

***Ab Initio* Determination of Accurate Electron Affinities of B, C, O, and F**Takeshi Noro^(a) and Megumu Yoshimine*IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099*

Masahiro Sekiya and Fukashi Sasaki

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

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Large-basis-set multireference singly and doubly excited configuration-interaction calculations give electron affinities (EA's) 0.278, 1.264, 1.454, and 3.363 eV for atoms B, C, O, and F, in excellent agreement with observed values 0.28, 1.268, 1.462, and 3.399 eV. The study relies on systematic expansion of reference space and curves of energy versus weight of reference configurations to obtain EA's within 0.01 eV of the full configuration-interaction limit for the chosen basis.

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Ab initio calculation of electron affinities (EA's) of even small atoms is notoriously difficult. Despite many attempts,¹⁻¹⁰ EA's of atomic B, C, O, and F have not been calculated to "chemical accuracy," 1kcal/mol (0.04 eV). Computational methods have included configuration interaction (CI), perturbation theory, and quantum Monte Carlo (QMC). A recent QMC study¹⁰ gives 3.45 ± 0.11 eV for the EA of F, spanning the observed¹¹ 3.399 eV with a large error bar. Perturbation methods appear to overestimate EA's,^{1,12} and it is difficult to establish error bars.^{8,9} The CI approach has been hampered by small basis sets for orbital expansion and/or inadequate approximation to the complete CI configuration space. Sasaki and Yoshimine¹ were the first to use an adequate basis (10*s*,9*p*,8*d*,8*f*,6*g*,4*h*,2*i* Slater type), but their configuration space, limited to Hartree-Fock plus single and double orbital excitations [self-consistent-field single and double configuration interaction (SCF-SDCI)], was only enough to give EA's substantially smaller (as much as 0.5 eV) than observed values. Expanding the configuration space to include selected triple and quadruple excitations from Hartree-Fock gave only marginally improved values of 0.15, 1.11, 1.13, and 3.12 eV for B, C, O, and F, compared with observed values of 0.28, 1.268, 1.462, and 3.399 eV.¹¹ Botch and Dunning² expanded the reference space by adding the $2p^2 \rightarrow 3p^2$ excitation and reported Monte Carlo self-consistent-field multireference configuration-interaction (MCSCF-MRCI) results with a small contracted Gaussian (4*s*,4*p*,3*d*) basis, which are comparable in accuracy to those of Sasaki and Yoshimine. Feller and Davidson⁴ reported MCSCF-MRCI calculations in a 8*s*,5*p*,4*d*,2*f*,1*g* contracted Gaussian-type basis with expanded reference spaces; including estimates of the effects of quadruple excitations, they obtained EA's clustered around 1.22 eV for C and 1.29 eV for O. They later extended their calculations¹² to larger basis sets, and, with the inclusion of an estimated 0.05-eV contribution from the unused configuration space, reported 1.36

eV for the EA of O. Bauschlicher and co-workers^{5,6} calibrated MCSCF-MRCI EA's for O and F atoms against complete CI values in modest sized basis sets, and concluded as did Feller and Davidson,¹² that differential correlation effects between neutral and anion are only reliably computed when a high percentage of the correlation energies has been recouped.

Noro and Yoshimine¹³ have proposed a simple, effective selected reference MRCI procedure using curves of energy versus weight of reference configurations in the MRCI wave function to determine the minimum level of electron correlation needed to obtain reliable EA's and establish error bars. Their calculated EA for the ³B₁ methylene radical is 0.604 ± 0.03 eV, in good agreement with the observed value, 0.628 ± 0.031 eV.¹⁴ The same approach is used here to show that the EA's of B, C, O, and F can be calculated to a 0.04 eV accuracy.

Our calculations use a 13*s*,11*p*,6*d*,5*f*,5*g*,5*h* contracted Gaussian basis. The tightest *s* function is a contraction of five *s* primitives with contraction coefficients from the 1*s* atomic orbital in neutral-atom SCF calculations. The tightest *p* function is a contraction of two *p* primitives with contraction coefficients from the 2*p* SCF neutral atom or anion orbital. The remaining functions are Gaussian primitives. The *s* and *p* exponents are derived from the 13*s*,8*p* set of van Duijneveldt¹⁵ by replacing the most diffuse three *s* and six *p* by sequences of seven and ten even-tempered functions (fixed ratio between successive exponents). The *d*,*f*,*g*,*h* sets are even tempered.¹⁶ The extensive literature on EA calculations summarized earlier has established that our basis is adequate for quantitative calculation.

Our MRCI calculations used natural orbitals (NO) of SCF-SDCI wave functions. They were first used in a NO-SDCI calculation. Then we computed a sequence of MRCI wave functions, labeled MRCI(*N*) according to the number *N* of reference configurations. The reference configurations were chosen for the largest weights in the

NO-SDCI wave functions, with the exception of the $2p^2 \rightarrow 3p^2$ excitation in B^- and C^- which was the second configuration chosen. This order adjustment gave superior curves of MRCI(N) energies versus weight of reference configurations, w , in the MRCI wave function for interpolation and extrapolation. The curves are shown in Fig. 1 where, in the boron and carbon panels, primed points were obtained when the reference configuration ordering was by weight; the smoother behavior with our adjusted order is readily apparent.

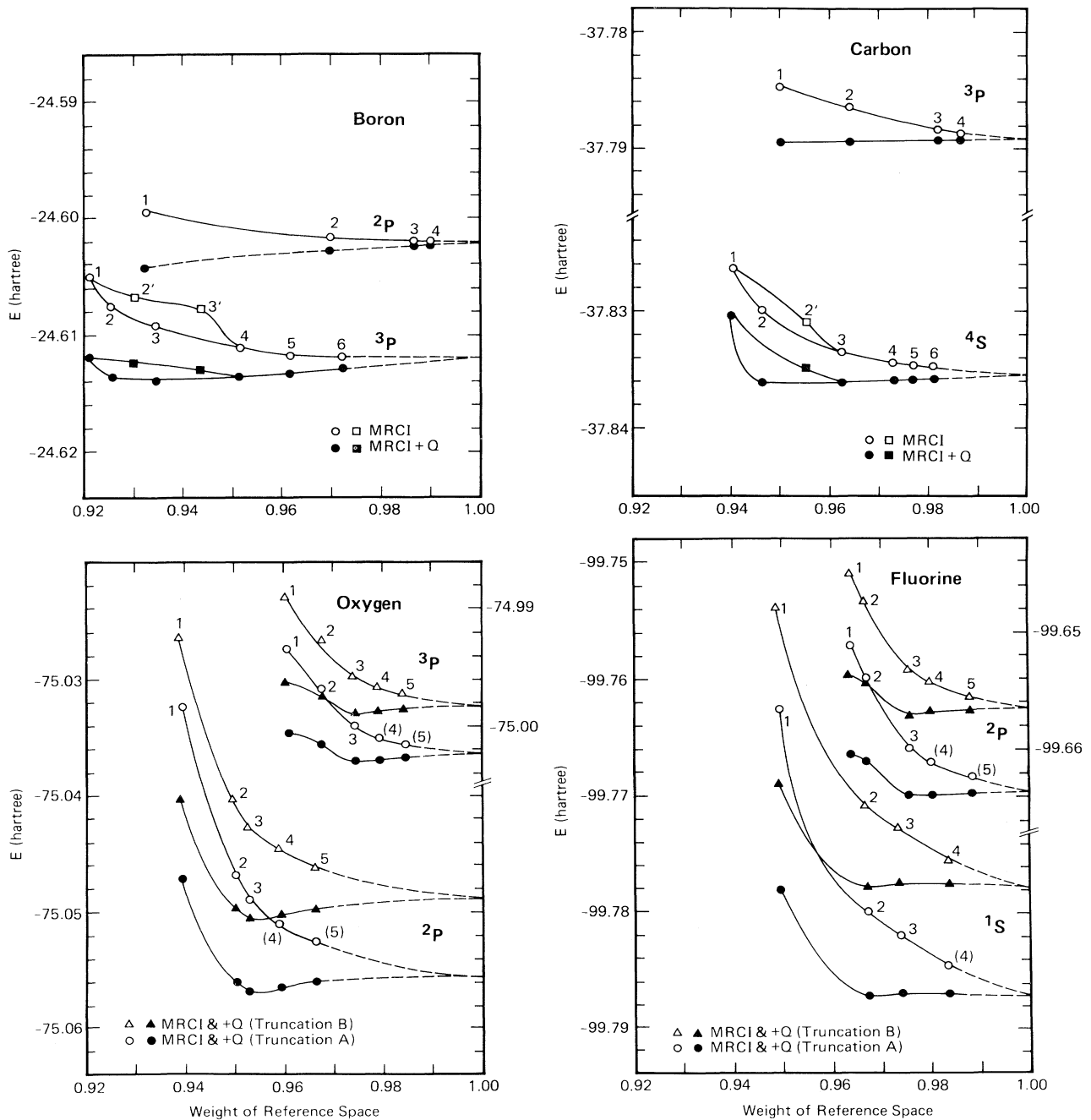


FIG. 1. MRCI and MRCI+Q energies, indicated by the open and solid symbols, respectively, as a function of the weight of reference space in MRCI wave functions for B, C, O, and F. Points in parentheses are estimated. $1s, 11p, 6d, 5f, 5g, 5h$ natural orbitals are used for B and C. Primed points are computed when reference configurations are added in order of weight in the NO-SDCI wave function. For O and F, curves are drawn for two basis sets, truncations A and B.

In all calculations the 1s electrons are uncorrelated —Sasaki and Yoshimine¹ showed that k shell and kl intershell correlation contributes less than 0.01 eV to first row EA's. Otherwise, the B and C calculations are as described above.

Calculations on O and F, because of the unmanageable dimensions of configuration spaces, required the additional approximation of dropping lowest occupation NO's. Truncation *A* limits single excitations to 13s,11p, 5d,4f,3g,2h and double excitations to 7s,7p,5d,4f, 3g,2h. The MRCI(1) EA's for O and F in truncation *A* differ from unapproximated ones by -0.011 and -0.013 eV. Truncation *B*, more severe, limits single excitations to 13s,11p,3d,2f,1g and doubles to 7s,7p, 3d,2f,1g; MRCI(1) EA's for O and F differ by -0.064 and -0.070 eV from unapproximated values. In the O and F panels of Fig. 1, MRCI(N) curves are shown through $N=1-5$ for truncation *B*. For truncation *A* we have $N=1-3$ computed points, and extend the curves by using truncation-*B* $N=3$ to 4 and $N=4$ to 5 energy differences. This estimate of truncation-*A* $N=4$ and 5 energies should be accurate to 0.0001 hartree, as suggested by the comparison of estimated lower- N energies against actual calculations.

Energy contributions E_Q due to quadrupole excitations from the reference configurations are estimated by

$$E_Q = \left[1 - \sum_{i=1}^N C_r^2 \right] (E_{\text{ref}} - E_{\text{CI}}), \quad (1)$$

where the sum is over reference configurations, E_{ref} is the expectation value of the Hamiltonian for a renormalized MRCI(N) wave function truncated to contain only the reference configurations, and E_{CI} is the MRCI(N) energy. Figure 1 shows these quadruple excitation effects in curves labeled MRCI+Q; the flatten out faster than the MRCI and, as we discuss below, assist in extracting accurate EA's from our calculations.

Calculations were done in atomic symmetry using a newer version of ATOMCI.¹⁷

From the curves of Fig. 1 we calculate electron affinities $EA(w)$, vertical energy differences between anion and neutral, which for large w become nearly constant [EA(1.0) is the extrapolated full CI EA]. Because the MRCI+Q curves are flatter, convergence to a constant EA is faster than with MRCI. While we have no proof that the curves smoothly extrapolate to $w=1.0$, it is plausible that they should. The fact that $EA(w)$ becomes nearly constant before we get into the extrapolated range is a strong indication. In addition, confidence in the extrapolation is enhanced by knowing that the MRCI and MRCI+Q curves must meet at $w=1.0$. We consider the vertical differencing of Fig. 1 curves to be the most reliable way to get EA's. Numerical results are given in Table I. Instead of the extrapolated EA(1.0), we give results for the w value corresponding to the highest N used for the neutral or the anion.

TABLE I. Electron affinities in eV calculated using best energies, $EA(M,N)$, and energies with the same weight of reference space, $EA(w)$. w values are from the best anion calculation for B, C, and F, and from the best neutral calculation for O.

Atom	B	C	O	F
	EA(M,N)			
(M,N)	(4,6)	(4,6)	(5,5)	(5,4)
MRCI	0.268	1.250	1.386	3.340
MRCI+Q	0.288	1.260	1.454	3.367
	EA(w)			
Weight	0.9721	0.9808	0.9839	0.9835
MRCI	0.278	1.267	1.453	3.363
MRCI+Q	0.273	1.264	1.454	3.363
Expt. ^a	0.28	1.268	1.462	3.399

^aReference 11.

For B, $w=0.9721$ corresponds to MRCI(6) for the anion energy which is subtracted from a linearly interpolated neutral energy to give $EA(0.9721)=0.278$ eV. This is our best value, ignoring E_Q because B has only three electrons correlated. This compares well with the nonvertical $EA(4,6)=0.268$ eV obtained by subtracting our best anion energy, MRCI(6), from the best neutral energy, MRCI(4), giving an indication of how close we are to the full CI limit.

The situation with C is similar. $EA(0.9808)=1.267$ eV comes from the MRCI(6) energy of the anion and the linearly interpolated neutral energy. Adding E_Q lowers it to 1.264 eV, our best value. $EA(4,6)=1.250$ eV is further away, reflecting the slopes of the MRCI(N) curves at w values corresponding to the MRCI(6) anion and MRCI(4) neutral. With E_Q , $EA(4,6)$ becomes 1.260 eV, due to the smaller slopes of the MRCI+Q curves.

O is different. At the MRCI(5) anion reference weight the anion and neutral curves have distinctly different slopes, even with E_Q . Therefore, we took the vertical difference at $w=0.9839$ corresponding to MRCI(5) of the neutral even though this required linear extrapolation of anion energy assuming the complete CI limit to be the MRCI(5)+Q value. $EA(0.9839)=1.453$ eV without E_Q is essentially identical to the converged MRCI+Q $EA(5,5)$ [$EA(N,N)$ are 1.462, 1.455, and 1.454 eV for $N=3, 4,$ and 5] which adds confidence to the best value of 1.454 eV. The best MRCI value, $EA(5,5)=1.386$ eV, is still far from converged.

The notoriously difficult F is better behaved than O. While the MRCI(N) curves are steep, they become remarkably flat with E_Q . $EA(0.9835)=3.363$ eV, unchanged by E_Q , is the best value. $EA(4,5)=3.367$ eV with E_Q agrees well while the value of 3.340 eV without E_Q is still not converged.

We have studied a variety of convergence patterns from our calculations and conclude that our best values,

0.278, 1.264, 1.454, and 3.363 eV for the EA's of B, C, O, and F, are within 0.01 eV of the full CI limits in our bases. Agreement with observed values 0.28, 1.268, 1.462, and 3.399 eV attests to the adequacy of our bases.

Our results put the work of previous investigators into perspective. The $2p^2 \rightarrow 3p^2$ excited configuration is the most important addition to the reference space, as pointed out by Botch and Dunning.² Our MRCI EA(1,2) = 0.22, 1.24, 1.46, and 3.50 eV values obtained when this configuration is added only to the anion reference space are within 0.1 eV of the observed values, considerably better than the MRCI EA(1,1) values of 0.15, 1.13, 1.08, and 3.04 eV. Other important additions are the $2s^2 \rightarrow 2p^2$ "near degeneracy" excitations in B and C, and the $2s \rightarrow 3d$ excitation in O and F. We confirm the necessity for obtaining a high percentage of the correlation energy in both neutral and anion in order to get high accuracy in EA's. The virtue of our calculations, particularly expressed in the form of Fig. 1, is that we see exactly what the high percentage is. It is interesting that even though the MRCI+Q results appear to overestimate the neutral and anionic correlation energies, the use of the E_Q correction is most helpful in speeding convergence of EA's; MRCI+Q EA(2,2)'s of 0.293, 1.267, 1.481, and 3.435 eV are remarkably good, already inside our desired error bar, and calculations beyond the (2,2) level show that the result is not fortuitous.

We have, for the first time, computed the EA's of B, C, O, and F atoms to a demonstratable accuracy of 0.04 eV. The claims to accuracy are based on a series of MRCI calculations charting the effect of systematically expanding the reference space. Plotting energy versus weight of reference configurations gives curves which demonstrate the requirements for convergence and the reliability of error bars. Estimating the effect of quadrupole excitations with respect to the reference configurations in MRCI calculations is shown to consid-

erably speed convergence of EA's to the full CI limit.

A report tabulating basis sets, data used for drawing Fig. 1, and tables of EA(M,N) convergence is available from one of us (M.Y.).¹⁶

^(a)Permanent address: Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan.

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