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Electron affinities of the first- and second-row atoms: Benchmark *ab initio* and density-functional calculations

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A benchmark *ab initio* and density-functional theory (DFT) study has been carried out on the electron affinities of the first- and second-row atoms. The *ab initio* study involves basis sets of $spdfgh$ and $spdfghi$ quality, extrapolations to the one-particle basis set limit, and a combination of the coupled cluster with all single, double (and triple) excitations [CCSD(T)], CCSDT, and full configuration-interaction electron correlation methods. Scalar relativistic and spin-orbit coupling effects were taken into account. On average, the best *ab initio* results agree to better than 0.001 eV with the most recent experimental results. Correcting for imperfections in the CCSD(T) method improves the mean absolute error by an order of magnitude, while for accurate results on the second-row atoms inclusion of relativistic corrections is essential. The latter are significantly overestimated at the self-consistent-field level; for accurate spin-orbit splitting constants of second-row atoms, inclusion of $2s,2p$ correlation is essential. In the DFT calculations it is found that results for the first-row atoms are very sensitive to the exchange functional, while those for second-row atoms are rather more sensitive to the correlation functional. While the Lee-Yang-Parr (LYP) correlation functional works best for first-row atoms, its PW91 counterpart appears to be preferable for second-row atoms. Among ''pure DFT'' (nonhybrid) functionals, G96PW91 (Gill 1996 exchange combined with Perdew-Wang 1991 correlation) puts in the best overall performance, actually slightly better than the popular hybrid B3LYP functional. B3PW91 outperforms B3LYP, while the recently proposed one-parameter hybrid functionals such as B1LYP seem clearly superior to B3LYP and B3PW91 for first-row atoms. The best results overall are obtained with the one-parameter hybrid modified Perdew-Wang (mPW1) exchange functionals of Adamo and Barone [J. Chem. Phys. **108**, 664 (1998)], with mPW1LYp yielding the best results for first-row, and mPW1PW91 for second-row atoms. Indications are that a hybrid of the type a mPW1LYP$+(1-a)$ mPW1PW91 yields better results than either of the constituent functionals. [S1050-2947(99)10908-9]

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I. INTRODUCTION

The electron affinity (EA) of a system is the energy required for the reaction

$$A^{-}\rightarrow A+e^{-}. \tag{1}$$

Electron affinities have traditionally been regarded as one of the hardest atomic or molecular properties to reproduce in an *ab initio* quantum mechanical calculation. For starters, they involve a change in the number of valence electrons correlated in the system, and hence are very taxing tests for any electron-correlation method. In addition, they involve a pronounced change in the spatial extent of the wave function, making them very demanding in terms of the basis set as well.

The electron affinities of the first-and second-row atoms have often been used as benchmarks [1–16] for high-level electronic structure methods since (a) many of them are known experimentally to very high precision (e.g., [17]); (b) no such complications as geometry relaxation are involved; and (c) the computational demands required are still relatively modest. Until recently, three of the first- and second-row atomic electron affinities were imprecisely known experimentally (B, Al, and Si). This situation was changed very recently by high-precision measurements in recent experiments for B [18], Al [19,20], and Si [21].

Density-functional theory (DFT) [22–24] allows a cost-effective introduction of electron correlation via the Kohn-Sham method [25] and the use of exchange-correlation functionals. However, since the systematic extension of these functionals towards the exact solution of the Schrödinger equations has not been possible hitherto, calculated results have to be compared with *ab initio* wave function calculations or experiment in order to judge their reliability and quality. In recent years, many studies have evolved that test the performance of density-functional methods in the calculation of atomic and molecular properties. One of these properties that can be used to critically test the available exchange-correlation functionals is electron affinities.

DFT electron affinities have already been obtained by a number of groups. Pople *et al.* investigated the performance of the Becke-Lee-Yang-Parr (BLYP) exchange-correlation functional in the calculation of atomization energies, ionization energies, electron affinities, and proton affinities using

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the 6-31$G(d)$, 6-31+$G(d)$, 6-311+$G(2df,p)$, and 6-311+$G(3df,2p)$ basis sets [26]. In a test performed on the molecules of the well-known G2 thermochemical data set [27], a mean absolute deviation from experiment of 0.137 eV for the electron affinities (25 molecules) was found for the largest basis set. In a previous contribution [28], two of us have studied ionization potentials and electron affinities using the hybrid functionals B3LYP and B3PW91 and Dunning's correlation-consistent basis sets [29]. For the largest basis set studied (i.e., [5*s*4*p*3*d*2*f*]), a mean absolute deviation from experiment of 0.13 eV for both of these functionals was found in the calculation of electron affinities for the G2 set of molecules. Schaefer and co-workers have studied electron affinities for a variety of systems: sulphur fluorides [30], phosphorus fluorides [31], monochlorine fluorides [32], and silicon fluorides [33]. Galbraith and Schaefer [34] also evaluated the electron affinities for F and F_2 using a number of exchange-correlation functionals and [4*s*3*p*2*d*], [5*s*4*p*3*d*2*f*], [6*s*5*p*4*d*3*f*2*g*], and [7*s*6*p*5*d*6*f*3*g*2*h*] basis sets. Moreover, they studied the atomic electron affinities for the first-row elements, 12 first-row diatomic and 15 first-row triatomic molecules, using six different functional, among which were some hybrid functionals [35]. It was found that for their series of tested molecules, the BLYP functional provided the best agreement with experiment, the overall absolute error being 0.21 eV. For the B3LYP, BP86, and BHLYP functionals, the absolute error lies around 0.3 eV, whereas the B3P86 and local-density-approximation (LDA) errors are around 0.7 eV. Recently, Curtiss *et al.* [36] studied the performance of density-functional methods in the calculation of ionization energies and electron affinities on the so-called G2 ion test set, which consists of the 63 atoms and molecules whose ionization energies and electron affinities were included in the original G2 test set, supplemented with 83 atoms and molecules. Thus, they determined the performance of the seven exchange-correlation functionals in the calculation of 58 electron affinities. It was concluded that for this set and the 6-311+$(3df,2p)$ basis set, the mean absolute deviations were 0.697 eV (LDA), 0.113 eV (BLYP), 0.121 eV (BPW91), 0.193 eV (BP86), 0.131 eV (B3LYP), 0.145 eV (B3PW91), and 0.596 eV (B3P86).

The purpose of the present work is twofold. First of all, we will try to establish whether present-day state-of-the-art wave-function-based methods will consistently yield ''the right result for the right reason.'' As a byproduct, we will obtain basis set limit values for the nonrelativistic, clamped-nuclei electron affinities, which will serve the second purpose. This involves the testing of the performance and basis set dependence of different exchange-correlation density functionals in the calculation of these electron affinities.

II. COMPUTATIONAL METHODS

A. Density-functional calculations

Density-functional calculations were performed using GAUSSIAN94 [37] running on the Cray J916/8-1024 of the Brussels Free Universities Computer Center, and GAUSSIAN98 [38] running on the SGI Origin 2000 of the Faculty of Chemistry at the Weizmann Institute of Science.

In order to account for possible errors in the numerical integration due to the diffuseness of the charge density, in particular of course for the anions, and the high angular momentum in the basis set, a fine grid of 590 angular Lebedev nodes and 99 radial nodes was used and tightened convergence criteria for the Kohn-Sham equations were specified, such that the tabulated results for the electron affinities can be considered precise to 10^{-4} eV.

A wide variety of exchange-correlation functionals E_{xc} was considered. Among the ''pure DFT'' functionals were the following.

(1) The local density approximation (LDA), which actually uses Slater's expression for exchange (*S*) [39] and Vosko, Wilk, and Nusair's expression for the correlation energy of the uniform electron gas [40], parametrized using Ceperley and Alder's quantum Monte Carlo results [41].

(2) The gradient-corrected B-LYP, B-P86, and B-PW91 functionals, which are combinations of Becke's 1988 (B88, or simply B) gradient-corrected exchange functional [42] with correlation functionals due to Lee, Yang, and Parr (LYP) (LYP) [43], Perdew (P86) [44], and Perdew and Wang (PW91) [45], respectively.

(3) The combination of the PW91 correlation functional with the exchange functional proposed in the same paper [45], a combination usually denoted by the acronym GGA91 for generalized gradient approximation–1991.

(4) Combinations of the LYP and PW91 correlation functionals with the 1996 exchange functional proposed by Gill [46], denoted G96LYP and G96PW91, respectively.

Among ''hybrid'' functionals (i.e., those having a nonzero coefficient for the true Hartree-Fock exchange E_x^{HF}), we have considered the following.

(1) The popular B3LYP [47,48] functional, which takes the form

$$E_{xc}=a_{x0}E_x^{LDA}+(1-a_{x0})E_x^{HF}+a_{x1}\Delta E_x^{B88}+(1-a_c)E_c^{LDA}+a_cE_c^{LYP}, \qquad (2)$$

in which the three constants $a_{x0}=0.80$, $a_{x1}=0.72$, $a_c=0.81$ were originally empirically determined by Becke [47] using the P86 correlation functional, and in which the implementation in the Gaussian series of programs [48] uses the Vosko-Wilk-Nusair (VWN) functional 3 [40] for E_c^{LDA} rather than the VWN functional 5 employed by Becke [47].

(2) The B3PW91 functional, which has the same form as the B3LYP functional except that E_c^{PW91} is used instead of E_c^{LYP}.

(3) A number of new one-parameter hybrid functionals proposed by Adamo and Barone:

$$E_{xc}=a_0E_x^{HF}+(1-a_0)(E_x^{LDA}+\Delta E_x^{GC})+E_c, \qquad (3)$$

in which ΔE_x^{GC} is some gradient correction to the exchange functional (e.g., B88, PW91, G96), and E_c represents any suitable correlation functional. From an analysis [49] based on perturbation theory, a_0 takes the nonempirical value $\frac{1}{4}$. In the present paper, we have considered B1LYP and B1PW91 [50] (i.e., the one-parameter analogs of B3LYP and B3PW91), as well as the newer LG1LYP functional [51] which uses the Lacks-Gordon [52] expression for E_x^{GC} and the mPW1LYP and mPW1PW91 functionals [53], in which the nonlocal exchange is given by a modification of E_x^{PW91}

TABLE I. Best *ab initio* computed electron affinities (in eV).

	SCF limit $A+B.C^n$	CCSD(T) limit $A+B/n^3$	Core corr. CCSD(T)/ MTav5z	Spin-orbit CAS-CI(all)/ ACVQZ MTav5z	Darwin+MV ACPF(all)/ACVQZ MTav5z	FCI corr. (see text)	Best Calc.	Experiment
H	−0.32877	1.08297	0.00000	0.00000	−0.00004	0.00000	0.75416	0.754195 [17]
B	−0.26754	0.52465	0.00427	−0.00060	−0.00127	0.01907	0.27858	0.277(10), 0.279723(25) [18]
C	0.54826	0.70047	0.00720	−0.00332	−0.00283	0.01309	1.26288	1.2629(3) [17]
N	–	–	–	–	–	–	–	–
O	−0.53902	1.99391	0.00173	−0.00222	−0.00588	0.01223	1.46075	1.461122(3) [17]
F	1.30727	2.11864	0.00430	−0.01652	−0.00928	0.00056	3.40496,3.40285[a]	3.401190(4) [17]
Al	0.04101	0.40219	−0.01617	−0.00385	−0.00536	0.01497	0.43277	0.441(10), 0.43283(5) [20], 0.44094(66) [19]
Si	0.95579	0.46046	−0.00965	−0.01806	−0.00787	0.00992	1.39060	1.385(5), 1.38946(6) [21]
P	−0.45796	1.19166	−0.00521	0.01229	−0.00937	0.01124	0.74264,0.74474[b]	0.7465(3) [17]
S	0.90388	1.18400	−0.00161	−0.00410	−0.01223	0.00441	2.07436,2.07544[b]	2.077104(1) [17]
Cl	2.52999	1.13398	0.00085	−0.03657	−0.01509	−0.00309	3.61008, 3.61113[b]	3.61269(6) [17], 3.612641(27)[c]

[a] Includes $A+B/l^3$ extrapolation of CCSDT–CCSD(T) difference from AVTZ and AVQZ basis sets (see text).

[b] Using dAVQZ and dAV5Z basis sets for valence correlation extrapolation.

[c] U. Berzinsh, M. Gustafsson, D. Hanstorp, A. Klinkmüller, U. Ljungblad, and A.-M. Mårtensson-Pendrill, Phys. Rev. A **51**, 231 (1995).

for better treatment of long-range interactions (the small-density, large-gradient regime).

B. *Ab initio* calculations

The CCSDT (coupled cluster with all single, double, and triple excitations [54]) calculations were carried out using ACES II [55] running on a DEC Alpha 500/500 workstation at the Weizmann Institute of Science; all other *ab initio* calculations reported in this work were carried out using MOLPRO98.1 [56] running on a Silicon Graphics Octane workstation at the Weizmann Institute.

The valence calculations were carried out using the augmented correlation-consistent valence n-tuple zeta (aug-cc-pVnZ, or AVnZ for short) basis sets of Kendall, Dunning, and Harrison [8]. The contracted sizes for the various AVnZ basis sets for [second-row/first-row/hydrogen] atoms are as follows: AVDZ $[5s4p2d/4s3p2d/3s2p]$, AVTZ $[6s5p3d2f/5s4p3d2f/4s3p2d]$, AVQZ $[7s6p4d3f2g/6s5p4d3f2g/5s4p3d2f]$, AV5Z $[8s7p5d4f3g2h/7s6p5d4f3g2h/6s5p4d3f2g]$; in addition, for first-row and hydrogen atoms only, we considered AV6Z $[8s7p6d5f4g3h2i/7s6p5d4f3g2h]$.

Except where indicated otherwise, restricted open-shell Hartree-Fock (ROHF) reference wave functions were used throughout.

The self-consistent-field (SCF) component of the total energy was extrapolated using a geometric expression [57] of the type $A+B/C^n$ applied to AVnZ energies with $n=$Q, 5, 6 for first-row atoms and $n=$T, Q, 5 for second-row atoms. The CCSD(T) (coupled cluster with all single and double excitations and a quasiperturbative treatment of connected triple excitations [58–60]) valence correlation energy was extrapolated using both the three-parameter expression $A+B/(n+\frac{1}{2})^{\alpha}$ proposed by one of us [61] and the two-parameter expression $A+B/n^3$ proposed by Halkier *et al.* [62]: both expressions are based on the known asymptotic convergence behavior [63,64] of pair correlation energies as a function of the maximum angular momentum present in the basis set.

Imperfections in the treatment of connected triple excitations are corrected by means of CCSDT calculations in the AVQZ basis set. Finally, the effect of connected quadruple and higher excitations is approximated by full configuration interaction (FCI) in the largest basis set where this is feasible with the Knowles-Handy [65] determinantal code. For B and Al, this is AVQZ; for C and Si, AVTZ; for the other elements AVDZ.

The effect of inner-shell correlation was determined as the difference between valence-only and all-electron CCSD(T) calculations using the Martin-Taylor [66,67] family of core-correlation basis sets. The MTavqz basis set corresponds to a completely uncontracted AVQZ basis set augmented with $1p3d2f$ high-exponent functions of which the exponents are obtained by successively multiplying the largest exponent already present in that angular momentum by a factor of 3.0. The MTav5z basis set was similarly obtained from the AV5Z basis set but with $1p3d2f1g$ high-exponent functions added.

Scalar relativistic effects were approximated by the first-order perturbation correction [68,69] of the Darwin and mass-velocity (DMV) terms. For technical reasons, these calculations were carried out at the averaged coupled pair functional (ACPF) [70] level. Since great flexibility in the s and p functions is essential for this type of effect, we employed the MTAVQZ basis set throughout for this contribution.

Spin-orbit coupling constants were evaluated at the CASSCF-CI level using the $spdf$ part of the MTav5z basis set. (For a recent review of the methodology involved, see Ref. [71].)

III. RESULTS AND DISCUSSION

A summary of our computed results and their different components is presented in Table I, together with the experimental results, while a selection of previously computed literature values is presented in Table II.

A. First-row atoms

An indication for the error introduced by our use of finite basis sets and extrapolations can be obtained from our results for the EA of the hydrogen atom, for which the computed results represent exact solutions within the respective finite basis sets.

The three-point geometric extrapolation for the SCF component adds only about 0.0001 eV to the largest-basis set (AV6Z) result. The two-point Halkier extrapolation, however, still adds about 0.0041 eV to the final result. The latter, 0.754 16 eV, agrees excellently with the most precise measurement, 0.754 195(19) eV [17]; the somewhat higher observed value for deuterium, 0.754 593(74) eV [17], suggests that deviations from the Born-Oppenheimer approximation (not considered in the present work) may account for 0.0002–0.0004 eV; hence this is probably a more realistic assessment of the residual error in our calculation than the difference of 0.000 04 eV between computed and observed EAs. The only term other than SCF and valence correlation that contributes to our computed result is an essentially negligible (4×10^{-5} eV) contribution of Darwin and mass-velocity (DMV) effects.

The electron affinity of the boron atom, imprecisely known for a long time, was very recently redetermined to high accuracy by Scheer, Bilodeau, and Haugen [18] as 0.279 723(25) eV, in perfect agreement with a very recent relativistic coupled cluster calculation by Eliav *et al.* [6] in an exceedingly large $[35s26p20d14f9g6h4i]$ basis set, as well as the numerical relativistic MCSCF calculation by Fischer, Ynnerman, and Gaigalas [7]. Our present best calculated result, 0.278 58 eV, meets the 0.001 eV accuracy target using no larger basis sets than $[8s7p6d5f4g3h2i]$. Again, the basis set extrapolation beyond AV6Z amounts to essentially nothing for the SCF contribution but 0.004 eV for the valence correlation energy. The *n*-particle space calibration, in this case, was carried out at the FCI/AVQZ level, and amounts to no less than 0.0191 eV—about three-quarters of which consists of imperfections in the treatment of connected triples. As a more extreme case of a general trend, the results reflect imbalance between the quality of the CCSD(T) treatment for neutral and anion—in this case close to exact for B but rather less so for B^-. Inner-shell correlation increases EA by 0.0043 eV, while DMV effects reduce EA by 0.0013 eV and spin-orbit effects by another 0.0006 eV.

Our best calculation for carbon, 1.262 98 eV, agrees to within experimental uncertainty with the experimental value 1.2629(3) eV. The amounts bridged by the extrapolation parallel those found for H and B. *n*-particle calibration accounts for 0.013 eV, split about 2:1 between imperfections in the treatment of connected triples and effects of connected higher excitations. Spin-orbit and scalar relativistic effects lower the EA by 0.003 eV each. Inner-shell correlation has the highest contribution of the first-row atoms, 0.007 eV.

The nitrogen atom has no bound anion. For oxygen, our best calculation is within 0.0005 eV of the very precisely known experimental value. In this case, extrapolation even from the AV6Z basis set contributes a solid 0.016 eV to the final result—it should be noted that the valence correlation component of EA is almost three times larger in absolute value than that in C. While the spin-orbit contributions largely compensate between neutral and anion (reflected in the fairly small EA contribution of -0.002 eV), the DMV contribution is relatively important at -0.006 eV (as expected). The *n*-particle correction, at 0.012 eV, largely consists of effects of connected quadruple and higher excitations—the difference between CCSDT and CCSD(T) only amounts to about 0.002 eV.

The EA for F has traditionally been known as one of the very hardest quantities to reproduce from a theoretical calculation. Our calculated value is 0.004 eV higher than the experimental result—which is still close to 0.1% accuracy relatively speaking. The basis set extrapolation covers similar amounts as in O, while both the spin-orbit (-0.016 eV) and DMV (-0.009 eV) contributions are quite sizable. Inner-shell correlation contributes a similar amount as in B. The main uncertain element in our calculation is the deceptively small *n*-particle calibration contribution of 0.0006 eV, which is actually the result of a cancellation between imperfections in the CCSD(T) treatment of connected triple excitations (-0.009 eV) on the one hand, and the effect of connected higher excitations ($+0.010$ eV) on the other hand. Unfortunately, the largest basis set in which we could carry out FCI calculations was AVDZ, but we expect the FCI-CCSDT difference to converge as fast as in the case of B or C. The considerable basis set variation of the CCSDT-CCSD(T) differences as well as the clear downward trend, progressing from $+0.003$ eV (AVDZ) over -0.006 eV (AVTZ) to -0.009 eV (AVQZ), strongly suggests that this difference would be substantially larger near the *n*-particle basis set limit. If we assume an $A+B/l^3$ extrapolation for this difference (equivalent to carrying out a valence correlation extrapolation on CCSDT rather than CCSD(T) values for this case) we obtain a further lowering by 0.002 eV, bringing the calculated EA down to 3.4031 eV, within 0.002 eV of the experimental value of 3.401 190(4) eV.

Of previously computed results for F, Gutsev *et al.* (CCSDT/AV5Z, 3.395eV) and Curtiss *et al.* (G3 theory, 3.400 eV) are both in excellent agreement with experiment. However, the former includes neither spin-orbit nor DMV contributions, and their inclusion would reduce the result to 3.370 eV. The G3 value does include spin-orbit terms (experimentally derived) but not DMV, and would be reduced to 3.391 eV upon inclusion of the latter.

B. Second-row atoms

The previously rather imprecisely known [17] EA of aluminum was very recently redetermined. Calabrese, Covington, and Thompson [19] obtained 0.440 94(66) eV, while Scheer *et al.* [20] obtained the more precise, and substantially lower, value of 0.432 83(5) eV. Our own calculations agree to four figures with this latter value. Extrapolation of the valence correlation contribution beyond AV5Z accounts for only 0.0036 eV, while inclusion of inner-shell correlation lowers EA by 0.016 eV, almost perfectly canceling the increase of 0.015 eV from *n*-particle correction. As in isovalent B, imperfections in the treatment of connected triples in

TABLE II. Comparison of presently computed *ab initio* electron affinities (eV) with earlier calculations. The prefixes NR and R indicate nonrelativistic and relativistic values/results, respectively; SO indicates values with only a correction for spin-orbit splitting applied (not for scalar relativistic effects).

	Year	Source	Ref.	Level of theory	Basis set	H	B	C	O	F
R	1999	This work		Best calc.		0.7542	0.2786	1.2629	1.4607	3.4029
R		Most recent experimental values				0.7542(2)	0.279723(25)	1.2629(3)	1.461122(3)	3.401190(4)
NR	1999	Gdanitz	[1]	r12-MRACPF	a	0.7542	0.2833	1.2655	1.454	3.398
R	1999	Gdanitz	[1]	r12-MRACPF	a,f	0.7538	0.2820	1.2623	1.445	3.385
NR	1998	Gutsev *et al.*	[2]	CCSDT	AV5Z	0.747	0.241	1.259	1.432	3.395
SO	1998	Curtiss *et al.*	[86]	G3 theory			0.204	1.193	1.336	3.400
R	1998	Gou-xin *et al.*	[3]	LDA	Numer.	0.637	0.282	1.220	1.292	2.180
R	1997-8	Wijesundera	[4,5]	MC Dirac-Fock	Numer.		0.260	1.210		
R	1997	Eliav *et al.*	[6]	CCSD (+T)	c		0.279			
R	1995	Fischer *et al.*	[7]	MCHF+core+val.	Numer.		0.2795			
R	1993	Hughes and Kaldor	[87]	Fock space CCSD	$13s9p6d4f2g$					3.421
NR	1992-3	Dunning *et al.*	[8]	FCIapprox	AVQZ	0.740	0.263	1.246	1.401	3.364
NR	1992	Strout and Scuseria	[88]	CCSD(T)	$23s26p10d5f3g$				1.415	
NR	1992	Moskowitz and Schmidt	[89]	Variational QMC			0.24(2)	1.27(2)	1.30(2)	3.46(4)
NR	1991	Noro *et al.*	[10]	MRCI	$13s11p6d5f5g5h$		0.278	1.264	1.454	3.363
R	1990	Sundholm and Olsen	[11]	d	Numer.		0.2668			
NR	1989	Novoa *et al.*	[12]	CIPSI-3	$7s6p4d2f$		0.28	1.22	1.23	3.16
e	1986	Bauschlicher *et al.*	[13,14]	FCI	b				1.287	3.040
NR	1985	Feller and Davidson	[15]	MR-CI+Q				1.235	1.405	
NR	1985	Raghavachari	[16]	CCD+ST(CCD)	$7s5p4d2f$		0.22	1.22	1.36	3.35

	Year	Source	Ref.	Level of theory	Basis set	Al	Si	P	S	Cl
R		This work		Best calc.		0.4328	1.3906	0.7467	2.0768	3.6111
R		Most recent experimental values				0.43283(5)	1.38946(6)	0.7465(3)	2.077104(1)	3.61264(3)
NR	1998	Gutsev *et al.*	[2]	CCSDT	AV5Z	0.433	1.405	0.714	2.059	3.623
R	1998	Curtiss *et al.*	[86]	G3 theory		0.390	1.379	0.711	2.064	3.608
R	1998	Gou-xin *et al.*	[3]	LDA	Numer.	0.450	1.372	0.748	1.996	3.332
R	1997-8	Wijesundera	[4,5]	MC Dirac-Fock	Numer.	0.433		0.702		
R	1997	Eliav *et al.*	[6]	CCSD (+T)	c	0.427				
NR	1996	Greeff *et al.*	[90]	Diffusion QMC		0.432(21)				
R	1995	Heinemann *et al.*	[91]	CCSD(T) [g]	$6s5p4d3f3g2h1i$				2.064(5)	
R	1993	Hughes and Kaldor	[87]	FS:CCSD	$13s9p6d4f2g$					3.608
SO	1992-3	Dunning *et al.*	[9]	FCIapprox	AVQZ	0.441	1.413	0.702	2.051	3.632
NR	1988	Yoshida *et al.*	[92]	Diffusion QMC+ECP						3.617(198)

[a] $19s14p7d5f3g2h$ (B,C), $19s14p8d6f4g3h1i$ (O,F), $11s5p4d3f2g$ (H).

[b] O: FCI($2p$ only)/[$6s5p3d2f$]; F: FCI (full valence)/[$5s4p2d$].

[c] $35s26p20d14f9g6h4i$.

[d] MCHF + core valence + relativistic corrections.

[e] R for oxygen, NR for fluorine.

[f] Relativistic corrections taken from numerical HF calculations, Ref. [72].

[g] Plus *n*-particle correction from valence FCI in the [$5s4p2d1f$] basis set (+0.005 eV); scalar relativistic (DMV) contribution from the MRCI+Q/$6s5p4d3f2g$ calculation (-0.008 eV); spin orbit from experiment (-0.004 eV).

TABLE III. Effect of electron correlation on the computed scalar relativistic corrections (eV).

	SCF MTavqz	ACPF/ MTavqz	SCF MTav5z	ACPF/ MTav5z	Num. HF [73]	Num. HF [72]
H	−0.00010	−0.00004	−0.00010	−0.00004	−0.00016	+0.0000
B	−0.00144	−0.00128	−0.00143	−0.00127	−0.00148	−0.0013
C	−0.00323	−0.00283	−0.00323	−0.00283	−0.00345	−0.0032
O	−0.00796	−0.00592	−0.00795	−0.00588	−0.00819	−0.0080
F	−0.01236	−0.00930	−0.01236	−0.00928	−0.01319	−0.0129
Al	−0.00528	−0.00536	−0.00529	−0.00536	−0.00538	−0.0054
Si	−0.00892	−0.00786	−0.00892	−0.00787	−0.00922	−0.0092
P	−0.01056	−0.00935	−0.01056	−0.00937	−0.01087	−0.0109
S	−0.01426	−0.01219	−0.01427	−0.01223	−0.01473	−0.0147
Cl	−0.01830	−0.01504	−0.01831	−0.01509	−0.01917	−0.0192

CCSD(T) make up the bulk of that effect. Spin-orbit coupling and scalar relativistic effects weigh in at −0.0038 and −0.0054 eV, respectively.

The EA of Si was very recently revised to 1.389 46(6) eV by Thogersen *et al.* [21]. Our own calculation comes within 0.001 eV of that value. With a substantial spin-orbit splitting in Si(^3P) and none at all in Si$^-$(^4S), we find the spin-orbit contribution to EA to be the second-largest of the atoms surveyed, −0.018 eV, while scalar relativistic effects are less substantial at −0.008 eV. The basis set extrapolation bridges are 0.006 eV in this case; inner-shell correlation is less prominent than in Al but still affects the result by −0.010 eV, which interestingly again nearly cancels the *n*-particle calibration correction. The latter is about evenly split between imperfections in the treatment of connected triple excitations and the effects of connected quadruple and higher excitations.

In the final three atoms, basis set convergence appears to be particularly slow, as witnessed by the fact that extrapolations from AVQZ and AV5Z results cover 0.023, 0.026, and 0.030 eV, respectively, for P, S, and Cl. When using AV5Z and AV6Z results for Cl, some 0.017 eV is still bridged. Under these circumstances, it is not surprising that accuracy would be somewhat lower; and indeed, our computed results for P, S, and Cl are too low by about 0.002 eV on average.

Given how diffuse particularly the P anion is (the isovalent N anion is not even bound), one might wonder whether even the AV*n*Z basis sets are sufficiently saturated in the anion region. In an attempt to establish this, we have carried out calculations for P, S, and Cl using dAV*n*Z (doubly-augmented V*n*Z) basis sets, in which the additional set of diffuse functions was generated simply by multiplying the lowest exponents already present by 0.25. Particularly for P, but less so for S and Cl, there is a nontrivial difference between AVQZ/AV5Z and dAVQZ/dAV5Z extrapolated limits: 0.0021 eV for P, and 0.0011 eV for S and Cl. This leads to revised values that are in perfect agreement with experiment for P and S, while the revised result for Cl is only 0.0015 eV too low.

Aside from these specific remarks, we can make some general observations.

First of all, the mean absolute deviation between our best computed *ab initio* values and the most recent experimental values is only 0.0009 eV, with the largest individual error, 0.0018 eV, seen for P. To the best of our knowledge (see Table II), this level of accuracy is unprecedented in the literature for this property.

The inclusion of corrections for imperfections in the CCSD(T) method is absolutely indispensable for this level of accuracy: neglecting them raises the mean absolute error by more than an order of magnitude, to 0.009 eV. This contribution, as noted above, is generally dominated by corrections for imperfections in the treatment of connected triple excitations, i.e., the difference between CCSD(T) and CCSDT.

The contribution of inner-shell correlation stabilizes the anion over the neutral in the first-row atoms: in absolute value, it goes through a maximum for C although in relative terms it monotonically decreases in importance from left to right in the Periodic Table. For second-row atoms, core correlation stabilizes the neutral over the anion, and monotonically decreases from left to right in the Periodic Table.

As expected, the contribution of scalar relativistic (Darwin and mass-velocity, DMV) effects mounts from left to right within each row, and is more important for the second row than for the first row. As seen in Table III, our relativistic contributions follow the same trends as those obtained in the numerical SCF calculations of García de la Vega [72] and of Koga *et al.* [73], particularly the consistent favoring of the more compact neutral atom over the more diffuse anion. However, in absolute value our ACPF/MTav5z-calculated DMV contributions are systematically smaller than the numerical HF results; the difference increases from left to right in the Periodic Table and becomes fairly substantial for F and Cl. As is readily seen by comparing SCF/MTav5z and ACPF/MTav5z results, this mostly reflects the effect of electron correlation on the correction, which one would intuitively expect to decrease the effect of a one-electron property that is most important for the inner-shell electrons. Comparison of MTavqz and MTav5z results reveals that our computed contributions are converged in terms of the basis set to $\leqslant 5\times10^{-5}$ eV at the ACPF level and $\leqslant 10^{-5}$ eV at the SCF level. The small difference between the present SCF level contributions and the numerical HF results reflects the inclusion of some additional scalar relativistic effects in the latter, particularly the two-electron Darwin term which we did not consider. Evidently, their importance, at the Hartree-Fock level, mounts from −0.00004 eV for B or −0.0001 eV for Al to about −0.0008 to −0.0009

TABLE IV. Effect of dynamical correlation on the computed atomic spin-orbit fine structures (cm^{-1}). Degeneracies are given in parentheses with the experimental values. Experimental results are taken from Ref. [93] unless indicated otherwise. Note that the degeneracies for Si(^3P_n) ($n=0,1,2$) in Ref. [93] are misprinted.

	Expt	MTavtz +CI(all)[a]	MTav5z CASSCF	MTav5z +CI(val)[b]	MTav5z +CI(subval)[c]	MTav5z +CI(all)[a]
B	0(2), 15.254(4)	14.4	14.9	14.2		14.7
B^-	0(1), 4(3), 9(5); 0(1), 3.23(3), 8.41(5) [18]	2.45,7.34	2.44,7.31	2.4,7.2		2.49,7.50
C	0(1), 16.40(3), 43.40(5)	13.2,39.5	13.1,39.2	13.2,39.6		13.4,40.2
O	0(5), 158.265(3), 226.977(1)	153.2,229.8	161.0,241.6	153.6,230.4		155.1,232.6
O^-	0(4), 177.08(2)	176.8	180.6	177.2		179.0
F	0(4), 404.1(2)	394.9	401.9	397.7		399.8
Al	0(2), 112.061(4)	114.6	103.2	90.0	115.0	115.4
Al^-	0(1), 26.0(3), 76.0(5); 0(1), 22.7±0.3(3), 68.4±0.4(5) [20]	22.8,68.3	19.6,58.9	18.6,55.7	22.9,68.8	22.9,68.8
Si	0(5), 77.113(3), 223.157(1)	72.7,218.0	63.8,191.3	61.7,185.1	72.8,218.5	72.8,218.5
P^-	0(5), 181(3), 263(1)	197.7,296.5	180.51,270.76	165.9,248.7	197.3,296.0	198.2,297.3
S	0(5), 396.09(3), 573.65(1)	394.4,592.6	366.3,549.5	347.7,521.5	394.3,591.4	395.3,593.0
S^-	0(4), 483.54(2)	492.8	452.9	436.3	492.7	493.8
Cl	0(4), 882.36(2)	883.1	823.2	799.3	883.5	884.8

[a] CASSCF-CI, also including excitations from $(1s)$ orbitals.

[b] CASSCF-CI, excitations only from the valence orbitals considered.

[c] CASSCF-CI, excitations from the valence orbitals as well as $(2s2p)$ subvalence orbitals considered.

eV for F and Cl. It is not *a priori* clear how electron correlation would affect these contributions, although a reduction in importance would seem plausible.

The spin-orbit contributions likewise mount from left to right and from top to bottom in the Periodic Table; however, because such systems as C^-, Si^-, and P do not exhibit any first-order spin-orbit splitting, the contributions to EA at first sight seem more erratic.

To the accuracy relevant here, it hardly appears to matter whether the observed or the best computed fine structures are used for calculating the spin-orbit contribution. As seen in Table IV, the computed values are clearly near convergence with respect to the basis set. For the first-row atoms, the CASSCF values are quite close to experiment but this holds much less true for the second-row atoms. Inclusion of external valence correlation usually seems to lower the computed values and bring them away from experiment, while the inclusion of $(2s,2p)$ correlation for the second-row atoms leads to a dramatic improvement in the quality of the results. Inclusion of correlation from the deep-lying $(1s)$ orbitals has little effect on the second-row results, as expected, but for first-row atoms a somewhat greater contribution is seen.

Of the previous calculations summarized in Table II, the one systematic study that most closely reproduces our present benchmark values are the very recent benchmark calculations of Gdanitz [1], which were carried out using a variant of the multireference ACPF [70] method involving explicit interelectronic distances, MRACPF-r_{12} [74]. (In fact, since the author of Ref. [1] was apparently unaware of the revised experimental EA of B [18], his accuracy for B is better than claimed in Ref. [1].) Nevertheless, even using this elaborate method, the errors in the O and F electron affinities obtained in that work [1] are still an order of magnitude larger than those in the present work. Part of the discrepancy is due to the reliance, for relativistic corrections, on the numerical Hartree-Fock values of García de la Vega [72], which we have seen above to be an overestimate for the scalar relativistic contribution.

C. Density-functional results

The suitability of DFT methods for calculating electron affinities has been the subject of some debate in the literature. It was noted early [75] that numerical LDA calculations on H^- do not yield a bound HOMO, and hence no electron affinities can be obtained unless the anion is artificially stabilized by a Watson-sphere potential [47]. Schaefer and coworkers [34,35] (see also Ref. [28]), however, carried out EA calculations using finite Gaussian basis sets with a variety of exchange-correlation functionals and found quite reasonable agreement with experiment. These at-first-sight contradictory findings were largely reconciled by Rösch and Trickey [76], whose arguments will be briefly summarized here.

The main cause of the problem is the fact that the spurious self-repulsion of the electron in the Coulomb potential is not exactly canceled by the corresponding term in the (approximate) exchange potential. (Exact cancellation occurs both for Hartree-Fock exchange and for the exact Kohn-Sham potential [77].) This ‘‘self-interaction error’’ results in an exchange-correlation potential which for large r approaches zero exponentially rather than the correct limit $-1/r$ [78]. As a result, Kohn-Sham orbital energies are artificially shifted upward by amounts on the order of several eV; while this is a mere annoyance for calculations on neutral systems, this is on the same order of magnitude as the highest occupied orbital energies in anions and leads to the latter becoming positive. Such an orbital (in an infinite basis set) is non-normalizable and in fact corresponds to a combination of incoming and outgoing scattered waves. However, a finite basis set of Slater or Gaussian basis functions, no matter how diffuse or extended, will in effect confine the orbital to a finite-sized sphere and thus render it artificially normalizable. The question as to whether a DFT calculation of the electron affinity as $E(A)-E(A^{-})$ will yield an acceptable result then largely hinges on whether the artificially normalizable orbital itself will be significantly affected by the incorrect asymptotic shape of the approximate potential, as well as how well the self-interaction error in the total energy cancels between neutral and anionic species.

The self-interaction error is mitigated by the use of ''hybrid'' functionals such as B3LYP or mPW1PW91, since the Hartree-Fock component is free of self-interaction. (In the present work, we found that all hybrid functionals yielded all-negative occupied orbital energies for Cl^{-}, as did all hybrid functionals other than B3PW91 for F^{-}. The other anions still exhibit positive highest occupied orbital energies.) In addition, a rigorous self-interaction correction (SIC) [79] can be introduced, at the expense of introducing orbital-dependent potentials and orbital representation invariance problems [80]. Numerical orbital calculations with such self-interaction corrected DFT methods (e.g., [81,82]) yield agreement with experiment for atomic electron affinities comparable to that with the better hybrid functionals studied here. (However, initial SIC-LDA results [83] for molecular binding energies and geometries were in fact poorer than with standard LDA, and even more so compared with generalized gradient approximations).

We note that the prime application for DFT calculations of electron affinities would be large molecules where no other approach is currently computationally feasible, and that the spatial extent of the charge distribution in such systems would help reduce the self-repulsion error [76]. By comparison, atoms represent a ''worst-case scenario,'' so it would definitely be of interest to know if accurate atomic EAs can be obtained at all using modern pure DFT and hybrid exchange-correlation functionals and finite basis sets. We will demonstrate here that not only is this the case, but that accuracies are comparable to some of the older *ab initio* calibration work in Table II.

Computed DFT electron affinities are compared with the best nonrelativistic *ab initio* values in Table V, while basis set convergence in the DFT results is depicted in Table VI for two representative DFT functionals, one pure, the other hybrid.

As seen in Table VI, basis set convergence for the DFT results is quite rapid. Convergence is essentially achieved from AVTZ basis sets onwards, and extrapolations of any kind would add little to the quality of the results. In the remainder of our discussion, we will therefore employ the unextrapolated results with the largest basis set, AV5Z.

The most striking feature of Table V is that performance with many of the functionals is qualitatively different for first-row and second-row atoms. As could be expected, the worst performance is put in by LDA, with a global mean absolute deviation of 0.377 eV; however, the results for this functional are substantially better for second-row than for first-row atoms, the performance being almost as good as for the BP86 functional. Upon closer inspection (as exemplified by comparison of the BPW91, B3PW91, and G96PW91 results), it seems that the results for the first row (aside from hydrogen) are quite sensitive to the nature of the exchange functional, while this is much less the case for the second-row atoms, where the results are rather dominated by the correlation functional. The performance of many of the exchange-correlation functionals, however, for the simplest of systems, i.e., the hydrogen atom, leaves a lot to be desired. Considering first the pure DFT (nonhydrid) exchange-correlation functionals as a group, it appears that the PW91 correlation functional performs somewhat better than its LYP counterpart, particularly for the second row. For exchange, B88 works somewhat better than PW91 for the first row, although there seems to be little difference between them for the second row. The 1996 Gill exchange functional however appears to be markedly superior to both of them, the differences again being most conspicuous for the first row. Compared to G96LYP, the different correlation functional in G96PW91 cuts the error for the second row in half even though the overall performance for the first row is comparable to that of B3LYP. Overall, G96PW91 emerges as the best pure DFT functional for the criterion used here, with a mean absolute error of 0.11 eV for atomic electron affinities (only 0.06 eV in the second row). The contention that the PW91 correlation functional is best used in conjunction with the PW91 exchange functional does not appear to be borne out by the present results.

Turning now to the hybrid functionals, we note that the popular B3LYP functional in fact performs slightly less well than G96PW91. Performance for B3PW91 is in fact markedly better than that of B3LYP, and the best of all the pre-1996 functionals considered. In line with the general observation that the first-row EAs appear to be much more sensitive to the exchange part of the functional than their second-row counterparts, the admixture of Hartree-Fock exchange also has the largest effect for the first row.

Interestingly, the one-parameter B1LYP represents a dramatic improvement over the three-parameter B3LYP for first-row atoms. In fact, its performance for the first-row electron affinities is not dissimilar to some of the *ab initio* calibration studies done in the past. Performance for the second row is marred by a particularly poor result for Si. LG1LYP yields marginally better results than B1LYP for the second-row atoms, but slightly worse ones (on average) for the first row. The mPW1LYP functional, on the other hand, exhibits a slight performance improvement over B1LYP for both first-and second-row atoms: residual errors for the first row are down to $+0.02$ eV (H), $+0.05$ eV (B), -0.06 eV (C), $+0.03$ eV (O), and -0.11 eV (F). Again the weakest performance for the second row is put in for Si (-0.21 eV).

Interestingly enough, substitution of the PW91 correlation functional leads to a serious deterioration of results for the first-row atoms: this is perhaps to some extent related to the fact that the LYP correlation functional was itself based on a fit [84] to estimated correlation energies for the first-row atoms. The mPW1PW91 functional, on the other hand, yields very good results for the second-row atoms, with residual errors of -0.10 eV (Al), $+0.04$ eV (Si), $+0.07$ eV (P), -0.01 eV (S), and -0.08 eV (Cl).

The fact that mPW1LYP seems to put in the best performance for the first row and mPW1PW91 for the second row naturally leads to the suggestion that perhaps a hybrid of the two correlation functionals may lead to the best results overall. If we were to assume that the Kohn-Sham orbitals do not differ greatly between the mPW1LYP and mPW1PW91 ap-

TABLE V. Performance of different exchange-correlation functionals for atomic electron affinities (eV). The AV5Z basis set was used throughout.

		Nonhybrid functionals						
	Best nonrel. [a]	LDA	B-LYP	B-P86	B-PW91	PW91-PW91	G96-LYP	G96-PW91
H	0.75420	0.952	0.881	1.037	0.760	0.767	0.841	0.721
B	0.28045	0.756	0.468	0.701	0.605	0.659	0.422	0.557
C	1.26903	1.814	1.367	1.646	1.562	1.630	1.325	1.519
O	1.46885	2.071	1.839	1.918	1.726	1.841	1.719	1.604
F	3.43077	4.128	3.681	3.759	3.601	3.724	3.592	3.511
Al	0.44199	0.646	0.390	0.657	0.569	0.610	0.356	0.535
Si	1.41653	1.593	1.231	1.552	1.473	1.521	1.202	1.444
P	0.73973	1.039	0.911	1.076	0.870	0.931	0.842	0.802
S	2.09069	2.393	2.129	2.310	2.136	2.216	2.060	2.068
Cl	3.66173	3.929	3.571	3.765	3.617	3.702	3.515	3.562
Mean abs. error		0.377	0.157	0.287	0.145	0.205	0.128	0.108
	First row	0.504	0.206	0.372	0.210	0.283	0.139	0.155
	Second row	0.250	0.108	0.202	0.081	0.126	0.116	0.061

		Hybrid functionals						
	Best nonrel. [a]	B3-LYP	B3-PW91	B1-LYP	LG1-LYP	mPW1-PW91	mPW1-LYP	b
H	0.75420	0.926	0.761	0.765	0.827	0.659	0.770	0.733
B	0.28045	0.476	0.522	0.308	0.352	0.487	0.332	0.383
C	1.26903	1.380	1.470	1.183	1.213	1.425	1.211	1.282
O	1.46885	1.688	1.509	1.454	1.583	1.403	1.502	1.469
F	3.43077	3.527	3.376	3.270	3.347	3.253	3.318	3.297
Al	0.44199	0.466	0.551	0.324	0.342	0.539	0.341	0.407
Si	1.41653	1.345	1.473	1.184	1.192	1.463	1.204	1.290
P	0.73973	0.964	0.854	0.804	0.859	0.806	0.831	0.823
S	2.09069	2.203	2.128	2.029	2.070	2.083	2.063	2.069
Cl	3.66173	3.672	3.626	3.490	3.517	3.583	3.524	3.544
Mean abs. error		0.124	0.090	0.095	0.101	0.100	0.084	0.065
	First row	0.159	0.109	0.060	0.080	0.140	0.054	0.054
	Second row	0.088	0.071	0.130	0.122	0.059	0.114	0.077

[a] This work: best *ab initio* minus spin-orbit and scalar relativistic contributions.

[b] $(\frac{2}{3})$mPW1LYP$+(\frac{1}{3})$mPW1PW91.

TABLE VI. Basis set convergence of computed electron affinities (in eV) for selected exchange-correlation functionals.

	G96PW91/				mPW1LYP/			
	AVDZ	AVTZ	AVQZ	AV5Z	AVDZ	AVTZ	AVQZ	AV5Z
H	0.6825	0.7019	0.7054	0.7210	0.7270	0.7504	0.7550	0.7703
B	0.5289	0.5376	0.5422	0.5565	0.3064	0.3123	0.3205	0.3317
C	1.5097	1.5141	1.5132	1.5194	1.1998	1.2004	1.2050	1.2113
O	1.5914	1.5929	1.5950	1.6041	1.4921	1.4910	1.4950	1.5015
F	3.5496	3.5189	3.5096	3.5106	3.3590	3.3216	3.3170	3.3184
Al	0.5372	0.5374	0.5315	0.5346	0.3342	0.3341	0.3381	0.3412
Si	1.4580	1.4555	1.4434	1.4439	1.2094	1.2060	1.2035	1.2042
P	0.7601	0.8025	0.7961	0.8021	0.7932	0.8285	0.8268	0.8312
S	2.0850	2.0751	2.0668	2.0676	2.0747	2.0642	2.0623	2.0626
Cl	3.6204	3.5749	3.5637	3.5621	3.5769	3.5301	3.5259	3.5244

proaches, then the optimum hybrid could be determined by minimizing the mean absolute error of a linear combination $aEA_{\mathrm{mPW1LYP}}+(1-a)EA_{\mathrm{mPW1PW91}}$ in terms of a. This procedure shows some similarity with the ''empirical density functionals'' recently proposed by Adamson, Gill, and Pople [85]. As it happens, we find the optimum value of a to be 0.669, or almost exactly $\frac{2}{3}$. This yields an overall mean absolute error of 0.07 eV, or 0.05 eV for first-row atoms and 0.08 eV for second-row atoms. Individual errors are for H -0.02, for B $+0.10$, for C $+0.01$, for O $+0.00$, for F -0.13, for Al -0.04, for Si -0.13, for P $+0.08$, for S -0.02, and for Cl -0.12 eV—in fact, the value for O accidentally agrees with the *ab initio* value to four figures. The present results can be considered very promising for the accurate calculation of electron affinities of large molecular systems.

IV. CONCLUSIONS

We have carried out *ab initio* calibration calculations of the electron affinities of the first-and second-row atoms. Our calculations include extrapolations to the infinite-basis limit as well as corrections for scalar relativistic and spin-orbit effects. Our best *ab initio* values agree with the most recent experimental values to within better than 0.001 eV on average. Neglect of correlation effects beyond CCSD(T) causes an increase in the mean absolute error by an order of magnitude. Inner-shell correlation is most important for the early second-row elements, while scalar relativistic effects are quite important for the later second-row elements. Neglect of electron correlation effects on the scalar relativistic contributions leads to significant overestimates, while inclusion of subvalence correlation is essential for accurate spin-orbit splitting constants for the second-row elements.

The DFT results are essentially converged with respect to extension of the basis set at the AVTZ level. The performance of DFT methods for the first-row atoms is very strongly dependent on the quality of the exchange functional, while this is not the case for second-row atoms, where the correlation functional appears to be rather more important. While the LYP correlation functional works best for first-row atoms, its PW91 counterpart appears to be preferable for second-row atoms. Among pure DFT (nonhybrid) functionals, G96PW91 (Gill 1996 exchange combinated with Perdew-Wang 1991 correlation) puts in the best overall performance, actually slightly better than the popular hybrid B3LYP functional. B3PW91 outperforms B3LYP, while the recently proposed one-parameter hybrid functionals such as B1LYP appear to be clearly superior to B3LYP and B3PW91 for first-row atoms. mPW1LYP puts in the overall best performance for first-row atoms, while mPW1PW91 yields the best results for second-row atoms. The best overall performance appears to be afforded by an empirical superposition of these functionals, $(\frac{2}{3})$mPW1LYP $+(\frac{1}{3})$mPW1PW91.

Note added in proof. After acceptance of the present paper, we became aware of a recent study [M. Scheer, R. C. Bilodeau, C. A. Brodie, and H. K. Haugen, Phys. Rev. A **58**, 2844 (1998)] concerning remeasurements of the electron affinities of C, Si, Ge, and Sn. While the improved EA(Si) reported, 1.389 521(20) eV, differs insignificantly (for our purposes) from the previous measurement [21] of 1.389 46(6) eV quoted in Table I, the new EA(C) of 1.262 119(20) eV represents a slight downward revision of the experimental value of 1.2629(3) eV [17] quoted in Table I. Hence, our best calculated EA(C), which agreed to four figures with Ref. [17], in fact lies 0.000 77 above the best available experimental result.

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