

Benchmark correlation energies for small molecules

DARRAGH P. O'NEILL and PETER M. W. GILL*

School of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK

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We present estimates of the exact correlation energies for 56 small molecules whose experimental atomization energies are known accurately. These should prove useful in the assessment and parameterization of new quantum chemical methods.

1. Introduction

The prediction of thermochemical quantities to high accuracy ($\sim 1 \text{ kcal mol}^{-1}$) is an important and challenging goal in quantum chemistry and a purely *ab initio* approach requires the use of highly accurate and computationally expensive treatments of electron correlation and relativistic effects. Many of the popular, more computationally accessible, but more empirical quantum chemical models, such as B3LYP [1] or the Gaussian-*n* methods [2–5], are parameterized to reproduce such thermochemical data and while this is clearly a desirable quality in any method, an even more satisfying target is to reproduce accurately atomic and molecular total energies: this too would lead to accurate thermochemistry, but without depending upon unphysical error cancellation. Clearly, to parameterize or to assess the performance of a method requires an accurate data set. Although there are papers [6–11] which contain estimates of the total energy of one or several small molecules, we are not aware of a large systematic set of such data in the chemical physics literature. In this article we use a combination of accurately determined experimental and theoretical quantities to do so for 56 small molecules, viz. the 55 neutral molecules in the G1 set [2, 3] and H_2 . In particular, we list the non-relativistic (NR) total and electronic energies, the restricted and unrestricted Hartree–Fock (HF) energies and the corresponding correlation energies. We aim to determine these quantities to within a millihartree (mE_h).

2. Method

The atomization energy, ΣD_0 , of an *N*-atom molecule *M* is calculated using

$$\Sigma D_0 = \sum_i^N E_e^i - E_0^M + \Delta E_{\text{Rel}}, \quad (1)$$

where E_e^i is the total NR electronic energy of the *i*th atom in *M*, E_0^M is the NR energy of the lowest vibronic state of the molecule, and ΔE_{Rel} corrects the calculated atomization energy for the effects of relativity. E_0^M is given by

$$E_0^M = E_e^M + E_{\text{ZPVE}}^M, \quad (2)$$

where E_e^M is the total NR electronic energy of *M* if the nuclei were held fixed at positions corresponding to the potential minimum and E_{ZPVE}^M is the zero-point vibrational energy. E_e^M can be written as

$$E_e^M = E_{\text{HF}}^M + E_{\text{corr}}^M, \quad (3)$$

where E_{HF}^M is the HF energy and E_{corr}^M the correlation energy of *M*. Given the atomization energies, the relativistic corrections, the zero-point corrections, the total atomic energies and the HF energies, we can now determine E_0^M , E_e^M and E_{corr}^M ,

$$E_0^M = \sum_i^N E_e^i + \Delta E_{\text{Rel}} - \Sigma D_0, \quad (4)$$

$$E_e^M = E_0^M - E_{\text{ZPVE}}^M, \quad (5)$$

$$E_{\text{corr}}^M = E_e^M - E_{\text{HF}}^M. \quad (6)$$

* Corresponding author. e-mail: p.gill@anu.edu.au.

Present address: Research School of Chemistry, Australian National University, ACT 0200, Australia.

Table 1. Methods used to derive required quantities.

Quantity	Method
ΣD_0	Experimental
E_{ZPVE}	MP2/6-31G* ZPVE scaled by 0.9661
E_{HF}	HF/cc-pV5Z-h/(Exp. or QCISD/ G3MP2Large)
ΔE_{Rel}	CISD(FC)/cc-pVTZ//CCSD(T)(FC)/ aug-cc-pVTZ for one-electron scalar relativistic corrections.
E_c	Spin-orbit corrections from experiment Total atomic energies from [18]

3. Results

The quality of the results we obtain using equations (4)–(6) is clearly dependent on the accuracy of the data we use. The methods used to obtain these data are summarized in table 1. We obtain the atomization energy from experiment, specifically we take those listed in [4] for the G1 molecules (correcting the value for CN to that quoted in [12]) and the value for H₂ from [13]. The majority of these have error bars less than 1 mE_h and we assume they are accurate for our purposes.

Table 2. Geometry^a, atomization energy ΣD_0 ^b, zero-point vibrational energy E_{ZPVE} ^c, relativistic correction ΔE_{Rel} ^d, non-relativistic energy of lowest vibronic state E_0 , non-relativistic electronic energy E_c ^e, HF energy E_{HF} ^f, and correlation energy E_{corr} for atoms and molecules. All energies are in Hartrees.

Species	Geom.	$\Sigma D_0 \times 10^3$	$E_{ZPVE} \times 10^3$	$\Delta E_{Rel} \times 10^3$	E_0	E_c	E_{HF}		$E_{corr} \times 10^3$	
							UHF	RHF	UHF	RHF
H	–	–	–	–	–	–0.5000	–0.5000	–0.5000	–0	–0
He	–	–	–	–	–	–2.9037	–2.8616	–2.8616	–42	–42
Li	–	–	–	–	–	–7.4781	–7.4327	–7.4327	–45	–45
Be	–	–	–	–	–	–14.6674	–14.5730	–14.5730	–94	–94
B	–	–	–	–	–	–24.6539	–24.5331	–24.5291	–121	–125
C	–	–	–	–	–	–37.8450	–37.6937	–37.6886	–151	–156
N	–	–	–	–	–	–54.5892	–54.4045	–54.4009	–185	–188
O	–	–	–	–	–	–75.0673	–74.8188	–74.8122	–249	–255
F	–	–	–	–	–	–99.7339	–99.4161	–99.4112	–318	–323
Ne	–	–	–	–	–	–128.9376	–128.5468	–128.5468	–391	–391
Na	–	–	–	–	–	–162.2546	–161.8587	–161.8587	–396	–396
Mg	–	–	–	–	–	–200.0530	–199.6146	–199.6146	–438	–438
Al	–	–	–	–	–	–242.3460	–241.8808	–241.8768	–465	–469
Si	–	–	–	–	–	–289.3590	–288.8588	–288.8544	–500	–505
P	–	–	–	–	–	–341.2590	–340.7192	–340.7187	–540	–540
S	–	–	–	–	–	–398.1100	–397.5132	–397.5071	–597	–603
Cl	–	–	–	–	–	–460.1480	–459.4897	–459.4838	–658	–664
Ar	–	–	–	–	–	–527.5400	–526.8173	–526.8173	–723	–723
H ₂	HH	164.6	9.8	0.0	–1.1646	–1.1745	–1.1336	–1.1336	–41	–41
LiH	HH	89.2	3.1	0.0	–8.0673	–8.0704	–7.9873	–7.9873	–83	–83
BeH	HH	74.7	4.7	0.0	–15.2421	–15.2468	–15.1536	–15.1532	–93	–94
CH	HH	127.3	6.5	0.0	–38.4723	–38.4788	–38.2844	–38.2798	–194	–199
CH ₂ (³ B ₁)	KU	286.2	16.7	–0.5	–39.1317	–39.1484	–38.9408	–38.9353	–208	–213
CH ₂ (¹ A ₁)	KU	271.9	17.4	–0.3	–39.1172	–39.1346	–38.8959	–38.8959	–239	–239
CH ₃	KU	460.9	29.5	–0.2	–39.8060	–39.8355	–39.5811	–39.5766	–254	–259
CH ₄	KU	625.5	44.8	–0.5	–40.4710	–40.5158	–40.2170	–40.2170	–299	–299
NH	HH	125.9	7.4	–0.2	–55.2153	–55.2227	–54.9862	–54.9783	–236	–244
NH ₂	KU	270.9	18.9	–0.3	–55.8604	–55.8794	–55.5920	–55.5870	–287	–292
NH ₃	QCI	440.9	34.1	–0.5	–56.5306	–56.5647	–56.2249	–56.2249	–340	–340
OH	HH	161.4	8.2	–0.2	–75.7289	–75.7371	–75.4278	–75.4228	–309	–314
OH ₂	KU	349.5	20.8	–0.8	–76.4176	–76.4383	–76.0672	–76.0672	–371	–371
FH	HH	215.5	8.9	–1.0	–100.4503	–100.4592	–100.0706	–100.0706	–389	–389
SiH ₂ (¹ A ₁)	QCI	230.1	11.8	–1.0	–290.5901	–290.6019	–290.0352	–290.0352	–567	–567
SiH ₂ (³ B ₁)	KU	196.7	12.2	–1.3	–290.5569	–290.5692	–290.0288	–290.0268	–540	–542
SiH ₃	QCI	341.0	20.4	–1.3	–291.2013	–291.2217	–290.6467	–290.6451	–575	–577
SiH ₄	QCI	482.5	31.3	–1.6	–291.8431	–291.8744	–291.2682	–291.2682	–606	–606
PH ₂	QCI	230.6	13.6	–0.3	–342.4899	–342.5035	–341.8929	–341.8872	–611	–616
PH ₃	KU	362.4	24.2	–0.6	–343.1220	–343.1462	–342.4943	–342.4943	–652	–652
SH ₂	KU	276.0	15.2	–1.4	–399.3874	–399.4026	–398.7198	–398.7198	–683	–683
ClH	HH	162.9	6.7	–1.6	–460.8125	–460.8192	–460.1125	–460.1125	–707	–707
Li ₂	HH	38.2	0.8	0.0	–14.9944	–14.9951	–14.8716	–14.8716	–124	–124

(continued)

Table 2. Continued.

Species	Geom.	$\Sigma D_0 \times 10^3$	$E_{ZPVE} \times 10^3$	$\Delta E_{\text{Rel}} \times 10^3$	E_0	E_e	E_{HF}		$E_{\text{corr}} \times 10^3$	
							UHF	RHF	UHF	RHF
LiF	HH	219.3	2.2	-1.0	-107.4322	-107.4344	-106.9931	-106.9931	-441	-441
HCCH	QCI	619.8	25.0	-0.8	-77.3105	-77.3355	-76.8555	-76.8555	-480	-480
H ₂ CCH ₂	QCI	847.6	50.3	-0.8	-78.5384	-78.5888	-78.0706	-78.0706	-518	-518
H ₃ CCH ₃	QCI	1061.8	74.6	-1.0	-79.7528	-79.8274	-79.2665	-79.2665	-561	-561
CN	HH	284.3	6.3	-0.2	-92.7187	-92.7250	-92.2422	-92.2250	-483	-500
HCN	KU	480.9	15.5	-0.5	-93.4156	-93.4311	-92.9157	-92.9157	-515	-515
CO	HH	408.3	4.7	-0.8	-113.3214	-113.3261	-112.7907	-112.7907	-535	-535
HCO	KU	430.8	13.0	-1.0	-113.8440	-113.8570	-113.3035	-113.2981	-553	-559
H ₂ CO	QCI	569.2	26.4	-1.1	-114.4826	-114.5090	-113.9231	-113.9231	-586	-586
H ₃ COH	QCI	766.2	50.8	-1.3	-115.6798	-115.7306	-115.1017	-115.1017	-629	-629
N ₂	HH	358.7	4.8	-0.2	-109.5373	-109.5421	-108.9929	-108.9929	-549	-549
H ₂ NNH ₂	QCI	646.0	52.9	-0.3	-111.8248	-111.8776	-111.2364	-111.2364	-641	-641
NO	HH	239.2	8.6	-0.5	-129.8962	-129.9047	-129.3087	-129.3009	-596	-604
O ₂	HH	188.0	3.1	-1.0	-150.3236	-150.3267	-149.6908	-149.6672	-636	-660
HOOH	QCI	402.1	25.4	-1.4	-151.5381	-151.5635	-150.8528	-150.8528	-711	-711
F ₂	HH	58.8	2.2	-1.4	-199.5280	-199.5303	-198.7729	-198.7729	-757	-757
CO ₂	KU	608.6	11.2	-1.8	-188.5899	-188.6011	-187.7250	-187.7250	-876	-876
Na ₂	HH	26.5	0.4	0.0	-324.5357	-324.5360	-323.7165	-323.7165	-819	-819
Si ₂	HH	117.9	1.1	-1.6	-578.8375	-578.8386	-577.7615	-577.7549	-1077	-1084
P ₂	HH	185.0	1.6	0.3	-682.7027	-682.7043	-681.4995	-681.4995	-1205	-1205
S ₂	HH	160.5	1.5	-2.2	-796.3827	-796.3842	-795.1090	-795.0933	-1275	-1291
Cl ₂	HH	91.2	1.2	-1.6	-920.3887	-920.3899	-919.0101	-919.0101	-1380	-1380
NaCl	HH	155.4	0.8	-1.8	-622.5597	-622.5605	-621.4600	-621.4600	-1101	-1101
SiO	HH	303.6	2.6	-1.3	-364.7312	-364.7337	-363.8545	-363.8545	-879	-879
SC	HH	270.1	2.9	-1.1	-436.2262	-436.2291	-435.3618	-435.3618	-867	-867
SO	HH	196.8	2.4	-1.8	-473.3759	-473.3783	-472.4210	-472.4039	-957	-974
ClO	HH	100.9	1.9	-2.1	-535.3182	-535.3201	-534.3183	-534.3106	-1002	-1009
ClF	HH	96.1	1.8	-2.2	-559.9802	-559.9820	-558.9194	-558.9194	-1063	-1063
Si ₂ H ₆	QCI	797.0	49.1	-3.2	-582.5181	-582.5672	-581.3842	-581.3842	-1183	-1183
CH ₃ Cl	KU	591.2	37.8	-2.2	-500.0865	-500.1243	-499.1564	-499.1564	-968	-968
CH ₃ SH	QCI	709.3	46.2	-1.9	-438.6662	-438.7124	-437.7665	-437.7665	-946	-946
HOCl	KU	249.1	12.7	-2.4	-535.9668	-535.9795	-534.9340	-534.9340	-1045	-1045
SO ₂	KU	404.8	6.3	-3.0	-548.6524	-548.6588	-547.3250	-547.3250	-1334	-1334

^aGeometries are denoted by HH = Huber and Herzberg (experimental r_e from [13]), KU = Kuchitsu (experimental r_e from [19]) and QCI = geometry calculated using QCISD/G3MP2Large.

^bTaken from [4], with the exception of CN from [12] and H₂ from [13].

^cMP2/6-31G* ZPVE scaled by 0.9661 [14] taken from [15].

^dScalar relativistic and spin-orbit corrections taken from [16].

^eAtomic total energies taken from [18].

^fCalculated using cc-pV5Z- h .

The zero-point vibrational energies are obtained by scaling the ZPVE from a MP2/6-31G* harmonic frequency calculation by 0.9661 [14] and are taken from [15]. The RMS error of this method with the 39 molecules used to parameterize it is approximately $0.3 mE_h$.

We use the relativistic corrections to the atomization energies listed by Feller and Peterson [16] which consist of scalar relativistic corrections (one-electron Darwin and mass-velocity terms in the Breit-Pauli Hamiltonian) obtained using a CISD(FC)/cc-pVTZ//CCSD(T)(FC)/aug-cc-pVTZ wavefunction, and also a spin-orbit correction based on experimental results. The scalar relativistic corrections are expected to be within

$1 mE_h$ of four-component or Douglas-Kroll results. Although the geometries at which the relativistic corrections are calculated are not the experimental geometries, the differences are expected to be negligible and, furthermore, it has been shown that these corrections have a very weak dependence on geometry [17].

The NR electronic energies of the atoms are taken from [18] and are taken to have errors of less than $1 mE_h$. The molecular HF energies are calculated using experimental r_e structures (taken from [13, 19]) which are available for 42 of the species under investigation. The remaining 14 HF energies are calculated at the QCISD/G3MP2Large [20–22] geometries. The HF results are obtained using the cc-pV5Z [23, 24] basis

set with the h -functions removed (cc-pV5Z- h). Halkier *et al.* have studied the convergence of the HF energy using correlation consistent basis sets and report that using the cc-pV5Z basis yields energies within $1 mE_h$ of the HF limit [25]. All HF energies are calculated using the Q-CHEM package [26].

In table 2 we present all of the quantities described above. The correlation energy depends upon whether a restricted (RHF) or unrestricted (UHF) wavefunction is used and we therefore list both. We note that the atomic correlation energies given here are different to those given by Chakravorty *et al.* [18] as they have used numerical HF energies [27] which are symmetry restricted and therefore higher than either the RHF or UHF energies shown here. We would recommend, when assessing a post-HF method using a RHF/UHF wavefunction to estimate the correlation energy, the use of the energies listed here rather than those of [18].

Ideally, we would like to be able to compare our results with exact solutions (within an infinite basis set) of the Schrödinger equation, but in the two decades since this was done for water [28] (within a double-zeta basis set) we have not moved much closer to this goal. Although quantum Monte Carlo offers estimates to the exact energy, quantifying the error due to the fixed node approximation requires the use of experimentally derived energies like the ones listed in the table. We hope that the data listed here will not only be useful, but also highlight the need for theoretical methods which can produce benchmark data like these without approximation or experimental data.

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