. The ATcT value [16] for the latter represents a considerable revision upward, to 170.06 ± 0.02 kcal/mol [16]: this leads to TAE<sub>0</sub>[C<sub>2</sub>H<sub>6</sub>] = 666.26 ± 0.11 kcal/mol, closer to our calculations but still with an unexplained gap of 0.3 kcal/mol. In fact, the ATcT value is a bit lower, 666.18 ± 0.06 kcal/mol.

Naively, one might suspect the effect of the internal rotation on the heat content function  $H_{298} - E_0$ , but the difference between the Pitzer–Gwinn value quoted in Gurvich and the rigid rotor-harmonic oscillator approximation is less than 0.05 kcal/mol, making it unlikely that this causes a major error in converting the heat of formation to absolute zero.

### 3.3. Improved zero-point vibrational energy

Our first suspect was the zero-point vibrational energy. We recalculated the harmonic frequencies at the CCSD(T)/cc-pVQZ level (see Table 3), but this affects the ZPVE by less than 0.01 kcal/mol.

We then proceeded to calculate quartic force fields at the B3LYP/pc-2 and B97-1/pc-2 levels of theory, where pc-2 is one of the polarization consistent basis sets of Jensen [45–48] – identical in size to cc-pVTZ, but optimized for

density functional theory calculations. The zero-point vibrational energy was obtained using the simplified formula of Allen and coworkers [49], which is expressed directly in terms of the force constants rather than anharmonicities and  $G_0$ . As the DFT harmonic frequencies are known to be insufficiently accurate for the purpose, we substituted the CCSD(T)/cc-pVQZ harmonic frequencies in the analysis. (It was shown repeatedly before, e.g. [50], that this dramatically improves the quality of predicted vibrational fundamentals.)

We were then startled to find that the B3LYP/pc-2 and B97-1/pc-2 force fields, combined with CCSD(T)/cc-pVQZ harmonic frequencies, yielded significantly different zero-point vibrational energies. Detailed inspection revealed that essentially all the difference resulted from the quartic term, rather than from the cubic and kinetic energy terms.

Although the Allen formula is valid for both asymmetric and symmetric tops, we suspected a symmetry issue, and therefore repeated both calculations with the molecular symmetry slightly (10 μÅ) perturbed. To our surprise, the gap between the two methods narrowed by an order of magnitude, the B97-1 force field being most affected.

In all these calculations, Gaussian's "ultrafine" grid – a pruned (99,590) Euler–Lebedev product grid – had been used for energies and gradients, and the "medium" grid – a pruned (50,194) Euler–Lebedev product grid – for solving the coupled perturbed Kohn–Sham equations. Enlarging the latter to a "fine" (75,302) grid did not significantly affect results. However, when we switched to a pruned (140,590) grid for energies and gradients – the "huge" grid of our locally modified G03 installation – the difference between the two functionals, and between the symmetric and perturbed geometries, basically disappeared. (Like lowering the symmetry, the *pruned* "huge" grid approximately doubled CPU time.) Proceeding to an even more elaborate pruned (199,974) grid did not

Table 3  
Basis set convergence of geometry (Å, degrees) and harmonic frequencies for C<sub>2</sub>H<sub>6</sub> (in cm<sup>−1</sup>)

	CCSD(T)				Best estimate
	VTZ val	VQZ val	MTsmall val	MTsmall all	
r <sub>CC</sub>	1.5290	1.5265	1.5261	1.5231	1.5227
r <sub>CH</sub>	1.0918	1.0908	1.0906	1.0892	1.0890
θ <sub>CCH</sub>	111.197	111.207	111.211	111.230	111.226
ω <sub>1</sub>	3119.79	3122.59	3125.82	3132.03	3128.80
ω <sub>2</sub>	3096.58	3099.95	3102.97	3109.03	3106.01
ω <sub>3</sub>	3039.21	3039.93	3045.07	3050.93	3045.79
ω <sub>4</sub>	3037.75	3039.42	3043.35	3049.53	3045.60
ω <sub>5</sub>	1512.49	1512.27	1517.21	1519.45	1514.51
ω <sub>6</sub>	1510.81	1510.39	1514.99	1517.38	1512.78
ω <sub>7</sub>	1427.38	1427.91	1431.00	1433.88	1430.79
ω <sub>8</sub>	1406.57	1408.46	1411.85	1415.06	1411.67
ω <sub>9</sub>	1224.77	1225.01	1227.50	1229.95	1227.46
ω <sub>10</sub>	1013.83	1014.67	1013.30	1017.05	1018.42
ω <sub>11</sub>	820.90	820.75	822.64	826.15	824.26
ω <sub>12</sub>	309.62	305.65	313.07	309.66	302.24

For additional theoretical and experimental geometry data, see Ref. [42].



significantly affect results further. We note that throughout, the B97-1 functional displays greater grid sensitivity than the B3LYP one, possibly because the former involves higher powers of the reduced density gradient.

Our revised ZPVE, with CCSD(T)/cc-pVQZ harmonic frequencies and the B97-1/pc-2 anharmonic force field with “huge” grids, amounts to 46.29 kcal/mol. Thus  $TAE_0$  shifts down to 666.36 kcal/mol.

It was found earlier[51] for  $C_2H_4$  that inclusion of inner-shell correlation on the harmonic frequencies significantly improves agreement between calculated and observed fundamentals. We estimated the core correlation contribution in the present case as the difference between CCSD(T)/MTsmall calculations with and without ‘frozen’ core electrons. (MTsmall stands for the ‘small’ Martin–Taylor core correlation basis set introduced in Ref. [3]. We verified for  $C_2H_4$  that it recovers nearly all of the effect of the ordinary Martin–Taylor core correlation basis set[52].) This suggests a shift upward by 0.10 kcal/mol in the zero-point vibrational energy, and  $TAE_0$  thus shifts down to 666.26 kcal/mol, where the nominal 0.16 kcal/mol uncertainty interval encloses the ATcT value.

However, it was shown before (e.g., [53]) that harmonic frequencies for X–H stretches at the CCSD(T) level are overestimated by several  $cm^{-1}$  at the basis set limit with all electrons correlated, and in a molecule with six C–H stretches this can add up to a nontrivial amount. It can therefore not be ruled out that our best ZPVE is in fact on the order of 0.05 kcal/mol too high.

### 3.4. Post-SCF corrections to the diagonal Born–Oppenheimer correction

It was assumed in the original W4 paper – as in the HEAT papers [8,9] – that the diagonal Born–Oppenheimer corrections were well reproduced at the HF/AVTZ level. Initial investigations by Valeev and Sherrill [54] seemed to indicate that correlation corrections to the DBOC are rather unimportant – with the notable exception of the hydrogen molecule. However, from results reported in a recent paper [55] on the implementation of CCSD and higher-level DBOCs, a somewhat different picture emerges.

While we do not have the implementation of these authors at our disposal, they found that size-consistency

errors in CISD relative to CCSD are quite unimportant, at least for small molecules. So CISD calculations – which we were able to carry out using PSI3 [24] – should be helpful in resolving our question.

Furthermore, as can be seen in Table 4, basis set convergence of the correlation contribution to DBOC is quite rapid, at least in terms of our needs for the present application. We conclude that even at the CISD/cc-pVDZ level, we recover a sufficient chunk of the correction for our purposes, and essentially all of it for systems that do not have highly polar bonds.

W4 values with CISD/cc-pVDZ correlation corrections to DBOC are tabulated in Table 1, together with the original W4 values. Error statistics, broken down by category, are given in Table 5.

The overall RMS error is marginally improved for W4 theory, as well as for the post-W4 methods W4.2 and W4.3. However, if H-containing molecules are considered separately, a somewhat more marked improvement is seen, from an RMSD of 0.062 kcal/mol to one of 0.049 kcal/mol.

Essentially across the board, inclusion of electron correlation lowers the DBOC. In the case of H-containing systems, the effects are quite significant in relative terms, albeit still small on an absolute scale. For the molecules  $CH_4$ ,  $C_2H_2$ , and  $C_2H_4$ , we find DBOC correlation corrections of  $-0.04$ ,  $-0.03$ , and  $-0.05$  kcal/mol, respectively – 45%, 30%, and 45%, respectively, of the Hartree–Fock DBOCs.

It should then not come as a surprise that there would be an even larger correction for  $C_2H_6$ , and here we indeed find  $-0.07$  kcal/mol, or 46% of the SCF-level contribution. This, in fact, brings our best calculated  $TAE_0$  of  $C_2H_6$  down to 666.19 kcal/mol, in perfect agreement with the ATcT value.

A cross-check on our results is delivered by the two successive hydrogenation reactions of acetylene and ethylene, and by the disproportionation reaction of two ethylenes into acetylene and ethane. It can be seen in Table 2 that not only are the W4 values in excellent agreement with experiment, but the calculated values at the bottom of the well converge fairly rapidly with the theoretical treatment – in particular, a very large portion of all three reaction energies is recovered at the SCF level, and the overall

Table 4  
Basis set convergence of diagonal Born–Oppenheimer contributions to total atomization energies (kcal/mol)

	HF VDZ	HF AVDZ	HF VTZ	HF AVTZ	CISD–HF VDZ	CISD–HF AVDZ	CISD–HF VTZ	CISD–HF AVTZ
H <sub>2</sub>	0.057	0.060	0.053	0.053	–0.036	–0.038	–0.039	–0.039
BH	–0.101	–0.101	–0.102	–0.103	–0.029	–0.029	–0.028	–0.028
BH <sub>3</sub>	–0.013	–0.011	–0.017	–0.017	–0.048	–0.051	–0.048	N/A
CH <sub>4</sub>	0.109	0.106	0.100	0.099	–0.045	–0.046	–0.043	N/A
NH <sub>3</sub>	0.128	0.137	0.131	0.135	–0.039	–0.036	–0.034	N/A
H <sub>2</sub> O	0.110	0.124	0.121	0.126	–0.031	–0.026	–0.026	N/A
HF	0.069	0.078	0.078	0.080	–0.018	–0.014	–0.014	–0.013
CO	0.013	0.014	0.016	0.016	–0.010	–0.009	–0.008	N/A

Table 5  
Error statistics (kcal/mol) for various W4 theory variants with and without correlation corrections to the DBOC

CISD DBOC	W4		W4.2		W4.3	
	NO	YES	NO	YES	NO	YES
<i>Mean signed error</i>						
All	−0.013	−0.032	−0.009	−0.029	0.024	0.008
1st row	−0.012	−0.034	−0.004	−0.026	0.030	0.011
2nd row	−0.016	−0.027	−0.033	−0.043	0.009	−0.001
H containing	0.038	0.007	0.033	0.001	0.031	0.003
Non H containing	−0.068	−0.074	−0.055	−0.062	0.018	0.012
<i>Mean absolute deviation</i>						
All	0.066	0.061	0.058	0.055	0.044	0.038
1st row	0.066	0.062	0.057	0.055	0.038	0.035
2nd row	0.066	0.059	0.064	0.058	0.059	0.049
H containing	0.052	0.039	0.048	0.039	0.030	0.022
Non H containing	0.081	0.085	0.069	0.073	0.060	0.057
<i>Root mean square deviation</i>						
All	0.083	0.080	0.073	0.069	0.057	0.052
1st row	0.085	0.081	0.069	0.065	0.051	0.048
2nd row	0.078	0.075	0.088	0.086	0.069	0.061
H containing	0.062	0.049	0.060	0.048	0.039	0.030
Non H containing	0.101	0.103	0.084	0.086	0.072	0.068

post-CCSD(T) contributions are quite modest. Note that for both hydrogenation reactions, the DBOCs are significantly reduced when correlation contributions to the DBOC are included, while both DBOC and correlation correction thereto are small to begin with for the disproportionation reaction.

#### 4. Conclusions

Our benchmark W4 calculation of the total atomization energy of ethane reproduces the best available experimental value basically exactly, provided adequate precautions are taken in the calculation of the zero-point vibrational energy.

The combination of large-basis set CCSD(T) harmonic frequencies with quartic force fields obtained from density functional theory appears to be a very useful approach for zero-point vibrational energies in situations where a large basis set CCSD(T) quartic force field would be computationally intractable. When doing so, very large grids must be used in the solution of the Kohn–Sham equations to ensure adequate grid convergence of the quartic term. (The internal rotation in C<sub>2</sub>H<sub>6</sub> turned out not to be a significant obstacle, as the internal rotation barrier is substantially greater than RT.)

Post-SCF contributions to the diagonal Born–Oppenheimer correction can be thermochemically significant (at least, at W4-like accuracy levels) in molecules with many hydrogens. Even at the CISD/cc-pVDZ level, useful post-SCF DBOC contributions can be obtained.

Finally, the presently reported experience leads us to conclude that the main factor limiting accuracy in computational thermochemistry on small organic molecules and radicals may well no longer be primarily the solution of the relativistic, clamped-nuclei Schrödinger equation, and

that increasing attention will have to be paid to nuclear-motion related issues such as the diagonal Born–Oppenheimer correction and anharmonic corrections to the zero-point vibrational energy.

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#### Appendix A. Brief note on the H<sub>2</sub> molecule

The simplest possible molecule with a conventional two-electron bond would seem to be the H<sub>2</sub> diatomic. For this simple system, basically exact answers are available from the literature. Thus, the reader might wonder how well W4 theory fares here.

Furthermore,  $\text{H}_2$  enters not just into the hydrogenation reactions discussed above, but also into all sorts of isodesmic reaction cycles involving  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$ .

An accurate nonrelativistic, clamped-nuclei dissociation energy of  $\text{H}_2$  is  $38293.0 \text{ cm}^{-1}$ , or  $109.485 \text{ kcal/mol}$  [58]. Our calculations were carried out at the CCSD(T)/cc-pVQZ reference geometry,  $r_e = 0.74189 \text{ \AA}$ , rather than the experimental  $r_e = 0.74144 \text{ \AA}$ : from the potentials in Ref. [58], the geometry difference would cause a change in the total energy on the order of less than  $0.04 \text{ cm}^{-1}$ , which is negligible for our purposes. At our reference geometry, the numerical Hartree–Fock dissociation energy as computed using the 2DHF (two-dimensional finite-difference Hartree–Fock) program [60] is  $83.8467 \text{ kcal/mol}$ , which is reproduced almost exactly by the W4 SCF contribution,  $83.8461 \text{ kcal/mol}$ . Subtracting the numerical Hartree–Fock dissociation energy from  $109.485 \text{ kcal/mol}$  leaves us with an ‘experimental correlation energy’ of  $25.638 \text{ kcal/mol}$  at the CCSD(T)/cc-pVQZ geometry. (At the experimental geometry, the exact SCF and correlation components are  $83.8499$  and  $25.635 \text{ kcal/mol}$ , respectively – this illustrates the redistribution of binding energies between SCF and correlation components that occurs as a bond is stretched or compressed.)

It is, in fact, in the correlation contribution that the only significant discrepancy between theory and experiment is found. For main-group systems including atoms other than hydrogen, the value of  $L$  used in the  $A + B/L^3$  extrapolation formula is equal to both the cardinal number  $N$  in the AVNZ basis sets used, and the largest angular momentum actually present in the basis set  $L_{\text{max}}$ . For  $\text{H}_2$ , of course,  $L_{\text{max}} = N - 1$ , creating an ambiguity as to which choice is preferred. Using  $L = L_{\text{max}}$  with the AV{5,6}Z basis sets leads to an extrapolated correlation energy of  $25.629 \text{ kcal/mol}$ , while  $L = N$  yields  $25.650 \text{ kcal/mol}$  instead. The two numbers are seen to bracket the ‘experimental’ correlation energy, with the former choice being slightly closer to experiment. With the AV{6,7}Z basis sets, the two corresponding values are  $25.632$  and  $25.642 \text{ kcal/mol}$ , respectively, once again bracketing the ‘experimental’ value.

(Another prototype system that might shed some light on this is the helium atom. The exact, nonrelativistic, clamped-nuclei total energy is  $-2.903724$  hartree [61]: subtracting the numerical SCF energy of  $-2.861680$  hartree found in the present work using 2DHF, we obtain an exact correlation energy of  $0.042044$  hartree, or  $26.383 \text{ kcal/mol}$ . Using  $L = L_{\text{max}}$  with the AV{5,6}Z basis sets leads to an extrapolated correlation energy of  $26.356 \text{ kcal/mol}$ , while  $L = N$  yields  $26.399 \text{ kcal/mol}$  instead. Once again, the exact correlation energy is bracketed by both choices.)

The exact numerical adiabatic correction found by Bishop and Cheung [58] for  $^1\text{H}_2$  is  $114.618 \text{ cm}^{-1}$ ; the exact answer for the  $^1\text{H}$  atom is of course simply [59]  $R_\infty / (1 + M_p/m_e) = 59.732 \text{ cm}^{-1}$ , where  $R_\infty$  is the Rydberg constant for an infinitely heavy nucleus and  $M_p$  and  $m_e$  are the proton and electron masses, respectively. We thus find that

the exact DBOC contribution to  $D_e(^1\text{H}_2) = 0.0139 \text{ kcal/mol}$ . The CISD/AVTZ calculated value from the present work,  $0.014 \text{ kcal/mol}$ , is in perfect agreement therewith. Note that the HF/AVTZ DBOC of  $0.053 \text{ kcal/mol}$  used in W4 theory causes by itself an error of  $0.039 \text{ kcal/mol}$ .

The relativistic correction to  $D_e$  found in that work,  $-0.54 \text{ cm}^{-1}$  or  $-0.0015 \text{ kcal/mol}$ , is too small to be of thermochemical interest. Yet the W4 level contribution,  $-0.0016 \text{ kcal/mol}$ , is in very good agreement.

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