

Boron Hydrides: LCAO-MO and Resonance Studies

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The results of an LCAO-MO calculation for the boron hydrides and hydride ions B_2H_6 , B_4H_{10} , B_5H_9 , B_6H_{11} , B_6H_{10} , B_7H_{13} , $B_{10}H_{14}$, $B_{10}H_{16}$, BH_4^- , $B_3H_8^-$, $B_9H_{14}^-$, $B_{10}H_{10}^{-2}$, $B_{10}H_{14}^{-2}$, $B_{12}H_{12}^{-2}$ are reported. Charge distributions and overlap populations are calculated from the wavefunctions for real distances and for idealized molecules with all distances equal. The three-center bond theory is extended to incorporate unsymmetric equivalent structures with concomitant improvement in charge distributions. These are compared with the presumably better LCAO-MO charges. The valence structure of a new boron hydride, $B_{18}H_{22}$, is discussed.

WE present in this paper the results of an LCAO-MO calculation on those boron hydrides and boron hydride ions whose structures or analogues have been definitely established by x-ray diffraction, electron diffraction or spectroscopic methods. Fourteen molecular species qualify: B_2H_6 , B_4H_{10} , B_5H_9 , B_6H_{11} , B_6H_{10} , B_7H_{13} , $B_{10}H_{14}$, $B_{10}H_{16}$, BH_4^- , $B_3H_8^-$, $B_9H_{14}^-$, $B_{10}H_{14}^{-2}$, $B_{10}H_{10}^{-2}$, $B_{12}H_{12}^{-2}$. Energy levels and wavefunctions have been computed and, from the latter, charge distributions and overlap populations have also been calculated. Before embarking on a discussion of computational details and results, we wish to make some remarks concerning the three-center bond theory for the boron hydrides.¹

EQUIVALENT AND RESONANCE STRUCTURES FOR THE BORON HYDRIDES

The three-center bond formalism for describing the valence structures of the boron hydrides is only eight years old.² Its youth has not precluded the development of misleading ideas and bad habits regarding the capabilities of the theory, primarily based on over-literal interpretations of the little graphs which we, in our present state of less than blissful ignorance, draw to give an inkling of the filled orbital nature and the electron distribution in these molecules. The prime example is the case of decaborane. The original structure presented (structure 1 of Table VI) has single

bonds linking positions 2 and 6, and 4 and 9, three-center bonds connecting other borons. Is the 2-6 or 4-9 bond weaker or stronger than any other connection in the molecule? The original structure also gave a charge distribution whose primary disturbing feature was that borons 6 and 9 came out nonpositive, in contradiction to the considerable evidence for the predominance of nucleophilic attack at these positions. How is this to be explained?

We would like here to answer these rhetorical questions and couple them with some warnings. Our contention is that a more realistic charge distribution and perhaps bond-order gradation may be brought about by consideration of *all* of the equivalent and resonance structures of a boron hydride, not only the most symmetric ones. An unstated procedure of the original three-center bond theory was that only structures satisfying the molecular symmetry should be considered. The analogy may be drawn to the singling out of Kekulé structures in the simplified valence-bond approach to aromatics. In principle there is no objection to structures of lower symmetry, which when coupled as several resonance forms, yield the full molecular symmetry in the population analysis. This problem was already clear from the failure to write a three-center structure of C_{4v} symmetry for B_5H_9 ; one instead had to compromise on a pair of C_{2v} resonance hybrids.

We would like, at this point, to delineate the distinction between resonance and equivalent structures. The former, as for B_3H_9 , are a set of symmetry equivalent structures which when considered as a group, have the molecular symmetry. The latter, as the two usual

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¹ W. N. Lipscomb, in *Advances in Inorg. Chem. Radiochem.* **1**, 117 (1959) and references therein.

² W. H. Eberhardt, B. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.* **22**, 989 (1954).

structures drawn for B_nH_m , are distinct ways of relative arrangements of single bonds and three-center bonds in the boron framework. While symmetry demands that all the resonance structures of a given equivalent form enter the wavefunction or the population analysis with equal coefficients, there are no such symmetry requirements on different equivalent forms. The fact that we will weigh them equally in the subsequent discussion only indicates the symmetry of our ignorance.

The problem, then, is to find *all* the equivalent and resonance structures of a molecule. Our experience in this matter has shown that the human mind is both a fallible and extremely efficient mechanism. The latter point has become clear recently as we have attempted to program that most efficient and most unimaginative of man's tools, the digital computer, to find all the structures for us. The problem is one of combinatorics and of logic, and we have been surprised to find that human logic has so far been very efficient. Unfortunately the program has not yet yielded results. On the other hand, we are continuing with its development, since the computer does well in combinatorial problems, in exhausting all the possibilities. We have often thought that we had all the equivalent structures, only to find a week, or a year, later that we had missed some very obvious ones. The listing of boron hydride structures which we present is to the best of our present knowledge complete. This does not mean that it is absolutely complete. The saving grace here is that once we have written down most of the structures, the discovery of the few we had omitted does not affect greatly the ordering in the population analysis. The latter stabilizes very quickly.^{2a}

Figure 1 shows some of the boron hydride frameworks. The various structures we have derived for the neutral boron hydrides are listed in Table I. Column three of Table I contains the number of resonance forms belonging to the particular equivalent structure. Only one of the resonance forms is described; the others may be generated by applying the symmetry opera-

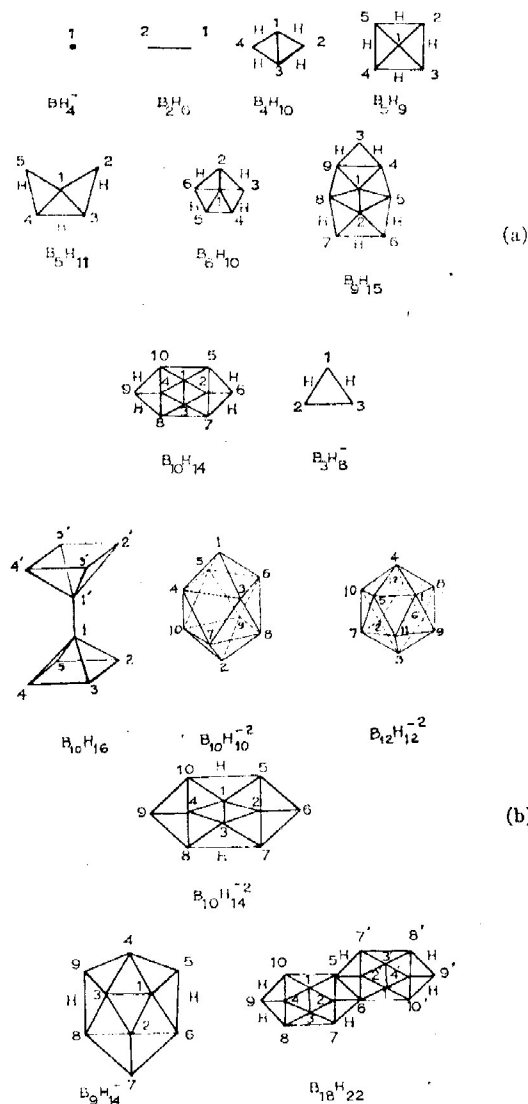


FIG. 1. Numbering convention for the boron hydrides.

^{2a} Note added in proof: The computer program mentioned has been induced to produce results. The structures listed in Table I now represent all possible reasonable three-center bond patterns. We have excluded those in which the same two borons are bonded by both a central three-center bond and either an open three-center or normal single bond. We have also excluded those patterns in which borons are bonded by either a single bond or open three-center bond and either another open three-center bond or hydrogen bridge. The initial human effort produced 26 out of 30 structures for B_9H_{15} , 109 out of 111 structures for $B_{10}H_{14}$. For $B_9H_{14}^-$ there are altogether three structures with the following charge distribution:

1,3	0.00	5,9	-0.17
2	-0.11	6,8	+0.11
4	0.00	7	-0.78.

For $B_{10}H_{14}^{-2}$ there are altogether 87 structures with the charge distribution

1,2	-0.27	5,7,8,10	-0.01
3,4	-0.10	6,9	-0.62.

tions of Column 2 to the listed form. In order to simplify the compilation we give only the position of single bonds and open three-center bonds. This procedure is sufficient since the central three-center bonds can be filled in uniquely in order to complete the particular valence pattern of the molecule. B_2H_6 and B_4H_{10} allow only one structure each, and are therefore absent from the listing.

These structures contain some in which two open three-center bonds cross and a single bond originates at the crossing. Such structures, though not explicitly barred, were not considered in the first three-center bond treatments, because the necessary hybridization at the central boron seemed difficult to achieve. Although less favorable, these structures are not impos-

TABLE I. Three-center bond isomerism in the boron hydrides.

Molecule	Generating symmetry	Number of resonance structures	B-B	B $\overbrace{\quad}$ B	Molecule	Generating symmetry	Number of resonance structures	B-B	B $\overbrace{\quad}$ B
B ₃ H ₃					B ₉ H ₁₅ (continued)				
1	C ₂	2	1-2, 1-4	3-1-5	11	σ_v	2	4-5, 2-7	6-2-8
2	C _s	4	1-2, 1-3		12	σ_v	2	4-5, 1-8	2-8-9
		6			13	σ_v	2	1-4, 2-7	9-4-5, 6-2-8
B ₄ H ₁₁					14	σ_v	2	1-4, 2-8	9-4-5
1		1		5-1-2	15	σ_v	2	1-4, 2-6	9-4-5
2		1			16	σ_v	2	2-5, 8-9	
3		1		5-1-3, 2-1-4	17	σ_v	2	2-7, 8-9	
		3					30		
B ₅ H ₁₀					B ₁₀ H ₁₄				
1		1	1-2, 4-5		1		1	4-9, 2-6	5-2-7, 10-4-8
2		1	1-2, 4-5	3-1-5, 4-1-6	2	σ_v'	2	4-9, 2-6	5-2-3, 7-2-1, 10-4-8
3	σ_v	2	1-6, 4-5	2-1-4, 3-1-5	3	σ_v	2	2-5, 4-10	
4	σ_v	2	1-4, 4-5	2-1-5, 3-1-6	4	σ_v	2	2-7, 4-10	
5	σ_v	2	1-6, 4-5	2-1-5	5	σ_v	2	1-3, 5-10	2-3-4
6	σ_v	2	1-4, 4-5	3-1-5	6	σ_v, σ_v'	4	4-9, 5-10	
7	σ_v	2	1-4, 4-5	3-1-5	7	σ_v, σ_v'	4	4-9, 5-10	1-3-7, 3-2-6, 2-7-8
		12			8	σ_v, σ_v'	4	4-9, 2-5	10-4-8, 1-2-6
B ₁₀ H ₁₆					9	σ_v, σ_v'	4	4-9, 2-5	10-4-8, 1-2-7, 3-2-6
half structures	A C ₂ B C _s C C _s	2 4 4	1-2, 1-4 1-2, 1-3 1-2, 1-3, 1-4	3-1-5 3-1-5 1'-1-5	10	σ_v, σ_v'	4	4-9, 2-5	10-4-8
A-A		4			11	σ_v, σ_v'	4	4-9, 1-2	10-4-8, 5-2-7, 3-2-6
B-B		16			12	σ_v, σ_v'	4	4-9, 1-2	10-4-8, 5-2-3
A-B		16			13	σ_v, σ_v'	4	4-9, 1-2	10-4-8
A-C		16			14	σ_v, σ_v'	4	4-9, 1-5	10-5-2
B-C		32			15	σ_v, σ_v'	4	4-9, 2-5	
		84			16	σ_v, σ_v'	4	4-9, 2-5	10-4-3, 1-4-8
B ₉ H ₁₅					17	σ_v, σ_v'	4	10-4, 2-5	1-4-8, 3-4-9
1		1	4-9, 1-2		18	σ_v, σ_v'	4	10-4, 2-5	1-4-9
2		1	4-9, 1-2	5-2-8	19	σ_v, σ_v'	4	10-4, 2-7	1-4-8, 3-4-9
3		1	4-5, 8-9		20	σ_v, σ_v'	4	10-4, 2-7	1-4-9
4		1	4-9, 1-2	5-2-7, 6-2-8	21	σ_v, σ_v'	4	10-4, 3-7	1-4-9, 2-7-8
5	σ_v	2	4-9, 2-7	1-2-6, 5-2-8	22	σ_v, σ_v'	4	10-4, 7-8	1-4-9
6	σ_v	2	4-9, 2-7	6-2-8	23	σ_v, σ_v'	4	10-4, 1-2	5-2-7, 3-2-6
7	σ_v	2	4-9, 2-7		24	σ_v, σ_v'	4	10-4, 1-2	3-2-5
8	σ_v	2	4-9, 2-5	1-2-7, 6-2-8	25	σ_v, σ_v'	4	10-4, 1-2	
9	σ_v	2	4-9, 2-5	1-2-6	26	σ_v, σ_v'	4	10-4, 2-3	5-2-7, 1-2-6
10	σ_v	2	4-9, 2-5		27	σ_v, σ_v'	4	10-4, 2-3	
					28	σ_v, σ_v'	4	10-4, 2-3	1-2-7
					29	σ_v, σ_v'	4	1-4, 3-7	2-7-8
					30	σ_v, σ_v'	4	1-4, 7-8	
					31	σ_v'	2	2-6, 4-9	10-4-8

111

sible, and hence in order to see their effect we have performed the population analysis with and without them.

Bond orders are defined³ simply as $2C_iC_j$, summed over all orbitals. There are thus four possible component bond orders: $\frac{1}{2}$ for 2 borons bonded by an *H* bridge, 1 for a normal single bond, $\frac{2}{3}$ for 2 borons bonded by a central three-center bond, $1/\sqrt{2}$ for an open B-B-B three-center bond.

In Table II we compare charge distributions obtained from analyzing all three-center structures with

³ R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.* **36**, 2179 (1962).

those obtained from some limited subset. In Table III we see the three-center bond orders, together with a comparison of various subsets for B₆H₁₀ and B₁₀H₁₄. In the Appendix we derive the equivalent structures and charge distribution for a newly discovered⁴ higher hydride, B₁₈H₂₂, whose structure determination has just now been completed in this laboratory.⁵ Postponing, for the present, an evaluation of the charge

⁴ A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.* **84**, 3218 (1962).

⁵ P. G. Simpson and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S. A.* **48**, 1490 (1962).

distributions obtained with all three-center bond structures, we now turn to the LCAO-MO calculations.

COMPUTATION

A computer program described previously^{3,6} has been extended to calculate the energy levels and wavefunctions of the known boron hydrides and borohydride ions. The input parameters consist of the Cartesian coordinates of N arbitrarily situated boron atoms and M hydrogens ($4N+M \leq 68$, but this limitation is an artificial one imposed by the size of the computer memory, and may be easily removed), boron $2s$ and $2p$ and hydrogen $1s$ Coulomb integrals, and the proportionality constant K , in the relation $\beta_{rs} = K S_{rs}$, where S is the overlap between Slater orbitals and K is taken equal for all interactions. The set of equations $\sum_s (H_{rs} - ES_{rs}) C_s = 0$ is solved with all interactions or overlaps included. The program also performs a Mulliken population analysis on the resulting molecular orbitals, calculating overlap populations and gross atomic populations (charges). The boron Coulomb integrals were rather arbitrarily set equal to the corresponding valence state ionization potentials: $\alpha(2s) =$

-15.36 eV, $\alpha(2p) = -8.63$ eV. The value of K was set equal to -21 eV throughout, primarily to compare with calculations carried out with the same value by Moore *et al.*⁷

The input coordinates for the known boron hydrides were taken from the best x-ray or electron-diffraction parameters⁸; in some cases ($B_{10}H_{14}$, B_9H_{16} , $B_{10}H_{12}^{2-}$, $B_{12}H_{12}^{2-}$) these were adjusted to yield the apparent symmetry planes; in the others the original parameters were retained and the symmetrization, when appropriate, applied to the results of the population analysis. For B_6H_9 , considerations of consistency led us to use the x-ray determined distances rather than the presumably more accurate microwave values. The ions $B_{10}H_{14}^{2-}$ and $B_9H_{14}^-$ were included even though the structure determinations have been performed only on their acetonitrile analogs, $B_{10}H_{12}(NCCH_3)_2$ and $B_9H_{13}NCCH_3$. The substituted hydrogens were replaced in these molecules at a distance of 1.21 Å from the substituted boron, in the direction of the acetonitrile N, the latter direction determined in the corresponding x-ray study. The framework projections and the labeling convention used in this paper are given in Fig. 1.

In the first calculation on B_2H_6 the Coulomb integral for all hydrogens was set equal to -13.61 eV. The resulting charge distribution was

B	+0.233,
H _t	-0.156,
H _b	+0.080.

These charges are in disagreement with the nonempirical *SCF* calculation of Yamazaki,⁹ who obtains

B	+0.22,
H _t	+0.01,
H _b	-0.24.

Molecule	All structures	"Good" structures*	Symmetric structures	Most symmetric
$B_{10}H_{14}$	111	81	9	1
1, 3	-0.03	-0.07	-0.11	0
2, 4	-0.46	-0.36	-0.30	-0.67
6, 9	+0.29	+0.29	+0.22	0
5, 7, 8, 10	+0.10	+0.07	+0.09	+0.33
B_9H_{15}	30	25	3	
1	-0.09	-0.09	-0.22	
2	-0.50	-0.45	-0.33	
3	0	0	0	
4, 9	-0.10	-0.09	-0.17	
5, 8	+0.09	+0.06	+0.11	
6, 7	+0.30	+0.31	+0.33	
B_6H_{10}	12	9	1	
1	-0.72	-0.63	-0.33	
2	+0.36	+0.37	0	
3, 6	+0.35	+0.30	+0.33	
4, 5	-0.17	-0.17	-0.17	
B_5H_{11}	3	2		
1	-0.67	-0.50		
2, 5	-0.06	-0.08		
3, 4	+0.39	+0.33		
B_4H_9	6			2
1	-0.78			-1.00
2, 3, 4, 5	+0.20			+0.25
$B_{10}H_{16}$	84			
1, 1'	-0.70			
2'-5, 2'-5'	+0.18			

* Structures with 2 three-center bonds crossing eliminated.

⁶ R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.* **36**, 3489 (1962).

⁷ E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.* **35**, 1329 (1961); **37**, 675 (1962).

⁸ B_2H_6 : K. Hedberg and V. Schomaker, *J. Am. Chem. Soc.* **73**, 1482 (1951). B_4H_{10} , B_5H_{11} , $B_{10}H_{14}$: E. B. Moore, R. E. Dickerson, and W. N. Lipscomb, *J. Chem. Phys.* **27**, 209 (1957) and references therein. B_6H_{12} : W. J. Dulmage and W. N. Lipscomb, *Acta Cryst.* **5**, 260 (1952). B_6H_{10} : F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, Jr., and W. N. Lipscomb, *J. Chem. Phys.* **28**, 56 (1958). B_9H_{15} : Refined parameters were kindly communicated to us by P. G. Simpson. See P. G. Simpson and W. N. Lipscomb, *ibid.* **35**, 1340 (1961). $B_{10}H_{16}$: The distances given in R. Grimes, F. E. Wang, R. Lewin and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S. A.* **47**, 996 (1961) are very rough and H atoms were not located. The molecule used in this calculation was simply constructed from two pyramids of B_5H_5 structure, 1.74 Å apart. BH_4^- : P. J. Ford and R. E. Richards, *Discussions Faraday Soc.* **19**, 230 (1955). $B_3H_8^-$: C. R. Peters and C. E. Nordman, *J. Am. Chem. Soc.* **82**, 5758 (1960). $B_3H_4^-$: B_3H_3 (CH_3CN) F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Chem. Phys.* **35**, 1335 (1961). There are some errors in Table III of this reference. x, y, z for $H_{6,5',8,8'}$ should be replaced by $1-x, 1-y, 1-z$; indices 6 and 6' should be switched with 8 and 8' for hydrogens. Primed and unprimed atoms in Fig. 2 must also be interchanged. $B_{10}H_{12}^{2-}$: $B_{10}H_{12}(CH_3CN)_2$ J. v. d. M. Reddy and W. N. Lipscomb, *ibid.* **31**, 610 (1959). $B_{10}H_{14}^{2-}$: R. Dobrott and W. N. Lipscomb, *ibid.* **37**, 1779 (1962). $B_{12}H_{12}^{2-}$: J. A. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.* **82**, 4427 (1960).

⁹ M. Yamazaki, *J. Chem. Phys.* **27**, 1401 (1957).

TABLE III. Three-center bond orders.

Bond	Distance	All structures	"Good" structures*	Symmetric structures	Most symmetric
B₁₀H₁₄					
		111	81	9	1
5-10	2.01	0.70	0.71	0.70	0.67
1-2	1.79	0.73	0.74	0.67	0.67
1-5	1.78	0.74	0.75	0.74	0.67
2-5	1.78	0.75	0.74	0.75	0.71
2-6	1.72	0.76	0.75	0.77	1.00
1-3	1.71	0.73	0.75	1.11	1.33
5-H-6	1.77	0.68	0.72	0.61	0.50
B₆H₁₀					
		12	7	1	
1-4	1.80	0.77	0.77	0.67	
1-3	1.75	0.74	0.72	0.67	
1-2	1.74	0.74	0.73	1.00	
4-5	1.60	1.00	1.00	1.00	
2-H-6	1.74	0.61	0.69	0.50	
3-H-4	1.74	0.67	0.79	1.17	
B₁₀H₁₆					
		84			
1-2	1.66	0.86			
1-1'	1.74	0.83			
2-H-3	1.77	0.58			
B₉H₁₅					
		30			
4-5	1.98	0.73			
2-5	1.83	0.73			
1-4	1.83	0.77			
4-9	1.80	0.84			
1-5	1.77	0.74			
1-2	1.77	0.73			
2-6	1.76	0.76			
5-H-6	1.82	0.61			
6-H-7	1.78	0.72			
3-H-4	1.76	0.50			
B₈H₉					
		6			
1-2	1.66	0.84			
2-H-3	1.77	0.61			
B₈H₁₁					
		3			
1-2	1.87	0.69			
1-3	1.72	0.68			
3-H-4	1.77	0.72			
2-H-3	1.76	0.72			

* Structures with 2 three-center bonds crossing eliminated.

There is, however, better agreement for the overlap populations:

<i>n</i>	Ours	Yamazaki
H _t -B	0.86	0.85
H _b -B	0.45	0.39
B-B	0.38	0.34

No reasonable variation of any Coulomb integral or of *K* was found which would make the terminal hydrogens more positive than those on the bridge, while preserving actual B-H distances. When the computation was repeated omitting the terminal hydrogens and the four *sp*³ boron hybrids pointing toward them, the bridge hydrogens showed up negative, a result to be expected in view of the greater magnitude of the H Coulomb integral. The procedure of dropping the terminal hydrogens was deemed inadvisable for the higher hydrides, since certain boron orbitals would have to be omitted

as well, and no consistent procedure for doing so was discovered.

The alternative chosen was to perform each calculation twice; once with all hydrogen Coulomb integrals equal to -13.61 eV (Method I) and again after forcing the bridge hydrogens to be negative by using a different Coulomb integral for bridge and terminal hydrogens. If in diborane we take $\alpha(H_t) = -11.60$ eV, $\alpha(H_b) = -15.75$ eV (Method II), we obtain the charge distribution

$$\begin{aligned} B & +0.147, \\ H_t & -0.004, \\ H_b & -0.135. \end{aligned}$$

This same choice of $\alpha(H)$ kept the charge on the bridge hydrogens between -0.08 and -0.17, and that on the terminal hydrogens between -0.03 and +0.05 for all the hydrides, with the exception of the unique terminal hydrogen in B₆H₁₁ which showed up very positive (+0.30). We optimistically anticipated that the boron charge distribution would not depend drastically on either choice of the hydrogen Coulomb integral.

IDEALIZED BORON HYDRIDES

In the standard Hückel treatment of aromatic molecules one determines energies and wave functions setting all nearest-neighbor distances equal. Bond orders calculated from such wavefunctions presumably indicate the direction of the deviation of the actual bond distances from the value used in the initial calculation. We have attempted to carry through a similar treatment for the boron hydrides. The following assumptions were made concerning a set of idealized boron hydrides.

(1) For all molecules: B-B distance 1.75 Å, B-H_b 1.33 Å, B-H_t 1.21 Å.

(2) B₄H₁₀, B₆H₁₂, B₆H₁₀, B₉H₁₅, B₁₀H₁₄, B₁₂H₁₂²⁻, B₁₀H₁₄²⁻, B₉H₁₄⁻, B₈H₈⁻ were all constructed as fragments of a perfect icosahedron, with terminal hydrogens radially displaced from the borons, and bridge hydrogens radially located over the midpoints of icosahedral edges. This choice of coordinates put in one plane two borons, their respective terminal hydrogens, and any bridge hydrogen that might be between them. Such a situation, leading to a short H_t-H_b contact of 1.51 Å, and H_b-H_b on adjacent edges 1.49 Å, is, of course, avoided in the actual hydrides. When two terminal H atoms were necessary on a given B atom, one was placed normally, i.e., radially out, and the other along an icosahedral edge, or in one case (B₁₀H₁₄²⁻) in an icosahedral plane. This created two anomalously short contact distances between terminal hydrogens on different borons: H_t-H_t of 0.58 Å in B₁₀H₁₄²⁻, and 0.80 in B₉H₁₄⁻. These sacrifices were deemed necessary to obtain a consistent procedure.

(3) B₁₀H₁₀²⁻ was chosen as a perfect deltahedron, i.e., with all faces equilateral triangles. B₅H₉ was con-

TABLE IV. Highest occupied orbital energies and gaps to lowest unfilled orbitals in the boron hydrides.

Molecule	Real				Idealized				Number of filled orbitals	Experimental IP (eV)
	<i>E</i> top filled I	<i>E</i> top filled II	Gap (eV) I	Gap (eV) II	<i>E</i> top filled I	<i>E</i> top filled II	Gap (eV) I	Gap (eV) II		
B ₂ H ₆	-14.08	-12.95	9.21	8.18	-14.05	-12.90	9.42	8.27	6	12.1 ^a 11.9 ^b 11-12 ^c
B ₄ H ₁₀	-13.04	-13.05	12.59	12.48	-9.55	-9.09	5.01	2.85	11	
B ₆ H ₈	-12.21	-11.90	9.81	9.75	-11.08	-11.34	7.21	5.99	12	10.8 ^d 10.4 ^e 10.9 ^f
B ₈ H ₁₁	-12.62	-12.26	8.86	8.39	-11.08	-11.09	6.14	5.79	13	
B ₆ H ₁₀	-12.37	-12.08	7.93	7.23	-11.56	-11.52	7.92	6.44	14	
B ₉ H ₁₅	-11.84	-11.48	6.59	6.07	-9.73	-9.44	4.91	4.37	21	
B ₁₀ H ₁₄	-12.83	-12.38	6.75	6.32	-8.87	-8.58	2.13	1.94	22	11.0 ^d 10.7 ^g 10.26 ^h
B ₁₀ H ₁₆	-11.38	-11.24	8.64	8.73	-9.96	-10.16	6.07	4.80	23	
B ₁₀ H ₁₀ ²⁻	-11.68	-11.56	9.13	9.22	-11.25	-11.05	9.13	9.11	21	
B ₁₀ H ₁₄ ²⁻	-11.34	-11.16	9.57	9.73	-9.91	-9.39	8.42	6.82	23	
B ₁₂ H ₁₂ ²⁻	-12.60	-11.98	14.11	13.49	-12.75	-12.04	14.69	13.98	25	
BH ₄ ⁻	-14.67	-13.75	26.54	29.28	-14.65	-13.75	29.12	32.27	4	
B ₃ H ₈ ⁻	-13.58	-12.63	15.24	13.59	-11.58	-11.46	11.77	11.38	9	
B ₉ H ₁₄ ⁻	-11.89	-11.32	6.59	6.67	-9.92	-9.34	5.75	5.54	21	

^a J. L. Margrave, *J. Chem. Phys.* **51**, 38 (1956).

^b W. S. Koski, J. J. Kaufman, C. F. Pachuki, and F. J. Shipko, *J. Am. Chem. Soc.* **80**, 3202 (1958).

^c W. C. Price, *J. Chem. Phys.* **16**, 894 (1948).

^d J. L. Margrave, *J. Chem. Phys.* **32**, 1889 (1960).

^e J. J. Kaufman, ONR Rept. No. 4, RIAS.

^f R. M. Reese, quoted by V. H. Dibeler, quoted by J. L. Margrave in reference d.

^g J. J. Kaufman *et al.*, ONR Rept. No. 2, RIAS, (March 19, 1962).

structured as an octahedral fragment, and B₁₀H₁₆ as a compound of two octahedral fragments. In both cases the bridge and terminal hydrogens were placed in the plane of the base of the pyramid. B₂H₆, which would be hard to idealize under any circumstances, was made with a H₁-B-H₂ angle of 120°. BH₄⁻ was tetrahedral.

As in the case of the real hydrides, the idealized molecules were processed with the two different assumptions about Coulomb integrals. It was observed that with either choice the idealized hydrides had more positive hydrogens than their real counterparts; this is reflected in the predominance of negative borons in the population analysis.

DISCUSSION

The full presentation of the wavefunctions and energy levels would be too space-consuming and perhaps over-ambitious, considering that the choice of parameters in the calculation was fairly arbitrary and may be modified in the future. We therefore confine ourselves to presenting the salient features of the calculated results.

A cursory comparison of energy gaps, top filled orbitals, binding energies, charge distributions, and overlap populations reveals that the idealized structures are a poor approximation to the real boron hydrides. They yield worthwhile results only when the idealization is slight, as in B₁₀H₁₀²⁻. It could be argued

that our particular manner of idealization, *vide supra*, is unrealistic; yet it is hard to imagine another systematic procedure. The fact of the matter is that the subtle adjustments that bridge hydrogens and terminal borons make in "going" from the idealized to the real structure are energetically very beneficial to the molecule; they also change considerably the electronic distribution in the molecule. This fact is naturally disappointing since one cannot hope to explore all the pathways of distortion in such complicated molecules. Indeed the failure of the idealized structures to yield information of value damages critically our expectation that the LCAO-MO method may help decide which as yet unknown boron hydrides should be stable. Perhaps our hope was overambitious—we therefore let the case of the idealized structures rest here.

The calculations for the real structures are much more encouraging. Large energy gaps are obtained, a surprising additivity is encountered for the electronic energies, and the charge distributions appear realistic. We discuss these results in order.

Energy Gaps and Ionization Potentials

The energies of the top occupied orbital and the magnitude of the gap to the lowest unfilled orbital are given in Table IV. The gaps are nicely large, with no striking discrepancy between calculations I and II. It is notoriously difficult to predict electronic absorp-

TABLE V. Total electronic and binding energies.

Molecule	Three-center bond parameters			Total energy ΣE_i (eV)				Binding energy ^b $\Sigma E_i^{\infty} - \Sigma E_i$				Calculated ΣE_i	
	s'	t	y	Real		Idealized		Real		Idealized		I ^c	II ^d
				I	II	I	II	I	II				
B ₂ H ₆	2	0	0	-191.57	-188.68	-191.53	-188.35	44.67	45.54	44.63	45.41	-190.48	-187.14
B ₄ H ₁₀	4	0	1	-346.97	-344.39	-334.77	-330.26	80.39	81.31	68.19	67.18	-346.80	-343.74
B ₄ H ₈	4	1	2	-375.27	-374.40	-366.99	-365.03	89.68	90.30	81.40	80.93	-374.80	-373.62
B ₄ H ₁₁	3	2	0	-408.15	-401.40	-399.32	-391.81	95.34	98.25	86.51	88.66	-410.40	-401.55
B ₆ H ₁₀	4	2	2	-437.52	-434.84	-426.88	-422.71	105.70	106.52	95.06	94.39	-436.96	-434.04
B ₆ H ₁₂	5	4	2	-655.49	-648.38	-640.93	-632.41	157.76	160.05	143.20	144.08	-656.22	-648.45
B ₁₀ H ₁₄	4	6	2	-686.11	-676.91	-673.51	-662.78	169.37	171.71	156.77	157.58	-685.60	-675.72
B ₁₀ H ₁₆	8	2	5	-715.42	-716.70	-698.71	-697.73	171.46	171.70	154.75	152.73	-715.44	-716.70
B ₁₀ H ₁₈	0	8	3	-643.60	-628.54	-640.56	-625.07	181.30	186.34	178.26	182.87	-643.60	-628.54
B ₁₂ H ₁₆	0	10	3	-768.44	-750.60	-768.31	-749.14	213.68	219.96	213.55	218.50	-767.92	-749.38
B ₁₀ H ₁₂ ⁺	2	6	3	-706.95	-691.83	-694.81	-679.60	190.21	194.93	178.07	174.40	-709.76	-694.84
B ₈ H ₈ ⁺	2	0	1	-280.72	-275.00	-275.56	-269.43	73.98	76.04	68.82	70.47	-280.72	-275.00
B ₆ H ₆ ⁺	2	6	1	-649.73	-635.33	-639.08	-624.19	165.61	171.05	154.96	159.91	-653.68	-637.52
BH ₄ ⁻	0	0	4	-124.62	-118.41	-124.67	-118.56	37.56	39.39	37.61	39.54	-124.40	-118.40

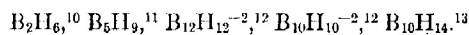
^a s' is the number of hydrogen bridges, t the number of boron-boron three-center bonds, y the number of boron-boron single bonds, and x' the number of normal boron-hydrogen bonds.

^b For negative ions, ΣE_i^{∞} is for neutral core only, and does not include $E_i^{\infty}(e^-)$ at ∞ . $E_i^{\infty}(B) = 2\alpha(2\beta B) + \alpha(2\beta B)$; $E_i^{\infty}(H) = \alpha(15H)$.

^c $s = 33.04$, $t = 21.06$, $y = 28.04$, $x' = 31.10$, $R_B = \Sigma E_{B_{10}} - E_{B_{12}} - E_{B_{16}} / \Sigma E_{B_{10}} = 0.0019$.

^d $s = 34.37$, $t = 22.82$, $y = 28.66$, $x' = 29.60$, $R_B = 0.0017$.

tion spectra from calculations which do not explicitly incorporate electronic interactions. Experimentally the situation is not entirely adequate. The following is a list of boron hydrides in estimated order of increasing wavelength of the first intense absorption band:



The order is in fair agreement with the order of the corresponding calculated energy gaps.

Ionization potentials have fared poorly experimentally. To our knowledge only three have been measured by various workers; these are reproduced in the last column of Table IV. The number is too small to make a comparison, but it is clear that the calculated ionization potentials, i.e., the energies of the top filled orbitals, are somewhat too large, a situation which may be remedied by an appropriate adjustment of parameters.

Electronic Energy

The energies in Table V do not include nuclear repulsion. In the Hückel theory the one electron energies are the eigenvalues of a Hamiltonian matrix, the matrix elements of which are integrals with respect to an unspecified Hamiltonian H_{eff} . Now in constructing this Hamiltonian one may or may not subtract out nuclear repulsions before hand. The choice is purely formal, since one never carries out any quadratures with H_{eff} , but only guesses at its matrix elements. From many as yet unpublished calculations on the conformations of simple molecules we have amassed a considerable body of evidence showing that it is unnecessary to add nuclear repulsions to the energies obtained, as the repulsions are largely simulated by our choice of the matrix elements of H_{eff} .

Also listed in Table V are "binding energies," i.e., energies of the corresponding number of B and H atoms removed to infinity minus the total electronic energy. The energy E of B at infinity is taken as $\alpha(2s\text{B}) + 2\alpha(2p\text{B})$, and the E at infinity of H is taken as $\alpha(\text{H})$. The choice of the $(2s)(2p)^2$ state for B is discussed below. A difficulty arises for negative ions, since it is impossible to define uniquely the energy of an electron at infinity. The bonding energies listed for the negative ions are those for the neutral core only, and thus the actual bonding is less than that given.

A calculation has also been carried out for various BH_3 geometries. The molecule seems to prefer a planar equilateral triangle conformation with $\Sigma E_i = -95.63$ eV for all $\text{B} \cdots \text{H} = 1.21$ Å (Calculation of type I), and $\Sigma E_i = -95.02$ eV for a geometry of half of B_2H_6 . Thus diborane is calculated with our parameters to be 1.53

¹⁰ W. C. Price, J. Chem. Phys. **16**, 894 (1948).

¹¹ J. R. Platt, H. B. Klevens, and G. W. Schaeffer, J. Chem. Phys. **15**, 598 (1947).

¹² R. Hoffmann (unpublished data). $\lambda_{\text{max}} \text{B}_{10}\text{H}_{10}^{2-} \sim 1950$ Å, $\lambda_{\text{max}} \text{B}_{12}\text{H}_{12}^{2-} < 1850$ Å.

¹³ G. C. Pimentel and K. S. Pitzer, J. Chem. Phys. **17**, 882 (1949).

TABLE VI. Heats of atomization and binding energies for the boron hydrides.

Molecule	ΔH_a (eV)	ΔH_a	B.E.	ΣE
		$\Delta H_a(\text{B}_2\text{H}_6)$	B.E. (B_2H_6)	$\Sigma E(\text{B}_2\text{H}_6)$
B_2H_6	24.94	1	(1)	(1)
B_3H_{10}	45.43	1.822	1.800	1.811
B_5H_9	48.98	1.964	2.008	1.959
B_5H_{11}	53.18	2.132	2.134	2.131
B_6H_{10}	56.90	2.281	2.366	2.284
$\text{B}_{10}\text{H}_{14}$	90.10	3.613	3.792	3.582
BH_3	11.85	0.475	0.497*	0.499*

* For most stable, i.e. planar, BH_3 configuration.

eV more stable than 2 BH_3 of diborane fragment geometry and 0.31 eV more stable than the most favorable BH_3 conformation.¹⁴

Gunn and Green¹⁵ have measured the heats of formation of most of the boron hydrides, and have obtained for the heats of atomization the values listed in the second column on Table VI. In the next column these are given as multiples of the heat of atomization of B_2H_6 . It is clear that our calculated bonding energies are too large. In this type of calculation the binding energies can be made of arbitrary size by varying the overlap proportionality constant K ; since our calculated energies are too large, it is indicated that K should be decreased, a change which would also move the ionization potentials in the desired direction. What is interesting to compare, assuming a rough proportionality of binding energy to K , is the relative calculated binding energy, which again is given for calculation I in multiples of the B_2H_6 binding energy, in the fourth column of Table VI. The agreement is good, and it would not be so if we had chosen our bonding energies with B at infinity in the $(2s)^2(2p)$ configuration. The agreement is not good enough to allow a calculated estimate of the heats of formation. However, we are encouraged to think that calculations with lower K may even yield predictions of these relatively small (less than 1 eV) energies. The last column of Table VI shows the ratios of the total energies relative to diborane, to be compared with values in column II!

There are other astonishingly good additivities among these energies. In view of the small values of the heats of formation relative to the heats of atomization one might expect that the bonding and total energies for the neutral boron hydrides could be fitted well with a set of two parameters, corresponding to the energy per boron and hydrogen, respectively. This is indeed true. Even better is the fit where the 14 total energies and binding energies are calculated with four

¹⁴ Compare with 1.23 eV estimated heat of dissociation of $\text{B}_2\text{H}_6 \rightarrow 2\text{BH}_3$. S. H. Bauer, in *Borax to Boranes* (American Chemical Society, Washington, 1961).

¹⁵ S. R. Gunn and L. G. Green, J. Phys. Chem. **65**, 2173 (1961).

TABLE VII. Charge distributions in the boron hydrides.

Molecule	Atoms	Real ^a		Three-center bonds ^b	Ideal	
		I ^c	II ^d		I ^c	II ^d
B ₂ H ₆	1, 2	+0.23	+0.14	0	+0.24	+0.15
B ₄ H ₁₀	1, 3	+0.04	+0.14	0	-0.30	-0.27
	2, 4	+0.15	+0.03	0	+0.01	-0.10
B ₅ H ₉	1	-0.23	-0.36	-0.78	-0.47	-0.66
	2, 3, 4, 5	+0.19	+0.25	+0.20	+0.04	+0.11
B ₆ H ₁₁	2, 5	+0.09	-0.14	-0.06	-0.07	-0.30
	3, 4	+0.19	+0.24	+0.33	-0.08	-0.05
	1	-0.10	-0.30	-0.67	-0.01	-0.23
B ₆ H ₁₀	1	+0.02	-0.12	-0.72	+0.13	-0.01
	4, 5	-0.03	-0.07	-0.17	-0.26	-0.30
	3, 6	+0.24	+0.30	+0.35	-0.11	-0.10
	2	+0.20	+0.28	+0.36	-0.08	-0.06
B ₉ H ₁₅	3	+0.09	-0.05	0.00	-0.17	-0.23
	4, 9	+0.05	+0.03	-0.10	-0.06	-0.12
	1	+0.11	-0.02	-0.09	+0.14	+0.02
	5, 8	+0.11	+0.07	+0.09	-0.07	-0.12
	2	-0.01	-0.17	-0.50	+0.10	-0.04
	6, 7	+0.18	+0.24	+0.30	+0.00	+0.02
B ₁₀ H ₁₄	5, 7, 8, 10	+0.17	+0.12	+0.10	+0.03	-0.02
	2, 4	+0.04	-0.10	-0.46	+0.06	-0.08
	6, 9	+0.29	+0.33	+0.29	-0.12	-0.12
	1, 3	+0.10	-0.04	-0.03	+0.09	-0.05
B ₁₀ H ₁₆	1, 1'	-0.35	-0.32	-0.70	-0.56	-0.61
	2-5, 2'-5'	+0.18	+0.24	+0.18	+0.02	+0.10
B ₁₀ H ₁₀ ²⁻	1, 2	-0.15	-0.29	-0.33	-0.16	-0.29
	3, 10	-0.01	-0.17	-0.17	+0.00	-0.16
BH ₄ ⁻	1	-0.25	-0.92	-1.00	-0.31	-0.96
B ₁₂ H ₁₂ ²⁻	1-12	-0.02	-0.17	-0.17	+0.02	-0.13
B ₃ H ₈ ⁻	1	+0.12	-0.05	0	-0.03	-0.12
	2, 3	-0.16	-0.30	-0.50	-0.34	-0.55
B ₁₀ H ₁₄ ²⁻	1, 3	-0.04	-0.19	-0.33	-0.02	-0.18
	2, 4	+0.07	-0.07	-0.33	+0.06	-0.08
	5, 7, 8, 10	+0.00	-0.05	+0.33	-0.11	-0.17
	6, 9	-0.27	-0.56	-1.00	-0.43	-0.66
B ₉ H ₁₄ ⁻	7	-0.20	-0.50	-1.00	-0.38	-0.66
	2	+0.06	-0.08	-0.33	+0.08	-0.07
	4	+0.15	-0.08	0.00	+0.32	+0.14
	1, 3	+0.02	-0.14	0.00	-0.00	-0.17
	6, 8	+0.05	+0.00	+0.33	+0.04	-0.03
	5, 9	-0.01	-0.16	-0.17	-0.23	-0.37

^a Averaged over the apparent symmetry planes for B₄H₁₀, B₅H₁₁, B₁₀H₁₄, B₁₀H₁₀²⁻, B₁₂H₁₂²⁻.

^b For all structures, see text. For B₁₀H₁₄²⁻, B₉H₁₄⁻, one structure only. For B₁₀H₁₀²⁻ only structures with central 3 center bonds.

^c $\alpha(\text{H}) = -13.61$ eV for all H's.

^d $\alpha(\text{H}) = -13.75$ eV for bridge H's, -11.60 eV for terminal H's.

energy parameters corresponding to the four variables of the three-center bond theory (energy per hydrogen bridge, three-center BBB bond, single BB bond, normal BH bond). The average deviation from the observed energy in this fit is less than an electron volt per molecule; or to use the crystallographers notation, with an $R_E = \sum |E_{\text{obs}} - E_{\text{calc}}| / \sum |E_{\text{obs}}| = 0.002$, which is slightly better than terrestrial crystallographers can do. A set of such computed total energies may be examined in the last columns of Table V.

Charge Distribution

The results are tabulated in Table VII. As mentioned above, we had hoped that the difference between Calculations I and II, i.e., different Coulomb integrals for bridge and terminal hydrogens, would not affect the boron charge distributions. This has largely proved true with the following exceptions: atoms 1, 3 vs 2, 4 in B₄H₁₀; atom 1 vs 4, 5 in B₆H₁₀; atoms 4, 9 in B₉H₁₅; atoms 2, 4 vs 5, 7, 8, 10 in B₁₀H₁₄²⁻; atom 4 vs 6, 8 in B₉H₁₄⁻. Note that the charge order in B₁₀H₁₄ is in agree-

TABLE VIII. Overlap populations in the boron hydrides.

Molecule	Bond	Distance	Real		Three-center bond order	Idealized	
			I	II		I	II
B ₂ H ₆	1-H-2	1.77	0.38	0.20	1.00	0.39	0.20
B ₄ H ₁₀	1-3	1.71	0.63	0.63	1.00	0.32	0.32
	1-H-2	1.84	0.35	0.27	0.50	0.48	0.39
B ₅ H ₉	1-2	1.66	0.63	0.62	0.84	0.53	0.55
	2-H-3	1.77	0.37	0.30	0.61	0.43	0.33
B ₆ H ₁₁	1-2	1.87	0.42	0.43	0.68	0.48	0.51
	1-3	1.72	0.54	0.54	0.69	0.37	0.36
	3-H-4	1.77	0.36	0.28	0.72	0.68	0.61
	2-H-3	1.76	0.43	0.34	0.72	0.52	0.43
B ₆ H ₁₀	1-4	1.80	0.44	0.43	0.77	0.42	0.41
	1-3	1.75	0.52	0.52	0.74	0.34	0.33
	1-2	1.74	0.52	0.51	0.74	0.37	0.36
	4-5	1.60	1.00	0.97	1.00	0.85	0.82
	2-H-6	1.79	0.44	0.36	0.61	0.64	0.57
	3-H-4	1.74	0.45	0.36	0.67	0.64	0.58
B ₁₀ H ₁₄	5-10	2.01	0.42	0.40	0.70	0.60	0.59
	1-2	1.79	0.45	0.42	0.73	0.51	0.49
	2-5	1.78	0.49	0.48	0.75	0.44	0.43
	1-5	1.78	0.51	0.50	0.74	0.47	0.45
	2-6	1.72	0.57	0.58	0.76	0.36	0.35
	1-3	1.71	0.55	0.54	0.73	0.49	0.48
	5-H-6	1.77	0.43	0.35	0.68	0.62	0.54
B ₉ H ₁₅	4-5	1.98	0.43	0.40	0.73	0.72	0.70
	1-4	1.83	0.45	0.42	0.77	0.47	0.43
	2-5	1.83	0.47	0.47	0.73	0.45	0.45
	4-9	1.80	0.52	0.52	0.84	0.45	0.48
	1-5	1.77	0.56	0.55	0.74	0.46	0.45
	1-2	1.77	0.42	0.40	0.73	0.53	0.52
	2-6	1.76	0.54	0.54	0.76	0.36	0.35
	5-H-6	1.82	0.37	0.29	0.61	0.55	0.46
	6-H-7	1.78	0.46	0.38	0.72	0.74	0.67
	3-H-4	1.76	0.40	0.33	0.50	0.46	0.39
B ₁₀ H ₁₆ ^a	1-1'	1.74	1.00	1.00	0.83	0.98	0.98
	1-2	1.66	0.61	0.62	0.86	0.50	0.53
	2-H-3	1.77	0.38	0.30	0.58	0.43	0.33
B ₁₀ H ₁₀ ²⁻	3-4	1.86	0.39	0.37	0.72 ^b	0.43	0.41
	3-8	1.81	0.52	0.51	0.75	0.53	0.52
	1-3	1.73	0.58	0.56	0.92	0.56	0.54
B ₃ H ₈ ⁻	2-3	1.80	0.64	0.60	1.00	0.78	0.77
	1-H-2	1.77	0.44	0.38	0.50	0.38	0.29
B ₁₂ H ₁₂ ²⁻	1-5	1.77	0.49	0.48	0.77 ^c	0.50	0.48
B ₁₀ H ₁₄ ²⁻	5-6	1.86	0.56	0.55	0.71 ^d	0.76	0.74
	1-3	1.84	0.43	0.42	1.00	0.50	0.49
	1-5	1.78	0.50	0.50	0.67	0.45	0.45
	1-2	1.76	0.50	0.48	0.67	0.51	0.48
	2-5	1.75	0.50	0.48	0.67	0.49	0.46
	2-6	1.74	0.48	0.46	1.00	0.43	0.42
	5-H-10	1.88	0.31	0.22	0.50	0.46	0.34
B ₉ H ₁₄ ⁻	4-5	1.87	0.48	0.50	0.67 ^d	0.45	0.45
	6-7	1.87	0.51	0.50	0.71	0.61	0.61
	1-3	1.83	0.44	0.42	0.67	0.49	0.47
	1-6	1.78	0.48	0.48	0.67	0.44	0.44
	1-2	1.76	0.48	0.46	0.67	0.50	0.48
	1-4	1.76	0.52	0.49	1.33	0.53	0.50
	2-6	1.75	0.51	0.49	0.67	0.50	0.47
	2-7	1.74	0.52	0.50	1.00	0.46	0.44
	1-5	1.72	0.54	0.54	0.67	0.46	0.46
	5-H-6	1.85	0.34	0.25	0.50	0.46	0.36

^a See reference 8 regarding distances.^b 80 structures with central 3-center bonds only.^c Total number of structures large and unknown. Bond order obtained by symmetry.^d One structure only.

TABLE IX. Dipole moments (in D) from charges.

Molecule	I	II	3-center ^a	Obs
B ₄ H ₁₀	1.54	0.80	0	0.56 ^b
B ₅ H ₉	5.59	1.04	4.07	2.13 ^c
B ₅ H ₁₁	3.76	1.28	2.36	
B ₆ H ₁₀	6.64	4.07	6.67	
B ₉ H ₁₆	7.20	3.69	5.66	
B ₁₀ H ₁₄	6.75	0.13	10.20	3.52 ^d

^a Charges on borons only, taken from all structures.

^b J. R. Weaver, C. W. Heitsch, and R. W. Parry, *J. Chem. Phys.* **30**, 1075 (1959).

^c H. J. Irotowski, R. J. Myers, G. C. Pimentel, *J. Chem. Phys.* **20**, 518 (1952).

^d A. W. Laubeigayer and R. Bottci, *J. Am. Chem. Soc.* **74**, 1618 (1952).

ment with that calculated by Moore *et al.*⁷ and is in accordance with experimental evidence.

In Table VII are also listed charges derived from an analysis of, for the main part all, three-center structures, as discussed in the first section. If we define "improvement" as increasing similarity to both experimentally inferred and LCAO-MO computed charge distributions, then the inclusion of unsymmetrical structures clearly improves the three-center bond theoretical results. Decaborane is here the best example.

With the conviction that the LCAO-MO charge distributions are more realistic than those derived previously, we earnestly implore that they be tested in the interpretation of experimental facts such as reactivities. Where ambiguities exist, we hope that, while better calculations are not immediately forthcoming, a choice may be made on empirical grounds between methods I and II. No clear choice can be made at present.

Overlap Populations and Bond Lengths

The results are presented in Table VIII. For organic molecules bond orders calculated with equal distances can be related to bond lengths. This was one of the motivating factors in building up a set of idealized boron hydrides; however, these proved to be of little value.¹⁶ The overlap populations for the real hydrides also do not enlarge our knowledge, since their evident proportionality to bond lengths has been installed *a priori* by use of the proper distances in the calculations.

Some further points should be noted. (1) It is clear that boron-boron distances spanned by bridge hydrogens show less variation in length than other B—B distances and do not fall on the same bond length-overlap population curve as the latter.

(2) The difference between methods I and II is manifested only in the overlap populations between borons connected by bridge hydrogens.

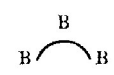
¹⁶ Except, as already implied, when there was little to idealize. For example, in delta-hedral B₁₀H₁₀²⁺ the idealized overlap populations show the trend of the actual bond lengths.

(3) It must be said to the credit of the three-center bond orders, also arising from an idealized structure, that they render a much better, though inadequate, representation of reality than do the idealized LCAO-MO structures.

Other Physical Properties

Dipole moments have been measured for 3 of the 6 hydrides which should possess them. The experimental values and those calculated from the charge distribu-

TABLE X. B₁₈H₂₂ half-structures.

	B—B	B  B
1	2-7, 4-8	
2	2-7, 4-10	
3	4-9, 7-8	
4	4-9, 2-7	10-4-8
5	4-9, 2-3	10-4-8, 1-2-7
6	4-9, 1-2	10-4-8
7	4-9, 3-7	2-7-8
8	4-9, 2-7	
9	4-8, 2-7	10-4-3, 1-4-9
10	4-8, 2-7	9-4-3
11	4-10, 2-7	1-4-8, 3-4-9
12	4-10, 3-7	1-4-9, 2-7-8
13	4-10, 7-8	1-4-9
14	4-10, 2-7	1-4-9
15	3-4, 2-7	1-4-9, 10-4-8
16	4-9, 2-7	3-4-10, 1-4-8
17	1-4, 2-7	10-4-8, 3-4-9
18	4-10, 1-2	
19	3-4, 2-7	
20	4-8, 1-2	
21	1-4, 2-7	
22	4-10, 2-3	1-2-7
23	1-4, 2-7	3-4-10
24	4-8, 2-3	1-2-7
25	3-4, 2-7	1-4-8
26	1-4, 3-7	2-7-8
27	1-2, 3-8	4-8-7
28	1-4, 7-8	
29	1-2, 7-8	
30	1-3, 7-8	2-1-4
B ₁₈ H ₂₂ ²⁺		
1	5-6	10-5-2', 2-6-10'
2	5-6	10-5-2', 2-6-10', 1-3-8, 7-8-4, 9-4-3
B ₁₃ H ₂₂ ²⁺		
1	5-6, 4-9, 1-3, 7-8	10-5-2', 2-6-10'

tions are shown in Table IX. A calculation with parameters between those of I and II would seem to give fair agreement. There is no reason to expect good dipole moments from wavefunctions as approximate as ours.

Chemical shifts in NMR spectra of boron hydrides are not simply related to charge distributions in the molecules; one has to take into account diamagnetic currents and possibly local atomic paramagnetism as well. Detailed consideration of NMR phenomena will be deferred to a forthcoming publication.

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APPENDIX

$B_{18}H_{22}$

The structure of a new boron hydride, $B_{18}H_{22}$, has just recently been determined.⁵ This centrosymmetric molecule may be thought of as two decaborane cages sharing a common (5-6) edge, but opening up in opposite directions. The framework is shown in Fig. 1.

A cursory examination of the bonding situation about the common edge, 5-6, shows that the only centrosymmetric structures are those in Fig. 2. (a) leads to

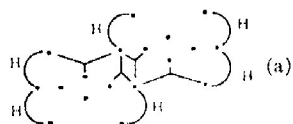
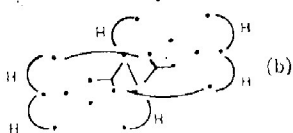


FIG. 2. Possible centrosymmetric bond arrangements for $B_{18}H_{22}$.



6.12.4.0 $B_{18}H_{22}$ structures, while (b) yields only 6.14.1.0 $B_{18}H_{22}^{2+}$ and 6.10.7.0 $B_{18}H_{22}^{2-}$. Thus all the centrosymmetric $B_{18}H_{22}$ graphs may be derived from a complete listing of $B_{10}H_{14}$ structures. Fortunately we have compiled what we hope is an exhaustive, or at least nearly complete, list of the latter. From this we obtain the 30 centrosymmetric structures described in Table X. An obvious derivation gives 870 unsymmetrical (no center of inversion) structures for a grand total of 900. An equally facile examination of the 900 structures, equally weighted, yields the following charge distribution:

atom	1	2	3	4	5
Q	-0.07	-0.27	-0.09	-0.50	+0.50
atom	6	7	8	9	10
Q	+0.50	-0.10	+0.09	+0.30	+0.13

Other unsymmetrical structures are multitudinous but we have not felt that an effort to find all of them is worthwhile.

The following bond orders are computed:

1-2	0.73	2-6	0.67	4-10	0.76
1-3	0.74	2-7	0.84	5-6	1.33
1-4	0.73	3-4	0.73	5-10	0.67
1-5	0.67	3-7	0.74	6-7	0.50
1-10	0.78	3-8	0.77	7-9	0.73
2-3	0.77	4-8	0.73	8-9	0.61
2-5	0.67	4-9	0.76	9-10	0.72

These are in disappointing disagreement with the observed distances.

Positions 5 and 6 appear to be the most positive ones in the molecule. They are, however, sterically inaccessible to nucleophilic reagents. Position 9 is next most positive and it is probable that this is the region from which the hydrogen dissociates in the formation of $B_{18}H_{21}^-$, the existence of which has been reported.⁴ In general, the molecule should be more reactive toward electrophilic attacking groups and less reactive toward nucleophiles than decaborane. Positions 2 and 4 remain negative, but 4 is easily singled out as the most negative site in the molecule.