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Rick A. Kendall, Thom H. Dunning, and Robert J. Harrison

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Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions

Rick A. Kendall and Thom H. Dunning, Jr.

Molecular Science Software Group; Theory, Modeling, and Simulation; Molecular Science Research Center; Pacific Northwest Laboratory; Richland, Washington 99352

Robert J. Harrison

Theoretical Chemistry Group, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

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The calculation of accurate electron affinities (EAs) of atomic or molecular species is one of the most challenging tasks in quantum chemistry. We describe a reliable procedure for calculating the electron affinity of an atom and present results for hydrogen, boron, carbon, oxygen, and fluorine (hydrogen is included for completeness). This procedure involves the use of the recently proposed correlation-consistent basis sets augmented with functions to describe the more diffuse character of the atomic anion coupled with a straightforward, uniform expansion of the reference space for multireference singles and doubles configuration-interaction (MRSD-CI) calculations. Comparison with previous results and with corresponding full CI calculations are given. The most accurate EAs obtained from the MRSD-CI calculations are (with experimental values in parentheses) hydrogen 0.740 eV (0.754), boron 0.258 (0.277), carbon 1.245 (1.263), oxygen 1.384 (1.461), and fluorine 3.337 (3.401). The EAs obtained from the MR-SDCI calculations differ by less than 0.03 eV from those predicted by the full CI calculations.

I. INTRODUCTION

The calculation of accurate atomic or molecular electron affinities (EAs),

$$\begin{aligned} \text{EA} &= E(\text{neutral}) - E(\text{anion}) \\ &= [E_{\text{HF}}(\text{neutral}) - E_{\text{HF}}(\text{anion})] \\ &\quad + [E_{\text{corr}}(\text{neutral}) - E_{\text{corr}}(\text{anion})] \\ &= \Delta E_{\text{HF}}(\text{EA}) + \Delta E_{\text{corr}}(\text{EA}), \end{aligned} \quad (1)$$

has proven to be one of the most difficult tasks facing modern computational quantum chemistry.¹⁻²⁰ The inability of the Hartree-Fock (HF) or self-consistent-field (SCF) and small multiconfiguration SCF (MCSCF) approaches to predict accurate EAs is well documented.¹⁻²⁰ The correlation energy of the anion with an additional, though weakly bound, electron is substantially larger than that of the neutral. As a result, high levels of electron correlation are required to obtain a balanced description of the correlation energies of the two moieties.¹⁻⁴ Over the years, the full range of variational and perturbative methodologies have been applied to this problem with limited success. This has been attributed to inadequacies of the basis sets and/or the wave functions used in the calculations. The basis sets and wave functions must be chosen carefully as to not bias the calculation toward either moiety and to obtain a comparable level of correlation energy in each calculation.

This study utilizes a series of basis sets that systematically increase in size and flexibility coupled with a methodology that accounts for a systematic increase in the fraction of electron correlation energy recovered. Both the basis sets and wave functions are expanded in a consistent and straightforward manner to produce accurate predictions of the electron affinities of hydrogen, boron, carbon, oxygen, and fluorine.

Nitrogen and neon have near-zero or negative electron affinities and are not specifically included in this study,¹⁰ although basis sets will be reported for both of these atoms.

The purpose of this paper is to show that atomic EAs can be predicted in an effective and efficient manner with the proper choice of basis sets and wave functions. In addition, we report basis sets that can be used for molecular anion calculations or, in fact, any calculation that is dependent on an accurate description of the long-range nature of the wave function (e.g., hydrogen bonded systems).²¹ In Sec. II, we briefly describe the basis sets and wave functions used. In Sec. III, the results of our calculations are presented. A comparison to previous work and discussion is presented in Sec. IV and conclusions are drawn in Sec. V.

II. METHODOLOGY

A. Basis sets

The basis sets used to calculate the EAs of the first-row atoms are derived from the recently proposed correlation-optimized basis sets.²² These basis sets were considered as the "root" neutral sets. To describe the more diffuse charge distributions of the anions the neutral sets were augmented with additional functions optimized for the atomic anions. Briefly, a set of primitive *s* and *p* functions was added to the (*sp*) sets of each of the correlation-consistent basis sets, polarized valence double-zeta (cc-pVDZ), triple-zeta (cc-pVTZ), and quadruple-zeta (cc-pVQZ), of the neutral atom and the exponents optimized for the anion SCF energy. Then, an additional primitive polarization function was added to each of the *l*-polarization sets present in the neutral basis set, and the exponents of these functions were optimized for the Hartree-Fock plus single and doubles configuration-interaction (HF-SDCI) energy of the anion. This

procedure leads to three basis sets of ordered size and level of accuracy. The *augmented* correlation-consistent polarized valence double-zeta, triple-zeta, and quadruple-zeta basis sets obtained in this way have 23, 46, and 80 basis functions, respectively; the basis sets will be referred to as aug-cc-pVDZ, -pVTZ, and -pVQZ, respectively. (For each polarization function only the 5 *d* functions, 7 *f* functions, and 9 *g* functions were included.) The aug-cc-pVDZ basis has a primitive set of 10 *s* functions, 5 *p* functions, and 2 *d* functions generally contracted to 4*s*, 3*p*, and 2*d* functions [i.e., (10*s*5*p*2*d*)/[4*s*3*p*2*d*]]. The aug-cc-pVTZ and -pVQZ basis sets are (11*s*6*p*3*d* 2*f*)/[5*s*4*p*3*d* 2*f*] and (13*s*7*p*4*d* 3*f*2*g*)/[6*s*5*p*4*d* 3*f*2*g*], respectively.

Since the basis sets employed here are valence basis sets, no attempt has been made to estimate or recover contributions associated with correlation effects involving the 1*s* core orbital. Both Sasakai and Yoshimine⁹ and Feller and Davidson² found that exclusion of core and core-valence interactions increased the calculated EAs by less than 0.02 eV. Also, no estimate has been made for the contribution of relativistic effects. For all except hydrogen, the anions differ from the neutrals by addition of an electron in a 2*p* orbital. Thus, relativistic effects should contribute insignificantly to the calculated electron affinities.^{1-4,8,9}

B. Wave functions

The wave functions used in the present calculations are multireference singles and doubles configuration-interaction wave functions (MR-SDCI) with selected orbital sets and excitation levels included in the MCSCF reference space. To generate a systematic series of reference spaces, the orbitals used in each MCSCF reference space were {2*s*2*p*2*p'*}, {2*s*2*s'*2*p*2*p'*}, {2*s*2*s'*2*p*2*p'*2*p''*}, and {2*s*2*s'*2*p*2*p'*3*d*}; the HF reference space is, of course, just {2*s*2*p*}. For each of these orbital sets, two MCSCF wave functions were considered. The first was the standard com-

plete-active-space MCSCF (CAS SCF) wave function and the other was an “*n*-electron reduced CAS” (*n*-CAS) wave function. In the *n*-electron reduced CAS wave function, only *n* electrons are allowed in the non-HF valence orbitals. With *n* = 2, the *n*-electron reduced CAS reproduces the full CAS SCF and CAS MR-SDCI results quite well (see Tables III–VI) while significantly reducing the total cost of the calculation. Note that the most important triple and quadruple excitations (relative to the HF) are included in the “*n*-electron reduced CAS” MR-SDCI wave functions as single and double excitations from the important single and double excitations included in the 2-CAS wave function. We have chosen a total of seven different reference wave functions for use in this study: HF, CAS(2*s*2*p*2*p'*), 2-CAS(2*s*2*p*2*p'*), CAS(2*s*2*s'*2*p*2*p'*), 2-CAS(2*s*2*s'*2*p*2*p'*), 2-CAS(2*s*2*s'*2*p*2*p'*2*p''*), and 2-CAS(2*s*2*s'*2*p*2*p'*3*d*). All MCSCF and MR-SDCI calculations were done with the COLUMBUS suite of electronic structure codes.²³ The HF calculations were performed with the GVB164 code of the QUEST package.²⁴

The effect of higher excitations is estimated by the use of the MCSCF analog of the Davidson correction,²⁵ (MR-SDCI + Q):

$$E_{+Q} = \left(1 - \sum C_{\text{ref}}^2\right)(E_{\text{CI}} - E_{\text{ref}}), \quad (3)$$

where the sum is over all of the configurations included in the reference set, E_{ref} is the corresponding expectation value, and E_{CI} is the MR-SDCI energy. Where possible, a full CI calculation was also done to establish the accuracy of the wave functions described above. The full CI calculations were based on HF orbitals with symmetry and equivalence restrictions and with the 1*s* core orbital frozen.²⁶ When the full CI expansion was prohibitively large, the “selection-plus-perturbation-correction” scheme of Harrison²⁷ was used. This approach affords us the ability to estimate the full

TABLE I. Optimum exponents (ζ) of the augmenting functions for describing the oxygen anion. HF-SDCI energies are in hartree, electron affinities (EA) in eV. Δ EA is the difference between the current and preceding EA, i.e., the incremental increase in the EA.

Basis Set	$\zeta(s,p,d,f,g)$	$E_{\text{HF-SDCI}}$			
		$E(\text{anion})$	$E(\text{atom})$	EA	Δ EA
aug-cc-pVDZ					
cc-pVDZ		− 74.868 76	− 74.907 26	− 1.048	
+ (<i>sp</i>)	0.078 96(<i>s</i>), 0.068 56(<i>p</i>)	− 74.942 12	− 74.913 53	0.778	1.825
+ (<i>spd</i>)	0.332(<i>d</i>)	− 74.956 40	− 74.921 49	0.950	0.172
aug-cc-pVTZ					
cc-pVTZ		− 74.970 00	− 74.968 45	0.042	
+ (<i>sp</i>)	0.073 76(<i>s</i>), 0.059 74(<i>p</i>)	− 75.002 43	− 74.969 82	0.887	0.845
+ (<i>spd</i>)	0.214(<i>d</i>)	− 75.006 29	− 74.970 85	0.964	0.077
+ (<i>spdf</i>)	0.500(<i>f</i>)	− 75.009 90	− 74.972 78	1.010	0.046
aug-cc-pVQZ					
cc-pVQZ		− 75.006 98	− 74.987 07	0.542	
+ (<i>sp</i>)	0.069 59(<i>s</i>), 0.053 48(<i>p</i>)	− 75.023 92	− 74.987 44	0.993	0.451
+ (<i>spd</i>)	0.154(<i>d</i>)	− 75.025 14	− 74.987 60	1.022	0.029
+ (<i>spdf</i>)	0.324(<i>f</i>)	− 75.026 18	− 74.987 93	1.041	0.019
+ (<i>spdfg</i>)	0.714(<i>g</i>)	− 75.027 47	− 74.988 53	1.060	0.019

CI energy for relatively large basis sets. The "selection-plus-perturbation-correction" methodology is superior to other selection schemes^{28,2,29-31} due to the lack of *ad hoc* or extrapolation procedures. Harrison's implementation also facilitates the efficient use of the distributed parallel computing environment available to us. Without parallel software the CPU cycles needed to compute the estimated full CI results would not have been available to us. Our parallel computing environment consists of two Intel iPSC/860 machines (one with 16 nodes, the other with 64 nodes³²) and of a distributed network of workstations (Sun 1's, 1 + 's, 4/330's, SGI 4D/35's and a 4D/340, and a DECStation 5000).

III. RESULTS

The exponents of the primitive Gaussian functions used to augment the neutral correlation-consistent basis sets of the oxygen atom for anionic calculations are listed in Table I along with the corresponding energies of the oxygen anion and atom. The incremental increases in the calculated EAs resulting from addition of the diffuse functions to the neutral basis sets are plotted in Fig. 1. As can be seen, addition of a set of diffuse (*sp*) functions to the neutral basis sets is critical for an accurate description of the anion, increasing the EAs by 1.825 (-pVDZ), 0.845 (-pVTZ), and 0.451 eV (-pVQZ); in line with previous experience, the effect of the diffuse *p* function is dominant. There is a nearly exponential decrease in $\Delta EA(+sp)$ as the neutral basis set increases in size.

Addition of diffuse (*dfg*) functions to the neutral basis set has a far less dramatic effect on the calculated EAs, although they are quantitatively important, increasing the calculated EAs by 0.172 (-pVDZ), 0.123 (-pVTZ), and 0.067 eV (-pVQZ). There is also a nearly exponential decrease in $\Delta EA(+d)$ as the neutral basis set increases in size. Although the general trend is for $\Delta EA(l)$ to decrease with increasing *l*-quantum number, $\Delta EA(g)$ is the same as $\Delta EA(f)$ for the aug-cc-pVQZ basis set.

Optimum exponents for the diffuse primitive Gaussian functions used to augment the cc-pVDZ, -pVTZ, and

TABLE II. Optimum exponents for the diffuse functions to augment the neutral basis sets for hydrogen and the first-row atoms B–Ne. The exponents quoted for the polarization functions of nitrogen (and all of the functions for neon) were obtained by polynomial interpolation (extrapolation) from the exponents of B–F.

	Augmenting functions				
	$\zeta(s)$	$\zeta(p)$	$\zeta(d)$	$\zeta(f)$	$\zeta(g)$
Hydrogen					
cc-pVDZ	0.029 74	0.727			
cc-pVTZ	0.025 26	0.102	0.247		
cc-pVQZ	0.023 63	0.084 8	0.190	0.360	
Boron					
cc-pVDZ	0.031 05	0.023 78	0.0904		
cc-pVTZ	0.029 14	0.020 96	0.0604	0.163	
cc-pVQZ	0.027 21	0.018 78	0.0466	0.113	0.273
Carbon					
cc-pVDZ	0.046 90	0.040 41	0.151		
cc-pVTZ	0.044 02	0.035 69	0.100	0.268	
cc-pVQZ	0.041 45	0.032 18	0.0766	0.187	0.424
Nitrogen					
cc-pVDZ	0.061 24 ^a	0.056 11 ^a	0.230		
cc-pVTZ	0.057 60 ^b	0.049 10 ^b	0.151	0.364	
cc-pVQZ	0.054 64 ^c	0.044 02 ^c	0.111	0.245	0.559
Oxygen					
cc-pVDZ	0.078 96	0.068 56	0.332		
cc-pVTZ	0.073 76	0.059 74	0.214	0.500	
cc-pVQZ	0.069 59	0.053 48	0.154	0.324	0.714
Fluorine					
cc-pVDZ	0.098 63	0.085 02	0.464		
cc-pVTZ	0.091 58	0.073 61	0.292	0.724	
cc-pVQZ	0.085 94	0.065 68	0.207	0.460	0.924
Neon					
cc-pVDZ	0.123 0	0.106 4	0.631		
cc-pVTZ	0.113 3	0.091 75	0.386	1.084	
cc-pVQZ	0.105 4	0.081 78	0.273	0.689	1.224

^a The interpolated (*sp*) exponents for the cc-pVDZ set are 0.062 29(*s*) and 0.054 52(*p*).

^b The interpolated (*sp*) exponents for the cc-pVTZ set are 0.058 40(*s*) and 0.047 86(*p*).

^c The interpolated (*sp*) exponents for the cc-pVQZ set are 0.055 17(*s*) and 0.043 03(*p*).

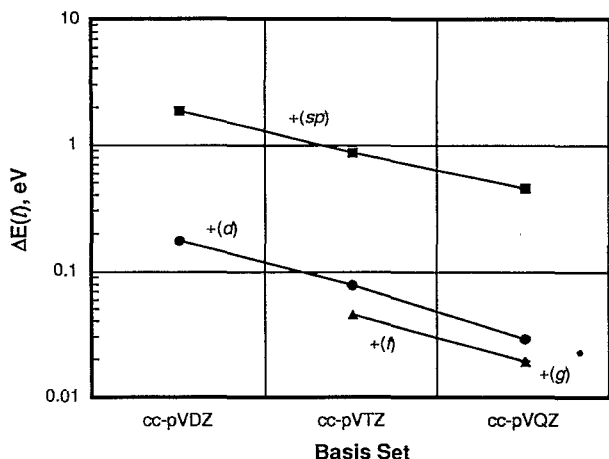


FIG. 1. Incremental increases in the calculated electron affinity (EA) of the oxygen atom resulting from the addition of diffuse functions to the neutral basis set.

-pVQZ basis sets for the hydrogen atom and the first-row atoms boron–neon are listed in Table II. Complete listings of both the correlation-consistent and augmented correlation-consistent basis sets will be published elsewhere.³³ Exponents for both nitrogen and neon are reported in Table II despite the fact that bound negative ions do not exist for these atoms. The exponents of the (*sp*) diffuse functions for the nitrogen atom were obtained from HF calculations on the ³P state of N⁻. Because of the use of symmetry and equivalence restrictions in these calculations, the wave functions so obtained for the nitrogen anion are not the lowest-energy solution that would correspond to N(⁴S) + e. The exponents for the augmenting polarization functions for nitrogen (and all of the exponents for the neon atom) were obtained by interpolation (extrapolation) of a cubic polynomial obtained from the calculated exponents of B, C, O, and F. For nitrogen, the calculated and interpolated exponents for the (*sp*) functions differ by less than 3% (see Table II).

TABLE III. HF-SDCI, MR-SDCI, and full CI energies for the boron atom and anion* (in hartree); electron affinities (EA) in eV.

Basis	Reference	E_{CI} (anion)	E_{CI} (atom)	EA
aug-cc-pVDZ	HF	-24.595 18	-24.591 26	0.107
	2-CAS(2p2p')	-24.596 24	-24.590 43	0.158
	CAS(2p2p')	-24.596 24	-24.590 43	0.158
	2-CAS(2s2s'2p2p')	-24.597 94	-24.591 36	0.179
	CAS(2s2s'2p2p')	-24.597 95	-24.591 36	0.179
	2-CAS(2s2s'2p2p'2p'')	-24.598 15	-24.591 37	0.185
	2-CAS(2s2s'2p2p'3d)	-24.598 34	-24.591 49	0.187
	Full CI	-24.598 46	-24.591 49	0.190
	aug-cc-pVTZ	HF	-24.604 03	-24.598 55
2-CAS(2p2p')		-24.604 43	-24.597 01	0.202
CAS(2p2p')		-24.604 42	-24.597 01	0.202
2-CAS(2s2s'2p2p')		-24.607 14	-24.598 83	0.226
CAS(2s2s'2p2p')		-24.607 15	-24.599 02	0.221
2-CAS(2s2s'2p2p'2p'')		-24.607 44	-24.598 85	0.234
2-CAS(2s2s'2p2p'3d)		-24.607 88	-24.598 86	0.245
Full CI		-24.608 03	-24.598 86	0.249
aug-cc-pVQZ		HF	-24.606 76	-24.600 99
	2-CAS(2p2p')	-24.607 02	-24.599 38	0.208
	CAS(2p2p')	-24.607 02	-24.599 38	0.208
	2-CAS(2s2s'2p2p')	-24.609 99	-24.601 20	0.239
	CAS(2s2s'2p2p')	-24.610 00	-24.601 29	0.237
	2-CAS(2s2s'2p2p'2p'')	-24.610 32	-24.601 31	0.245
	2-CAS(2s2s'2p2p'3d)	-24.610 80	-24.601 33	0.258
	Full CI	-24.610 97	-24.601 33	0.263
	EA (measured)			0.277
EA (error)			0.014	

* The electrons in the 1s core orbital were not correlated.

TABLE IV. HF-SDCI, MR-SDCI, and full/estimated full CI energies for the carbon atom and anion* (in hartree); electron affinities (EA) in eV.

Basis	Reference	E_{CI} (anion)	E_{CI} (atom)	EA
aug-cc-pVDZ	HF	-37.802 70	-37.764 07	1.051
	2-CAS(2p2p')	-37.805 95	-37.764 05	1.140
	CAS(2p2p')	-37.805 97	-37.764 05	1.141
	2-CAS(2s2s'2p2p')	-37.807 03	-37.765 09	1.141
	CAS(2s2s'2p2p')	-37.807 06	-37.765 09	1.142
	2-CAS(2s2s'2p2p'2p'')	-37.807 13	-37.765 09	1.144
	2-CAS(2s2s'2p2p'3d)	-37.807 70	-37.765 25	1.155
	Full CI	-37.807 74	-37.765 24	1.156
	aug-cc-pVTZ	HF	-37.820 86	-37.780 62
2-CAS(2p2p')		-37.824 75	-37.780 36	1.208
CAS(2p2p')		-37.824 77	-37.780 36	1.208
2-CAS(2s2s'2p2p')		-37.826 18	-37.781 84	1.207
CAS(2s2s'2p2p')		-37.826 22	-37.781 84	1.208
2-CAS(2s2s'2p2p'2p'')		-37.826 40	-37.781 90	1.211
2-CAS(2s2s'2p2p'3d)		-37.827 45	-37.782 27	1.229
Full CI		-37.827 54	-37.782 27	1.232
aug-cc-pVQZ		HF	-37.826 10	-37.785 50
	2-CAS(2p2p')	-37.830 13	-37.785 21	1.223
	CAS(2p2p')	-37.830 15	-37.785 21	1.223
	2-CAS(2s2s'2p2p')	-37.831 66	-37.786 54	1.228
	CAS(2s2s'2p2p')	-37.831 70	-37.786 78	1.222
	2-CAS(2s2s'2p2p'2p'')	-37.831 89	-37.786 62	1.232
	2-CAS(2s2s'2p2p'3d)	-37.833 07	-37.787 32	1.245
	Full CI ^b	-37.833 03	-37.787 23	1.246
	EA (measured)			1.263
EA (error)			0.017	

* The electrons in the 1s core orbital were not correlated.

^b Full CI estimate using the "selection plus perturbation theory" methodology (Ref. 27).

TABLE V. HF-SDCI, MR-SDCI, and full/estimated full CI energies for the oxygen atom and anion* (in hartree); electron affinities (EA) in eV.

Basis	Reference	E_{CI} (anion)	E_{CI} (atom)	EA
aug-cc-pVDZ	HF	-74.956 33	-74.921 63	0.944
	2-CAS(2p2p')	-74.967 21	-74.924 35	1.166
	CAS(2p2p')	-74.967 51	-74.924 37	1.174
	2-CAS(2s2s'2p2p')	-74.968 78	-74.925 37	1.181
	CAS(2s2s'2p2p')	-74.968 96	-74.925 39	1.186
	2-CAS(2s2s'2p2p'2p'')	-74.969 11	-74.925 41	1.189
	2-CAS(2s2s'2p2p'3d)	-74.970 02	-74.926 13	1.194
	Full CI	-74.970 35	-74.925 91	1.209
	aug-cc-pVTZ	HF	-75.009 95	-74.972 81
2-CAS(2p2p')		-75.023 42	-74.976 45	1.278
CAS(2p2p')		-75.023 81	-74.976 49	1.288
2-CAS(2s2s'2p2p')		-75.025 11	-74.977 68	1.290
CAS(2s2s'2p2p')		-75.025 70	-74.977 72	1.306
2-CAS(2s2s'2p2p'2p'')		-75.026 08	-74.977 88	1.311
2-CAS(2s2s'2p2p'3d)		-75.027 81	-74.979 25	1.321
Full CI ^b		-75.028 51	-74.979 13	1.344
aug-cc-pVQZ		HF	-75.027 47	-74.988 53
	2-CAS(2p2p')	-75.041 45	-74.992 32	1.337
	CAS(2p2p')	-75.041 85	-74.992 37	1.347
	2-CAS(2s2s'2p2p')	-75.043 31	-74.993 59	1.353
	CAS(2s2s'2p2p')	-75.043 93	-74.993 63	1.369
	2-CAS(2s2s'2p2p'2p'')	-75.044 37	-74.993 87	1.374
	2-CAS(2s2s'2p2p'3d)	-75.046 31	-74.995 44	1.384
	Full CI ^b	-75.046 67	-74.995 19	1.401
	EA (measured)			1.461
EA (error)			0.060	

*The electrons in the 1s core orbital were not correlated.

^bFull CI estimate using the "selection plus perturbation theory" methodology (Ref. 27).

TABLE VI. HF-SDCI, MR-SDCI, and estimated full CI energies for the fluorine atom and anion* (in hartree); electron affinities (EA) in eV.

Basis	Reference	E_{CI} (anion)	E_{CI} (atom)	EA
aug-cc-pVDZ	HF	-99.653 35	-99.544 10	2.973
	2-CAS(2p2p')	-99.666 06	-99.548 52	3.199
	CAS(2p2p')	-99.666 58	-99.548 56	3.211
	2-CAS(2s2s'2p2p')	-99.667 20	-99.549 39	3.206
	CAS(2s2s'2p2p')	-99.667 88	-99.549 44	3.223
	2-CAS(2s2s'2p2p'2p'')	-99.667 76	-99.549 45	3.219
	2-CAS(2s2s'2p2p'3d)	-99.668 67	-99.550 39	3.219
	Full CI ^b	-99.669 32	-99.550 29	3.239
	aug-cc-pVTZ	HF	-99.727 85	-99.618 62
2-CAS(2p2p')		-99.743 83	-99.624 65	3.243
CAS(2p2p')		-99.744 55	-99.624 73	3.260
2-CAS(2s2s'2p2p')		-99.745 34	-99.625 66	3.257
CAS(2s2s'2p2p')		-99.746 30	-99.625 79	3.279
2-CAS(2s2s'2p2p'2p'')		-99.746 39	-99.625 95	3.277
2-CAS(2s2s'2p2p'3d)		-99.748 21	-99.627 80	3.276
Full CI ^b		-99.749 46	-99.627 88	3.308
aug-cc-pVQZ		HF	-99.753 70	-99.642 79
	2-CAS(2p2p')	-99.770 40	-99.649 13	3.300
	CAS(2p2p')	-99.771 12	-99.649 21	3.317
	2-CAS(2s2s'2p2p')	-99.772 14	-99.650 35	3.314
	CAS(2s2s'2p2p')	-99.773 12	-99.650 48	3.337
	2-CAS(2s2s'2p2p'2p'')	-99.773 25	-99.650 58	3.338
	2-CAS(2s2s'2p2p'3d)	-99.775 32	-99.652 69	3.337
	Full CI ^b	-99.776 17	-99.652 55	3.364
	EA (measured)			3.401
EA (error)			0.037	

*The electrons in the 1s core orbital were not correlated.

^bFull CI estimate using the "selection plus perturbation theory" methodology (Ref. 27).

TABLE VII. Full CI energies for the hydrogen atom and anion^a (in hartree); electron affinities (EA) are in eV.

Basis	Calculation	$E(\text{anion})$	$E(\text{atom})$	EA
aug-cc-pVDZ	HF + 1 + 2	-0.524 03	-0.499 33	0.672
aug-cc-pVTZ	HF + 1 + 2	-0.526 56	-0.499 82	0.728
aug-cc-pVQZ	HF + 1 + 2	-0.527 14	-0.499 95	0.740
EA (measured)				0.754
EA (error)				0.014

Tables III–VI contain the atomic and anionic MR-SDCI and full (or estimated full) CI energies and EAs for boron–fluorine for each of the seven reference functions (HF and six MCSCF wave functions) and the three basis sets considered here. For completeness, Table VII includes the corresponding data for hydrogen. Since our goal is to systematically determine the EA for a given atom, we have done so by systematically varying the size and flexibility of both the basis set and the reference wave function as discussed above. The convergence of the calculated EA as a function of these two global parameters is shown in Fig. 2 for the oxygen atom. As the flexibility of the basis set and reference wave function increases, the predicted EA approaches the experimental result. The convergence pattern displayed in Fig. 2 for oxygen is qualitatively the same for the rest of the first-row atoms considered in this work.

IV. DISCUSSION

In the following four subsections, we discuss the results of the MR-SDCI and full CI calculations of the electron affinities of the boron, carbon, oxygen, and fluorine atoms. In the first subsection, we discuss the effect of a systematic expansion of the reference space for the most accurate basis

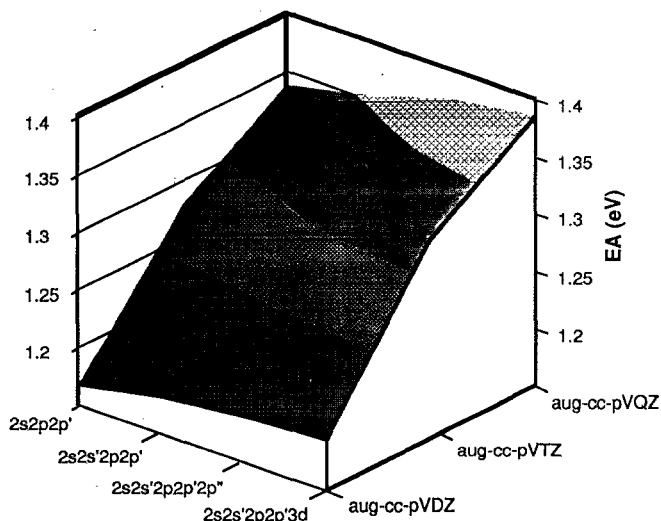


FIG. 2. Convergence of the electron affinity of oxygen with reference space and basis set.

set considered here, the aug-cc-pVQZ set. In the second subsection, we discuss the effect of increasing flexibility in the basis set for both the 2-CAS($2s2s'2p2p'3d$) MR-SDCI and full CI calculations. Finally, in the last two subsections, we compare the present calculations with experimental results and with a selection of prior calculations.

A. Systematic expansion of the orbital reference space

The errors in the EAs obtained by systematic expansion of the orbital reference space in the MR-SDCI calculations, relative to the full CI results, are plotted in Fig. 3 for the aug-cc-pVQZ basis set. To begin, it should be noted that the errors in the HF-SDCI EAs are approximately equal for bo-

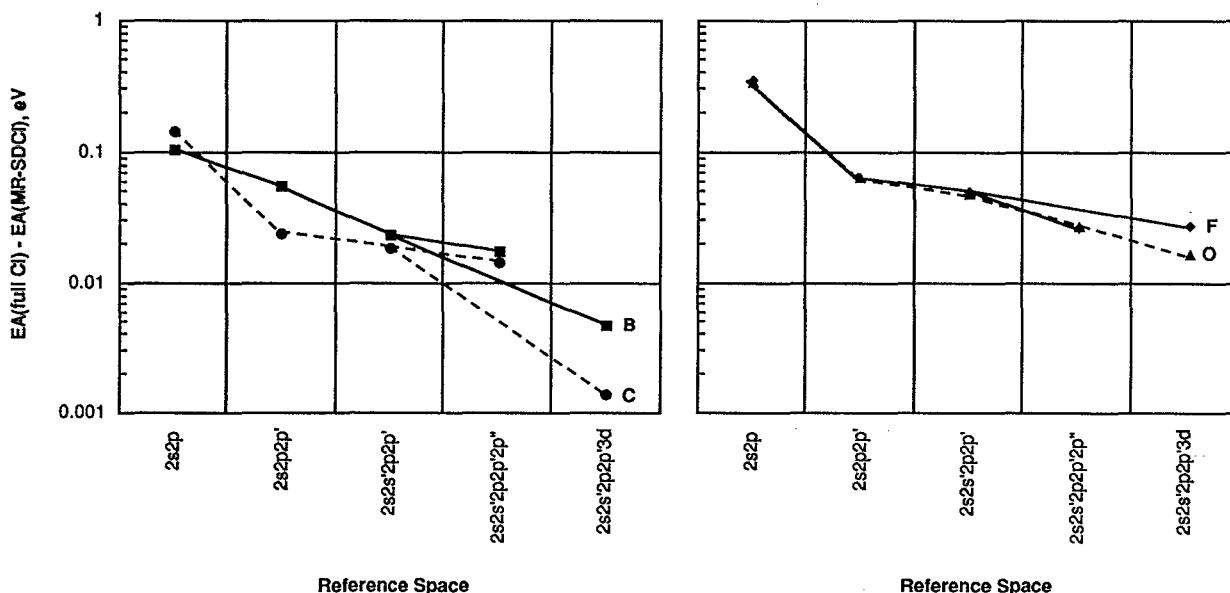


FIG. 3. Errors in the electron affinities obtained from the MR-SDCI calculations relative to those from the corresponding full CI calculations.

ron and carbon (0.105 vs 0.142 eV) and for oxygen and fluorine (0.341 vs 0.346 eV). That the errors are substantially larger for oxygen and fluorine is expected since, for these atoms, addition of the "extra" electron gives rise to an additional doubly occupied orbital in the HF wave function.

For boron the single most important orbital to add to the ($2s2p$) Hartree-Fock space is the $2p'$ orbital. Inclusion of the $2p'$ orbital in the reference space reduces the error in the calculated EA, measured relative to the full CI result, by 48% for the aug-cc-pVQZ basis set. For the other first-row atoms, the $2p'$ orbital is even more important, reducing the errors in the calculated EAs by 83% (C), 81% (O), and 82% (F). The importance of the $2p'$ orbital was first noted and discussed by Botch and Dunning.⁷ As those authors pointed out, atomic negative ions are best described by the configuration $2p^n 2p_{n+1}$. The $2p$ orbital in the anion is similar to the $2p$ orbital of the neutral atom; the $2p_{n+1}$ orbital, on the other hand, is weakly bound ($\epsilon \approx -EA$) and, thus, is far more diffuse. This wave function is well described by the two configurations: $2s^2 2p^n - \lambda 2s 2p^n - 2p'^2$.

Addition of the $2s'$ orbital to the reference space in boron reduces the error in the calculated EA by another 30%. For carbon, oxygen, and fluorine, on the other hand, inclusion of the $2s'$ orbital in the reference set reduces the error by only 4%–5%. Although the percentage correction is large for the boron atom, it should be noted that the absolute magnitude, 0.021 eV, is quite small. In his calculations on the neutral first-row atoms, Dunning²² found that s functions were far more important for boron than for the other first-row atoms. The present results indicate that s orbitals are more important for a proper description of the boron anion than for the other first-row anions.

Addition of a $2p''$ orbital to the ($2s2s'2p2p'$) reference space reduces the error by only 3% for carbon and 6%–7% for boron, oxygen, and fluorine. Addition of a $3d$ orbital to this same reference space reduces the error by a larger, but steadily declining, amount from boron to fluorine: 18% (B), 12% (C), 9% (O), and 7% (F). Of course, the absolute energy lowering resulting from the addition of the $3d$ orbital to the reference space increases substantially from boron (neutral: 0.0035 eV; anion: 0.022 eV) to fluorine (neutral: 0.064 eV; anion: 0.087 eV). However, the incremental change, $\Delta E(\text{anion-neutral})$, varies only slightly (B: 0.019 eV; C: 0.017 eV; O: 0.031; F: 0.023 eV) and that, coupled with the increasing errors in the HF-SDCI EAs along the series, accounts for the steady decline noted above.

In summary, for all of the atoms, except boron, the importance of the orbitals included in the reference space decreases in the series: $2p' \gg 3d > 2p'' \approx 2s'$. For boron, the $2s'$ orbital is more important than the $3d$ orbital, although the absolute difference is small (0.01 eV). The 2-CAS($2s2s'2p2p'3d$) MR-SDCI calculations obtain over 98% of the corresponding full CI EAs. This indicates that the aug-cc-pVQZ basis set and 2-CAS($2s2s'2p2p'3d$) wave functions do indeed yield a well-balanced description of both the neutral and the anion.

The electron affinities obtained using the Davidson correction are compared with the uncorrected and full CI results in Table VIII for the 2-CAS($2s2s'2p2p'3d$) MR-SDCI

TABLE VIII. Electron affinities (EAs) obtained from MR-SDCI calculations, with and without the Davidson correction and full CI calculations. The MR-SDCI calculations were based on the 2-CAS($2s2s'2p2p'3d$) reference space and used the aug-cc-pVQZ basis set.

	MR-SDCI	MR-SDCI + Q	Full CI
Boron	0.258	0.276	0.263
Carbon	1.245	1.252	1.246
Oxygen	1.384	1.415	1.401
Fluorine	3.337	3.363	3.364

calculations. For all of the atoms, except fluorine, use of the Davidson correction results in EAs that are larger than those obtained from the full CI calculations.

Finally, the data for carbon in Table IV exhibit the expected variational behavior with two exceptions: the full CI energies for both the neutral and anion are higher than the 2-CAS($2s2s'2p2p'3d$) MR-SDCI energies. This can be attributed to the difference in the $1s$ core orbital used in the two calculations.

B. Systematic expansion of the basis set

The errors in the EAs obtained from the MR-SDCI calculations with the $2s2s'2p2p'3d$ reference space for each of the basis sets considered here are plotted in Fig. 4. As expected, the errors are larger for oxygen and fluorine than for the boron and carbon, with the error decreasing monotonically with expansion of the basis set. For oxygen the error drops nearly exponentially from 0.267 (-pVDZ) to 0.140 (-pVTZ) to 0.077 eV (-pVQZ). For fluorine, on the other hand, the error decreases nearly linearly from 0.182 (-pVDZ) to 0.124 (-pVTZ) to 0.064 eV (-pVQZ). For both boron and carbon, the error decreases dramatically as the basis is expanded from -pVDZ to -pVTZ, from 0.091 to 0.032 eV for boron and from 0.108 to 0.034 eV for carbon. Further expansion, to the -pVQZ basis set, decreases the errors only slightly to 0.019 (B) and 0.018 eV (C).

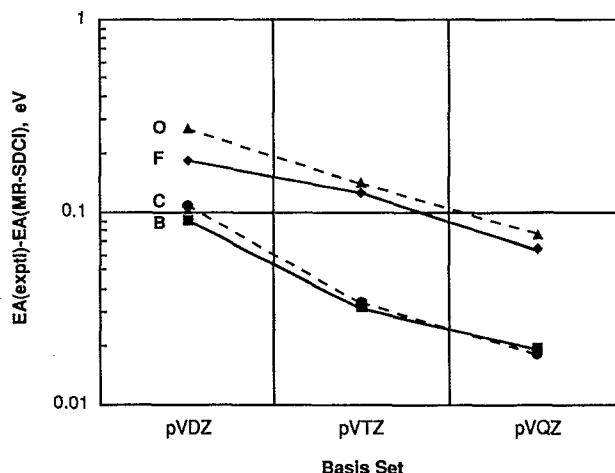


FIG. 4. Errors (relative to experiment) in the electron affinities from the MR-SDCI calculations with the ($2s2s'2p2p'3d$) reference space.

C. Comparison with experimental results

The recommended value for the EA of boron is 0.277 ± 0.010 eV.^{34–36} The EA obtained from the 2-CAS(2s2s'2p2p'3d) MR-SDCI calculations with the aug-cc-pVQZ basis set is 0.258 eV, which is less than the measured value by just 0.019 ± 0.010 eV. The full CI result for the aug-cc-pVQZ basis is 0.263 eV, which is in error by only 0.014 ± 0.010 eV. The EA estimated by adding the Davidson correction to the above MR-SDCI calculation, MR-SDCI + Q, is 0.276 eV, which is larger than that obtained from the full CI calculation and fortuitously equals the recommended value within experimental error.

The recommended EA of carbon is 1.2629 ± 0.0003 eV.^{34,35,37} The most accurate MR-SDCI and MR-SDCI + Q results are 1.245 and 1.252 eV, respectively. Thus, the EA obtained from the MR-SDCI calculations with the aug-cc-pVQZ basis set is in error by less than 1.5%. The estimated full CI result for the aug-cc-pVQZ basis set is 1.246 eV; this is not a complete CI expansion but an estimate based on Harrison's "selection plus perturbation correction" method.²⁷

The recommended EA for oxygen is 1.461122 ± 0.000003 eV.^{34,35,38} The estimated full CI result for the aug-cc-pVQZ basis set is 1.401 eV. This is 0.06 eV, or slightly over 4%, below the measured value. This is the largest error reported in the present work. The best MR-SDCI value (see Table IV) is 1.384 eV, which is 0.08 eV below the experimental value and 0.02 eV below that obtained in the full CI calculations. The MR-SDCI + Q result for the same basis and reference wave function is 1.415 eV, just 0.05 eV below the experimental value.

Because of the large error in the calculated EA of oxygen, let us consider this case further. There are three sources of error in the calculated EAs: truncation of the reference orbital space, the *n*-electron space limitation, and truncation of the basis set. The data listed in Table V allow us to estimate the magnitude of these errors. For example, by comparing the 2-CAS(2s2s'2p2p') and 2-CAS(2s2s'2p2p'2p''), we see that omission of the 2p'' orbital in the reference space reduces the calculated EA by 0.021 eV. Similarly, comparing the 2-CAS(2s2s'2p2p') and CAS(2s2s'2p2p') calculations, we find that limiting the number of electrons in the unoccupied HF orbitals in the CAS wave function to two decreases the calculated EA by 0.016 eV. Finally, from the nearly exponential decrease in the error with increasing basis set size, we estimate that expansion of the basis set to an aug-cc-pV5Z set would reduce the error by 0.035 eV. If these three errors are assumed to be additive, which is a reasonable assumption given the nature of the errors, they account for nearly all of the difference between the calculated and experimental EA.

Finally, the recommended EA for fluorine is 3.401190 ± 0.000004 eV.³⁹ The MR-SDCI calculations with the aug-cc-pVQZ basis set yield 3.337 eV; addition of the Davidson correction yields 3.363 eV. The calculated EAs are 0.06 and 0.04 eV below the recommended value, respectively. The EA obtained from the full CI calculations with this basis set is 3.364 eV, which differs from experimental result by just 0.04 eV or slightly more than 1%.

As is evident from the previous discussion, use of the Davidson correction often yields an EA that is more accurate than that obtained from the corresponding full CI calculations. It might be argued that the MR-SDCI + Q method overestimates the correction to the anion energy and, thus, fortuitously predicts a more accurate EA. This is quite likely the case, but we cannot be absolutely certain because the full CI calculations were performed with the averaged HF orbitals and not the MCSCF orbitals of the 2-CAS(2s2s'2p2p'3d) wave functions. Therefore, both the core energies and the core–valence interactions will be somewhat different for the two CI calculations. This could account for a significant fraction of the observed differences of 0.01–0.03 eV in the calculated EAs.^{1,5,8,9}

Table VII contains the full CI data and EAs for the hydrogen atom. The aug-cc-pVQZ basis yields an EA of 0.740 eV which is 0.014 eV below the recommended value of 0.754 eV.^{34,35,40} The results for hydrogen are included here simply for completeness; there will be no further discussion of these results.

D. Comparison with previous calculations

First, it should be noted that, for the basis sets used in the current study, the HF EAs differ from the exact HF EAs (Ref. 41) by only 0.001 eV (-pVDZ)–0.0001 eV (-pVQZ) for boron to 0.06 eV (-pVDZ)–0.005 eV (-pVQZ) eV for fluorine. Thus, in Eq. (2), ΔE_{HF} converges rapidly compared to ΔE_{corr} . The challenge in computing accurate EAs lies in computation of the differences in the correlation energies of the neutral and anion.

Table IX contains a comparison of our work with a selection of other computational studies of the electron affinity of the first-row atoms. Let us first consider Raghavachari's work.⁶ This author used a basis set of approximately valence pVTZ quality, (7s6p4d2f), and Møller–Plesset perturbation theory through fourth order (MP4).⁴² He also used coupled-cluster theory including all double substitutions with various approximations for the effect of single and triple substitutions [CCD + (ST)].⁴³ The MP4 EAs reported for boron, carbon, and oxygen are quite impressive, although the EA obtained for fluorine overestimates the observed result by 0.09 eV. The CCD + (ST) results are less impressive but predict the EAs to within 0.1 eV (see Table IX). Feller and Davidson² showed that these methods typically overestimate the full CI EA by as much as 0.1 eV. The EAs obtained from the full CI calculations with the aug-cc-pVTZ and -pVQZ basis sets reconfirm this finding. For example, the EA reported for carbon by Raghavachari is 1.26 eV. The present full CI calculations yield 1.23 eV (aug-cc-pVTZ) and 1.25 eV (aug-cc-pVQZ). If the MP4 methodology actually recovered most of the correlation energy, one would expect the MP4 result to be no more than 1.24 eV.

The MCSCF calculations of Botch and Dunning⁷ are similar in spirit to the MR-SDCI calculations reported here. The EAs obtained by these authors are less than those obtained here by 0.06–0.14 eV for carbon, 0.10–0.28 eV for oxygen, and 0.039–0.16 eV for fluorine. These differences can be attributed to the balanced and consistent nature of the basis sets used in the current work. Such differences are also

TABLE IX. Comparison of present calculations with previous calculations of the electron affinities (EAs) of the first-row atoms.

	Basis set			EA (eV)	Δ EA (eV)	Percent error	
	Ref.	Size	Method				
Boron							
<i>Recommended</i>				0.277			
Raghavachari	6	59	<i>spdf</i>	MP4	0.270	0.007	2.53
				CCD + ST	0.220	0.057	20.58
Noro <i>et al.</i>	1	211	<i>spdfgh</i>	MR-CI	0.268	0.009	3.25
				MR-CI extrap.	0.278	-0.001	-0.36
Present calculations							
aug-cc-pVDZ		23	<i>spd</i>	MR-SDCI	0.187	0.090	32.66
				FCI	0.190	0.087	31.49
aug-cc-pVTZ		46	<i>spdf</i>	MR-SDCI	0.245	0.032	11.45
				FCI	0.249	0.028	9.94
aug-cc-pVQZ		80	<i>spdfg</i>	MR-SDCI	0.258	0.019	6.94
				FCI	0.263	0.014	5.22
Carbon							
<i>Recommended</i>				1.263			
Raghavachari	6	59	<i>spdf</i>	MP4	1.260	0.003	0.23
				CCD + ST	1.220	0.043	3.40
Feller and Davidson	5	81	<i>spdfg</i>	MR-SDCI	1.203	0.060	4.74
				MR-SDQCI	1.235	0.028	2.21
Botch and Dunning	7	31	<i>spd</i>	MR-SDCI	1.080	0.183	14.48
Noro <i>et al.</i>	1	211	<i>spdfgh</i>	MR-CI	1.250	0.013	1.02
				MR-CI extrap.	1.267	-0.004	-0.32
Present calculations							
aug-cc-pVDZ		23	<i>spd</i>	MR-SDCI	1.155	0.108	8.54
				FCI	1.156	0.107	8.44
aug-cc-pVTZ		46	<i>spdf</i>	MR-SDCI	1.229	0.034	2.67
				FCI	1.232	0.031	2.46
aug-cc-pVQZ		80	<i>spdfg</i>	MR-SDCI	1.245	0.018	1.41
				FCI	1.246	0.017	1.33
Oxygen							
<i>Recommended</i>				1.461			
Raghavachari	6	59	<i>spdf</i>	MP4	1.390	0.071	4.87
				CCD + ST	1.360	0.101	6.92
Feller and Davidson	5	81	<i>spdfg</i>	MR-SDCI	1.265	0.196	13.42
				MR-SDQCI	1.322	0.139	9.52
Bauschlicher <i>et al.</i>	4	50	<i>spdf</i>	full CI	1.287	0.174	11.92
Feller and Davidson	2	171	<i>spdfg</i>	MR-CI (sel)	1.341	0.120	8.22
				MR-CI + Q	1.405	0.056	3.84
Botch and Dunning	7	31	<i>spd</i>	MR-SDCI	1.090	0.371	25.40
Noro <i>et al.</i>	1	211	<i>spdfgh</i>	MR-CI	1.386	0.075	5.14
				MR-CI extrap.	1.453	0.008	0.56
Present calculations							
aug-cc-pVDZ		23	<i>spd</i>	MR-SDCI	1.194	0.267	18.26
				FCI	1.209	0.252	17.22
aug-cc-pVTZ		46	<i>spdf</i>	MR-SDCI	1.321	0.140	9.57
				FCI	1.344	0.117	8.02
aug-cc-pVQZ		80	<i>spdfg</i>	MR-SDCI	1.384	0.077	5.25
				FCI	1.401	0.060	4.12
Fluorine							
<i>Recommended</i>				3.401			
Raghavachari	6	59	<i>spdf</i>	MP4	3.490	-0.089	-2.61
				CCD + ST	3.350	0.051	1.51
Botch and Dunning	7	38	<i>spdf</i>	MR-SDCI	3.180	0.221	6.50
Bauschlicher and Taylor	3	27	<i>spd</i>	FCI	3.040	0.361	10.62
Noro <i>et al.</i>	1	211	<i>spdfgh</i>	MR-CI	3.340	0.061	1.80
				MR-CI extrap.	3.363	0.038	1.12
Present calculations							
aug-cc-pVDZ		23	<i>spd</i>	MR-SDCI	3.219	0.182	5.37
				FCI	3.239	0.162	4.77
aug-cc-pVTZ		46	<i>spdf</i>	MR-SDCI	3.276	0.125	3.67
				FCI	3.308	0.093	2.73
aug-cc-pVQZ		80	<i>spdfg</i>	MR-SDCI	3.337	0.064	1.89
				FCI	3.364	0.037	1.10

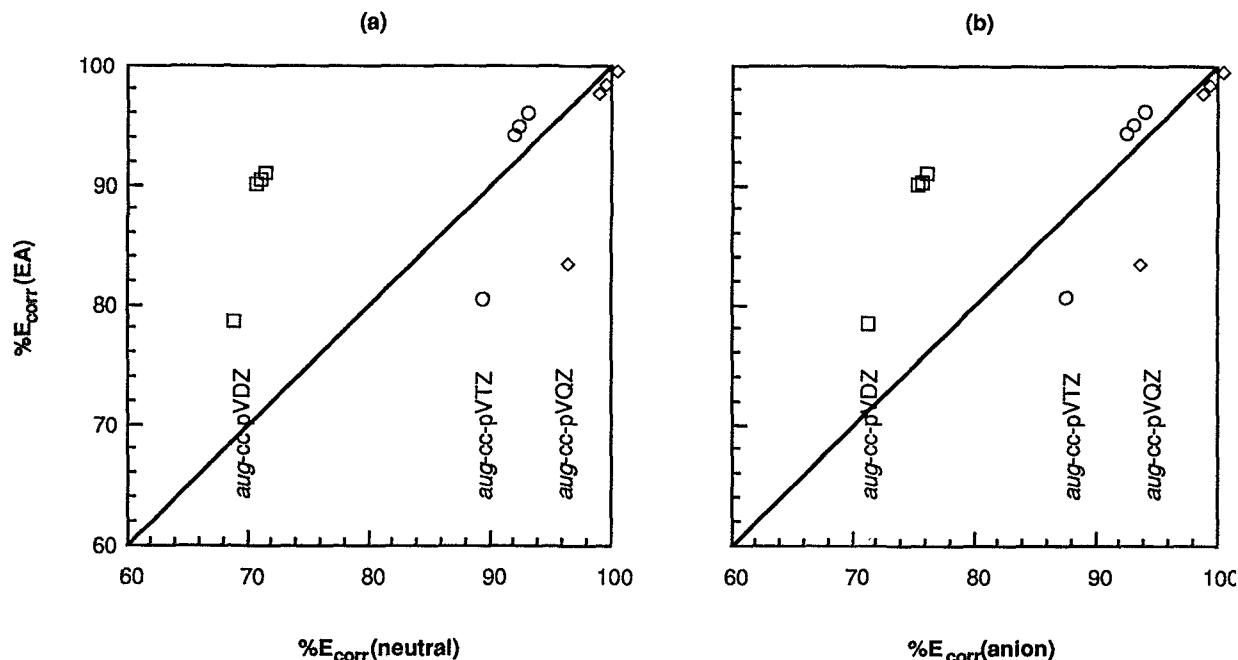


FIG. 5. Convergence of the correlation energy contribution to the calculated electron affinities (EA) of fluorine. The fractional correlation energy contribution to EA (F) obtained from a given calculation is plotted against the fractional total valence correlation energy of the neutral atom (a) and anion (b) obtained from that same calculation (expressed as percentages). All values are relative to the correlation energies obtained with the 2-CAS(2s2s'2p2p'3d) MR-CI wave function with the aug-cc-pVQZ basis set.

evident in comparison with the early work of Feller and Davidson on carbon and oxygen,⁵ except their EAs are more accurate than those of Botch and Dunning. Feller and Davidson later expanded their work on oxygen to a very large basis set and a thorough correlation treatment to recover $\sim 95\%$ of the correlation energy.²

There has been considerable discussion in the literature of the convergence of $\Delta E_{\text{corr}}(\text{EA})$ relative to that of $E_{\text{corr}}(\text{neutral})$ or $E_{\text{corr}}(\text{anion})$. Bauschlicher *et al.*⁴ stated the accepted notion, namely, that "methods which obtain 90% of the total correlation energy ... should yield 90% of the differential correlation energy contribution to the EA." In support of this, Feller and Davidson² found that the calculated EA of oxygen does not converge any faster than the calculated total correlation energies. In Fig. 5, we plot the fraction of $\Delta E_{\text{corr}}(\text{EA})$ obtained in a given calculation vs the fraction of the total valence correlation energies recovered in that same calculation, $E_{\text{corr}}(\text{neutral})$ and $E_{\text{corr}}(\text{anion})$. The plotted values are relative to the E_{corr} values obtained from the MR-SDCI calculation with the 2-CAS(2s2s'2p2p'3d) reference space and aug-cc-pVQZ basis set and are expressed as percentages. Results are given for the aug-cc-pVDZ, -pVTZ, and -pVQZ basis sets and for HF-SDCI and MR-SDCI wave functions based on the 2-CAS(2s2p2p'), 2-CAS(2s2s'2p2p'), and 2-CAS(2s2s'2p2p'3d) reference spaces.

From Fig. 5 it is evident that all calculations, except for the HF-SDCI calculations with the aug-cc-pVTZ and -pVQZ basis sets and the MR-SDCI calculations with the aug-cc-pVQZ basis set, recover a larger fraction of

$\Delta E_{\text{corr}}(\text{EA})$ than of $E_{\text{corr}}(\text{neutral})$ or $E_{\text{corr}}(\text{anion})$. The difference is particularly marked for calculations with the aug-cc-pVDZ basis set where the MR-SDCI calculations recover $\sim 75\%$ of the correlation energy of the anion, $\sim 71\%$ of the correlation energy of the neutral, and $\sim 91\%$ of the differential correlation energy contribution to EA. Thus, the two smaller basis sets seem to be biased towards the anion, although for the aug-cc-pVTZ set the differences between the fractions of $E_{\text{corr}}(\text{neutral})$ and $E_{\text{corr}}(\text{anion})$ recovered in the MR-SDCI calculations are less than 1%. For the aug-cc-pVQZ basis set the MR-SDCI calculations recover a slightly larger fraction of $E_{\text{corr}}(\text{neutral})$ than of $E_{\text{corr}}(\text{anion})$, although the differences never exceed 0.1%. These results are contrary to the notion expressed by Bauschlicher *et al.*⁴ and the results of Feller and Davidson,² although the latter calculations are most directly comparable to the MR-SDCI calculations with the aug-cc-pVQZ basis for which we do indeed find that 98.5%–99.0% of $E_{\text{corr}}(\text{neutral})$ and $E_{\text{corr}}(\text{anion})$ are recovered while 98.1%–98.9% of $\Delta E_{\text{corr}}(\text{EA})$ is recovered.

The most recent and complete study of the EAs of the first-row atoms is that of Noro *et al.*¹ They report the results of very large basis-set MR-CI calculations, including a novel extrapolation procedure. The accuracy of their predicted EAs is impressive as is the size of their basis sets. Noro *et al.* report *extrapolated* MR-CI EAs that are within 0.04 eV of the observed values (see Table IX). However, the raw calculated EAs are in error by as much as 0.08 eV and are essentially the same as those obtained here at a *much* reduced cost (our largest basis set contains 80 functions vs the 211 func-

tions contained in the largest set of Noro *et al.*). Both studies find that the most difficult atom for which to calculate an accurate EA is oxygen.

V. CONCLUSIONS

In this work, we presented a series of basis sets and MR-SDCI wave functions that, when used in calculations on neutral and anionic atoms, show a monotonic convergence toward the observed or recommended EAs. We reconfirm that accurate EAs can only be obtained if a large portion of the correlation energy is obtained. The correlation energy of the anion usually converges more slowly than that of the corresponding neutral species, although this is basis set and wave function dependent. The compactness of the basis sets presented here makes them far more feasible for use in molecular anion studies than the basis sets previously employed to obtain comparable accuracy.

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