

Calculation of the Electron Affinity of Boron*

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(Received 8 January 1968)

Ab initio calculations have been made for the ground states of neutral B and B⁻ using configuration-interaction wave functions which included the Hartree-Fock configuration, single excitations, and double excitations of the types (1*s*,2*p*), (2*s*,2*s*), (2*s*,2*p*), and (2*p*,2*p*). These calculations indicate that B⁻ is stable and that the electron affinity of B is 0.0028 Hartrees (0.08 eV). Contributions from the omitted types of correlations were investigated by making separate-pair calculations for the (1*s*,1*s*) and (1*s*,2*s*) pairs. These contributions do not affect the qualitative conclusions. Consideration of the probable errors in the calculations leads to the definite conclusion that B⁻ is stable and to an estimate of 0.25 eV for the electron affinity of boron.

INTRODUCTION

THE problem of determining the existence or non-existence of atomic negative ions is of interest both as an end in itself and in its relation to other problems of atomic physics. Of use are not only the atomic electron affinities themselves, but also descriptions of the negative ions, which may be applied in discussions of processes such as electron photodetachment or the scattering of electrons by atoms. Two recent review articles^{1,2} summarize the work which has been done in this field to date and discuss more fully some of the problems related to negative ions.

Among first-row atoms, the electron affinities of Li, C, O, and F are known from experiment,³ while the electron affinities of Be, B, and N have not been determined experimentally. This situation has aroused considerable interest in predicting the stabilities of negative ions, and a number of procedures have been advanced for estimating the electron affinities of first-row atoms.⁴⁻⁹ The procedure which appears to us to have the most reliable theoretical grounding is that of Clementi and McLean,⁹ who obtain approximate atomic and negative-ion energies by extrapolation from accurate Hartree-Fock calculations.

Unextrapolated Hartree-Fock energies do not provide a sound basis for estimating electron affinities. For example, Hartree-Fock results predict C⁻ and F⁻ to be stable but indicate instability for Li⁻ and O⁻. There are two principal reasons why Hartree-Fock energies of atoms and negative ions are not directly comparable. The first is that the orbital-occupancy and symmetry

requirements of the restricted Hartree-Fock method are not equally restrictive for an atom and its ion. The calculated stability of C⁻, for example, is largely due to the fact that its ⁴S state is particularly well approximated by a restricted Hartree-Fock wave function. A second, and more systematic, discrepancy between atom and negative-ion Hartree-Fock energies is due to the inability of the Hartree-Fock method to describe electron correlation. An atom and its ion will have different correlation energies, not only because the ion contains an additional electron, but also because the distribution of all the valence-shell electrons will be quite different in the two systems. The correlation energy of a negative ion is invariably larger than that of the corresponding neutral atom, and the difference between these two correlation energies is often comparable to the electron affinity. Clementi and McLean's extrapolation involves estimates of the correlation energies, which vary rather smoothly with the nuclear charge and the number of electrons.

Because the correlation energies are large compared to the electron affinities under study, it would be desirable to have more accurate atomic and negative-ion calculations. Efforts in this direction have been relatively limited, particularly with respect to the ions. The most commonly used method of more accurate calculations is that of configuration interaction (CI), and the largest negative ion for which an accurate CI study has been reported is Li⁻, which Weiss¹⁰ found to be bound in 1961. Very recently Weiss¹¹ has reported very interesting but less complete *ab initio* CI results for the electron affinities of Na and K. In these calculations, Weiss compares the neutral-atom Hartree-Fock energies with the energies of negative-ion CI wave functions which include the Hartree-Fock function plus configurations in which the outer pair of *s* electrons (3*s*² for Na⁻ and 4*s*² for K⁻) are excited to different virtual orbitals. The present authors have made CI calculations¹² on the ground states of N and N⁻, and O and O⁻. These calculations are slightly less extensive than

* Supported in part by the National Science Foundation (Grant No. GP-5555).

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¹ L. M. Branscomb, *Atomic and Molecular Processes* (Academic Press Inc., New York, 1962), p. 100.

² B. L. Moiseiwitsch, *Advances in Atomic and Molecular Physics* (Academic Press Inc., New York, 1965), Vol. 1, p. 61.

³ B. Ya'akobi, *Phys. Letters* **23**, 655 (1966).

⁴ G. Glockler, *Phys. Rev.* **46**, 111 (1934).

⁵ H. R. Johnson and F. Rohrlach, *J. Chem. Phys.* **30**, 1608 (1959).

⁶ B. Edlen, *J. Chem. Phys.* **33**, 98 (1960).

⁷ M. Kaufman, *Astrophys. J.* **137**, 1296 (1963).

⁸ R. J. S. Crossley, *Proc. Phys. Soc. (London)* **83**, 375 (1964).

⁹ E. Clementi and A. D. McLean, *Phys. Rev.* **133**, A419 (1964).

¹⁰ A. W. Weiss, *Phys. Rev.* **122**, 1826 (1961).

¹¹ A. W. Weiss, *Phys. Rev.* **166**, 70 (1968).

¹² H. F. Schaefer and F. E. Harris (unpublished).

those reported in this work and indicate that N^- remains unstable as in the Hartree-Fock approximation, but that O^- is stable.

Although Branscomb and Smith¹³ have reported the occurrence of B^- in a discharge in BF_3 , the electron affinity of B is not known experimentally. Several estimation procedures⁵⁻⁹ predict B^- to be stable, but one⁴ does not. The purpose of the present research is to determine by *ab initio* CI calculations the stability of the 3P ground state of B^- relative to the 2P state of neutral B. This paper contains the results of the calculations and the conclusions which may be drawn from them by consideration of the known pattern of accuracy of studies of this kind.

METHOD

While it is within the realm of possibility to make essentially complete calculations of the correlation energy in B^- , as the present authors have recently done¹⁴ for neutral B, the computational labor would be excessive and, in the light of experience, unnecessary. The alternative chosen here was to calculate explicitly that part of the correlation energy which might be expected to be substantially different in B and B^- , after which marginally significant contributions could be added in an approximate manner.

The specific approach taken was to start from CI calculations for B and B^- which contained all configurations necessary to give a good description of all the *L*-shell correlations and of the $1s$ - $2p$ intershell correlation, the latter being expected to be significant because B^- has one more $2p$ electron than B. The remaining types of correlation were initially omitted on the premise that they would be nearly the same in both systems and would enter nearly additively. More complete estimates of the correlation energies of B and B^- were then obtained by explicit evaluation and addition of the omitted types of correlation.

The approximation of additive pair correlations is based on ideas introduced by Brueckner¹⁵ and Bethe and Goldstone,¹⁶ and applied more specifically to electronic systems by Sinanoglu¹⁷ and by Nesbet.^{18,19} The pair correlations used in this study were obtained by the CI procedure described by Nesbet. In terms of this formulation, the present authors' earlier study of neutral boron indicated that different pair correlations were additive to within about 2% of the total correlation energy, thereby validating the approach to be used here.

The actual computations were carried out by the procedure described in detail in previous work.¹⁴

L-SHELL CI CALCULATIONS FOR B AND B^-

The starting points for these calculations were the Hartree-Fock functions of Bagus and Gilbert²⁰ for B and of Clementi and McLean⁹ for B^- . The Hartree-Fock basis set of each system was augmented by the addition of six virtual atomic orbitals denoted, according to their symmetry, s_I , s_{II} , p_I , p_{II} , d_I , and d_{II} . These virtual orbitals consisted of *M*- and *N*-shell Slater-type basis orbitals which had been orthogonalized to each other and to the Hartree-Fock orbitals. For example, the p_{II} virtual orbital was constructed by orthogonalizing a $4p$ orbital to both the $2p$ Hartree-Fock orbital and the previously constructed p_I orbital.

The Hartree-Fock orbitals (denoted $1s$, $2s$, and $2p$) and the virtual orbitals were used to construct nearly all possible configurations describable as single or double excitations from the Hartree-Fock *L*-shell orbitals. For neutral B the configurations formed in this way are those numbered 2 through 27 in Table I, while those formed for the B^- ion appear as configurations 2 through 33 in Table II. For each system, configuration 1 is the Hartree-Fock wave function. The configurations for B and B^- correspond except that six configurations of B^- of the type $2p^2 \rightarrow xy$ (numbers 20 through 25 in Table II) do not exist for neutral B, which has only a single $2p$ electron.

The 27- and 33- configuration wave functions defined in the preceding paragraph were first used to determine optimum orbital exponents for the virtual orbitals. As an initial approximation, the added basis orbitals were all given the same orbital exponent. This technique has been used successfully by Nesbet¹⁸ with somewhat larger basis sets in Bethe-Goldstone calculations. By minimization of the CI energies, optimum orbital exponents were determined to be 1.38 for B and 0.99 for B^- . The smaller value for B^- reflects the fact that the electron distribution in the negative ion is more diffuse than in the corresponding neutral atom.

Next, the virtual orbital exponents were optimized individually in two cycles. Table III shows the orbital exponents and corresponding energies of B and B^- for the optimum single exponents and after each cycle of individual optimization. The most important result in Table III is that the energy improvement obtained by optimizing the exponents individually is much greater for B^- (0.004447 hartrees) than for neutral B (0.000092 hartrees). This fact indicates how much more difficult it is to describe the electron distribution in B^- than in neutral B. The much smaller improvement in the second cycle of individual optimizations leads the authors to believe that further optimization of the exponents would

¹³ L. M. Branscomb and S. J. Smith, *J. Chem. Phys.* **25**, 598 (1956).

¹⁴ H. F. Schaefer and F. E. Harris, *Phys. Rev.* **167**, 67 (1968).

¹⁵ K. A. Brueckner, *Phys. Rev.* **96**, 508 (1954); **97**, 1353 (1955).

¹⁶ H. A. Bethe and J. Goldstone, *Proc. Roy. Soc. (London)* **A238**, 551 (1957).

¹⁷ O. Sinanoglu, *J. Chem. Phys.* **36**, 706 (1962).

¹⁸ R. K. Nesbet, *Phys. Rev.* **155**, 51 (1967).

¹⁹ R. K. Nesbet, *Phys. Rev.* **155**, 56 (1967).

²⁰ This function appears in a supplement to a paper by A. D. McLean and M. Yoshimine [*IBM J. Res. Develop.* (to be published)].

TABLE I. Configuration-interaction wave function for the 2P ground state of the boron atom.

Cfg. No. n	Configuration	Energy contribution $E(n) - E(n-1)$ (hartrees)	Coefficient in 39-cfg. eigenvector	Energy $E(n)$ of n -cfg. function (hartrees)
1	$1s^2 2s^2 2p$...	0.96459476	-24.52905860
2	$1s^2 2s s_I 2p$	-0.00020852	0.02880765	-24.52926713
3	$1s^2 2s s_{II} 2p$	-0.00007156	0.00773885	-24.52933869
4	$1s^2 2s d_I 2p$	-0.02004634	0.12985626	-24.54938503
5	$1s^2 2s d_{II} 2p$	-0.00064986	0.01725152	-24.55003489
6	$1s^2 s_I^2 2p$	-0.00307631	-0.03373559	-24.55311120
7	$1s^2 s_{II}^2 2p$	-0.00022215	-0.00519801	-24.55333335
8	$1s^2 (s_I s_{II})^1 S 2p$	-0.00002717	0.00338765	-24.55336052
9	$1s^2 2p^3$	-0.02899551	-0.19990818	-24.58235602
10	$1s^2 (p_I^2)^1 S 2p$	-0.00005226	0.00418044	-24.58240828
11	$1s^2 (p_{II}^2)^1 S 2p$	-0.00032247	0.01922158	-24.58273075
12	$1s^2 (p_I p_{II})^1 S 2p$	-0.00006202	-0.00762166	-24.58279278
13	$1s^2 p_I 2p^2$	-0.00000498	0.00773348	-24.58279775
14	$1s^2 p_{II} 2p^2$	-0.00459976	0.06456434	-24.58739752
15	$1s^2 (d_I^2)^1 S 2p$	-0.00184624	0.02994734	-24.58924375
16	$1s^2 (d_{II}^2)^1 S 2p$	-0.00007810	0.00506702	-24.58932185
17	$1s^2 (d_I d_{II})^1 S 2p$	-0.00000745	0.00144928	-24.58932929
18	$1s^2 2s^2 p_I$	-0.00001129	-0.00409358	-24.58934059
19	$1s^2 2s^2 p_{II}$	-0.00001193	-0.00590861	-24.58935251
20	$1s^2 2s s_I p_I$	-0.00212607	0.03606961	-24.59147858
21	$1s^2 2s s_I p_{II}$	-0.00301605	0.04860416	-24.59449463
22	$1s^2 2s s_{II} p_I$	-0.00017846	0.00679412	-24.59467309
23	$1s^2 2s s_{II} p_{II}$	-0.00004266	0.00415265	-24.59471576
24	$1s^2 2s p_I d_I$	-0.00000079	0.00050760	-24.59471654
25	$1s^2 2s p_I d_{II}$	-0.00011521	0.00620416	-24.59483175
26	$1s^2 2s p_{II} d_I$	-0.00144759	0.02838748	-24.59627934
27	$1s^2 2s p_{II} d_{II}$	-0.00007180	0.00588616	-24.59635114
28	$1s 2s^2 s_I 2p$	-0.00001653	0.00151816	-24.59636767
29	$1s 2s^2 s_{II} 2p$	-0.00000171	0.00030223	-24.59636938
30	$1s 2s^2 d_I 2p$	-0.00008221	0.00326115	-24.59645160
31	$1s 2s^2 d_{II} 2p$	-0.00004974	0.00181806	-24.59650133
32	$1s 2s^2 s_I p_I$	-0.00018586	0.00429566	-24.59668720
33	$1s 2s^2 s_I p_{II}$	-0.00011619	0.00282352	-24.59680338
34	$1s 2s^2 s_{II} p_I$	-0.00003386	0.00125749	-24.59683725
35	$1s 2s^2 s_{II} p_{II}$	-0.00009067	0.00194278	-24.59692792
36	$1s 2s^2 p_I d_I$	-0.00028748	0.00521053	-24.59721540
37	$1s 2s^2 p_I d_{II}$	-0.00025602	0.00371788	-24.59747142
38	$1s 2s^2 p_{II} d_I$	-0.00012268	0.00283002	-24.59759410
39	$1s 2s^2 p_{II} d_{II}$	-0.00031302	0.00377397	-24.59790712

result in an energy improvement of no more than 0.0001 hartree for either system. The exponents listed in the rows labeled "second cycle" in Table III were therefore adopted for use in subsequent calculations.

A more vivid picture of the significance of the exponent optimization is provided by examining radial plots of the Hartree-Fock and optimized virtual orbitals. Figures 1 and 2 show values of $rR(r)$ for these orbitals, where $R(r)$ is an orbital radial dependence. The plots show that the major difference in the Hartree-Fock functions of B and B⁻ is in the $2p$ orbital, and that, except for d_I , the virtual orbitals parallel the difference in the $2p$ orbitals. This does not happen for d_I because its most important function is to treat $2s$ excitations.

An interpretation of the results obtained to this point requires a closer examination of the configurations used in the calculations. Each configuration in Tables I and II refers to a simultaneous eigenfunction of orbital and spin angular momentum (an " L - S eigenfunction"). For some configurations, only a single L - S eigenfunction exists, and that is of course what is referred to. For other configurations, however, there exist several L - S eigen-

functions. In some cases the eigenfunction described by a particular vector coupling scheme is known (from previous calculations on neutral B) to be far more important than the other possible eigenfunctions. In these cases, the important eigenfunction was arbitrarily used for both B and B⁻, and the vector coupling is indicated in the specification of the configuration in Tables I and II. An example of this situation is given in configuration 8 of Table I, where the s_I and s_{II} electrons are coupled to form a 1S two-electron eigenfunction. The other possible 2P boron wave function which can be formed from the orbital occupancy $1s^2 s_I s_{II} 2p$ can be thought of as involving the coupling of the s_I and s_{II} electrons to form a two-electron 3S state. This second L - S eigenfunction has a far smaller contribution to the energy of B than does the first. For configurations where explicit vector couplings are not shown, all the linearly independent L - S eigenfunctions were included in the calculations, and an optimum vector coupling was determined *via* the CI. This single optimally-coupled eigenfunction is that associated with the results given in Tables I and II.

TABLE II. Configuration-interaction wave function for the 3P ground state of the boron negative ion.

Cfg. No. n	Configuration	Energy contribution $E(n) - E(n-1)$ (hartrees)	Coefficient in 45-cfg. eigenvector	Energy $E(n)$ of n -cfg. function (hartrees)
1	$1s^2 2s^2 2p^2$...	0.95708467	-24.51919154
2	$1s^2 2s s_{II} 2p^2$	-0.00000006	0.01229132	-24.51919161
3	$1s^2 2s s_{II} 2p^2$	-0.00008151	0.02177714	-24.51927311
4	$1s^2 2s d_I 2p^2$	-0.02187009	0.14294895	-24.54114321
5	$1s^2 2s d_{II} 2p^2$	-0.00299286	0.04843178	-24.54413607
6	$1s^2 s_I^2 2p^2$	-0.00237550	-0.02866914	-24.54651157
7	$1s^2 s_{II}^2 2p^2$	-0.00017387	-0.01654516	-24.54668544
8	$1s^2 (s_I s_{II})^1 S 2p^2$	-0.00127507	-0.02148612	-24.54796051
9	$1s^2 2p^4$	-0.00922896	0.11263329	-24.55718947
10	$1s^2 (p_I^2)^1 S 2p^2$	-0.00086187	0.02229578	-24.55805134
11	$1s^2 (p_{II}^2)^1 S 2p^2$	-0.00070664	0.03907560	-24.55875798
12	$1s^2 (p_I p_{II})^1 S 2p^2$	-0.00095313	-0.03258123	-24.55971111
13	$1s^2 p_I 2p^3$	-0.00182164	0.03658689	-24.56153274
14	$1s^2 p_{II} 2p^3$	-0.00719844	0.00673450	-24.56873118
15	$1s^2 (d_I^2)^1 S 2p^2$	-0.00263206	0.00251699	-24.57136325
16	$1s^2 (d_{II}^2)^1 S 2p^2$	-0.00007095	0.04057667	-24.57143420
17	$1s^2 (d_I d_{II})^1 S 2p^2$	-0.00002207	0.09361624	-24.57145627
18	$1s^2 2s^2 2p p_I$	-0.00000735	0.02197220	-24.57146362
19	$1s^2 2s^2 2p p_{II}$	-0.00000481	-0.01853393	-24.57146843
20	$1s^2 2s^2 p_I^2$	-0.00157138	-0.03176566	-24.57303981
21	$1s^2 2s^2 p_{II}^2$	-0.00227654	-0.08564278	-24.57531635
22	$1s^2 2s^2 p_I p_{II}$	-0.00300929	0.05705958	-24.57832563
23	$1s^2 2s^2 d_I^2$	-0.00153174	0.03558762	-24.57985737
24	$1s^2 2s^2 d_{II}^2$	-0.00009412	0.01565641	-24.57995149
25	$1s^2 2s^2 d_I d_{II}$	-0.00045695	0.01809221	-24.58040844
26	$1s^2 2s 2p s_I p_I$	-0.00509252	0.05954524	-24.58550096
27	$1s^2 2s 2p s_I p_{II}$	-0.00158457	0.04819689	-24.58708553
28	$1s^2 2s 2p s_{II} p_I$	-0.00204138	0.04616757	-24.58912691
29	$1s^2 2s 2p s_{II} p_{II}$	-0.00304132	0.06151398	-24.59216823
30	$1s^2 2s 2p p_I d_I$	-0.00106623	0.02289596	-24.59323446
31	$1s^2 2s 2p p_I d_{II}$	-0.00051198	0.01819460	-24.59374644
32	$1s^2 2s 2p p_{II} d_I$	-0.00433841	0.06429322	-24.59808485
33	$1s^2 2s 2p p_{II} d_{II}$	-0.00029592	0.01574037	-24.59838077
34	$1s^2 s^2 2p^2 s_I$	-0.00002265	0.00173352	-24.59840342
35	$1s^2 s^2 2p^2 s_{II}$	-0.00000336	0.00047372	-24.59840678
36	$1s^2 s^2 2p^2 d_I$	-0.00005133	0.00254869	-24.59845811
37	$1s^2 s^2 2p^2 d_{II}$	-0.00004206	0.00178664	-24.59850018
38	$1s^2 s^2 2p s_I p_I$	-0.00014295	0.00390986	-24.59864313
39	$1s^2 s^2 2p s_I p_{II}$	-0.00043360	0.00556515	-24.59907672
40	$1s^2 s^2 2p s_{II} p_I$	-0.00002156	0.00121088	-24.59909828
41	$1s^2 s^2 2p s_{II} p_{II}$	-0.00019042	0.00321531	-24.59928870
42	$1s^2 s^2 2p p_I d_I$	-0.00019249	0.00454304	-24.59948119
43	$1s^2 s^2 2p p_I d_{II}$	-0.00020115	0.00368132	-24.59968234
44	$1s^2 s^2 2p p_{II} d_I$	-0.00033383	0.00489028	-24.60001617
45	$1s^2 s^2 2p p_{II} d_{II}$	-0.00073023	0.00626338	-24.60074640

The foregoing discussion indicates that, for practical purposes, the present calculations are complete with respect to the multiplicity of L - S eigenfunctions for each orbital occupancy. The only other single or double

L -shell excitations which have been omitted from the calculations are those of the type $2s^2 \rightarrow s_i d_j$. These configurations were of negligible importance in neutral B and presumably also in B^- . Triple and quadruple exci-

TABLE III. Optimization of orbital exponents in L -shell CI calculations. Energies are in hartrees.

	Orbital exponents						Energy	Energy improvement
	3s	3p	3d	4s	4p	4d		
2P boron atom								
Single orbital exponent	1.38	1.38	1.38	1.38	1.38	1.38	-24.596259	...
First cycle of individual optimizations	1.25	1.38	1.52	1.40	1.35	1.62	-24.596341	0.000082
Second cycle	1.26	1.47	1.62	1.42	1.33	1.64	-24.596351	0.000010
3P boron negative ion								
Single orbital exponent	0.99	0.99	0.99	0.99	0.99	0.99	-24.593934	...
First cycle of individual optimizations	1.27	0.99	1.50	1.15	0.67	1.16	-24.598323	0.004389
Second cycle	1.44	0.99	1.56	1.14	0.67	1.18	-24.598381	0.000058

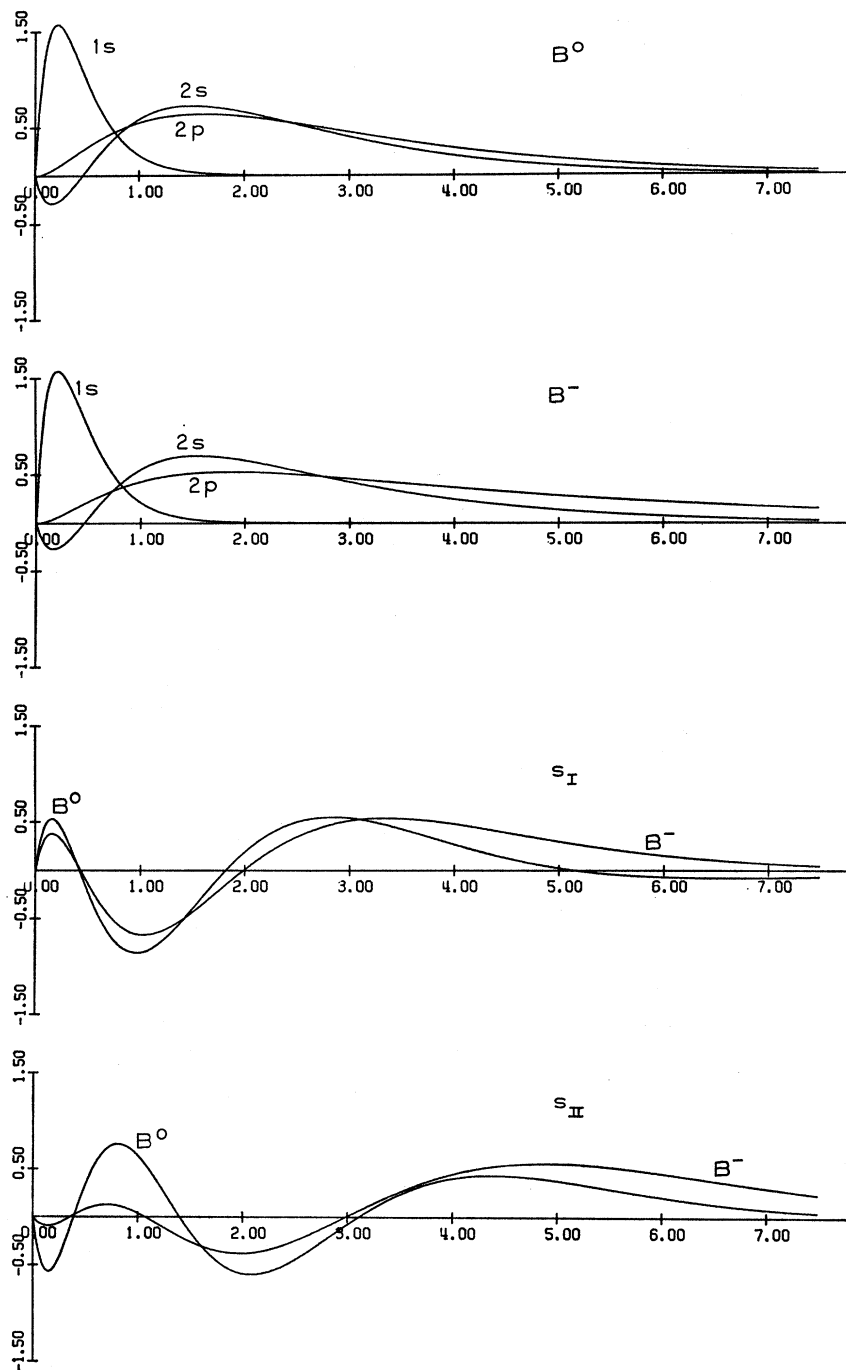


FIG. 1. Hartree-Fock orbitals and virtual s orbitals used to describe L -shell correlation in B and B^- .

tations are also believed to be small so that the present calculations are reasonably complete L -shell CI's with the virtual orbitals in use here.

The Hartree-Fock and various L -shell CI's of this work are summarized in the first three lines of Table IV. The table shows that the CI, and particularly the individual orbital exponent optimizations, have qualitatively altered the Hartree-Fock indication of the instability of B^- . However, the omission of the $(1s, 2p)$ cor-

relation, and the fact that much of the correlation energy of neutral B is still unaccounted for, renders tentative any conclusions at this level of approximation.

ADDITION OF $(1s, 2p)$ CORRELATION TO THE CI'S

Having obtained virtual orbitals and configurations suitable for describing the L -shell correlation, the next

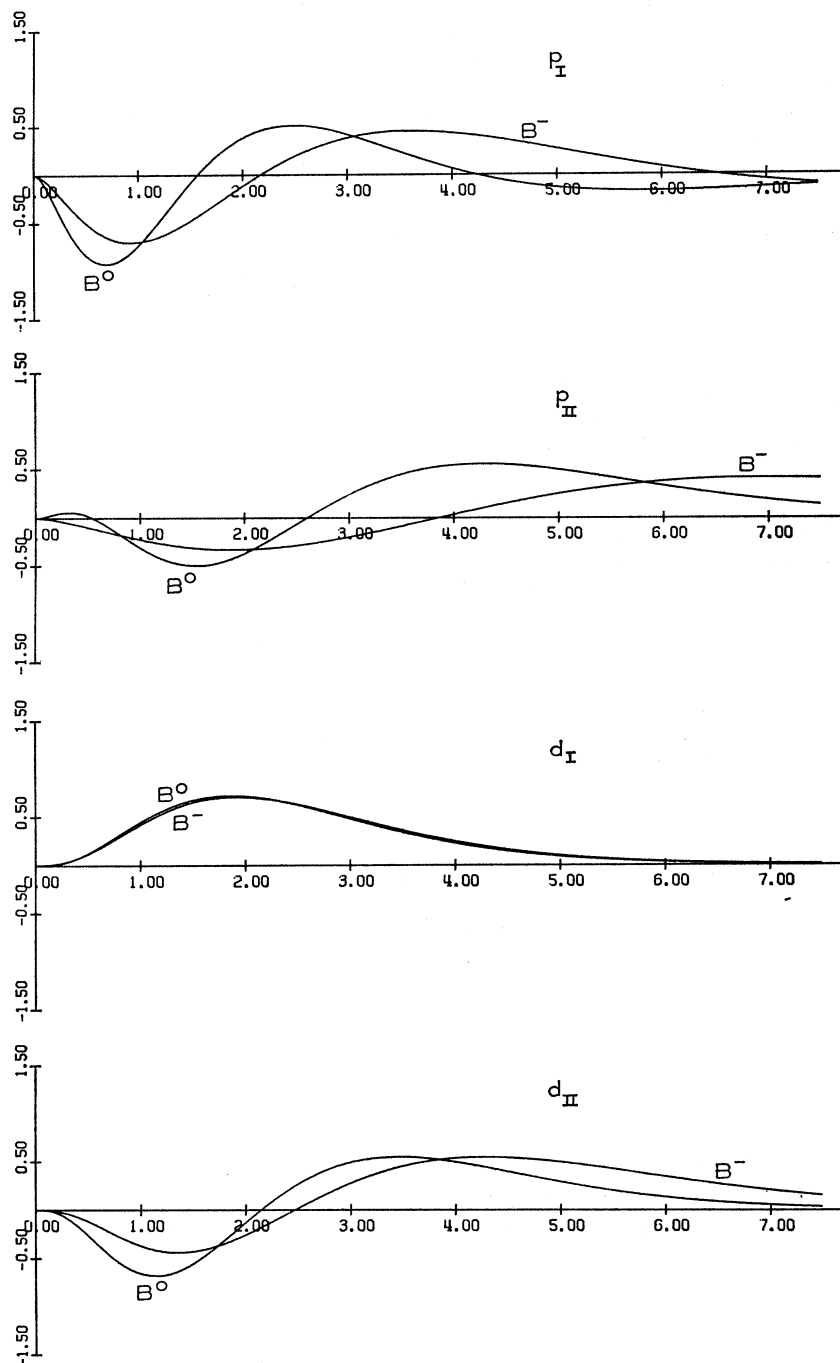


FIG. 2. Virtual p and d orbitals used to describe L -shell correlation in B and B^- .

step was to add orbitals and configurations needed to characterize the $(1s, 2p)$ correlation. Previous work has shown that the virtual orbitals which best describe an intershell correlation lie in a region of space between the Hartree-Fock orbitals of the two shells in question. Since the virtual orbitals used for the L -shell CI's lie in the region of the $2s$ and $2p$ Hartree-Fock orbitals or farther from the nucleus, it was deemed necessary to add to the basis set three more virtual orbitals s_{III} ,

p_{III} , and d_{III} , which would be expected to lie closer to the $1s$ orbital region. These new orbitals were constructed by orthogonalizing $2s$, $2p$, and $3d$ basis orbitals to the previously selected atomic orbitals. The new virtual orbitals were used in conjunction with virtual orbitals s_I , p_I , and d_I to describe the $(1s, 2p)$ correlation.

Using the six chosen virtual orbitals, all possible configurations corresponding to $(1s, 2p)$ excitations were added to the previous CI functions. Because the con-

TABLE IV. Calculated energies of B and B⁻ and the electron affinity of B. Energies are in hartrees.

	B	B ⁻	Electron affinity
Hartree-Fock ^a	-24.529059	-24.519192	-0.009867
L-shell CI, best single orbital exponent	-24.596259	-24.593934	-0.002325
L-shell CI, individually optimized exponents	-24.596351	-24.598381	+0.002030
Above + (1s) and (1s,2p) excitations	-24.597907	-24.600746	+0.002839
Above + (1s,1s) and (1s,2s) pair energies	-24.644123	-24.646306	+0.002183
Experiment (relativistic contributions deducted) ^b	-24.654

^a Reference 9.^b Reference 25.

figurations in use involve 1s excitations, it was also desirable to add the single excitations of (1s) type. For B, the new configurations are numbered 28 through 39 in Table I; for B⁻, they are numbered 34 through 45 in Table II. The energies of the enlarged CI's were then minimized as a function of the orbital exponents of the added orbitals; the optimized 2s, 2p, and 3d orbital exponents were, for neutral B, 2.7, 4.3, and 4.2, and for the B⁻ ion, 2.6, 4.3, and 3.9, respectively.

The fourth line in Table IV indicates how the energies were affected by the (1s,2p) correlation. As expected, the contribution for B⁻ is significantly larger than for B, increasing the calculated electron affinity. However, it may be noted that the two 2p electrons of B⁻ contribute far less than twice the energy of the single 2p electron of B, probably because the more diffuse L shell

TABLE V. Calculated single and pair excitation energies.

	No. of cfs used	Energy (hartrees)	
		B	B ⁻
e(1s)	7	-0.000186	-0.000117
e(1s,1s)	29	-0.040033	-0.040156
e(1s,2s)	29	-0.006183	-0.005404

of B⁻ tends to reduce the electron interaction with the K shell.

(1s,1s) AND (1s,2s) PAIR CALCULATIONS FOR B AND B⁻

To verify that the omitted types of correlation were similar for B and B⁻, and to indicate that these contributions accounted for most of the remainder of the correlation energy, calculations were carried out for the correlations of the (1s,1s) and (1s,2s) pairs. Because individual pair calculations involve a limited class of single and double excitations, it is possible to use larger basis sets in these calculations than in the more complete CI's already discussed. Each pair calculation was therefore carried out using nine virtual orbitals s_I, s_{II}, s_{III}, p_I, p_{II}, p_{III}, d_I, d_{II}, and d_{III}. These orbitals were formed by orthogonalizing 2s, 3s, 4s, 2p, 3p, 4p, 3d, 4d, and 5d orbitals to the previously selected atomic orbitals. Since a large number of virtual orbitals was used in

these calculations, the basis orbitals from which they were constructed were all given the same orbital exponent. An optimum value of this exponent was determined for each pair calculation of B and of B⁻.

The (1s,1s) pair calculations were made using the Hartree-Fock function and all single and double excitations of the 1s² pair except for those of the type 1s² → s_id_j, which, as in the L-shell calculation, were negligible. The optimized orbital exponents were 6.9 for both B and B⁻. The energy increments, which are listed in Table V, are quite similar for B and B⁻.

Similar calculations were then carried out for the (1s,2s) pair. The 1s2s → s_id_j excitations were omitted and only single excitations of the types 1s → s_i and 2s → s_j were included. The optimized orbital exponents

TABLE VI. Correlation energy estimates for the ground states of B and B⁻. Energies in hartrees.

	$E(1s)$ + $E(1s,1s)$	$E(1s,2s)$	$E(2s)$ + $E(2p)$ + $E(1s,2p)$ + $E(2s,2s)$ + $E(2s,2p)$ + $E(2p,2p)$	Multiple excitations	Total
² P B ⁰	-0.0415	-0.0062	-0.0738	-0.0035	-0.125
² P B ⁻	-0.0415	-0.0054	-0.0916	-0.0055	-0.144

were 4.8 for B and 4.6 for B⁻. The results of these calculations also appear in Table V.

There is some ambiguity as to the best way to interpret the results of these pair calculations, because the CI results of the previous section include some configurations with (1s) excitations. Adopting a relatively conservative view, a good measure of the heretofore omitted correlation energy might be simply the sum of the increments e(1s,1s) and e(1s,2s), it being assumed that e(1s) is already more or less included in the CI calculations. Energies computed on this basis are given in the fifth row of Table IV. It may be seen that the energy increments account for most of the previously omitted correlation energy for neutral B, and leave unaffected the qualitative relationship of the B and B⁻ energies. Since the computed electron affinity is now a substantial fraction of the remaining error in the B calculation,

TABLE VII. Electron affinity of boron.

	hartrees	eV
Hartree-Fock calculation ^a	-0.0099	-0.27
Estimates		
Glockler ^b	-0.0037	-0.10
Johnson and Rohrlich ^c	+0.030	+0.82
Edlen ^d	+0.012	+0.33
Kaufman ^e	+0.014	+0.39
Crossley ^f	+0.0059	+0.16
Clementi and McLean ^a	+0.011	+0.30
This work		
Calculated	+0.0022	+0.06
Best estimate	+0.009	+0.25

^a Reference 9.^c Reference 5.^e Reference 7.^b Reference 4.^d Reference 6.^f Reference 8.

one may with some certainty conclude that the stability of B^- has been demonstrated.

ELECTRON AFFINITY OF BORON

Although the calculations described here provide a convincing demonstration of the stability of B^- , the unadjusted numerical results do not indicate the most probable value of the electron affinity of boron. A better estimate may be obtained by considering the probable magnitudes of the errors in the B and B^- calculations.

A potentially important error in both calculations is the neglect of relativistic effects. Clementi and McLean⁹ estimate the relativistic corrections to the energy to be -0.00610 hartrees for neutral B, and -0.00605 hartrees for B^- . These are so nearly equal that they will not be considered further.

The most significant remaining error in both calculations is the underestimation of the various correlation effects. A systematic estimation of the various types of correlation is presented in Table VI. The values given there are based in part upon the present work and in part upon other studies. The values of $e(1s)+e(1s,1s)$ were arrived at by consideration of the results of Table V of this work, some recent work^{18,21-23} on Be, and a comparison of the Bethe-Goldstone results of Nesbet²⁴ for Be (-0.0418 hartrees) and B (-0.0411 hartrees). The value for $e(1s,2s)$ was taken from Table V of this work because it was thought that the lack of pair additivity and the incompleteness of the basis set would largely cancel in their effect. The estimate of the energy

contribution of multiple excitations in neutral B was based on the authors's previous work.¹⁴ The corresponding estimate for B^- was obtained by adding to the B value a reasonable guess for the contribution of configurations such as $1s^2 2p^2 \rightarrow wxyz$ and $2s^2 2p^2 \rightarrow wxyz$. The third column of Table VI contains the L -shell pair correlation energies. The calculated values of these energies were -0.0688 hartrees for B and -0.0816 hartrees for B^- . The value given for B in Table VI was obtained by forcing the total correlation energy to conform to Clementi's²⁵ experimental value of -0.125 hartrees. This required an adjustment of the calculated value by -0.005 hartrees. Taking into account the greater difficulty in obtaining an exactly comparable calculation for B^- , the adjustment estimated for the L -shell pair correlation energy in B^- was -0.010 hartrees—twice that for neutral B. These estimates lead to a correlation energy of -0.144 hartrees for B^- , and to an electron affinity of $+0.009$ hartrees.

Table VII gives the results of previous estimates of the electron affinity of boron, plus the calculated and "best estimated" values from the present work. Since the authors are wary of the estimates (including their own), it is only claimed that the true value of the electron affinity is positive, almost certainly lying between the value given by Crossley⁶ (0.0059 hartrees) and that of Kaufman⁷ (0.014 hartrees).

ACKNOWLEDGMENTS

All computations reported here were performed at the Stanford University Computation Center. One of us (H. F. S.) acknowledges many helpful conversations with Ralph Young.

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