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The electron affinity of 2s2p^2 ^{4}P in boron

Charlotte Froese Fischer† and Gediminas Gaigalas‡

† Vanderbilt University, Box 1679B, Nashville, TN 37235, USA
‡ Institute of Theoretical Physics and Astronomy, Lithuanian Academy of Sciences, A Goštauto 12, Vilnius 232600, Lithuania

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Abstract. Systematic MCHF procedures are applied to the study of the electron affinity of boron relative to the 2s2p^2 ^{4}P state. Several models are used. An electron affinity of 1.072(2) eV is predicted.

1. Introduction

The *ab initio* calculation of electron affinities (EAs) for even small systems has been a challenge for many atomic and molecular codes. Quantum chemical calculations strive for 'chemical accuracy' of 1 kcal mol^{-1} (40 meV). In experimental atomic physics the measured accuracy varies by orders of magnitude for different systems [1] but accuracies to a few meV are common. New resonant ionization, spectroscopic methods for negative ions can yield EAs to an accuracy of 0.1–0.2 meV [2]. A recent measurement for the electron affinity of Al [3] has reduced the uncertainty of an earlier measurement from 10 meV to only 0.3 meV. Thus considerable progress has been made in experimental techniques. With present day high-performance computers, similar improvements in accuracy should be possible for *ab initio* results.

Many calculations for electron affinities have been performed for the first row elements, including boron. For a review of early calculations for a range of systems, see Bunge and Bunge [4]. More recently, most calculations have relied on quantum chemical basis set methods [5] 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* [6] using an extensive basis in a multi-reference configuration interaction (MRCI) calculation. Only single and double (SD) replacements are included and the method relies on corrections that estimate the effect of the omitted triple and quadruple excitations. Uncertainty estimates are not usually provided.

Recently, an MCHF electron affinity of 279.5(20) meV was reported for the electron affinity of the boron ground state [7] to be compared with a measured value of 277(10) meV [1]. Most difficult to estimate is the uncertainty in the computed result. Only more accurate experimental data will determine the validity of the assumptions about uncertainty. Another interesting case is the electron affinity of the excited 2s2p^2 ^{4}P state. With the binding of an extra 2p electron to form the negative ion, the lowest state is 2s2p^3 ^{5}S for which the selection rules greatly reduce the size of the expansions needed in an MCHF calculation. This case was investigated by Bunge and Bunge [4] almost two decades ago who reported an EA of 0.89(2) eV. In this paper we revisit this problem and report results from systematic MCHF calculations. Several different computational models are used which are important in assessing the uncertainty.

2. MCHF calculations for the electron affinity

In an MCHF calculation [8], the wavefunction is expressed as a linear combination of configuration state functions (CSFs) which are antisymmetrized products of one-electron spin-orbitals. A set of orbitals, or active set (AS), determines the set of all possible CSFs or the complete active space (CAS) for an MCHF calculation. The latter grows rapidly with the number of electrons and also the size of the active set. Thus most MCHF expansions are limited to a restricted active space (RAS). Several different notations have been proposed for defining the RAS. Some are expressed in terms of single (S), double (D), triple (T) and quadruple (Q) excitations from one or more reference CSFs [9]. In systematic MCHF calculations it has been found convenient to define the RAS in terms of principal quantum numbers which, for virtual orbitals, merely define the order in which they are introduced into the basis. CSFs may be expressed in a canonical form by associating with each CSF an integer (or sequence) constructed from the one-electron principal quantum numbers assumed to be in increasing left to right order. There may, of course, be many different spin-angular couplings associated with a given integer. The latter may then be used to define an order for the CSFs and by specifying the highest integer provides a simple notation for defining the RAS, at least for few-electron systems. For example, (1 1 3 4) defines a RAS where the $1s^2$ core is inactive, the maximum principal quantum number is 4 but at least one outer electron must have $n \leqslant 3$. One feature of large-scale computation is that, as the AS is increased, the important CSFs containing high-n orbitals approach the CSFs obtained from SD excitations of a multi-reference (MR) set. The members of this set cannot always be identified in advance and adaptive techniques may be used [11]. In previous publications [7, 10] we have described computational models in terms of 'layers' specifying the range of principal quantum numbers for each group of electrons. In this paper, we specify instead, the range of principal quantum numbers for each electron. Since the lowest principal quantum numbers are determined by symmetry, parity, and the exclusion principle, only the highest need to be specified. From the set of principal quantum numbers, all possible CSFs are generated with the orbital angular quantum number restricted to $l \leqslant 6$ (i orbitals). Another restriction in our codes is that orbitals with $l \geqslant 3$ can be at most doubly occupied, a restriction not expected to be significant in the present study.

The electron affinity of an atom is an outer-electron property. In the valence correlation model, which we describe first, the $1s^2$ core is considered to be inactive and the atom and negative ion (or anion) can be treated as three- and four-electron systems, respectively. Up to the active set containing all orbitals with principal quantum numbers $\leqslant 7$ (called the $n = 7$ AS) all possible CSFs were included. However, deletion of CSFs with coefficients less than 10^{-6} did not affect the total energy to the digits reported. In the case of ^{5}S, the last CSF had principal quantum numbers (1 1 5 6 7 7). This observation was used to restrict the new CSFs for the $n = 8$ calculation. In the case of the ^{4}P, orbitals with $n = 8$ were constrained to be doubly occupied. The range of principal quantum numbers for this calculation is summarized in table 1. Notice that, because two schemes were used for the anion the RAS for ^{5}S consists of a union of two sequences.

The calculation for a specific n consists of the subset of the RAS defined in table 1. Table 2 reports the size of the RAS, the individually optimized energy, and the electron affinity. The latter may be defined as $E_n(^4\mathrm{P}) - E_n(^5\mathrm{S})$ (the $\Delta n = 0$ electron affinity) but another definition, motivated by the fact that more orbitals are needed to represent the

Table 1. The range of principal quantum numbers defining the restricted active space for two different computational models.

B(^{4}P)	B$^-$(^{5}S)
Valence correlation	
1 1 7 8 8	1 1 7 7 7 7 ∪ 1 1 5 6 8 8
With core polarization	
1 1 5 5 5	1 1 5 5 5 5
∪ 1 2 3 8 8	∪ 1 2 3 4 5 5 ∪ 1 2 3 3 8 8

Table 2. Systematic MCHF energies for restricted active space calculations with an increasing active set of orbitals. For each calculation, n specifies the maximum quantum number; angular quantum numbers were restricted to $l \leqslant 6$; orbitals were separately optimized for both states.

	B ^{4}P		B$^-$ ^{5}S		EA (eV)	
Expansion	CSF	E_n	CSF	E_n	$\Delta n = 0$	$\Delta n = 1$
Valence correlation only						
$n = 3$	11	−24.467 169 2	14	−24.502 744 6	0.968 06	
$n = 4$	64	−24.469 344 6	141	−24.507 948 0	1.050 45	
$n = 5$	240	−24.469 714 1	866	−24.508 882 5	1.065 83	1.075 88
$n = 6$	699	−24.469 803 0	3 921	−24.509 101 8	1.069 38	1.071 79
$n = 7$	1 755	−24.469 831 9	14 131	−24.509 167 7	1.070 38	1.071 17
$n = 8$	3 475	−24.469 839 5	18 057	−24.509 186 4	1.070 68	1.070 89
Estimated non-relativistic limit					1.0708(1)	
Estimated limit with relativistic correction					1.0700(1)	
Valence correlation + core polarization						
$n = 4$	1 381	−24.487 859 9	2 667	−24.524 801 8	1.005 24	
$n = 5$	2 119	−24.490 686 3	8 603	−24.529 351 4	1.052 13	
$n = 6$	4 622	−24.491 259 5	13 701	−24.530 456 7	1.066 105	1.082 21
$n = 7$	8 486	−24.491 473 0	21 753	−24.530 818 0	1.070 632	1.076 44
$n = 8$	11 611	−24.491 560 9	23 203	−24.530 962 9	1.072 17	1.074 58
Estimated non-relativistic limit					1.0733(3)	
Estimated limit with relativistic correction					1.0724(4)	

negative ion, could be $E_{n-1}(^4\mathrm{P}) - E_n(^5\mathrm{S})$ (the $\Delta n = 1$ electron affinity). Table 1 shows that the former is increasing with n whereas the latter is decreasing. Both can be extrapolated approximately; however, in this case the results are so well converged that one can also use the average of the last two values with the uncertainty being the difference between the average and the computed values. These are modified by a relativistic shift which from an $n = 6$ calculation was found to be $-0.000\,78$ eV.

But the outer correlation model will have some error associated with it arising from the neglect of correlation with the 1s^2 core which represents the polarization of the core by the outer electrons. Table 1 lists the range of principal quantum numbers for this model which includes a single excitation from the core. All calculations start by including all the CAS from an $n = 5$ valence correlation calculation, but when the 1s^2 core is opened, the second electron must have a principal quantum number no greater than 2; the third, no greater than 3 at which point the RAS begin to differ for the two cases. In all calculations, high-n orbitals need to be doubly occupied. Since ^{4}P has fewer electrons, there are also fewer in the 'core'. At the $n = 5$ level, the four-electron 'core' is (1 2 3 4) whereas for $n \geqslant 6$ it has been restricted further to (1 2 3 3). Notice also that this valence + core-polarization calculation has restricted valence correlation appreciably more than the first model calculation. The

$\Delta n = 0$ and $\Delta n = 1$ electron affinities can each be extrapolated approximately. A fairly reliable technique is to use the ratio (r) of the last two changes. Then, if Δ is the last change, assuming the remaining corrections form a geometric series, the remainder can be shown to be $r\Delta/(1-r)$. In this case the average of the two electron affinities is slowly decreasing and this may also be used in determining the limit and its uncertainty. These extrapolated values too need to be corrected for a relativistic shift of $-0.000\,935$ eV.

Finally, a calculation was performed that treats both systems as a whole. Now the configuration space needs to be constricted even more and a MR-SD pair-correlation scheme was employed similar to the one used by Noro *et al* [6] for outer correlation. Basically, SD replacements are applied to the most important components of the wavefunction and coupled as pair-correlation functions of the reference CSF. These are listed in table 3 for the two states. Table 4 reports the number of CSFs and the energies from increasing active sets. The latter increase rapidly with the size of the active set.

Table 3. The multi-reference configuration states for a full correlation MR-SD study that includes core–core correction.

^{4}P	2s2p^2,	2s3p^2,	2s3d^2,	2p^{2}3d,	2p3s3p
^{5}S	2s2p^3,	2s2p3p^2,	2s2p3d^2,	2p^{2}3s3p,	2p^{2}3p3d

Table 4. Systematic MCHF results for multi-reference SD pair-correlation excitations.

	B 4P		B$^-$ 5S		EA (eV)	
Expansion	CSF	E_n	CSF	E_n	$\Delta n = 0$	$\Delta n = 1$
$n = 4$	681	−24.510 810 4	757	−24.546 749 4		
$n = 5$	1 590	−24.517 483 1	1 953	−24.554 478 4		
$n = 6$	2 987	−24.5197691	3 876	−24.558 030 2		
$n = 7$	4 971	−24.520 8036	6 674	−24.559 651 8		
$n = 8$	7 549	−24.521 280 8	10 356	−24.560 343 6	1.062 95	1.075 90
$n = 9$	10 721	−24.521 504 7	14 922	−24.560 664 2	1.065 58	1.071 68
$n = 10$	14 487	−24.521 618 6	20 372	−24.560 826 8	1.066 93	1.070 03
Extrapolated MR-CI limit					1.068 48	
With Davidson correction					1.072 94	
Estimated limit with relativistic correction					1.071 76	

For large n, the weight of the reference set converges to 0.9974 and 0.9948, respectively, for ^{4}P and ^{5}S. This small difference of 0.26% requires a small correction. In arriving at accurate electron affinities for boron using the MR-SD scheme, Noro *et al* applied a Davidson correction [13] to estimate omitted correlation. Though a number of different schemes have been proposed (see [14] for a discussion), we use the same correction used by Noro *et al*, namely

$$\Delta E = \left[1 - \sum_i c_i^2\right](E_{\mathrm{ref}} - E_{\mathrm{MCHF}})$$

where the sum is over the reference configuration states, and E_{ref} is the energy of the interaction matrix restricted to the reference configuations.

Table 4 also reports the corrected energies. The electron affinity is increased by 0.004 46 eV by this correction and, as in earlier models, decreased when relativistic corrections are included. In the full-correlation model the relativistic shift increased in magnitude to −0.001 1821 eV. Table 5 compares various relativistic shift calculations. For MCHF calculations this effect depends on the wavefunction approximation, increasing as more inner-shell correlation is included. However, the latter is in good agreement with the difference of a Hartree–Fock and fully relativistic GRASP [15] calculation.

Table 5. Estimates of relativistic corrections (in eV) from various approximations where (r) refers to the inclusion of relativistic shift corrections and GRASP is a fully relativistic variational calculation. The HF electron affinity is 0.5252 eV.

Approx.	Rel. corr.
HF(r) − HF	−0.000 951
GRASP − HF	−0.001 111
MCHF(r) − MCHF $(n = 6)$	
Core-pol.	−0.000 935
Full corr.	−0.001 182

In the study of Ca^- [12] core polarization was found to reduce the electron affinity substantially, but it increased the electron affinity for the boron ground state and we see a similar effect here. Our final estimate of the electron affinity is 1.072 (2) eV. The second model is expected to be the more reliable since the full correlation calculation for a six-electron system is a much more difficult calculation requiring fairly large corrections. Even so, the final answer is close to that of the valence correlation with core-polarization model. The uncertainty of 2 meV is based on the difference in the EA for the first two models. This result differs significantly from the value of 0.89(2) eV determined by Bunge and Bunge [4]. Their 1978 calculations were restricted to relatively small orbital sets, the highest angular momentum orbital being a single f orbital.

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