

# Multiconfiguration-Hartree-Fock calculations for the electron affinity of boron

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Systematic multiconfiguration-Hartree-Fock procedures are applied to the study of the electron affinity of boron. For a valence correlation calculation, an electron affinity of 273.2(2) meV is obtained, which is reduced by 1.1 meV by a relativistic correction. Core polarization and core rearrangement were found to increase the electron affinity to 279.5(20) meV. The latter agrees well with the experimental value of 277(10) meV. Results are compared also with other theories.

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## I. INTRODUCTION

*Ab initio* calculations of electron affinities (EA's, denoted as  $E_a$  in this paper) for even small systems have been a challenge for many atomic and molecular codes. Quantum chemical calculations strive for "chemical accuracy" of 1 kcal/mol (about 40 meV), but in experimental atomic physics an accuracy of a few meV is desirable. Though the electron affinity of carbon has been measured to an accuracy of 0.3 meV [5], the experimental uncertainty in the electron affinity of boron is 10 meV [5].

Many calculations for electron affinities have been performed for the first row elements, including boron. Most are quantum chemical basis-set methods [1,2] where basis-set truncation errors are present as well as errors arising from an unbalanced treatment of correlation in the atom and anion. Some very accurate valence correlation results have been reported by Noro *et al.* [3] using an extensive orbital basis along with single and double (SD) replacements from a multireference configuration interaction (MRCI) calculation with a quadrupole correction for excitations from the rest of the wave function. The best results were obtained when the weight of the reference states was the same in both systems. In boron the quadrupole correction appeared not to be needed since it changed their value of 278 meV to 273 meV. The former compared well with the experimental value of 277(10) meV [5] but, in fact, both are within experimental uncertainty. For carbon, their corrected value of 1.264 eV was the more accurate when compared with the most recent electron affinity of 1.2629(3) eV [5]. Unfortunately, the authors compared their results with a 1975 tabulation of electron affinities [6] where a value of 1.268 eV was quoted and so the accuracy of the corrected value was not evident. The calculations reported by Sundholm and Olsen [4] are finite element multiconfiguration Hartree-Fock (MCHF) calculations which do not suffer from basis-set limitations. A systematic series of calculations had been performed and a small relativistic effect and a core-valence contribution included. They reported a final value of  $266.8 \pm 3.0$  meV, also within experimental uncertainty. Unfortunately, the large error bar in the

experimental value has prevented a clear evaluation of these different theoretical results.

Recently, some large-scale MCHF calculations have been undertaken. The theoretical electron affinity for Li was computed: the value of 0.6176(1) eV [7] compared favorably with the experimental value of 0.6176(2) eV [8]. In order to speed up the execution of computer codes for the many angular integrations needed for obtaining energy expressions, the angular codes were modified using the concepts of quasispin and reduced coefficients of fractional parentage [9,10]. The programs have also been modified for parallel execution on a network of computer workstations using the parallel virtual machine (PVM) software [11]. The present work was undertaken as a first application of these improved codes in order to check their performance and to resolve the difference in the two theoretical results by attempting to obtain an estimate of the electron affinity to within a few meV.

## II. MCHF CALCULATION FOR THE ELECTRON AFFINITY

### A. Valence correlation calculation

The electron affinity of boron is the difference of the energy of the  $2s^2 2p^2 \ ^3P$  state of  $B^-$  and the  $2s^2 2p \ ^2P$  ground state of boron. To a large extent the  $1s^2$  shell can be treated as inactive and so our first calculation is a valence correlation calculation where the negative ion (or anion) and the neutral atom are treated as four- and three-electron systems, respectively. Systematic calculations were undertaken with orbital sets of increasing size, characterized by the largest principal quantum number. Thus an  $n = 4$  calculation includes all orbitals with principal quantum number  $n \leq 4$  and  $l \leq 3$ . Configuration state functions (CSF's) are generated from these orbitals. For few-electron systems, with  $1s$  inactive, the wave function expansions may include all configuration states that can be generated from the orbital set, at least for  $n = 3$  and  $n = 4$ : such a calculation is referred to as a complete active space (CAS) calculation. But for larger  $n$ , the ex-

TABLE I. Models for the generation of configuration state functions for MCHF wave function expansions.

$n$	B $^2P$	B $^-$ $^3P$
(i) Valence correlation		
3, 4	$1s^2\{2, \dots, n\}^3$	$1s^2\{2, \dots, n\}^4$
5, 6, 7	$1s^2\{2, 3, 4\}\{2, \dots, n\}^2$	$1s^2\{2, 3, 4\}^2\{2, \dots, n\}^2$
8, 9	$1s^2\{2, 3\}\{2, \dots, n\}^2$	$1s^2\{2, 3\}^2\{2, \dots, n\}^2$
(ii) Valence correlation and core polarization		
3, 4	$1s\{1, 2, \dots, n\}^4$	$1s\{1, 2, \dots, n\}^5$
5, 6, 7	$1s\{1, 2\}\{2, 3\}\{2, \dots, n\}^2$	$1s\{1, 2\}\{2, 3\}\{2, 3, 4\}\{2, \dots, n\}^2$
8, 9	$1s\{1, 2\}\{2, 3\}\{2, \dots, n\}^2$	$1s\{1, 2\}\{2, 3\}^2\{2, \dots, n\}^2$

pansions get rather large and, in fact, many of the CSF's do not contribute significantly. Some restriction needs to be applied. The models used are given in Table I. The notation  $\{2, 3, 4\}^2$ , for example, implies all possible configurations with two electrons that have principal quantum numbers in the range 2–4. The many-electron configuration may be viewed as consisting of “layers” where, for valence correlation the first two electrons are always  $1s$ , the next two have a restricted range depending on the highest principal quantum number, and electrons with large principal quantum numbers are at most doubly occupied. When core polarization is included, we start with a  $1s$  and a CAS for the remaining four or five electrons. But when configuration states are included with some principal quantum numbers greater than 4, the choices for inner electrons are constrained; the first electron is  $1s$ , the second either  $1s$ ,  $2s$ , or  $2p$ , and the third either  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ , or  $3d$ , etc. as shown in Table I. For high  $n$ , the angular quantum number was restricted to  $l \leq 6$  ( $i$  orbitals). CSF's with expansion coefficients less than 0.000 01 were deleted before the new CSF's from the next stage were added to the wave function expansion.

Table II reports results for these calculations. Included in the table are the number of configuration states in the expansion, the total energies, and the predicted electron affinity. The notation  $n = 8i$ , for example, is used to indicate that the  $n = 8$  orbital set was restricted to orbitals with  $l \leq 6$ . Orbitals were separately optimized for the two states. In fact, the B $^-$  system needs an extra “layer”

of orbitals to represent the diffuse nature of the negative ion. Let  $E_n$  be the energy of a system for the  $n$  orbital set. An interesting trend is  $E_a(n) = E_{n-1}(B) - E_n(B^-)$ , referred to as the  $\Delta n = 1$  electron affinity whereas the usual definition is a  $\Delta n = 0$  calculation. The latter EA is increasing with  $n$  and represents a lower bound (within the model) whereas the former is decreasing and predicts an upper bound. Both may be extrapolated (roughly); the average of the extrapolated value is the estimated limit and half the difference the error estimate for the model. The latter is reduced 1.1 meV due to relativistic shift effects.

### B. Core-polarization and nonuniqueness of MCHF expansions

In the case of Ca $^-$  it was found that core polarization was extremely important for an accurate calculation of the electron affinity [13]. In the present case, the  $1s^2$  core is more deeply embedded and not as “soft” as the argonlike core of calcium, but may still play a significant role in determining the electron affinity. Table III reports results for a calculation where excitations are allowed from the  $1s$  shell, though all CSF's must have at least one  $1s$  orbital. For  $n \leq 4$  no restrictions were placed on the CSF except that the  $1s$  orbital be occupied, but thereafter more restrictive models were used as shown in Table I. Even so, many CSF's are generated. To select

TABLE II. Valence correlation MCHF energies (in hartree) for complete active space (CAS) calculations with an inactive  $1s$  for an increasing active set. For each calculation,  $n$  specifies the maximum quantum number; angular quantum numbers were restricted to  $l \leq 6$ ; orbitals were separately optimized for both states.  $E_a(\Delta n = 0) = E_n(^2P) - E_n(^3P)$  whereas  $E_a(\Delta n = 1) = E_{n-1}(^2P) - E_n(^3P)$ , where  $E_a$  is an electron affinity.

Expansion	B $^2P$		B $^3P$		$E_a$ (meV)	
	No. CSF	$E$ (hartree)	No. CSF	$E$ (hartree)	$\Delta n = 0$	$\Delta n = 1$
$n = 3$	30	-24.596 215	83	-24.598 811	70.6	
$n = 4$	168	-24.600 745	1001	-24.608 684	166.6	
$n = 5$	614	-24.601 855	3149	-24.611 286	256.6	
$n = 6$	1329	-24.602 211	5905	-24.612 045	267.5	277.3
$n = 7$	2268	-24.602 365	7891	-24.612 326	271.0	275.2
$n = 8i$	3222	-24.602 420	8946	-24.612 425	272.3	273.7
$n = 9i$	2965	-24.602 440	9502	-24.612 465	272.8	273.4
Estimated nonrelativistic limit					273.2(1)	
Estimated limit with relativistic correction					272.1(1)	

TABLE III. Valence correlation and core-polarization MCHF energies (in hartree) for systematic calculations for different stationary solutions (see text). For each calculation,  $n$  specifies the maximum quantum number; angular quantum numbers were restricted to  $l \leq 6$  or 5, except for  $1s$  orbitals, which were separately optimized for both states.

Expansion	B $^2P$		B $^3P$		$E_a$ (meV)	
	No. CSF	$E$ (hartree)	No. CSF	$E$ (hartree)	$\Delta n = 0$	$\Delta n = 1$
<i>Calculation 1</i>						
$n = 3$	170	-24.596 625	516	-24.599 041	65.72	
$n = 4$	1948	-24.605 039	13181	-24.610 683	153.56	
$n = 5$	3491	-24.608 625	15062	-24.617 078	230.02	327.60
$n = 6$	6607	-24.609 895	24527	-24.619 362	257.63	292.18
$n = 7$	6634	-24.610 387	32807	-24.620 267	268.83	282.24
$n = 8i$	5382	-24.610 586	37869	-24.620 614	272.87	278.27
$n = 9i$	8434	-24.610 679	41664	-24.620 741	273.81	276.34
Estimated nonrelativistic limit					274.2(2)	
Estimated limit with relativistic correction					273.1(2)	
<i>Calculation 2</i>						
$n = 3$	170	-24.603 861	515	-24.601 342	-68.55	
$n = 4$	1948	-24.617 170	13178	-24.622 722	151.10	
$n = 5$	2936	-24.621 559	16530	-24.629 783	223.79	
$n = 6$	4756	-24.623 355	24736	-24.632 727	255.02	
$n = 7h$	5819	-24.624 031	28532	-24.633 960	270.18	288.59
$n = 8h$	6511	-24.624 317	29442	-24.634 435	275.31	283.10
$n = 9h$	6932	-24.624 450	29274	-24.634 643	277.39	280.98
Model limit					279.2	
Corrections: Type 1		-24.624 206		-24.634 662	279.5	
Corrections: Type 2		-24.624 481		-24.634 726	280.6	
Predicted electron affinity					279.5(20)	

from a new set when the orbital set size is increased, a technique used earlier in the study of the binding energy of Be and  $\text{Li}^-$  was applied [7]. A zero-order wave function consisting of CSF's with expansion coefficients greater than 0.001 is maintained and a first-order wave function calculation performed in which only the interaction of the new CSF's with the zero-order function is included. Then those CSF's with an expansion coefficient greater than 0.000 005 were retained for inclusion in the variational (MCHF) calculation of the orbitals, those less than this cutoff but greater than 0.000 002 were saved for a final CI correction: all other CSF's were neglected. The orbital basis now needs to represent intershell correlation as well as valence correlation and so, for the same size of the orbital set as before, convergence is a bit slower in that the  $n = 9$  calculation is not as well converged.

It has generally been assumed that the stationary solution for a given wave function expansion with a specific dominant component would be unique. In this study it was found that, with the same wave function expansions, both the  $n = 3$  and  $n = 4$  expansions had two stationary solutions when all orbitals were varied. The same may be true for other expansions but here only the  $^2P$  was investigated fully. The first solution had  $1s$  and  $2s$  orbitals close to their Hartree-Fock values and an outer  $3s$  orbital whereas in the second, the  $1s$  orbital acquired a larger mean radius, the  $2s$  contracted slightly, and the  $3s$  became an inner core-polarization orbital. The total energy of the latter solution was appreciably lower though the self-consistent field procedure was less sta-

ble making it more difficult to obtain a well converged result. It should be pointed out that for both systems the Hartree-Fock solutions are unique *only* through the application of Koopmann's theorem, that is, by selecting the solution for which the Lagrange multiplier ensuring the orthogonality between the two orbitals is set to zero [12]. Both valence correlation and core-polarization expansions break the  $1s, 2s$  symmetry—the two orbitals now play a different role in that it no longer is possible to interchange  $1s$  and  $2s$  and obtain the same wave function.

It should also be remembered that, in a CAS calculation, the orbitals are not uniquely defined—a transformation of the orbitals results in a transformation of the wave function. The latter requires that all the CSF's be present in the expansion. Such degrees of freedom can be removed, without affecting the energy, by deleting certain CSF's, which is referred to as "applying Brillouin's theorem," since the variational procedure then determines those orbitals for which the expansion coefficient for the deleted CSF is zero. Similar situations arise in the core polarization expansions.

Two sets of calculations were performed with some minor differences, but based on the two solutions, respectively. We will refer to them as calculations no. 1 and 2.

The first calculation started with the wave functions from outer correlation at the  $n = 3$  stage, each state separately optimized. The calculations converged rapidly to a solution. A large contributor to the wave function for

$B^-$  was  $1s^2 2s^2 2p 3p$ . Since our model for  $n \geq 5$  (see Table I) includes all double excitations from such configuration states (except from  $1s^2$ ) but not all from, say  $1s^2 2s^2 2p 5p$ , it was considered prudent to apply Brillouin's theorem and delete all  $1s^2 2s^2 2pnp$  CSF's. The variational  $3p$  orbital then includes these configuration states implicitly. The  $1s$  orbital was obtained from the  $n = 3$  calculation for the anion and kept fixed in all subsequent calculations: at the  $n = 3$  stage, fixing the  $1s$  orbital in this manner affected the electron affinity by less than 0.2 meV.

The second calculation initially was undertaken as a check on the first and to determine the effect of varying the  $1s$  orbital at every stage. It is not obvious how Brillouin's theorem should be applied. Ideally, one would like the most rapidly converging expansion, with a single dominant component, and the most stable self-consistent field procedure. In this calculation it was decided to break the  $2p, 3p, 4p$  symmetry by deleting the  $1s^2 2s^2 2p 3p$ ,  $1s^2 2s^2 2p 4p$ ,  $1s^2 2s^2 3p 4p$  configuration states as would be done in a natural orbital expansion [12] for valence correlation and indeed, as will be shown in a later section,  $2p^2$  now constituted a larger part of the wave function. It was at the  $n = 4$  stage of the  ${}^2P$  calculation that two solutions with different energies were found with the same wave function expansion, both satisfying the virial theorem to seven significant digits. With some effort, a second solution was also found for the  $n = 3$  expansion. This solution has a much larger core-polarization correction with a very contracted  $3s$  orbital. Orbitals from this lower solution were used at subsequent stages. The  $1s$  orbital was varied for the  ${}^2P$  and the same orbital used in the calculation for the negative ion. Convergence of the SCF iterations was extremely slow. Partly because of the difficulty of convergence, the orbital sets were restricted to  $l \leq 5$  ( $h$  orbitals).

Table III reports the results of both these calculations.

### III. DISCUSSION OF RESULTS

For the valence correlation calculation reported in Table II, the expansions are not extremely large and the two sets of electron affinities appear to be converging to similar limits. For the  $\Delta n = 0$  values, changes are decreasing by about a factor 3; assuming a geometric series for higher  $n$  differences, the extrapolation correction predicts a limit of 273.1 meV. The  $\Delta n = 1$  values are decreasing to a limit no larger than 273.3 meV. From the average of these two limits, the electron affinity predicted by this model is 273.2(1) meV, which is decreased by 1.1 meV for a relativistic correction. Notice that the error estimate has not included a number of small effects like the restriction on the  $l$  value.

In Table III, the size of the expansions for valence correlation together with core-polarization (sometimes referred to as core-valence) shows how much more demanding such calculations are even though the effect from the core is small.

The first calculation was one where  $1s$  and  $2s$  were similar to the valence correlation orbitals. This is re-

flected in the very similar trends in  $E_a(\Delta n = 0)$ . For the smaller basis sets, the  $E_a$ 's are somewhat smaller because the same number of orbitals must now account for more effects. However, for the large  $n$ , the  $E_a$ 's are slightly larger. The  $\Delta n = 0$  EA's are converging more rapidly than the  $\Delta n = 1$ : assuming ratios of 1/4 and 1/2, respectively, the predicted limits are 274.1 and 274.3 for an average of 274.2(1). The final correction for the selection-deletion process did not affect the electron affinity to this accuracy.

For the second core-polarization calculation, the energy of the neutral atom is now lower initially than for the negative anion but as the size of the orbital basis increases, the  $E_a$  trends are similar though they increase more rapidly with  $n$  than in the first calculation. In spite of the fact that the  $n = 7$  orbital set does not include the  $i$  orbitals,  $E_a(n = 7)$  is larger. The other striking feature is that the number of CSF's for large  $n$  is significantly smaller. In fact, these numbers are not monotonically increasing because, in going from  $8h$  to  $9h$  the expansion for  $8h$  is condensed as described earlier, and then selected new CSF's added to this set. In this case, more CSF's were deleted than added. In this calculation, the average of the last three  $\Delta n = 0$  and  $\Delta n = 1$  EA's is remarkably constant (279.39, 279.21, 279.19) and so we have taken the limit to be 279.2(1) meV. To this are added some contributions from the major CSF's omitted in the variational process. The first correction arises from CSF's deleted after having been included in a variational process whereas the second correction estimates the effect of the cutoff for selection from first-order calculations. The correction from the former is small but the latter is 1.1 meV in this case. When the relativistic correction is included the predicted estimate of the electron affinity is 279.5 meV.

This last calculation is considered the most accurate for several reasons. With respect to computational procedures where Hartree-Fock orbitals are fixed throughout the calculation, this calculation includes some core-core correlation, though the  $1s^2$  correlation is limited to radial correlation. It may be thought of as "core rearrangement." This accounts for the substantially lower total energies. The wave function expansion for this last calculation is also more dominant in that  $1s^2 2s^2 2p^2$  has the much larger weight. This can be seen in Table IV, where the coefficients of the major components of the wave function are tabulated for the two core-polarization calculations. In calculation no. 1, both  $2p^2$  and  $2p 3p$  are major contributors, whereas in calculation no. 2, only  $2p^2$  is a large contributor. This greater compactness accounts for the slower growth in the number of CSF's for large  $n$  and the larger effect from the corrections. Table IV also shows the large core-polarization component in both states for calculation no. 2 which is small in calculation no. 1.

In some sense, the neutral atom, five-electron system, is contained within the negative ion, six-electron system. As the orbital basis for the latter is expanded one would expect the latter also to represent the atom with reasonable accuracy. For outer correlation this can be checked since the  ${}^2P$  expansion without deletions can easily be

TABLE IV. Coefficients of CSF's that are major contributors in the wave function expansions for the MCHF core-polarization calculation.

${}^2P$			${}^3P$		
CSF	Calculation		CSF	Calculation	
	1	2		1	2
$1s^2 2s^2 2p$	0.9621	0.9489	$1s^2 2s^2 2p^2$	0.8081	0.9321
$1s^2 2p^3$	0.2067	0.1890	$1s^2 2s^2 2p 3p$	-0.5076	0.0
$1s^2 2s 2p ({}^1P) 3d$	-0.1074	-0.1029	$1s^2 2s 2p^2 ({}^3P) 3s$	-0.12068	-0.0246
$1s 2s^2 2p ({}^3P) 3s$	-0.0013	-0.1348	$1s^2 2p^4$	0.11917	0.1064
			$1s^2 2p^3 ({}^2P) 3p$	-0.11759	-0.0670
			$1s^2 2s 2p^2 ({}^1D) 3d$	0.11172	0.1086
			$1s^2 2s^2 3p^2 ({}^3P)$	-0.0077	-0.1398
			$1s 2s^2 2p^2 ({}^4P) 3s$	-0.0022	0.1153

generated (the deletions depend on the basis and need not be the same for both). In the present case an electron affinity of 273.6 meV is predicted, close to 273.2 meV, which we consider to be the limit. For the first core-polarization calculation, Table V attempts to show the inadequacy of the  ${}^3P$  basis for a  ${}^2P$  calculation. For each symmetry, orbital by orbital, the mean radius of the  ${}^3P$  orbital is larger than the corresponding orbital for  ${}^2P$ . Most noticeable is the lack of a contracted  $d$  orbital.

In the final value for the electron affinity an uncertainty of 2 meV is given. This has not been arrived at in a rigorous fashion. The computed  $E_a(n=9)$  was extrapolated by 2 meV, but this increase is clearly indicated by the trend. The orbital basis was truncated to  $h$

TABLE V. Mean radii (in a.u.) of the orbitals for  $B^-$  and  $B$ .

$nl$	$B ({}^2P)$	$B^- ({}^3P)$	$nl$	$B ({}^2P)$	$B^- ({}^3P)$
1s	0.32405	0.32405	4f	2.42618	2.57393
2s	1.95833	1.97291	5f	1.94303	3.56710
3s	3.02552	3.59112	6f	1.74601	1.97605
4s	2.06257	3.41506	7f	1.49749	1.95185
5s	1.46851	1.83578	8f	0.89793	0.92936
6s	2.07952	2.60770	9f	0.42672	0.45226
7s	2.01163	2.22650			
8s	1.25600	1.33280	5g	2.10798	2.27656
9s	0.36815	0.41519	6g	2.19568	3.20954
			7g	1.36687	1.81269
2p	2.11458	2.11912	8g	1.50104	1.62941
3p	3.73729	6.62635	9g	0.86071	1.40356
4p	1.42655	2.64403			
5p	1.04632	3.10157	6h	2.10472	2.28794
6p	1.61189	3.28033	7h	2.19745	2.78218
7p	2.53555	2.96312	8h	1.24921	1.83884
8p	1.01707	1.46329	9h	1.09102	1.28193
9p	0.47145	0.48308			
			7i	2.00756	2.26587
3d	2.51388	2.80658	8i	2.09750	2.46322
4d	2.24000	3.64965	9i	1.41920	1.94933
5d	1.19979	2.04584			
6d	2.45573	2.80165			
7d	1.17018	1.46144			
8d	0.70772	1.22960			
9d	0.48514	2.86314			

orbitals but inclusion of orbitals with higher  $l$  would increase the electron affinity by a fraction of an meV (Sundholm and Olsen [4] estimate this to be 0.5 meV). The biggest uncertainty comes from the model. Not all core-core correlation has been included but this effect is not expected to be as large as the core rearrangement already included. The present calculations have not included any relativistic splitting and represent the weighted average of the levels of each term. For the  ${}^2P$  the observed splitting is  $16 \text{ cm}^{-1}$ : a Breit-Pauli calculation for the valence correlation calculation yields  $14.3 \text{ cm}^{-1}$  which increases to  $15.47 \text{ cm}^{-1}$  for the calculation with core rearrangement. For the  ${}^3P$  calculation the Breit-Pauli calculation was performed only for the valence calculation yielding a splitting of  $(0, 2.66, 7.93) \text{ cm}^{-1}$  for the three  $J=(0, 1, 2)$  levels. Scaling the valence correlation results to agree with observation for the  ${}^2P$ , the electron affinity of  ${}^3P_0$  relative to  ${}^2P_{1/2}$  would be reduced about 0.6 meV.

#### IV. COMPARISON WITH OTHER THEORY AND EXPERIMENT

Table VI compares the present results with other theory and experiment.

Most theoretical results are for valence correlation. Let us consider this limit first, omitting the relativistic correction.

Because of the greater complexity of correlation in the anion, some correlation can easily be lost and most of the theories have predicted electron affinities that are too small. Raghavachari [2] used a perturbation scheme with which it is difficult to compare other than the final value. Kendell *et al.* [1] and Noro *et al.* [3] both used a multireference single and double configuration interaction (MR-SDCI) scheme but with different bases. The latter recognized the importance of computing energy differences from calculations where the weight to the reference configurations was the same in both states. They also used the Davidson correction [14] for estimating the remaining quadrupole corrections. Plots of the energies as a function of the weight of the reference state were flatter and easier to extrapolate. For boron, their estimate of the EA was 273 meV, though their uncorrected value of 278 meV appeared to be more accurate in that

TABLE VI. A comparison of the present nonrelativistic electron affinities (in meV) from different theories. The observed experimental value has been increased by 1 meV to account for relativistic effects.

Reference	Valence corr.	With core polarization
Present	273.2(2)	279.5(20)
Sundholm and Olsen [4]	268.6(17)	267.8(20)
Noro <i>et al.</i> (with correction) [3]	273	
Kendall and Dunning [1]	263	
Raghavachari [2]	269	

the agreement with experiment was better. However, we believe this limit is 273.2 meV, in agreement with their corrected value.

In many respects, the present calculations are most like those of Sundholm and Olsen [4]. In fact, for valence correlation up to  $n = 5$  our total energies are in perfect agreement. However, thereafter, Sundholm and Olsen estimate effects in a differential manner from which they determine the valence correlation limit to be 269.6(17) meV. It would appear that the different effects are enhanced when they are all considered together. Again, the effect of core-valence correlation was estimated from a small expansion including only  $s$  and  $p$  orbitals in the basis. A reduction in the electron affinity was predicted by this process whereas in our calculation a small increase was predicted for core-valence together with core rearrangement (calculation no. 2). Both of us agree on the reduction of the electron affinity by the relativistic effect though our estimate of  $-1.1$  meV was obtained from the  $n = 9$  valence correlation calculation using the non-fine-structure contributions of the Breit-Pauli Hamiltonian

(omitting the orbit-orbit interaction).

The experimental value of 277(10) meV has a rather large uncertainty. A more accurate value is needed to evaluate the different theories and the methods employed in determining the error estimates.

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