ACCURATE THEORETICAL ESTIMATES OF THE ELECTRON AFFINITIES OF AH$_n$ MOLECULES BY ISOGYRIC COMPARISONS. PROTON AFFINITIES OF AH$_n^-$ ANIONS

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Electron affinities of AH$_n$ molecules (A = Li to Cl) are estimated by ab initio molecular orbital theory, using isogyric comparisons with the hydrogen molecule. Results agree with experimental data to within 0.1 eV for first-row and most second-row compounds. Electron affinities are predicted for BH, BH$_2$, AlH and AlH$_2$. BH$_2^-$ is predicted to have a singlet $^1A_1$ ground state with the $^3B_1$ state lying 0.16 eV higher in energy; the corresponding singlet–triplet difference for AlH$_2^-$ is predicted to be larger, 0.73 eV. Theoretical proton affinities (PA)$_0$ for the AH$_n^-$ anions are derived from the same data set.

There have been many experimental studies of the electron affinities of small atoms and molecules, especially in the last fifteen years [*1]. Although some success has been achieved recently, theory has experienced difficulty in reproducing electron affinities of first-row atoms and their hydrides to an accuracy of 0.1 eV [*2], even with considerable computational effort. This is primarily because the stability of negative ions depends crucially on electron correlation. Indeed, most small anions are unbound at the single-configuration (Hartree–Fock) level of theory. It is widely recognized that an accurate description of the correlation between two electrons in the same orbital requires large basis sets and high levels of configuration interaction [3–5]. Can a more practical level of theory [*3] overcome these problems and achieve a uniform accuracy approaching 0.1 eV? This would permit prediction of missing entries in

experimental tabulations and identify experimental data which may be open to doubt and require reinvestigation.

The target accuracy of about 0.1 eV or 2 kcal/mol has been achieved in a recent study of the bond dissociation energies of the complete set of AH$_n$ neutral molecules, where A is a first-row atom [6]. A corresponding treatment of second-row hydrides is only slightly less accurate ($\approx$ 3 kcal/mol). The same procedure can be used to estimate the ionization energies and proton affinities of AH$_n^-$ species with comparable accuracy [7]. We now show that results of similar quality can be achieved when the same method is applied to the electron affinity problem, by examining all the first- and second-row AH$_n^-$ ions which can be formed by deprotonation of stable neutral species.

The method is almost identical to that used previously [6,7] and need not be described in detail. Equilibrium geometries and harmonic frequencies of the anions are obtained at the Hartree–Fock level, using the 6-31+G* basis (6-31G* for the neutral systems) [5] (see table 1). The diffuse basis functions (denoted by the "+" symbol) are included as they are known to lower the energies of anions and often to modify geometries substantially [5,8]. These geometries are then used for single-point energy cal-

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[*1] See ref. [1] for a review of atomic EAs and ref. [2] for a review of molecular EAs.
[*2] For leadings references, see ref. [3] for atoms and ref. [4] for molecules.
[*3] Essentially all the calculations reported in this paper required less than 72 h of CPU time with the GAUSSIAN 82 program [5] on a VAX 11/780 computer.
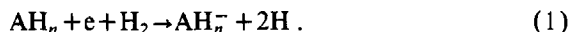
Table 1
HF/6-31+G* equilibrium geometries, energies and harmonic vibrational frequencies

Anion	Symmetry	Bond length (Å)	Bond angle (deg)	Energy (hartree)	Frequency (cm^{-1})	ZPE (kcal/mol) [a]
BeH$^-$	$C_{\infty v}$ ($^1\Sigma^+$)	1.419	–	−15.12681	1742	2.22
	$C_{\infty v}$ ($^3\Pi$)	1.365	–	−15.12643		
BH$^-$	$C_{\infty v}$ ($^2\Pi$)	1.245	–	−25.10507	2275	2.89
BH$_2^-$	C_{2v} ($^1A_1$)	1.237	105.5	−25.71034	1172(A_1), 2333(A_1), 2351(B_2)	7.45
	C_{2v} ($^3B_1$)	1.204	126.6	−25.73526	1043(A_1), 2550(A_1), 2665(B_2)	7.96
CH$^-$	$C_{\infty v}$ ($^3\Sigma^-$)	1.129	–	−38.28401	2722	3.46
CH$_2^-$	C_{2v} ($^2B_1$)	1.115	103.8	−38.88293	1417(A_1), 2862(A_1), 2901(B_2)	9.13
CH$_3^-$	C_{3v} ($^1A_1$)	1.097	109.7 [b]	−39.50415	880(A_1), 1577(E), 3045(A_1), 3109(E)	16.92
NH$^-$	$C_{\infty v}$ ($^2\Pi$)	1.029	–	−54.90437	3366	4.28
NH$_2^-$	C_{2v} ($^1A_1$)	1.017	103.6	−55.51808	1662(A_1), 3481(A_1), 3556(B_2)	11.07
OH$^-$	$C_{\infty v}$ ($^1\Sigma^+$)	0.953	–	−75.37642	3968	5.05
MgH$^-$	$C_{\infty v}$ ($^1\Sigma^+$)	1.863	–	−200.13263	1205	1.53
AlH$^-$	$C_{\infty v}$ ($^2\Pi$)	1.689	–	−242.42795	1573	2.00
AlH$_2^-$	C_{2v} ($^1A_1$)	1.686	96.0	−243.01012	898(A_1), 1566(B_2), 1588(A_1)	5.15
	C_{2v} ($^3B_1$)	1.622	117.9	−243.00838	782(A_1), 1818(A_1), 1820(B_2)	5.62
SiH$^-$	$C_{\infty v}$ ($^3\Sigma^-$)	1.545	–	−289.43865	1966	2.50
SiH$_2^-$	C_{2v} ($^2B_1$)	1.540	93.9	−290.02101	1064(A_1), 1977(B_2), 1998(A_1)	6.41
SiH$_3^-$	C_{3v} ($^1A_1$)	1.534	120.4 [b]	−290.61508	964(A_1), 1054(E), 2004(E), 2041(A_1)	11.61
PH$^-$	$C_{\infty v}$ ($^2\Pi$)	1.431	–	−341.25793	2380	3.03
PH$_2^-$	C_{2v} ($^1A_1$)	1.425	93.4	−341.85288	1213(A_1), 2411(B_2), 2420(A_1)	7.69
SH$^-$	$C_{\infty v}$ ($^1\Sigma^+$)	1.340	–	−398.10689	2782	3.54

[a] Scaled by applying a factor of 0.89 [5].
[b] Angle between the XH bond and the extension of the threefold axis.

culations with electron correlation included at the full fourth-order Møller–Plesset level, using the 6-311G** basis (6-31G** for second-row atoms), and three extensions which include diffuse functions, a second set of d-polarization functions, and f-polarization functions [5]. The energy lowerings due to each of these three extensions are then added, and the final combined energies are used to determine adiabatic electron affinities (EA)$_e$ (values corresponding to differences in the energy minima on the charged and neutral potential surfaces). This is done by means of isogyric [#4] comparisons, using the dissociation of H$_2$ as a reference and corresponding combined energies for the neutral systems [5]. Thus, for processes such as OH+e→OH$^-$, which lead to the creation of a new electron pair, the combined energies (derived as described above) for the anion and for the neutral species are used to determine the energy of the isogyric reaction

[#4] In *isogyric* reactions, the number of unpaired electron spins remains constant [6,7].

$$AH_n + e + H_2 \rightarrow AH_n^- + 2H . \tag{1}$$

Subtraction of the known exact value of $D_e(H_2)$ =0.17447 hartree [9] then leads to the predicted electron affinity.

For isogyric electron attachment processes, such as $C(^3P)+e\rightarrow C^-(^4S)$ (which do not involve any change in the number of paired electrons), the (EA)$_e$ is determined directly from the energy of

$$AH_n + e \rightarrow AH_n^- . \tag{2}$$

These electron affinities (EA)$_e$ are then corrected for zero-point vibration energies (estimated from theoretical harmonic frequencies corrected by a multiplicative factor of 0.89) [5] to give the final electron affinities, (EA)$_0$.

Use of the isogyric comparison (eq. (1)) partly avoids the difficulties associated with accurate computation of the correlation energy between paired electrons. The error in the computed correlation energy between the newly formed pair in eq. (1) is partly cancelled by the corresponding error in the hy-

drogen molecule. While the H_2 error will depend on the level of theory used, it is reasonable to expect that theoretical treatments of the energy of eq. (1) will converge more rapidly than efforts to compute the energy difference of AH_n and AH_n^- directly.

Both $(EA)_e$ and $(EA)_0$ results are presented in table 2, together with recent experimental values, where available. The target accuracy of 0.1 eV is clearly achieved for all the first-row compounds; in no case does the error exceed this amount [10]. For the

twelve comparisons with experiment currently possible, the mean absolute difference between theory and experiment is only 0.05 eV. This lends credence to the remaining predicted values for the beryllium and boron compounds. BeH^- was also investigated as a triplet ($^3\Pi$) but was found to be unstable with respect to electron loss. BH is predicted to have a small electron affinity of 0.13 eV. BH_2 is an interesting system, as the anion BH_2^- is isoelectronic with methylene, where the relation between singlet and

Table 2
Adiabatic electron affinities (eV)

Molecule	Neutral symmetry [a]	Anion symmetry [a]	Theory		Exp. [b,c] $(AE)_0$
			$(AE)_e$	$(AE)_0$	
Li	^2S	^1S	0.72	0.72	0.618
BeH	$^2\Sigma^+$	$^1\Sigma^+$	0.64	0.66	0.70±0.1
		$^3\Pi$	−0.28 [d]		
B	^2P	^3P	0.23 [d]	0.23	0.278±0.01
BH	$^1\Sigma^+$	$^2\Pi$	0.12 [d]	0.13	
BH_2	$^2A_1$	$^1A_1$	0.29	0.34	
		$^3B_1$	0.16 [d]	0.18	
C	^3P	^4S	1.23 [d]	1.23	1.263
CH	$^2\Pi$	$^3\Sigma^-$	1.14 [d]	1.16	1.238±0.008
CH_2	$^3B_1$	$^2B_1$	0.63	0.68	0.652±0.006
CH_3	$^2A_1$	$^1A_1$	0.10	0.10	0.08±0.03
NH	$^3\Sigma^-$	$^2\Pi$	0.29	0.30	0.381±0.014, 0.38±0.03
NH_2	$^2B_1$	$^1A_1$	0.77	0.78	0.744±0.022, 0.779±0.037
O	^3P	^2P	1.42	1.42	1.462
OH	$^2\Pi$	$^1\Sigma^+$	1.88	1.88	1.825±0.002, 1.828
F	^2P	^1S	3.49	3.49	3.399
Na	^2S	^1S	0.67	0.67	0.548
MgH	$^2\Sigma^+$	$^1\Sigma^+$	0.92	0.94	1.05±0.06
Al	^2P	^3P	0.32 [d]	0.32	0.442±0.01
AlH	$^1\Sigma^+$	$^2\Pi$	0.02 [d]	0.04	
AlH_2	$^2A_1$	$^1A_1$	1.02	1.05	
		$^3B_1$	0.31	0.32	
Si	^3P	^4S	1.34 [d]	1.34	1.385±0.005
SiH	$^2\Pi$	$^3\Sigma^-$	1.13 [d]	1.14	1.277±0.009
SiH_2	$^1A_1$	$^2B_1$	0.91 [d]	0.95	1.124±0.02
SiH_3	$^2A_1$	$^1A_1$	1.30	1.35	1.44±0.03
P	^4S	^3P	0.65	0.65	0.746±0.0003
PH	$^3\Sigma^-$	$^2\Pi$	0.95	0.96	1.028±0.01, 1.00±0.06
PH_2	$^2B_1$	$^1A_1$	1.20	1.23	1.26±0.03, 1.271±0.01
S	^3P	^2P	2.00	2.00	2.077
SH	$^2\Pi$	$^1\Sigma^+$	2.27	2.27	2.314±0.003, 2.317±0.005
Cl	^2P	^1S	3.58	3.58	3.615

[a] Point groups are C_{2v} for all triatomics and C_{3v} for all tetratomics except CH_3, which is D_{3h}.
[b] All atomic experimental values are from ref. [1].
[c] Representative molecular experimental values are from ref. [2]; see this compilation for other data.
[d] Calculated by eq. (2).

triplet states has long been subject of controversy [#5]. The present theory predicts that BH_2^- will have a *singlet ground state*, in contrast to methylene for which the triplet is lowest (by about 0.4 eV) and an EA of 0.34 eV [10]. The BH_2^- triplet ($^3B_1$) lies 0.16 eV (3.7 kcal/mol) higher than the $^1A_1$ state, but is still bound. The largest error is found in estimated electron affinity of lithium. The correlation energy for the two 2s electrons in Li^- is known to be small [10]. Apparently its magnitude is overestimated by the isogyric comparison.

The results for second-row compounds are somewhat less satisfactory. With the exception of sodium, the theoretical values are all lower than experiment, the largest deviation (0.17 eV) occurring for SiH_2. However, the mean absolute difference between the theoretical and experimental numbers is only 0.08 eV; the results for Cl and the PH_n and SH_n sets are within the desired ± 0.1 eV limit. Apart from SiH_2^-, this degree of agreement with experiment is not achieved by SiH and the Al and Na atoms. The origin of these variations is not apparent at present.

Predictions are made for MgH (which has a rather large experimental uncertainty), AlH and AlH_2. MgH is calculated to have a relatively large electron affinity (0.94 eV), greater than that for its first-row analog, BeH, and in agreement with the experimental value (1.05 ± 0.06 eV), within the combined limits of accuracy. On the other hand, AlH^- is close to being unstable relative to electron loss. AlH_2^- is predicted to have a singlet ground state ($^1A_1$), a bound triplet $^3B_1$ state, and a larger singlet–triplet separation, 0.73 eV, than BH_2^-.

We conclude that the present treatment, which involves a relatively modest computational effort (see footnote 3) gives EA estimates within 0.1 eV for the first-row and for most of the second-row atoms and hydrides.

Proton affinities of anions. The same data sets can be used to estimate the proton affinities $(PA)_e$ of all the AH_n^- species (table 3). Similar procedures have been used to calculate the proton affinities of the neutral molecules, AH_n [7]. The combined energies for AH_n^- are taken from table 4 and those for the protonated products, AH_{n+1}, from Pople et al.'s paper [6]. The theoretical $(PA)_0$ values, summarized

[#5] For a review see ref. [11]; see also ref. [12].

Table 3
Comparison of theoretical and experimental proton affinities $(PA)_0$ of AH_n^- anions in kcal/mol

Anion	Theory		Experiment	
	$(PA)_e$	$(PA)_0$, eq. (3)	$(PA)_0$ [a]	$(PA)_{298}$ [b]
Li^-	355.3	353.5	355.0 ± 0.1	
BeH^-	397.8	392.5		
B^-	388.3	385.1	385.7 ± 0.6	
BH^-	396.5	390.9		
BH_2^-	418.4	410.4		
C^-	365.1	361.2	364.5 ± 0.5	
CH^-	392.3	385.5	387.3 ± 1.1	
CH_2^-	417.2	409.0	406.2 ± 1.2	
CH_3^-	425.1	415.3	416.4 ± 0.3	416.6 ± 1.0
N^-	401.7	397.2	396.7 ± 2.5	
NH^-	405.9	398.7	396.6 ± 4.5	
NH_2^-	412.4	402.8	398.1 ± 3	403.6 ± 1.0
O^-	386.8	381.7	381.2 ± 3	382.1 ± 0.5
OH^-	396.1	388.3	389.6 ± 0.3	390.8 ± 0.4
F^-	374.3	368.7	370.3 ± 0.6	371.5 ± 0.7
Na^-	341.6	340.1	346.7 ± 0.2	
NgH^-	365.6	361.7		
Al^-	374.8	372.5	370.4 ± 6	
AlH^-	361.3	357.3		
AlH_2^-	411.9	406.6		
Si^-	350.5	349.0	350.4 ± 3	
SiH^-	369.5	364.9	360.1 ± 3.5	
SiH_2^-	364.0	357.6	358.2 ± 2.7	
SiH_3^-	380.3	373.0	370.2 ± 1.7	371.5 ± 2
P^-	368.6	365.3		
PH^-	371.0	366.0		
PH_2^-	372.9	365.9		370.4 ± 2
S^-	352.1	348.4	350.1 ± 1.7	
SH^-	355.5	349.8	349.3 ± 4.2	353.4 ± 2
Cl^-	335.6	331.5	332.3 ± 2	333.3 ± 0.3

[a] Calculated (eq. (4)) from data in ref. [14].
[b] Ref. [13].

in table 3, are corrected for the differences in zero-point energies (scaled) of AH_n^- and AH_{n+1}

$$(PA)_{0, AH_n^-} = E(\text{combined})_{AH_n^-}$$
$$-E(\text{combined})_{AH_{n+1}} + \Delta ZPE . \qquad (3)$$

Table 3 also provides a comparison with the available experimental values, but the situation is not very satisfactory as few directly measured values are available [13]. Relative acidities determined in the gas phase using ion cyclotron resonance or high-pressure mass spectrometry require "anchor" points to establish absolute acidity scales. These anchor points, as well as many other experimental $(PA)_0$ values for

Table 4
Anion energies (au) [a]

Anion		MP4SDTQ/ 6-311G(d,p) (6-31G(d,p)) [b]	MP4SDTQ/ 6-311+G(d,p) (6-31+G(d,p)) [b]	MP4SDTQ/ 6-311G(2d,p) (6-31G(2d,p)) [b]	MP4SDTQ/ 6-311G(df,p) (6-31G(df,p)) [b]	Combined [c]
Li$^-$	(^{1}S)	−7.44843	−7.45176	−7.44857	−7.44841	−7.45188
BeH$^-$	($^1\Sigma^+$)	−15.18962	−15.20102	−15.19443	−15.19275	−15.20896
	($^3\Pi$)	−15.16204	−15.17532	−15.16583	−15.16475	−15.18182
B$^-$	(^{3}P)	−24.56588	−24.58942	−24.57416	−24.56960	−24.60142
BH$^-$	($^2\Pi$)	−25.18860	−25.21009	−25.19726	−25.19445	−25.22460
BH$_2^-$	(^{1}A$_1$)	−25.82518	−25.84415	−25.83448	−25.83242	−25.86069
	(^{3}B$_1$)	−25.83344	−25.84890	−25.84075	−25.83975	−25.86252
C$^-$	(^{4}S)	−37.77486	−37.80210	−37.78687	−37.78194	−37.82119
CH$^-$	($^3\Sigma^-$)	−38.39483	−38.42246	−38.40743	−38.40458	−38.44481
CH$_2^-$	(^{2}B$_1$)	−39.03370	−39.06118	−39.04732	−39.04567	−39.08677
CH$_3^-$	(^{1}A$_1$)	−39.69067	−39.72094	−39.70454	−39.70447	−39.74861
N$^-$	(^{3}P)	−54.41351	−54.46223	−54.43061	−54.42846	−54.49428
NH$^-$	($^2\Pi$)	−55.05251	−55.10399	−55.06999	−55.06964	−55.13860
NH$_2^-$	(^{1}A$_1$)	−55.71877	−55.77109	−55.73611	−55.73756	−55.80722
O$^-$	(^{2}P)	−74.91447	−74.97193	−74.93683	−74.93480	−75.01462
OH$^-$	($^1\Sigma^+$)	−75.58290	−75.64966	−75.60470	−75.60489	−75.69343
F$^-$	(^{1}S)	−99.61710	−99.68443	−99.64449	−99.64081	−99.73553
Na$^-$		−161.85288	−161.85874	−161.85387	−161.85288	−161.85973
MgH$^-$		−200.18178	−200.18839	−200.18871	−200.18685	−200.20039
Al$^-$	(^{3}P)	−241.89122	−241.90266	−241.90515	−241.89496	−241.92033
AlH$^-$		−242.48724	−242.49809	−242.49961	−242.49524	−242.51846
AlH$_2^-$	(^{1}A$_1$)	−243.09444	−243.10253	−243.10593	−243.10571	−243.12529
	(^{3}B$_1$)	−243.07715	−243.08493	−243.08716	−243.08781	−243.10560
Si$^-$	(^{4}S)	−288.91400	−288.92700	−288.93444	−288.92194	−288.95538
SiH$^-$		−289.51160	−289.52500	−289.52963	−289.52411	−289.55554
SiH$_2^-$	(^{2}B$_1$)	−290.12154	−290.13464	−290.13852	−290.13766	−290.16774
SiH$_3^-$		−290.74236	−290.75431	−290.75859	−290.76103	−290.78921
P$^-$	(^{3}P)	−340.74027	−340.76402	−340.76479	−340.75890	−340.80717
PH$^-$	($^2\Pi$)	−341.35510	−341.37734	−341.37886	−341.37697	−341.42297
PH$_2^-$		−341.98422	−342.00507	−342.00699	−342.00841	−342.05203
S$^-$		−397.60559	−397.62581	−397.63295	−397.63312	−340.68070
SH$^-$		−398.24168	−398.26133	−398.26947	−398.27139	−398.31883
Cl$^-$		−459.66626	−459.68584	−459.69604	−459.70025	−459.74961

[a] For energies of the corresponding neutral species, see refs. [6,7]

[b] For second-row species.

[c] The energy lowerings in going from the MP4/6-311G(d,p) to each of the other three levels are added to the MP4/6-311G(d,p) values. The treatment for the second-row species was the same at MP4/6-31G(d,p), etc. levels.

the anions in table 3, can be determined from [13]

$$(PA)_{0, AH_n^-} = \Delta_f H(0 \text{ K})_{H^+} + \Delta_f H(0 \text{ K})_{AH_n^-}$$
$$- \Delta_f H(0 \text{ K})_{AH_{n+1}} \tag{4}$$

and the experimental data for each of the species (e.g. as given in the latest thermochemical compilations [14]).

Although many of the necessary heats of formation are not known with high accuracy, agreement of these data with the more directly measured values [13] as well as with our theoretical estimates is usually satisfactory and falls within 0.2 eV. The same is true of theoretical $(PA)_0$ values for these anions calculated directly at very high levels of theory [15].

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