

Assessment of Gaussian-2 and density functional theories for the computation of ionization potentials and electron affinities

Larry A. Curtiss and Paul C. Redfern

Chemistry Division/Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439-4828

Krishnan Raghavachari

Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974

John A. Pople

Chemistry Department, Northwestern University, Evanston, Illinois 60208

(Received 29 December 1997; accepted 13 February 1998)

A set of 146 well-established ionization potentials and electron affinities is presented. This set, referred to as the G2 ion test set, includes the 63 atoms and molecules whose ionization potentials and electron affinities were used to test Gaussian-2 (G2) theory [J. Chem. Phys. **94**, 7221 (1991)] and 83 new atoms and molecules. It is hoped that this new test set combined with the recently published test set of enthalpies of neutral molecules [J. Chem. Phys. **106**, 1063 (1997)] will provide a means for assessing and improving theoretical models. From an assessment of G2 and density functional theories on this test set, it is found that G2 theory is the most reliable method. It has an average absolute deviation of 0.06 eV for both ionization potentials and electron affinities. The two modified versions of G2 theory, G2(MP2,SVP) and G2(MP2) theory, have average absolute deviations of 0.08–0.09 eV for both ionization potentials and electron affinities. The hybrid B3LYP density functional method has the smallest average absolute deviation (0.18 eV) of the seven density functional methods tested for ionization potentials. The largest deviation for the density functional methods is for the ionization potential of CN (> 1 eV). The BLYP density functional method has the smallest average absolute deviation (0.11 eV) of the seven density functional methods tested for electron affinities, while the BPW91, B3LYP, and B3PW91 methods also do quite well. © 1998 American Institute of Physics. [S0021-9606(98)02519-7]

I. INTRODUCTION

Quantum chemical methods for the calculation of thermochemical data have developed beyond the level of just reproducing experimental data and can now make accurate predictions where the experimental data are unknown or uncertain. Critical documentation and evaluation of these methods is necessary if they are to be reliable for chemical investigations. One of these methods, Gaussian-2 theory (G2),¹ is a composite technique in which a sequence of well-defined *ab initio* molecular orbital calculations is performed to arrive at a total energy of a given molecular species. Originally, G2 theory was tested on a total of 125 reaction energies (atomization energies, ionization potentials, electron affinities, and proton affinities), chosen because they have well-established experimental values. The average absolute deviation for this set was 1.21 kcal/mol. All of the molecules contained only one or two nonhydrogen atoms with two exceptions (CO₂ and SO₂). In recent work,² we expanded the test set of atomization energies to include larger, more diverse molecules. In addition, enthalpies of formation at 298 K were used for comparison between experiment and theory instead of atomization energies. This set, referred to as the “enlarged G2 neutral test set,” included the original 55 molecules whose atomization energies were used to test G2 theory and 93 new molecules. The average absolute deviation for the full set was 1.58 kcal/mol. In Ref. 2 we also

tested other methods on the enlarged G2 neutral test set including two simplifications of G2 theory [G2(MP2),³ G2(MP2,SVP)⁴] and seven density functional methods (SVWN, BP86, BPW91, BLYP, B3P86, B3PW91, B3LYP). In addition, we have recently tested three complete basis set methods,^{5–7} [CBS-Q, CBS-q, CBS-4] on the new test set.⁸

In this paper we report on an evaluation of G2 theory for ionization potentials and electron affinities in an enlarged test set of these quantities. Included in this new set, referred to as the “G2-2 ion test set” (the original G2 test set will be referred to as the “G2-1 ion test set”) are 83 molecules that have up to seven nonhydrogen atoms, aromatic ring compounds, and halogen-containing molecules. We also examine the performance of several other G2 based methods [G2(MP2), G2(MP2,SVP)] and the seven density functional methods assessed in Ref. 2. In Sec. II we describe the theoretical methods. In Sec. III the molecules chosen for the test set and the sources of the experimental data are described. In Sec. IV the results are presented and discussed.

II. THEORETICAL METHODS

Gaussian-2 theory has been described in detail elsewhere.^{1,9} Gaussian-2 theory is a composite one, based on the 6-311G(*d,p*) basis set and several basis extensions. Geometries are calculated at the MP2(full)/6-31G(*d*) level, and scaled (0.8929) HF/6-31G(*d*) zero-point energies are in-

TABLE I. G2 total energies (in hartrees).

Molecule	E_e	E_o	Ion	E_e	E_o
H(2S)	-0.50000	-0.50000	H ⁺	0.00000	0.00000
He(1S)	-2.90026	-2.90026	He ⁺ (2P)	-1.99833	-1.99833
Ne(1S)	-128.81946	-128.81946	Ne ⁺ (2P)	-128.02524	-128.02524
Ar(1S)	-527.05570	-527.05570	Ar ⁺ (2S)	-526.47894	-526.47894
BF ₃ (1A_1)	-324.24933	-324.23744	BF ₃ ⁺ (2B_2)	-323.67328	-323.66367
BCl ₃ (1A_1)	-1404.14937	-1404.14214	BCl ₃ ⁺ (2B_2)	-1403.72365	-1403.71354
B ₂ F ₄ (1A_1)	-448.84650	-448.82818	B ₂ F ₄ ⁺ (2A_1)	-448.41405	-448.39632
CO ₂ ($^1\Sigma_g$)	-188.37269	-188.36131	CO ₂ ⁺ ($^2\Pi$)	-187.86442	-187.85759
CF ₂ (1A_1)	-237.46577	-237.45883	CF ₂ ⁺ (2A_1)	-237.04636	-237.03815
OCS($^1\Sigma^+$)	-510.95680	-510.94800	OCS ⁺ ($^2\Pi$)	-510.54585	-510.53790
CS ₂ ($^1\Sigma_g$)	-833.54006	-833.53355	CS ₂ ⁺ ($^2\Pi$)	-833.16754	-833.16241
CH ₂ (3B_1)	-39.08545	-39.06900	CH ₂ ⁺ (2A_1)	-38.70597	-38.69003
CH ₃ ($^2A_2'$)	-39.77274	-39.774509	CH ₃ ⁺ ($^1A_1'$)	-39.41569	-39.38559
C ₂ H ₅ ($^2A_1'$)	-79.02673	-78.97017	C ₂ H ₅ ⁺ (1A_1)	-78.73168	-78.67360
C ₃ H ₄ (cyclopropene)(1A_1)	-116.43532	-116.38129	C ₃ H ₄ ⁺ (2B_1)	-116.07341	-116.02259
CH ₂ =C=CH ₂ (1A_1)	-116.47092	-116.41784	CH ₂ =C=CH ₂ ⁺ (2A)	-116.10996	-116.06014
sec-C ₃ H ₇ ($^2A'$)	-118.28329	-118.19888	sec-C ₃ H ₇ ⁺ (1A)	-118.01182	-117.92706
C ₆ H ₆ ($^1A_{1g}$)	-231.87667	-231.78053	C ₆ H ₆ ⁺ ($^2B_{2g}$)	-231.53191	-231.43771
C ₆ H ₅ CH ₃ (toulene)($^1A'$) ^a	-271.12837	-271.00613	C ₆ H ₅ CH ₃ ⁺ ($^2A''$) ^a	-270.79759	-270.67767
CN($^2\Sigma$)	-92.58679	-92.58276	CN ⁺ ($^1\Sigma$)	-92.08252	-92.07805
CHO($^2A'$)	-113.71167	-113.69883	CHO ⁺ ($^1\Sigma$)	-113.41726	-113.40110
CH ₂ OH(2A)	-114.91748	-114.88156	CH ₂ OH ⁺ ($^1A'$)	-114.64688	-114.60775
CH ₃ O($^2A'$)	-114.90351	-114.86754	CH ₃ O ⁺ (3A_1)	-114.50618	-114.47126
CH ₃ OH($^1A'$)	-115.58430	-115.53489	CH ₃ OH ⁺ (2A)	-115.17850	-115.13219
CH ₃ F(1A_1)	-139.59211	-139.55422	CH ₃ F ⁺ ($^2A'$)	-139.11732	-139.08759
CH ₂ S(1A_1)	-436.95767	-436.93369	CH ₂ S ⁺ (2B_2)	-436.61207	-436.58912
CH ₂ SH(2A)	-437.52733	-437.49691	CH ₂ SH ⁺ ($^1A'$)	-437.25827	-437.22423
CH ₃ SH($^1A'$)	-438.19278	-438.14847	CH ₃ SH ⁺ ($^2A''$)	-437.84444	-437.80077
CH ₃ Cl(1A_1)	-499.59017	-499.55383	CH ₃ Cl ⁻ ($^2A'$)	-499.17211	-499.13848
C ₂ H ₅ OH($^1A'$)	-154.84126	-154.76445	C ₂ H ₅ OH ⁺ ($^2A''$)	-154.44642	-154.37294
CH ₃ CHO($^1A'$)	-153.63035	-153.57684	CH ₃ CHO ⁺ ($^2A'$)	-153.25004	-153.19802
CH ₃ OF($^1A'$)	-214.61513	-214.57355	CH ₃ OF ⁺ ($^2A''$)	-214.19398	-214.15443
C ₂ H ₄ S(thiirane)(1A_1)	-476.21752	-476.16447	C ₂ H ₄ S ⁺ (2B_1)	-475.88380	-475.83128
NCCN($^1\Sigma_g$)	-185.40273	-185.38648	NCCN ⁺ ($^2\Pi_g$)	-184.91047	-184.89606
C ₄ H ₄ O(furan)(1A_1)	-229.70023	-229.63261	C ₄ H ₄ O ⁺ (2A_2)	-229.37125	-229.30522
C ₄ H ₅ N(pyrrole)(1A_1)	-209.85764	-209.77838	C ₄ H ₅ N ⁺ (2A_2)	-209.55847	-209.48133
C ₆ H ₅ OH(phenol)($^1A'$) ^a	-307.01829	-306.91802	C ₆ H ₅ OH ⁺ ($^2A''$) ^a	-306.70017	-306.60081
C ₆ H ₅ NH ₂ (aniline)($^1A'$) ^a	-287.16324	-287.05108	C ₆ H ₅ NH ₂ ⁺ (2B_1) ^a	-286.87419	-286.76272
B ₂ H ₄ (1A_1)	-51.92006	-51.88248	B ₂ H ₄ ⁺ (2A_1)	-51.56673	-51.52857
NH(1A_1)	-55.14935	-55.14217	NH ⁺ ($^2\Pi$)	-54.65613	-54.64922
NH ₂ (2B_1)	-55.80738	-55.78902	NH ₂ ⁺ (3B_1)	-55.39460	-55.37835
N ₂ H ₂ (1A_g)	-110.50817	-110.48011	N ₂ H ₂ ⁺ (2A_g)	-110.15109	-110.12297
N ₂ H ₃ (2A)	-111.08793	-111.04965	N ₂ H ₃ ⁺ ($^2A'$)	-110.81375	-110.77254
HO($^1A'$)	-175.36731	-175.35340	HO ⁺ ($^2A''$)	-174.89880	-174.88646
SiH ₂ (1A_1)	-290.17902	-290.16771	SiH ₂ ⁺ (2A_1)	-289.84261	-289.83067
SiH ₃ (2A_1)	-290.79392	-290.77351	SiH ₃ ⁺ ($^2A_2'$)	-290.49916	-290.47764
Si ₂ H ₂ (1A_1)	-579.23640	-579.22189	Si ₂ H ₂ ⁺ (2A_1)	-578.93220	-578.91771
Si ₂ H ₄ (1A_g)	-580.45909	-580.42917	Si ₂ H ₄ ⁺ ($^2B_{3u}$)	-580.16108	-580.13080
Si ₂ H ₅ ($^2A'$)	-581.06513	-581.02700	Si ₂ H ₅ ⁺ ($^1A'$)	-580.78619	-580.74745
Si ₂ H ₆ ($^1A_{1g}$)	-581.71515	-581.66808	Si ₂ H ₆ ⁺ ($^2A_{1g}$)	-581.35747	-581.31147
Li(2S)	-7.43222	-7.43222	Li ⁻ (1S)	-7.45981	-7.45981
B(2P)	-24.60205	-24.60205	B ⁻ (3P)	-24.60905	-24.60905
Na(2S)	-161.84618	-161.84618	Na ⁻ (1S)	-161.87096	-161.87096
Al(2P)	-241.93097	-241.93097	Al ⁻ (3P)	-241.94403	-241.94403
C ₂ ($^1\Sigma_g^+$)	-75.80664	-75.80270	CC ⁻ ($^2\Sigma_g$)	-75.92077	-75.91673
C ₂ O(CCO)($^3\Sigma^-$)	-151.05096	-151.04222	C ₂ O ⁻ ($^2\Pi$)	-151.13697	-151.12769
CF ₂ (1A_1)	-237.46577	-237.45883	CF ₂ ⁻ (2B_1)	-237.46690	-237.46220
NCO($^2\Pi$)	167.79095	-167.78169	NCO ⁻ ($^1\Sigma^+$)	-167.92538	-167.91477
NO ₂ (ONO)(2A_1)	-204.84566	-204.83686	NO ₂ ⁻ (1A_1)	-204.93130	-204.92300
O ₃ (1A_1)	-225.18230	-225.17449	O ₃ ⁻ (2B_1)	-225.25619	-225.25039
OF($^2\Pi$)	-174.69866	-174.69627	OF ⁻ ($^1\Sigma^-$)	-174.78274	-174.78103
SO ₂ (1A_1)	-548.02288	-548.01572	SO ₂ ⁻ (2B_1)	-548.06404	-548.05817
S ₂ O($^1A'$)	-870.61372	-870.60846	S ₂ O ⁻ (SSO)($^2A''$)	-870.68292	-870.67875
C ₂ H($^2\Sigma$)	-76.48643	-76.47303	C ₂ H ⁻ ($^1\Sigma$)	-76.58608	-76.58646
C ₂ H ₃ ($^2A'$)	-77.77439	-77.73983	C ₂ H ₃ ⁻ ($^1A'$)	-77.80114	-77.76723

TABLE I. (Continued.)

Molecule	E_e	E_o	Ion	E_e	E_o
CH ₂ =C=C(¹ A ₁)	-115.14895	-115.11894	CH ₂ =C=C ⁻ (² B ₁)	-115.21074	-115.18311
CH ₂ =C=CH(² A')	-115.81131	-115.77330	CH ₂ =C=CH ⁻ (¹ A')	-115.84861	-115.80988
CH ₂ CHCH ₂ (² A ₂)	-117.06795	-117.00589	CH ₂ CHCH ₂ ⁻ (¹ A ₁)	-117.08512	-117.02515
CHO(² A')	-113.71167	-113.69883	CHO(¹ A')	-113.72099	-113.71128
CHF(¹ A')	-138.25921	-138.24708	HCF ⁻ (² A'')	-138.27386	-138.26404
CH ₃ O(² A')	-114.90351	-114.86754	CH ₃ O ⁻ (¹ A')	-114.96134	-114.92709
CH ₃ S(² A')	-437.54568	-437.51127	CH ₃ S ⁻ (¹ A')	-437.61445	-437.57979
CH ₂ S(¹ A ₁)	-436.95767	-436.93369	CH ₂ S ⁻ (² A')	-436.96874	-436.94786
CH ₂ CN(² B ₁)	-131.89837	-131.86953	CH ₂ CN ⁻ (¹ A')	-131.95700	-131.92772
CH ₂ NC(² B ₁)	-131.86203	-131.83336	CH ₂ NC ⁻ (¹ A')	-131.90549	-131.87653
CHCO(² A)	-151.71599	-151.69896	CHCO ⁻ (¹ Σ)	-151.80441	-151.78582
CH ₂ CHO(² A')	-152.96446	-152.92420	CH ₂ CHO ⁻ (¹ A')	-153.03366	-152.99325
CH ₃ CO(² A')	-152.97699	-152.93543	CH ₃ CO ⁻ (¹ A')	-152.99030	-152.95181
CH ₃ CH ₂ O(² A')	-154.15939	-154.09613	CH ₃ CH ₂ O ⁻ (¹ A')	-154.22467	-154.16264
CH ₃ CH ₂ S(² A)	-476.79987	-476.73755	CH ₃ CH ₂ S ⁻ (¹ A')	-476.87193	-476.80965
LiH(¹ Σ)	-8.02536	-8.02248	LiH ⁻ (² Σ)	-8.03650	-8.03424
HNO(¹ A')	-130.32975	-130.31539	HNO ⁻ (² A'')	-130.33664	-130.32434
HO ₂ (HOO)(² A'')	-150.74193	-150.72792	HO ₂ ⁻ (¹ A')	-150.78142	-150.76875

^aThis is a G2(MP2) energy; not done with G2 theory.

cluded in the final energies. Treatment of electron correlation is by Moller-Plesset (MP) perturbation theory¹⁰ and quadratic configuration interaction (QCI).¹¹ The final energies are effectively at the QCISD(T)/6-311+G(3df,2p) level, making certain assumptions about additivity¹² and appending a small higher-level empirical correction (HLC) to accommodate the remaining deficiencies. Since publication of the original G2 method, several modifications, such as G2(MP2)³ and G2(MP2,SVP)⁴ theory, have been proposed in which one or more of the steps have been changed to save computational time.

Seven density functional theories (DFT) are tested in this study: BLYP, B3LYP, BP86, B3P86, BPW91, B3PW91, and SVWN. The density functional models considered may be broadly divided into nonempirical and empirical types. The simplest is the local spin density functional, SVWN, which uses the Slater exchange functional¹³ and the Vosko, Wilk and Nusair¹⁴ correlation functional that is parameterized to random phase approximation results for a uniform electron gas. The more sophisticated functional BPW91 combines the 1988 exchange functional of Becke¹⁵ with the correlation functional of Perdew and Wang.¹⁶ Both components involve local density gradients as well as densities. The BP86 is similar, but uses an older correlation functional of Perdew.¹⁷ The BLYP¹⁸ functional also uses the Becke 1988 exchange functional, together with the correlation part of Lee *et al.*¹⁹ The other three functionals use parameters fitted to the data in the previous G2 test set.¹ There are three such (B3P86, B3PW91, B3LYP), giving functionals that are a linear combination of Hartree-Fock exchange, 1988 Becke exchange, and various correlation parts.^{20,21} This idea was introduced by Becke,²² and the resulting functionals are sometimes referred to as hybrid methods because of the mixing with Hartree-Fock exchange.

The electron affinities are calculated as the difference in total energies at 0 K of the anion and the corresponding

neutral, at their respective MP2(full)/6-31G(*d*) optimized geometries:

$$EA_0 = E_0(\text{neutral}) - E_0(\text{anion}).$$

Likewise, the ionization potentials are calculated as the difference in total energies at 0 K of the cation and the corresponding neutral, at their respective MP2(full)/6-31G(*d*) optimized geometries:

$$IP_0 = E_0(\text{cation}) - E_0(\text{neutral}).$$

The GAUSSIAN94²¹ computer program is used for all calculations. The basis set used in all of the density functional calculations is the 6-311+G(3df,2p) basis. Two smaller basis sets, 6-31+G(*d*) and 6-311+G(2df,*p*), were used to assess the basis set dependence of one of the DFT methods, B3LYP. The same set of geometries [MP2(full)/6-31G(*d*)] and zero-point energies [scaled HF/6-31G(*d*)] are used for all the G2-based and DFT methods used in this study. The geometries and zero-point energies for the full G2 ion test set as well as the neutral test set are available via the internet.²³

III. THE G2-2 ION TEST SET

The 83 molecules chosen for the new G2-2 ion test set were obtained from several sources including the thermochemical tables of Lias²⁴ and a recent review of Berkowitz *et al.*²⁵ The test set includes 50 ionization potentials (IPs) and 33 electron affinities (EAs). The criterion for choosing the ionization potentials and electron affinities is that the experimental values have a quoted uncertainty of 0.05 eV or less. This is not necessarily a guarantee of the accuracy of the experimental data; however, it is the best that we can do. Many of the molecules contain three or more nonhydrogen atoms, although there are some containing one or two that were not included in the original G2 test set. They have been added for completeness.

TABLE II. Deviation of G2, G2(MP2), and G2(MP2,SVP) ionization potentials from experiment.^a

Molecule	Expt.	Deviation (Expt. - Theory)			Ref. ^b
		G2	G2(MP2)	G2(MP2,SVP)	
<i>G2-1 test set</i>					
Li	5.39	0.05	0.05	0.05	c
Be	9.32	-0.09	-0.13	-0.18	c
B	8.30	0.10	0.12	0.15	c
C	11.26	0.08	0.12	0.14	c
N	14.54	0.06	0.11	0.10	c
O	13.61	0.08	0.14	0.13	c
F	17.42	0.03	0.06	0.04	c
Na	5.14	0.19	0.19	0.19	c
Mg	7.65	0.00	-0.03	-0.05	c
Al	5.98	0.05	0.10	0.11	c
Si	8.15	0.05	0.12	0.12	c
P	10.49	0.04	0.10	0.11	c
S	10.36	0.16	0.28	0.27	c
Cl	12.97	0.12	0.18	0.17	c
CH ₄	12.62	-0.06	-0.05	-0.05	c
NH ₃	10.18	-0.01	-0.01	-0.01	c
OH	13.01	0.03	0.06	0.07	c
OH ₂	12.62	-0.01	-0.01	0.00	c
FH	16.04	-0.05	-0.05	-0.06	c
SiH ₄	11.00	-0.01	0.02	0.05	c
PH	10.15	0.06	0.12	0.12	c
PH ₂	9.82	0.10	0.14	0.14	c
PH ₃	9.87	0.00	0.03	0.02	c
SH	10.37	0.06	0.12	0.11	c
SH ₂ (² B ₁ cation)	10.47	0.04	0.07	0.06	c
SH ₂ (² A ₁ cation)	12.78	0.03	0.03	0.02	c
ClH	12.75	0.03	0.05	0.03	c
C ₂ H ₂	11.40	-0.02	-0.02	-0.04	c
C ₂ H ₄	10.51	-0.07	-0.07	-0.10	c
CO	14.01	0.00	-0.01	-0.02	c
N ₂ (² Σ cation)	15.58	0.02	0.04	0.02	c
N ₂ (² Π cation)	16.70	0.03	0.06	0.04	c
O ₂	12.07	-0.10	-0.08	-0.06	c
P ₂	10.53	-0.01	0.03	0.02	c
S ₂	9.36	0.08	0.13	0.13	c
Cl ₂	11.50	-0.01	0.01	0.00	c
ClF	12.66	0.01	0.06	0.02	c
SC	11.33	-0.09	-0.09	-0.09	c
<i>G2-2 test set</i>					
H	13.60	-0.01	-0.01	-0.01	d
He	24.59	0.05	0.05	0.10	d
Ne	21.56	-0.05	-0.05	-0.02	d
Ar	15.76	0.07	0.07	0.13	d
BF ₃	15.56±0.03	-0.05	-0.04	-0.05	e
BCl ₃	11.60±0.02	-0.06	-0.03	-0.04	e
B ₂ F ₄	12.07±0.01	0.32	0.33	0.32	e
CO ₂	13.77±0.002	0.07	0.03	0.05	e
CF ₂	11.42±0.01	-0.03	-0.01	-0.02	e
OCS	11.17±0.002	0.01	-0.02	0.01	e
CS ₂	10.07±0.002	-0.03	-0.09	-0.03	e
CH ₂	10.40±0.003	0.08	0.10	0.11	f
CH ₃	9.84±0.002	0.06	0.07	0.07	f
C ₂ H ₅	8.12±0.008	0.05	0.06	0.07	f
C ₃ H ₄ (cyclopropene)	9.67±0.01	-0.09	-0.09	-0.11	e
CH ₂ =C=CH ₂	9.69±0.01	-0.04	-0.07	-0.08	e
sec-C ₃ H ₇	7.37±0.02	-0.03	-0.03	0.00	e
C ₆ H ₆	9.25±0.0002	-0.08	-0.09	-0.13	e
C ₆ H ₅ CH ₃	8.83±0.0006		-0.11	-0.15	e
CN	13.60±0.0001	-0.14	-0.07	-0.08	f
CHO	8.14±0.04	0.04	0.06	0.07	f
CH ₂ OH	7.55±0.006	0.10	0.12	0.13	f
CH ₃ O	10.73±0.008	-0.06	-0.05	-0.02	g
CH ₃ OH	10.85±0.01	-0.11	-0.12	-0.09	e

TABLE II. (Continued.)

Molecule	Expt.	Deviation (Expt. - Theory)			Ref. ^b
		G2	G2(MP2)	G2(MP2,SVP)	
CH ₃ F	12.47±0.02	-0.23	-0.22	-0.25	e
CH ₃ S	9.38±0.003	0.00	0.02	0.02	h
CH ₂ SH	7.54±0.003	0.12	0.16	0.17	f
CH ₃ SH	9.44±0.005	-0.02	0.00	0.00	e
CH ₃ Cl	11.22±0.02	-0.08	-0.07	-0.08	e
C ₂ H ₅ OH	10.47±0.02	-0.18	-0.19	-0.16	e
CH ₃ CHO	10.23±0.0007	-0.08	-0.04	-0.06	e
CH ₃ OF	11.34±0.008	-0.06	-0.05	-0.06	i
C ₂ H ₄ S (thiirane)	9.05±0.006	-0.02	0.02	-0.01	e
NCCN	13.37±0.01	-0.02	-0.02	-0.06	e
C ₄ H ₄ O (furan)	8.83±0.003	-0.08	-0.08	-0.10	e
C ₄ H ₅ N (pyrrole)	8.21±0.005	0.12	0.12	-0.04	e
C ₆ H ₅ OH (phenol)	8.51±0.001		-0.12	-0.16	j
C ₆ H ₅ NH ₂ (aniline)	7.72±0.02		-0.13	-0.16	e
B ₂ H ₄	9.70±0.02	0.07	0.08	0.07	f
NH	13.49±0.005	0.08	0.11	0.11	f
NH ₂	11.14±0.004	-0.04	-0.02	-0.01	f
N ₂ H ₂	9.59±0.007	-0.13	-0.13	-0.14	k
N ₂ H ₃	7.61±0.01	0.07	0.09	0.10	f,j
HOF	12.71±0.01	0.00	0.03	-0.01	l
SiH ₂	9.15±0.02	-0.02	0.02	0.01	f
SiH ₃	8.14±0.005	0.08	0.11	0.10	f
Si ₂ H ₂	8.20±0.02	-0.08	-0.03	-0.04	m
Si ₂ H ₄	8.09±0.03	-0.03	-0.04	-0.05	f,m
Si ₂ H ₅	7.60±0.05	-0.01	0.02	0.02	f,m
Si ₂ H ₆	9.74±0.02	0.04	0.06	0.06	n

^aIonization potentials and deviations in eV.^bReferences for the experimental ionization energies.^cSee Refs. 26 and 27 for experimental references.^d*Handbook of Chemistry and Physics*, edited by D. R. Lide (CRC, Boca Raton, 1996).^eReference 24.^fReference 25.^gB. Ruscic and J. Berkowitz, *J. Chem. Phys.* **95**, 4033 (1991).^hB. Ruscic and J. Berkowitz, *J. Chem. Phys.* **98**, 2568 (1993).ⁱB. Ruscic, E. H. Appelman, and J. Berkowitz, *J. Chem. Phys.* **95**, 7957 (1991).^jR. J. Lipert and S. D. Colson, *J. Chem. Phys.* **92**, 3240 (1990).^kB. Ruscic and J. Berkowitz, *J. Chem. Phys.* **95**, 4378 (1991).^lJ. Berkowitz, E. H. Appelman, and W. A. Chupka, *J. Chem. Phys.* **58**, 1950 (1973).^mB. Ruscic and J. Berkowitz, *J. Chem. Phys.* **95**, 2407 (1991).ⁿB. Ruscic and J. Berkowitz, *J. Chem. Phys.* **95**, 2416 (1991).

The original G2 test set (G2-1) contained 38 IPs and 25 EAs.^{1,26,27} In a number of cases more accurate values for these quantities have come to our attention, and we have used these new values in the comparison between theory and experiment in this work. New experimental data²⁵ are used for the electron affinities of NH₂, SiH₃, HS, and CN. The combined G2-1 and G2-2 ion test set provides a total of 146 IPs and EAs that can be used for testing of new quantum chemical methods for energy calculations. The combined set will be subsequently referred to as the "G2 ion test set."

The full set obtained by combining the complete G2 neutral set of Ref. 2, the complete G2 ion test set presented in this paper, the proton affinities in the original G2 test set, and the proton affinity of H₂ will be identified by the dated symbol G2/97. This comprehensive set contains 302 entries (148 neutral enthalpies of formation, 88 ionization potentials, 58 electron affinities, and 8 proton affinities).

IV. RESULTS AND DISCUSSION

The G2 total energies (E_e and E_0) for the 83 ions in the G2-2 ion test set are listed in Table I. Also listed in this table are the G2 energies for the corresponding neutral molecules. The deviations from experiment of the IPs with G2, G2(MP2), and G2(MP2,SVP) theories are given in Table II, while the deviations from experiment of the EAs from these theories are in Table III. The deviations of the seven DFT methods with experimental IPs and EAs are given in Tables IV and V, respectively. The average absolute deviations and maximum deviations for the various G2 and DFT methods are summarized in Tables VI for IPs and VII for EAs. In order to make the comparisons on an equal basis, five IPs are excluded from the summary. These include the IPs of three molecules (C₆H₅CH₃, C₆H₅OH, C₆H₅NH₂) that were not calculated at the G2 level of theory because of their size and the

TABLE III. Deviation of G2, G2(MP2), and G2(MP2,SVP) electron affinities from experiment.^a

Molecule	Expt.	Deviation (Expt. - Theory)			Ref. ^b
		G2	G2(MP2)	G2(MP2,SVP)	
<i>G2-1 test set</i>					
C	1.26	0.07	0.15	0.18	c
O	1.46	0.06	0.11	0.12	c
F	3.40	-0.08	-0.05	-0.07	c
Si	1.39	0.03	0.09	0.10	c
P	0.75	0.11	0.19	0.20	c
S	2.08	0.07	0.10	0.10	c
Cl	3.62	0.01	0.00	-0.02	c
CH	1.24	0.11	0.16	0.17	c
CH ₂	0.65	-0.01	0.00	0.00	c
CH ₃	0.08	0.04	0.04	0.02	c
NH	0.38	0.10	0.12	0.13	c
NH ₂	0.77	0.00	-0.03	-0.04	c,d
OH	1.83	-0.04	-0.05	-0.04	c
SiH	1.28	0.09	0.15	0.16	c
SiH ₂	1.12	0.14	0.18	0.18	c
SiH ₃	1.41	-0.01	0.03	0.02	c,d
PH	1.03	0.07	0.12	0.12	c
PH ₂	1.27	0.02	0.04	0.03	c
HS	2.36	0.06	0.05	0.04	c,d
O ₂	0.44	-0.03	0.02	0.02	c
NO	0.02	0.09	0.15	0.14	c
CN	3.86	-0.11	-0.10	-0.12	c,d
PO	1.09	0.05	0.12	0.13	c
S ₂	1.66	0.01	0.02	0.02	c
Cl ₂	2.39	0.01	0.06	0.06	c
<i>G2-2 test set</i>					
Li	0.62±0.0005	-0.13	-0.22	-0.28	e
B	0.28±0.01	0.09	0.18	0.22	e
Na	0.55±0.00002	-0.13	-0.21	-0.22	e
Al	0.44±0.01	0.09	0.14	0.15	e
C ₂	3.27±0.008	0.17	0.21	0.23	f
C ₂ O	2.29±0.018	-0.04	-0.02	-0.04	g
CF ₂	0.18±0.005	0.09	0.15	0.16	h
NCO	3.61±0.005	-0.01	-0.01	-0.02	i
NO ₂	2.27±0.005	-0.07	-0.04	-0.05	j
O ₃	2.10±0.003	0.04	0.09	0.10	k
OF	2.27±0.006	-0.03	0.02	0.01	l
SO ₂	1.11±0.008	-0.05	0.05	0.06	k
S ₂ O	1.88±0.008	-0.04	0.02	0.04	k
C ₂ H	2.97±0.009	-0.12	-0.13	-0.13	m
C ₂ H ₃	0.67±0.026	-0.08	-0.09	-0.09	m
CH ₂ =C=C	1.79±0.024	0.05	0.07	-0.06	k
CH ₂ =C=CH	0.89±0.026	-0.10	-0.13	-0.14	k
CH ₂ CHCH ₂	0.47±0.009	-0.05	-0.08	-0.10	m
HCO	0.31±0.005	-0.03	-0.02	-0.02	k
HCF	0.54±0.005	0.08	0.14	0.14	n
CH ₃ O	1.57±0.021	-0.05	-0.07	-0.05	m
CH ₃ S	1.87±0.013	0.00	0.00	-0.01	m
CH ₃ S	0.47±0.023	0.08	0.11	0.12	k
CH ₂ CN	1.54±0.013	-0.04	-0.05	-0.07	m
CH ₂ NC	1.06±0.026	-0.12	-0.11	-0.13	m
CHCO	2.35±0.022	-0.01	-0.02	-0.04	m
CH ₂ CHO	1.82±0.0004	-0.05	-0.06	-0.07	m
CH ₃ CO	0.42±0.04	-0.02	-0.01	-0.01	m
CH ₃ CH ₂ O	1.71±0.01	-0.10	-0.11	-0.09	m
CH ₃ CH ₂ S	1.95±0.004	-0.01	-0.01	-0.02	k
LiH	0.34±0.012	0.02	0.03	0.03	o
HNO	0.34±0.015	0.09	0.14	0.16	k
HO ₂ (HOO, ² A'')	1.08±0.017	-0.03	-0.01	-0.02	p

^aElectron affinities and deviations in eV.^bReferences for the experimental electron affinities.^cSee Refs. 26 and 27 for experimental references.^dRevised value from Ref. 25.^eH. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* **14**, 731 (1985).^fD. W. Arnold, S. E. Bradforth, T. N. Kitsopoulos, and D. M. Neumark, *J. Chem. Phys.* **95**, 8753 (1991).^gK. K. Murray, D. G. Leopold, T. M. Miller, and W. C. Lineberger, *J. Chem. Phys.* **89**, 5442 (1988).^hS. E. Bradforth, E. H. Kim, D. W. Arnold, and D. M. Neumark, *J. Chem. Phys.* **98**, 800 (1993).ⁱK. M. Ervin, J. Ho, and W. C. Lineberger, *J. Phys. Chem.* **92**, 5405 (1988).^jReference 24.^kM. K. Gilles, M. L. Polak, and W. C. Lineberger, *J. Chem. Phys.* **96**, 8012 (1992).^lReference 25.^mM. K. Gilles, K. M. Ervin, J. Ho, and W. C. Lineberger, *J. Phys. Chem.* **96**, 1130 (1992).ⁿH. W. Sarkas, J. H. Hendricks, S. T. Arnold, and K. H. Bowen, *J. Chem. Phys.* **100**, 1884 (1994).^oJ. M. Oakes, L. B. Harding, and G. B. Ellison, *J. Chem. Phys.* **83**, 5400 (1985).

TABLE IV. Deviation of DFT ionization potentials from experiment.^a

Molecule	Deviation (Expt. - Theory)						
	B3LYP	B3PW91	B3P86	BLYP	BPW91	BP86	SVWN
<i>G2-1 test set</i>							
Li	-0.23	-0.17	-0.59	-0.13	-0.15	-0.16	-0.48
Be	0.20	0.32	-0.24	0.34	0.38	0.21	-0.14
B	-0.44	-0.40	-0.92	-0.32	-0.39	-0.44	-0.79
C	-0.29	-0.32	-0.84	-0.15	-0.30	-0.33	-0.89
N	-0.14	-0.25	-0.76	0.03	-0.21	-0.23	-0.94
O	-0.55	-0.37	-1.02	-0.56	-0.46	-0.63	-0.99
F	-0.34	-0.20	-0.84	-0.32	-0.27	-0.40	-1.15
Na	-0.28	-0.13	-0.59	-0.21	-0.13	-0.19	-0.63
Mg	-0.08	0.10	-0.48	0.01	0.14	-0.06	-0.51
Al	-0.04	-0.14	-0.63	0.11	-0.11	-0.17	-0.47
Si	0.04	-0.09	-0.59	0.21	-0.05	-0.10	-0.52
P	0.11	-0.06	-0.56	0.31	0.00	-0.03	-0.60
S	-0.19	-0.12	-0.71	-0.05	-0.08	-0.24	-0.71
Cl	-0.10	-0.06	-0.65	0.06	-0.01	-0.14	-0.75
CH ₄	0.06	0.14	-0.44	0.25	0.23	0.12	-0.41
NH ₃	-0.01	0.06	-0.53	0.06	0.03	-0.09	-0.79
OH	-0.23	-0.11	-0.73	-0.18	-0.15	-0.30	-0.94
OH ₂	0.00	0.06	-0.54	0.07	0.03	-0.09	-0.87
FH	-0.06	0.01	-0.60	0.00	-0.03	-0.14	-1.01
SiH ₄	0.09	0.15	-0.42	0.34	0.30	0.18	-0.36
PH	-0.02	-0.15	-0.67	0.17	-0.10	-0.15	-0.65
PH ₂	-0.12	-0.22	-0.74	0.06	-0.16	-0.23	-0.64
PH ₃	0.03	0.08	-0.49	0.15	0.10	-0.02	-0.60
SH	-0.10	-0.05	-0.63	0.05	-0.01	-0.14	-0.86
SH ₂ (² B ₁ cation)	0.04	0.06	-0.50	0.20	0.11	-0.01	-1.00
SH ₂ (² A ₁ cation)	0.11	0.14	-0.43	b	b	b	b
ClH	0.00	0.01	-0.56	0.17	0.07	-0.04	-0.76
C ₂ H ₂	0.16	0.18	-0.39	0.28	0.19	0.08	-0.70
C ₂ H ₄	0.15	0.33	-0.41	0.23	0.14	0.02	-0.79
CO	-0.13	0.01	-0.59	0.10	0.14	-0.01	-0.56
N ₂ (² Σ cation)	-0.27	-0.20	-0.80	0.22	0.18	0.06	-0.59
N ₂ (² Π cation)	0.09	0.10	-0.49	b	b	b	b
O ₂	-0.79	-0.72	-1.28	-0.40	-0.42	-0.49	-1.06
P ₂	0.21	0.15	-0.40	0.39	0.20	0.10	-0.59
S ₂	-0.22	-0.28	-0.81	0.08	-0.09	-0.17	-0.63
Cl ₂	0.11	0.13	-0.44	0.44	0.34	0.24	-0.33
ClF	0.05	0.11	-0.46	0.33	0.29	0.18	-0.42
SC	-0.11	-0.03	-0.62	0.06	0.03	-0.11	-0.61
<i>G2-2 test set</i>							
H	-0.06	-0.11	-0.50	0.07	-0.11	0.00	0.11
He	-0.34	-0.12	-0.79	-0.20	-0.05	-0.25	-0.18
Ne	-0.21	-0.11	-0.72	-0.16	-0.16	-0.26	-1.25
Ar	-0.04	-0.04	-0.62	0.15	0.04	-0.06	-0.92
BF ₃	0.10	0.13	-0.50	0.49	0.40	0.27	-0.72
BCl ₃	0.28	0.26	-0.30	0.73	0.60	0.49	-0.04
B ₂ F ₄	0.56	0.64	0.06	0.94	0.92	0.80	0.17
CO ₂	0.12	0.13	-0.46	0.36	0.26	0.15	-0.63
CF ₂	0.07	0.22	-0.38	0.26	0.32	0.18	-0.31
COS	-0.02	-0.05	-0.62	0.15	-0.01	-0.12	-0.88
CS ₂	0.05	0.00	-0.55	0.23	0.06	-0.04	-0.66
CH ₂	-0.02	-0.14	-0.66	0.12	-0.13	-0.17	-0.71
CH ₃	-0.13	-0.21	-0.74	-0.02	-0.21	-0.28	-0.75
C ₂ H ₅	-0.10	-0.09	-0.63	0.08	-0.01	-0.09	-0.30
C ₂ H ₄ (cyclopropene)	0.24	0.26	-0.31	0.41	0.32	0.22	-0.36
CH ₂ =C=CH ₂	0.26	0.26	-0.30	0.46	0.34	0.24	-0.39
sec-C ₃ H ₇	0.00	-0.03	-0.56	0.23	0.10	0.02	-0.25
C ₆ H ₆	0.16	0.13	-0.44	0.35	0.20	0.09	-0.68
C ₆ H ₅ CH ₃	0.22	0.19	-0.38	0.42	0.28	0.17	-0.50
CN	-1.65	-1.67	-2.22	-1.02	-1.17	-1.20	-1.74
CHO	-0.38	-0.35	-0.90	-0.21	-0.28	-0.36	-0.72
CH ₂ OH	-0.13	-0.14	-0.67	0.04	-0.07	-0.15	-0.48
CH ₃ O	0.09	0.16	-0.43	0.37	0.34	0.22	-0.15
CH ₃ OH	0.19	0.23	-0.34	0.46	0.40	0.30	-0.22

TABLE IV. (Continued.)

Molecule	Deviation (Expt. - Theory)						
	B3LYP	B3PW91	B3P86	BLYP	BPW91	BP86	SVWN
CH ₃ F	0.11	0.17	-0.41	0.47	0.43	0.33	-0.11
CH ₃ S	0.09	0.10	-0.46	0.26	0.16	0.05	-0.51
CH ₂ SH	-0.13	0.17	-0.70	0.09	-0.05	-0.13	-0.48
CH ₃ SH	0.09	0.11	-0.45	0.30	0.20	0.09	-0.46
CH ₃ Cl	0.07	0.08	-0.49	0.36	0.25	0.15	-0.72
C ₂ H ₂ OH	0.24	0.30	-0.28	0.60	0.56	0.45	0.01
CH ₃ CHO	0.12	0.17	-0.42	0.33	0.28	0.17	-0.45
CH ₃ OF	0.15	0.26	-0.32	0.44	0.46	0.35	-0.13
C ₂ H ₄ S (thiirane)	0.11	0.11	-0.46	0.30	0.19	0.08	-0.54
NCCN	0.45	0.43	-0.14	0.68	0.55	0.44	-0.29
C ₄ H ₄ O (furan)	0.13	0.14	-0.44	0.26	0.16	0.05	-0.69
C ₄ H ₅ N (pyrrole)	0.15	0.16	-0.42	0.29	0.18	0.06	-0.67
C ₆ H ₅ OH (phenol)	0.18	0.17	-0.39	0.37	0.25	0.14	-0.49
C ₆ H ₅ NH ₂ (aniline)	0.20	0.19	-0.37	0.36	0.24	0.12	-0.43
B ₂ H ₄	0.18	0.22	-0.35	0.32	0.26	0.13	-0.55
NH	-0.20	-0.29	-0.82	-0.06	-0.27	-0.31	-0.92
NH ₂	-0.20	-0.07	-0.68	-0.15	-0.11	-0.26	-0.79
N ₂ H ₂	-0.02	0.03	-0.54	0.19	0.14	0.03	-0.39
N ₂ H ₃	-0.30	-0.27	-0.82	-0.10	-0.16	-0.26	-0.59
HOF	0.07	0.21	-0.38	0.29	0.34	0.23	-0.26
SiH ₂	0.10	0.15	-0.41	0.24	0.19	0.06	-0.45
SiH ₃	-0.05	-0.13	-0.65	0.10	-0.11	-0.18	-0.57
Si ₂ H ₂	0.15	0.11	-0.43	0.35	0.20	0.09	-0.47
Si ₂ H ₄	0.19	0.20	-0.35	0.28	0.18	0.06	-0.55
Si ₂ H ₅	-0.08	-0.17	-0.70	0.11	-0.11	-0.19	-0.58
Si ₂ H ₆	0.19	0.18	-0.38	0.42	0.28	0.18	-0.45

^a6-311+G(3df,2p) basis set results. Ionization energies and deviations in eV.

^bUnable to obtain convergence to excited state.

excited state IPs of SH₂ and N₂ that were not calculated with nonhybrid DFT methods. Thus a total of 83 IPs and 58 EAs are included in the average absolute deviations for the full G2 ion test set.

A. G2 theory

The average absolute deviation of G2 theory for the IPs in the full G2 ion test set is 0.063 eV (0.056 eV for the G2-1 test set and 0.070 for the new G2-2 test set). The IP in the G2-2 test set with the largest deviation is that of B₂F₄, which is off by 0.32 eV. Seven other molecules in this new test set deviate by more than 0.1 eV: CN (-0.14 eV), CH₃F (-0.23 eV), CH₃OH (-0.11 eV), C₂H₅OH (-0.18 eV), CH₂SH (0.12 eV), pyrrole (0.12 eV), and N₂H₂ (-0.13 eV). In the original test set three IPs, all atoms, deviated by more than 0.1 eV. The structures of the two molecules with the largest deviations, B₂F₄ and CH₃F, show significant changes upon ionization, including a Jahn-Teller distortion in CH₃F⁺. While the deviations in the theoretical IPs of B₂F₄ and CH₃F are larger than expected from theory, we have no reason at this time to discount the experimental results.

The average absolute deviation of G2 theory for the EAs in the full G2 ion test set is 0.061 eV (0.057 eV for the G2-1 test set and 0.064 for the new G2-2 test set). Five EAs in the G2-2 test set have deviations of more than 0.1 eV: Li (-0.13 eV), Na (-0.13 eV), C₂ (0.17 eV), C₂H (-0.12 eV), and CH₂NC (-0.12 eV). In the original test set, four EAs were off by more than 0.1 eV.

Overall G2 theory does quite well for the ionization potentials and electron affinities of the new test set with only a small decrease in performance. This is in contrast to results for the enthalpies in the new G2 neutral test set which had a larger average absolute deviation due to poor performance on halogen containing compounds and aromatic systems.

B. G2(MP2) and G2(MP2,SVP) theory

The two modified versions of G2 theory, G2(MP2) and G2(MP2,SVP), have average absolute deviations of 0.076 and 0.078 eV for the IPs in the full G2 ion test set with maximum deviations of 0.33 eV (B₂F₄) and 0.32 eV (B₂F₄), respectively. These two modifications perform slightly better on the G2-2 set of new IPs (0.072 and 0.073 eV, respectively) than on the original G2-1 test set (0.083 and 0.084 eV, respectively). The overall average absolute deviations for the G2(MP2) and G2(MP2,SVP) methods are about 0.015 eV larger than for G2 theory. The deviations for the three aromatic systems that were too large to be done with G2 theory range from 0.11 to 0.15 eV.

The two modified versions of G2 theory, G2(MP2) and G2(MP2,SVP) theory, have average absolute deviations of 0.084 and 0.091 eV for the EAs in the full G2 ion test set with maximum deviations of 0.22 eV (Li) and 0.28 eV (Li), respectively. These two modifications perform about the same on the G2-2 set of new EAs (0.083 and 0.093 eV, respectively) as on the original G2-1 test set (0.085 and 0.089 eV, respectively).

TABLE V. Deviation of DFT electron affinities from experiment.^a

Molecule	Deviation (Expt. - Theory)						
	B3LYP	B3PW91	B3P86	BLYP	BPW91	BP86	SVWN
<i>G2-1 test set</i>							
C	-0.10	-0.20	-0.71	-0.06	-0.27	-0.36	-0.94
O	-0.14	0.01	-0.61	-0.24	-0.16	-0.35	-1.02
F	-0.06	0.07	-0.54	-0.16	-0.12	-0.27	-1.15
Si	0.07	-0.07	-0.56	0.20	-0.06	-0.14	-0.59
P	-0.19	-0.09	-0.68	-0.13	-0.10	-0.31	-0.74
S	-0.11	-0.04	-0.62	-0.03	-0.04	-0.22	-0.67
Cl	-0.07	-0.03	-0.61	0.05	-0.01	-0.17	-0.81
CH	-0.12	-0.19	-0.71	-0.08	-0.26	-0.36	-0.91
CH ₂	-0.13	0.04	-0.56	-0.16	-0.05	-0.27	-0.79
CH ₃	0.06	0.15	-0.42	0.05	0.06	-0.12	-0.75
NH	-0.07	0.08	-0.53	-0.13	-0.05	-0.25	-0.85
NH ₂	0.04	0.14	-0.45	0.00	0.02	-0.16	-0.88
OH	0.06	0.17	-0.43	-0.01	0.01	-0.15	-0.94
SiH	0.02	-0.09	-0.59	0.15	-0.08	-0.17	-0.60
SiH ₂	-0.05	-0.13	-0.65	0.08	-0.12	-0.23	-0.62
SiH ₃	0.02	0.09	-0.47	0.10	0.08	-0.08	-0.62
PH	-0.09	-0.02	-0.59	-0.01	-0.02	-0.21	-0.73
PH ₂	0.01	0.05	-0.51	0.10	0.05	-0.11	-0.69
HS	-0.01	0.03	-0.54	0.08	0.03	-0.13	-0.81
O ₂	-0.12	0.05	-0.55	-0.06	0.03	-0.12	-0.51
NO	-0.30	-0.22	-0.76	-0.23	-0.22	-0.34	-0.77
CN	-0.21	-0.10	-0.69	0.00	0.02	-0.14	-0.67
PO	-0.20	-0.24	-0.77	0.00	-0.14	-0.24	-0.66
S ₂	-0.01	0.04	-0.52	0.16	0.12	-0.03	-0.35
Cl ₂	-0.47	-0.30	-0.85	-0.38	-0.27	-0.41	-0.57
<i>G2-2 test set</i>							
Li	0.06	0.11	-0.36	0.16	0.15	-0.02	-0.31
B	-0.13	-0.19	-0.69	-0.07	-0.24	-0.34	-0.80
Na	-0.04	0.04	-0.43	0.05	0.08	-0.09	-0.41
Al	0.06	-0.05	-0.53	0.17	-0.05	-0.14	-0.51
C ₂	-1.08	-1.06	-1.61	-0.69	-0.77	-0.88	-1.31
C ₂ O	-0.02	0.06	-0.53	0.09	0.08	-0.07	-0.71
CF ₂	-0.27	-0.17	-0.70	-0.21	-0.19	-0.29	-0.50
NCO	0.11	0.16	-0.43	0.24	0.19	0.05	-0.66
NO ₂	0.05	0.19	-0.40	0.24	0.32	0.16	-0.33
O ₃	-0.67	-0.57	-1.13	-0.19	-0.16	-0.27	-0.74
OF	0.00	0.17	-0.42	0.06	0.16	0.02	-0.54
SO ₂	-0.34	-0.29	-0.84	-0.11	-0.14	-0.25	-0.63
S ₂ O	-0.28	-0.27	-0.81	0.04	-0.04	-0.15	-0.56
C ₂ H	-0.12	0.00	-0.58	-0.06	-0.02	-0.21	-0.72
C ₂ H ₃	0.01	0.10	-0.47	0.05	0.06	-0.11	-0.62
CH ₂ =C=C	-0.18	-0.23	-0.77	0.02	-0.13	-0.24	-0.76
CH ₂ =C=CH	-0.05	0.00	-0.57	-0.03	-0.08	-0.23	-0.81
CH ₂ CHCH ₂	-0.03	0.03	-0.54	0.00	-0.04	-0.19	-0.82
HCO	-0.02	0.08	-0.49	0.04	0.05	-0.10	-0.54
HCF	-0.23	-0.20	-0.73	-0.18	-0.23	-0.34	-0.66
CH ₃ O	0.06	0.11	-0.48	0.06	0.02	-0.13	-0.84
CH ₃ S	0.05	0.10	-0.47	0.16	0.11	-0.04	-0.84
CH ₂ S	-0.22	-0.22	-0.76	-0.06	-0.15	-0.27	-0.65
CH ₂ CN	0.02	0.06	-0.51	0.06	0.01	-0.14	-0.79
CH ₂ NC	-0.01	0.05	-0.52	-0.01	-0.04	-0.19	-0.80
CHCO	0.11	0.16	-0.41	0.21	0.17	0.03	-0.62
CH ₂ CHO	-0.02	0.04	-0.53	0.00	-0.03	-0.18	-0.87
CH ₃ CO	0.07	0.20	-0.37	0.07	0.14	-0.04	-0.47
CH ₃ CH ₂ O	0.03	0.10	-0.49	0.00	-0.02	-0.17	-0.91
CH ₃ CH ₂ S	0.06	0.11	-0.50	0.16	0.12	-0.04	-0.62
LiH	-0.09	-0.10	-0.52	0.00	-0.10	-0.16	-0.44
HNO	-0.36	-0.28	-0.83	-0.24	-0.23	-0.36	-0.75
HO ₂ (HOO, ² A'')	0.10	0.27	-0.31	0.13	0.23	0.08	-0.39

^a6-311+G(3df,2p) basis set results. Electron affinities and deviations in eV.

TABLE VI. Summary of average absolute deviations and maximum deviations of ionization potentials (in eV) calculated by G2 and density functional methods.^a

Method	Test set						
	G2-1 (36)			G2-2 (47)			G2 (83)
	Avg. abs. dev.	Maximum deviation		Avg. abs. dev.	Maximum deviation	Avg. abs. dev.	
G2	0.056	0.19	-0.10	0.070	0.32	-0.23	0.063
G2(MP2)	0.083	0.28	-0.13	0.072	0.33	-0.22	0.076
G2(MP2,SVP)	0.084	0.27	-0.18	0.073	0.32	-0.25	0.078
SVWN	0.687	b	-1.15	0.516	0.17	-1.74	0.594
BLYP	0.196	0.44	-0.56	0.309	0.94	-1.02	0.260
BPW91	0.168	0.38	-0.46	0.263	0.92	-1.17	0.220
BP86	0.176	0.24	-0.63	0.220	0.80	-1.20	0.198
B3LYP	0.166	0.21	-0.79	0.187	0.56	-1.65	0.177
B3PW91	0.166	0.33	-0.72	0.207	0.64	-1.67	0.191
B3P86	0.623	b	-1.28	0.536	0.06	-2.22	0.570

^aThe average absolute deviations do not include the IPs of toluene, phenol, aniline, SH₂ (to the ²A₁ excited state) and N₂ (to the ²Π excited state) for reasons discussed in text. Number of quantities included in summaries is given in parentheses. DFT results are from 6-311+G(3df,2p) basis set.

^bAll are negative deviations.

C. Density functional methods

The DFT methods give a wide range of average absolute deviations (0.18–0.59 eV) for the IPs in the G2 test set as shown in the summaries in Table VI. The local density method (SVWN) and one of the gradient-corrected methods (B3P86) perform poorly with deviations of 0.59 and 0.57 eV, respectively. In nearly all the cases these two methods give IPs that are too large. For the gradient-corrected functionals, the average absolute deviation ranges from 0.18 to 0.57 eV. The Becke three-parameter functional performs better than the Becke exchange functional with the LYP and PW91 correlation functionals, but not with the P86 functional. The B3LYP gives the best agreement with experiment for the IPs in the G2 test set with an average absolute deviation of 0.18 eV, which is about three times that of G2 theory. The maximum deviation occurs for the IP of CN where the deviation

is 1.65 eV. The other DFT methods also give large errors for the IP of CN. The extremely large deviation is due to problems with the description of the CN cation by the DFT methods. The B3LYP method gives a reasonable account² of the enthalpy of formation of neutral CN and incorrectly gives CN⁺ to be a triplet state. If the triplet state energy is used, the error in the IP is reduced to about 0.5 eV. If the CN ionization potential is not included, the average absolute deviation for B3LYP decreases from 0.180 eV to 0.162 eV.

The DFT methods also give a wide range of average absolute deviations (0.11–0.70 eV) for the EAs in the G2 test set as shown in the summaries in Table VII. The local density method (SVWN) and one of the gradient-corrected methods (B3P86) perform poorly with deviations of 0.70 and 0.60 eV, respectively. In nearly all the cases these two methods give EAs that are too large. For the gradient-corrected

TABLE VII. Summary of average absolute deviations and maximum deviations of electron affinities (in eV) calculated by G2 and density functional methods.^a

Method	Test set						
	G2-1 (25)			G2-2 (33)			G2 (58)
	Avg. abs. dev.	Maximum deviation		Avg. abs. Dev.	Maximum deviation	Avg. abs. dev.	
G2	0.057	0.14	-0.11	0.064	0.17	-0.13	0.061
G2(MP2)	0.085	0.19	-0.10	0.083	0.21	-0.22	0.084
G2(MP2,SVP)	0.089	0.20	-0.12	0.093	0.23	-0.28	0.091
SVWN	0.740	b	-1.15	0.665	b	-1.31	0.697
BLYP	0.109	0.20	-0.38	0.117	0.24	-0.69	0.113
BPW91	0.100	0.12	-0.27	0.137	0.32	-0.77	0.121
BP86	0.208	b	-0.41	0.182	0.16	-0.88	0.193
B3LYP	0.107	0.07	-0.47	0.149	0.11	-1.08	0.131
B3PW91	0.106	0.17	-0.30	0.175	0.27	-1.06	0.145
B3P86	0.592	b	-0.85	0.598	b	-1.61	0.596

^aNumber of quantities included in summaries is given in parentheses. DFT results are from the 6-311+G(3df,2p) basis set.

^bAll are negative deviations.

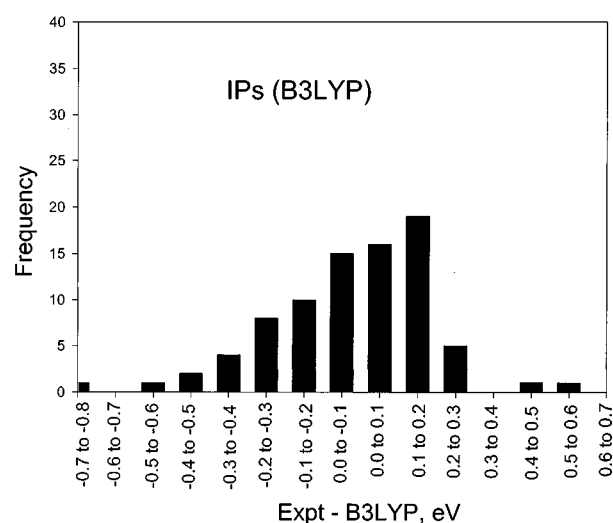
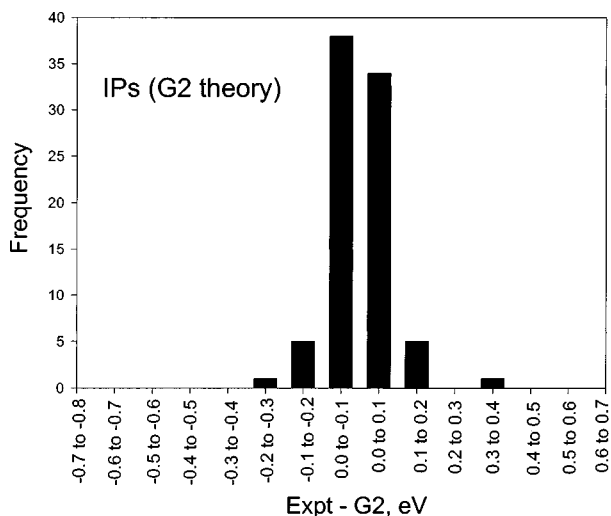


FIG. 1. Histogram of deviations with experiment of the ionization potentials in the G2 ion test set from G2 theory and the B3LYP density functional method. Each vertical bar represents deviations in a 0.1 eV range.

functionals other than B3P86, the average absolute deviation is much smaller and ranges from 0.11 to 0.19 eV. The BLYP and BPW91 methods give the best agreement with experiment for the EAs in the G2 test set with average absolute deviations of 0.113 and 0.121 eV, respectively, only about 60% greater than G2 theory. The B3LYP and B3PW91 hybrid density functional methods perform only slightly more poorly than the respective nonhybrid BLYP and BPW91 methods (average absolute deviations of 0.131 and 0.145 eV, respectively). The B3P86 method performs much worse than BP86 (see Table VII). Overall the DFT methods do quite well in predicting EAs in atoms and molecules. The largest deviation occurs for the electron affinity of C_2 , which has an error of ~ 1 eV for reasons similar to the case of the IP of CN (see above).

The maximum deviations of the DFT methods are significantly larger than those of the G2 methods (see summaries in Tables VI and VII). The distribution of deviations for G2 theory on the ionization potentials in the full G2 ion set is given in Fig. 1. About 87% of the G2 ionization potentials fall within 0.10 eV of the experimental value and 98% fall

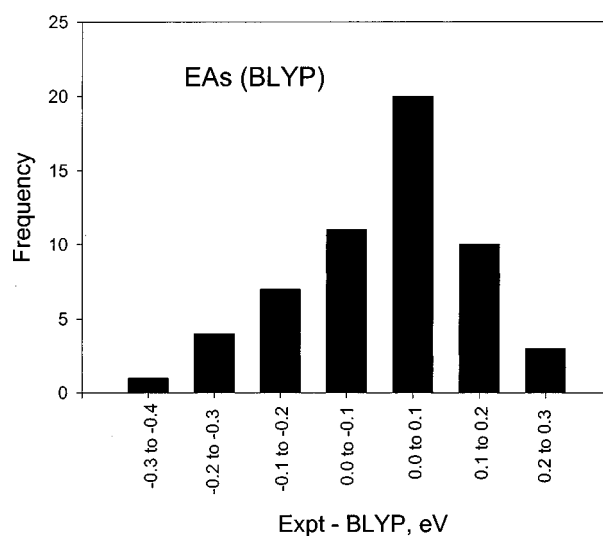
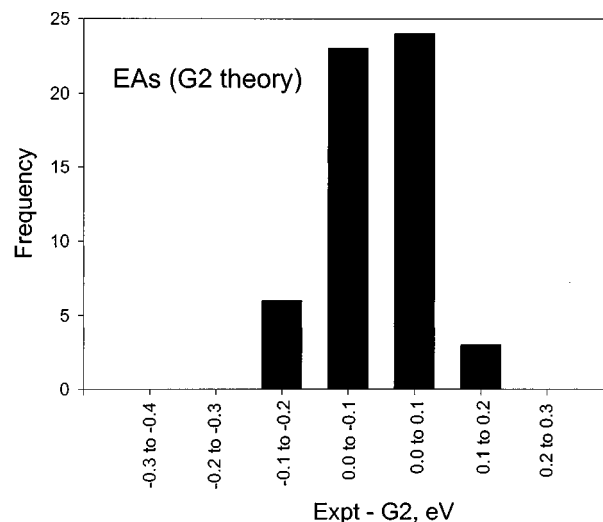


FIG. 2. Histogram of deviations with experiment of the electron affinities in the G2 ion test set from G2 theory and the BLYP density functional method. Each vertical bar represents deviations in a 0.1 eV range.

within 0.20 eV. The distribution of deviations for B3LYP, the best of the DFT methods for IPs, is also given in Fig. 1. Only about 40% of the B3LYP ionization potentials fall within 0.10 eV of the experimental value and 76% fall within 0.20 eV. The results in Fig. 1 indicate that both the G2 and B3LYP methods have a fairly equal distribution of positive and negative deviations. The B3LYP distribution covers a much larger range (-1.65 to 0.56 eV) than G2 theory (-0.23 to 0.32 eV). These considerations may be important for assessing the ionization potentials of systems where there is disagreement between theory and experiment or for making predictions for systems where there are no experimental measurements.

The distribution of deviations for G2 theory on electron affinities in the full G2 ion set is given in Fig. 2. About 84% of the G2 electron affinities fall within 0.10 eV of the experimental value and 100% fall within 0.20 eV. The distribution of deviations for BLYP, the best of the DFT methods for EAs, is also given in Fig. 2. About 59% of the G2 electron affinities fall within 0.10 eV of the experimental value and

TABLE VIII. Summary of average absolute deviations from experiment (in kcal/mol) for the G2/97 test set calculated by G2 and density functional methods.^a

	Enthalpies of Neutrals (148) ^b	IPs (83) ^c	EAs (58) ^d	PA (8) ^e	Total (297)
G2	1.59	1.47	1.41	1.08	1.50
G2(MP2)	2.04	1.78	1.94	0.77	1.91
G2(MP2,SVP)	1.93	1.79	2.10	0.91	1.90
SVWN	90.89	13.61	16.08	5.61	52.40
BLYP	7.09	6.00	2.62	1.96	5.77
BPW91	7.85	5.11	2.79	1.35	5.92
BP86	20.19	4.63	4.45	1.44	12.27
B3LYP	3.08	4.10	3.03	1.48	3.31
B3PW91	3.51	4.36	3.35	1.08	3.65
B3P86	17.97	13.24	13.73	1.04	15.36

^aFive IPs of the G2/97 test set are not included in the summaries (see text). All DFT calculations done with the 6-311+G(3df,2p) basis set. Number of quantities included in summaries is given in parentheses.

^bFrom Ref. 2.

^cThis work (Table VI).

^dThis work (Table VII).

^eThis work. Includes the seven proton affinities in Ref. 1 and the proton affinity of H₂.

nearly 85% fall within 0.20 eV. The results in Fig. 2 indicate that both the G2 and BLYP methods have a fairly equal distribution of positive and negative deviations for electron affinities. The BLYP distribution covers a larger range (−0.38 to 0.24 eV) than G2 theory (−0.13 to 0.14 eV).

Ten of the electron affinities correspond to adding an electron to a closed shell molecule (C₂, Cl₂, CF₂, O₃, SO₂, S₂O, H₂CCC, HCF, CH₂S, HNO). The DFT methods tend to have larger deviations for these electron affinities than for those corresponding to addition of an electron to an open shell molecule. For example, the average absolute deviation for BLYP for closed shell molecules is 0.16 eV (C₂ is excluded from this average because it is a problem case), which is about 60% larger than for the whole set of electron affinities. The performance of the hybrid methods is even worse. For example, the B3LYP method has an average absolute deviation of 0.33 eV for the electron affinities of closed shell molecules (excluding C₂); all of the deviations are negative. Much of the additional error for these closed shell electron affinities is due to the Hartree-Fock mixing in the hybrid methods. The average absolute deviation for G2 theory for the closed shell electron affinities is 0.06 eV, the same as for the whole set of electron affinities.

In recent work²⁸ we have calculated B3LYP/6-31G(*d*) geometries and zero-point energies for the G2 neutral test set and recalculated the B3LYP enthalpies [6-311+G(3df,2p) basis]. The use of unscaled B3LYP/6-31G(*d*) zero-point en-

ergies gives an average absolute deviation with experiment that is significantly larger than that obtained with scaled HF/6-31G(*d*) zero-point energies. Use of an appropriate scale factor for the B3LYP zero-point energies (0.96) gives an average absolute deviation with experiment that is similar to that obtained with scaled HF/6-31G(*d*) zero-point energies. The use of B3LYP/6-31G(*d*) geometries has little effect on the average absolute deviation. It is expected that similar results would be obtained for the ionization potentials and electron affinities in this test set.

D. Relation to other work

There have been several previous assessments of the performance of density functional methods for the calculation of ionization potentials and electron affinities. Gill *et al.*²⁹ investigated the performance of BLYP for ionization potentials and electron affinities in the original G2 test set (G2-1). With the 6-311+G(3df,2p) basis set they found an average absolute deviation of 0.195 eV for IPs and 0.137 eV for EAs, which is similar to our results. Their slightly larger deviation for EAs is due to use of an incorrect calculated electron affinity of CN.

De Profijt and Geerlings³⁰ have assessed several DFT methods including B3LYP, B3PW91, and BLYP on IPs and EAs in the original G2 test set (G2-1) using several correlation consistent basis sets,³¹ the largest being aug-cc-pVDZ.

TABLE IX. Summary of average absolute deviations from experiment (in kcal/mol) for the G2/97 test set calculated by B3LYP with different basis sets.^a

Basis set	Enthalpies of Neutrals (148)	IPs (83)	EAs (58)	PAs (8)	Total (297)
6-31+G(<i>d</i>)	8.75	4.19	3.72	4.26	6.37
6-311+G(2df, <i>p</i>)	3.92	4.11	3.11	1.56	3.75
6-311+G(3df,2p)	3.08	4.10	3.03	1.48	3.31

^aFive IPs of the G2/97 test set are not included in the summaries (see text). Number of quantities included in summaries is given in parentheses. MP2(full)/6-31G(*d*) geometries and scaled HF/6-31G(*d*) zero-point energies used in all calculations.

For IPs they obtained average absolute deviations of 0.15–0.20 eV, consistent with our results. For EAs they obtained average absolute deviations of 0.11–0.16 eV, also consistent with our results.

Tschumper and Schaefer³² have recently presented a systematic study of the electron affinities of 8 first row atoms, 12 diatomic molecules, and 15 triatomic molecules using 6 density functionals. They chose atoms and molecules with reasonably reliable (<0.14 eV) experimental electron affinities. They used a double-zeta basis set with polarization and diffuse functions. Similar to the findings of our investigation, they find that the BLYP method has the smallest average absolute deviation. However, their average absolute deviation with experiment of 0.23 eV for the BLYP method is more than twice as large as our deviation for this method. For atoms they found an average absolute deviation of 0.20 eV compared to 0.12 eV for all atoms in the G2 test set. If the comparison is made on the same set of first-row atoms (Li, B, C, O, F), they find an average absolute deviation of 0.21 eV compared to our value of 0.13 eV. Tschumper and Schaefer also found that the 12 diatomics are in poorer agreement with experiment (0.28 eV) using the BLYP method. In contrast, our BLYP results for the 13 diatomics in the G2 test set give an average absolute deviation (0.13 eV) that is similar to that of the atoms. It appears that the basis set used in this study performs better than the one used by Tschumper and Schaefer.

E. Combined G2 test set results

The average absolute deviations of the G2 and DFT methods for a combined G2 test set of neutral enthalpies,² ionization potentials, electron affinities, and proton affinities (for which all methods have been applied) are summarized in Table VIII. This combined set is G2/97 less five ionization potentials ($C_6H_5CH_3 \rightarrow C_6H_5CH_3^+$, $C_6H_5NH_2 \rightarrow C_6H_5NH_2^+$, $C_6H_5OH \rightarrow C_6H_5OH^+$, $N_2 \rightarrow N_2^+[{}^2\Pi]$, $SH_2 \rightarrow SH_2^+[{}^2A_1]$). For the 297 energies included in the summaries, G2 theory has the lowest average absolute deviation (1.50 kcal/mol) of all the methods examined, while the B3LYP method has the lowest average absolute deviation (3.31 kcal/mol) of the DFT methods.

We have also examined the basis set dependence of the results obtained for the B3LYP density functional method. Calculations of the enthalpies, IPs, and EAs in the combined G2 test set were carried out using the 6-31+G(*d*) and 6-311+G(2*df*,*p*) basis sets in place of the 6-311+G(3*df*,2*p*) basis set. The results are summarized in Table IX. The average absolute deviation for the combined set of energies is 6.37 kcal/mol for the 6-31+G(*d*) basis set and 3.75 kcal/mol for the 6-311+G(2*df*,*p*) basis set compared to 3.31 kcal/mol for the 6-311+G(3*df*,2*p*) basis set. The results in Table IX indicate a significant dependence on the basis set for the calculation of enthalpies of neutrals as has been found previously in DFT studies on the original G2 test set (G2-1) of atomization energies.^{29,33} The results in Table IX also indicate that the electron affinities and ionization potentials are not nearly as dependent on the size of the basis set as the enthalpies of the neutrals. This is also similar to

what has been found in DFT studies on the original G2 test set.²⁹

V. CONCLUSIONS

A set of 146 molecules having well-established ionization potentials and electron affinities has been presented. This set, referred to as the G2 ion test set, includes the 63 molecules whose ionization potentials and electron affinities were used to test G2 theory¹ and 83 new ones. We have used the new G2 test set to assess the performance of G2 and DFT theories in the calculation of these quantities. The DFT methods were assessed using the 6-311+G(3*df*,2*p*) basis with MP2(full)/6-31G(*d*) geometries and scaled HF/6-31G(*d*) zero-point energies. The following conclusions can be drawn from this study:

- (1) G2 theory has average absolute deviations of 0.06 eV for both ionization potentials and electron affinities. The two modified versions of G2 theory examined in this study, G2(MP2, SVP) and G2(MP2) theory, have average absolute deviations of 0.08–0.09 eV for both ionization potentials and electron affinities. Little degradation in the performance of the G2-based methods is observed in the new G2 ion test set.
- (2) The B3LYP method performs the best of the seven DFT methods investigated for ionization potentials, with an average absolute deviation of 0.18 eV, nearly three times that of G2 theory. It fails dramatically for the ionization potential of CN with an error of over 1 eV. The BPW91 method performs the best of the nonhybrid DFT methods, with an average absolute deviation of 0.22 eV.
- (3) The BLYP method performs the best of the seven DFT methods investigated for electron affinities, with an average absolute deviation of 0.11 eV, only about 60% larger than G2 theory. The B3LYP and B3PW91 hybrid methods and the BPW91 nonhybrid method perform only slightly worse than BLYP with average absolute deviations of 0.13, 0.14, and 0.11 eV, respectively.
- (4) The results for a combined G2 test set of neutral enthalpies, ionization potentials, electron affinities, and proton affinities indicate that G2 theory has the lowest average absolute deviation (1.50 kcal/mol) while the B3LYP has the lowest average absolute deviation (3.31 eV) of the DFT methods. This test set is referred to as G2/97. In an investigation of basis set dependence for B3LYP with the 6-31+G(*d*), 6-311+G(2*df*,*p*), and 6-31+G(3*df*,2*p*) basis sets on this test set, the enthalpies of formation are found to depend significantly on the basis set size, while the ionization potentials and electron affinities are not as sensitive.

ACKNOWLEDGMENTS

We acknowledge helpful discussion with Dr. Joseph Berkowitz. This work was supported by the U.S. Department of Energy, Division of Materials Sciences, under Contract No. W-31-109-ENG-38, and the National Science Foundation under Grant No. CHEM-89-18623. We acknowledge a grant of computer time at the National Energy Research Supercomputer Center.

- ¹L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).
- ²L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **106**, 1063 (1997).
- ³L. A. Curtiss, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.* **98**, 1293 (1993).
- ⁴(a) B. J. Smith and L. Radom, *J. Phys. Chem.* **99**, 6468 (1995); (b) L. A. Curtiss, P. C. Redfern, B. J. Smith, and L. Radom, *J. Chem. Phys.* **104**, 5148 (1996).
- ⁵G. A. Petersson, T. G. Tensfeldt, and J. A. Montgomery, Jr., *J. Chem. Phys.* **94**, 6091 (1991).
- ⁶J. A. Montgomery, Jr., J. W. Ochterski, and G. A. Petersson, *J. Chem. Phys.* **101**, 5900 (1994).
- ⁷J. W. Ochterski, G. A. Petersson, and K. Wiberg, *J. Am. Chem. Soc.* **117**, 11299 (1995); J. W. Ochterski, G. A. Petersson, and J. A. Montgomery, *J. Chem. Phys.* **104**, 2598 (1996).
- ⁸L. A. Curtiss, K. Raghavachari, P. C. Redfern, and B. B. Stefanov, *J. Chem. Phys.* **108**, 692 (1998).
- ⁹For reviews see, L. A. Curtiss and K. Raghavachari, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, edited by S. R. Langhoff (Kluwer Academic, The Netherlands, 1995), p. 139; K. Raghavachari and L. A. Curtiss, in *Modern Electronic Structure Theory*, edited by D. R. Yarkony (World Scientific, Singapore, 1995), p. 991; L. A. Curtiss and K. Raghavachari, in *Computational Thermochemistry*, edited by K. Irikura and D. J. Frurip (American Chemical Society Symposium Series 677) (1998).
- ¹⁰W. J. Hehre, L. Radom, J. A. Pople, and P. v. R. Schleyer, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1987).
- ¹¹J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987).
- ¹²L. A. Curtiss, J. E. Carpenter, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.* **96**, 9030 (1992).
- ¹³J. C. Slater, *The Self-Consistent Field for Molecules and Solids: Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4.
- ¹⁴S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
- ¹⁵A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- ¹⁶J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- ¹⁷J. P. Perdew, *Phys. Rev. B* **33**, 8822 (1986); **34**, 7406(E) (1986).
- ¹⁸P. M. W. Gill, B. G. Johnson, J. A. Pople, and M. J. Frisch, *Int. J. Quantum Chem.* **S26**, 319 (1992).
- ¹⁹C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- ²⁰P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **98**, 11623 (1994).
- ²¹M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, and J. A. Pople GAUSSIAN 94, Gaussian, Inc. Pittsburgh, PA, 1995.
- ²²A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ²³The MP2(full)/6-31G(d) geometries and zero-point energies may be obtained via anonymous FTP from axp.cmt.anl.gov. The files are located in the directory `g2testsets`. The geometries can also be down loaded from <http://chemistry.anl.gov/compmat/compterm.htm>.
- ²⁴S. G. Lias, J. E. Bartmess, J. E. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, *J. Phys. Chem. Ref. Data Suppl.* **1**, 17 (1988).
- ²⁵J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **78**, 2744 (1994).
- ²⁶J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, *J. Chem. Phys.* **90**, 5622 (1989).
- ²⁷L. A. Curtiss, C. Jones, G. W. Trucks, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.* **93**, 2537 (1990).
- ²⁸L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *Chem. Phys. Lett.* **270**, 419 (1997).
- ²⁹P. M. W. Gill, B. G. Johnson, J. A. Pople, and M. J. Frisch, *Chem. Phys. Lett.* **197**, 499 (1992); P. M. W. Gill, B. G. Johnson, J. A. Pople, and M. J. Frisch, *Int. J. Quantum Chem. Symp.* **26**, 319 (1992).
- ³⁰F. De Proft and P. Geerlings, *J. Chem. Phys.* **106**, 3270 (1997).
- ³¹T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989); R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- ³²G. S. Tschumper and H. F. Schaefer III, *J. Chem. Phys.* **107**, 2529 (1997).
- ³³C. W. Bauschlicher, *Chem. Phys. Lett.* **246**, 40 (1995).