Molecular Orbitals for Boron Hydrides Parametrized from SCF Model Calculations[1]

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Abstract: Recent development of a new molecular orbital method for complex molecules has led to an examination of molecular charge distributions, overlap populations, dipole moments, ionization potentials, and energies for a small, representative set of boron hydrides: BH_3, B_2H_6, B_4H_{10}, B_5H_9, and $B_{10}H_{14}$. Parameters were obtained from self-consistent field (SCF) results for B_2H_6. Comparisons of internal consistency with SCF results have been made for B_2H_6 and BH_3, and results for higher hydrides are compared with available experimental data. In addition, the effect on the wave functions of one-center, off-diagonal matrix elements of the molecular Hamiltonian is critically examined.

The boron hydrides have presented a challenge both as a test of existing theories and as a ground for development of new theories of structure and molecular properties. We have recently developed an essentially nonempirical molecular orbital theory[3] in which (a) the diagonal matrix elements for the potential energy part of the Hamiltonian are taken from exact SCF LCAO calculations[4] on simpler, closely related molecules (in this case, B_2H_6); (b) correction parameters K (defined below) for the Mulliken approximation to the off-diagonal potential energy matrix elements are also obtained from SCF results on simpler, related molecules; and (c) kinetic energy and overlap matrix elements are evaluated exactly for the molecule of interest. The only other parameters are the molecular geometry and the atomic orbital exponents for the basis set, discussed below.

Prior to these calculations, the most advanced method that had been applied to the higher hydrides was the extended Hückel theory,[5] which has shown substantial correlations with three-center resonance theory and experimental results pertaining to ionization potentials, binding energies, and charge distribution. However useful these correlations and predictions may be, we have felt it desirable to present calculations in which the somewhat arbitrary parameters and approximations of the earlier method have been dropped, and which can be directly compared to SCF results. In this paper we discuss the results for BH_3 and B_2H_6, for which exact SCF LCAO wave functions are available,[4] with respect to the averaging so necessary for transferring of parameters from one molecule to another.[3] After a series of internal checks of the theory for these two small molecules, we also examine the effects of these assumptions and parameters on the molecules B_4H_{10}, B_5H_9, and $B_{10}H_{14}$, for which fairly extensive experimental results are available. We also hope that SCF results on B_4H_{10} and B_5H_9 will be available in the foreseeable future for additional corroboration of the method. It is not our intention here to present an extended series of calculations for the higher boron hydrides, since a series of such calculations is in fact available in the doctoral dissertation of one of the present authors.[6]

Molecular Geometries and Basis Sets. Atomic positions of symmetry-unique atoms in a Cartesian coordinate system are listed in Table I. The corresponding molecular geometries were obtained from the most recent electron diffraction study[7] of B_2H_6, and from X-ray diffraction studies of B_4H_{10},[8] B_5H_9,[9] and $B_{10}H_{14}$,[10] but with modifications which give C_{2v}, C_{4v}, and C_{2v} symmetries, respectively, to these molecules, and which give B–H (terminal) and B–H_{BR} (bridge) distances which are not systematically shortened.[11] These distances are presented later (Table VII). The molecular structure of BH_3 is not established experimentally, but SCF calculations[12] predict the planar D_{3h} symmetry with a B–H distance of 1.19 A to be at the energy minimum. This bond distance corresponds very closely to the experimental value of 1.196 A for B–H (terminal) in B_2H_6.[7]

Throughout this series of papers a consistent set of basis functions is employed. A Slater-type basis set[13] is assumed with orbital exponents of 1.2 for H and Slater values[13] for all other atoms, *i.e.*, 4.7 for 1s and 1.3 for 2s and 2p for boron. Enough SCF calculations are available to indicate that 1.2 is close to optimized values for 1s of H in CH_2,[14] CH_4,[15] BH_3,[12] and both terminal and bridge H's in B_2H_6.[12] Correspondingly, Slater values[13] have been chosen in preference to best atom,[16a] because they are closer to the

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(1) Paper II in a series of four papers.

(2) National Science Foundation Predoctoral Fellow, 1964–1966.

(3) Paper I: M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353 (1966).

(4) Paper IV: W. E. Palke and W. N. Lipscomb, *ibid.*, **88**, 2384 (1966).

(5) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2872 (1962).

(6) An extended series of calculations for all the known boron hydrides, some carboranes, and various boron hydride derivatives is available in the doctoral dissertation of F. P. B. (Harvard University, April 1965). The wave functions successfully correlate a large body of experimental information. A slightly different basis set was used.

(7) L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, **42**, 1135 (1965).

(8) C. E. Nordman and W. N. Lipscomb, *ibid.*, **21**, 1856 (1953).

(9) W. J. Dulmage and W. N. Lipscomb, *Acta Cryst.*, **5**, 260 (1952).

(10) J. S. Kasper, C. M. Lucht, and D. Harker, *ibid.*, **3**, 436 (1950).

(11) For a summary and discussion see "Boron Hydrides," W. N. Lipscomb, Ed., The W. A. Benjamin Co., New York, N. Y., 1963, Chapter 1.

(12) W. E. Palke and W. N. Lipscomb, unpublished results. For a preliminary report, see M. D. Newton, F. P. Boer, W. E. Palke, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **53**, 1089 (1965).

(13) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

(14) J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 305 (1960).

(15) R. M. Pitzer, private communication.

(16) (a) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963). (b) The choice of a reference basis set is of course arbitrary, and the use of the Slater values of $\Sigma\epsilon_i^a(B) = -8.232$ au and $\Sigma\epsilon_i^a(B) = -16.263$ au will give somewhat larger binding energies. Since we use a

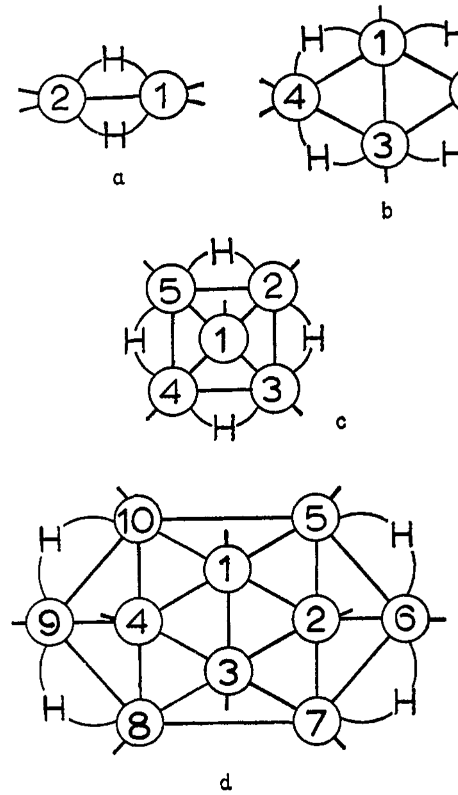

Figure 1. Numbering system and plane projection of boron hydrides: (a) B_2H_6, (b) B_4H_{10}, (c) B_5H_9, (d) $B_{10}H_{14}$.

SCF optimized values for 2s and 2p exponents in B_2H_6 and BH_3. It is, of course, clear that the systematic variation of orbital exponents upon energy minimization may in the future be used to choose basis functions when enough SCF calculations become available.

Procedure. As stated above, diagonal Hamiltonian elements are taken from the B_2H_6 SCF calculation while off-diagonal potential energy matrix elements are calculated according to eq 1[3]

$$U_{ij} = K_{ij}S_{ij}(U_{ii} + U_{jj})/2 \tag{1}$$

except for one-center 2s–2p ("zero-overlap") elements for which eq 2 is used[3]

$$F^{ZO}{}_{ij} = K^{ZO}\sum_{k} S_{ik}S_{jk}F_{kk} \tag{2}$$

A discussion of the two equations is available in ref 3. The Hamiltonian matrix elements[17] obtained from the B_2H_6 SCF calculation are listed as $F^{SCF}{}_{ij}$ in Table II, along with the values of K_{ij} calculated from the overlap matrix and eq 1. To guarantee rotational invariance[3] of the wave functions of polyhedral boron hydrides, we are forced to use a single average diagonal Hamiltonian element for all the 2p orbitals on a given B atom. Similarly, only one coefficient K may be used to calibrate eq 1 for all interactions between atomic orbitals of the same types (the relevant types are enumerated in Table III). In other words, we are forced to average over local anisotropies in the parameters. Unfortunately, this limitation seems more severe for the boron hydrides than for the alkanes, where anisotropies are much smaller,[18] or for planar unsaturated hydrocarbons, where σ–π separation is permitted.[18]

Table I. Cartesian Coordinates for Nonequivalent Atomic Positions

Atom	Center	X	Y	Z
		A. B_2H_6[a]		
B1	A	0.887	0	0
B2	B	−0.887	0	0
H1	C	1.494	1.030	0
H1′	D	1.494	−1.030	0
H2	E	−1.494	1.030	0
H2′	F	−1.494	−1.030	0
H_{BR}	G	0	0	1.002
H_{BR}'	H	0	0	−1.002
		B. B_4H_{10}		
B1		0.854	0	0
B2		0	1.400	0.831
H1		1.398	0	−1.058
H2		0	1.325	2.018
H2′		0	2.394	0.177
H_{BR}		1.264	0.990	0.787
		C. B_5H_9		
B1		0	0	1.087
B2		1.253	0	0
H1		0	0	2.297
H2		2.348	0	0.495
H_{BR}		0.974	0.974	−0.888
		D. $B_{10}H_{14}$		
B1		0.854	0	0
B2		0	1.522	0.403
B5		1.411	1.003	1.357
B6		0	1.774	2.101
H1		1.648	0	−0.846
H2		0	2.422	−0.460
H5		2.517	1.638	1.357
H6		0	2.951	2.607
H_{BR}		1.133	1.024	2.644

[a] For B_2H_6, all centers are listed (labeled A–H) since they will be referred to in Table II.

In diborane, the SCF values of α_{2p} are −0.440 au along the B–B axis (p_x), −0.388 in the plane of the terminal H atoms (p_y), and −0.183 in the plane of the bridge H atoms (p_z). A large anisotropy is also present in the $2p\pi$–$2p\pi$ (π with respect to the B–B axis) interactions, even though the kinetic energy and mutual overlap integrals are identical; these off-diagonal matrix elements (F's) are −0.280 in the plane of the bridge hydrogens and only −0.160 in the plane of the terminal hydrogens. This particular anisotropy also occurs in the values of $K(2p_z$–$2p_z) = 1.37$ and $K(2p_y$–$2p_y) = 0.73$, which show large deviations from the value of $K = 1$ (the Mulliken approximation). The pattern of these anisotropies is very similar to that in ethylene,[4] as shown in the following tabulation

	B_2H_6	C_2H_4
$\alpha(2p_x)$	−0.440	−0.549
$\alpha(2p_y)$	−0.388	−0.411
$\alpha(2p_z)$	−0.183	−0.146
$F(2p_x$–$2p_x)$	0.281	0.294
$F(2p_y$–$2p_y)$	−0.160	−0.232
$F(2p_z$–$2p_z)$	−0.280	−0.324

where the H atoms of C_2H_4 are in the xy plane. The ethylenic nature of the electronic structure of B_2H_6 has been noted many times earlier.[19] In addition to these

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hydrogen exponent of 1.2, the Slater set seems no more suitable as a reference.

(17) In accordance with the notation established in paper I (ref 3), diagonal and off-diagonal elements of the one-electron Hamiltonian matrix are respectively denoted by F_{ii} or α_i, and F_{ij} or $F(i - j)$. All energies are in atomic units (au).

(18) Paper III: M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2367 (1966).

Table II. Unique Nonzero Hamiltonian Elements[a,b]

		A. B_2H_6		
Element[c]	K_{ij}	I F_{ij}	II F_{ij}	III F_{ij}
A1s–A1s	1.000	−7.706	−7.706	−7.706
A1s–A2s	0.655	−1.728	−1.728	−1.728
A1s–A2p_x[d]	...	+0.009	0.000	0.000
A1s–Bls	...[f]	0.000	0.000	0.000
A1s–B2s	0.810	−0.317	−0.317	−0.317
A1s–B2p_x	0.820	−0.537	−0.538	−0.535
A1s–C1s	0.814	−0.580	−0.577	−0.577
A1s–E1s	0.795	−0.026	−0.027	−0.027
A1s–G1s	0.805	−0.426	−0.429	−0.429
A2s–A2s	1.000	−1.081	−1.081	−1.081
A2s–A2p_x[e]	...	+0.104	+0.104	+0.104
A2s–B2s	1.052	−0.536	−0.537	−0.537
A2s–B2p_x	1.107	−0.497	−0.498	−0.475
A2s–C1s	1.031	−0.584	−0.589	−0.589
A2s–E1s	1.052	−0.134	−0.132	−0.132
A2s–G1s	1.044	−0.564	−0.561	−0.561
A2p_x-A2p_x	1.000	−0.440	−0.440	−0.337*
A2p_x–B2p_x	1.129	+0.281	+0.281	+0.243
A2p_x–Cls	0.924	−0.188	−0.230*	−0.215
A2p_x–Els	1.134	+0.166	+0.154	+0.148
A2p_x–Gls	1.167	+0.372	+0.332*	+0.305*
A2p_y–A2p_y	1.000	−0.388	−0.388	−0.337*
A2p_y–B2p_y	0.730	−0.160	−0.160	−0.265*
A2p_y–Cls	1.010	−0.355	−0.377	−0.365
A2p_y–Els	0.832	−0.052	−0.065	−0.064
A2p_z–A2p_z	1.000	−0.183	−0.183	−0.337*
A2p_z–B2p_z	1.372	−0.280	−0.280	−0.265
A2p_z–G1	1.018	−0.301	−0.314	−0.344*
C1s–C1s	1.000	−0.464	−0.464	−0.464
C1s–D1s	1.175	−0.179	−0.173	−0.173
C1s–E1s	0.837	−0.032	−0.041	−0.041
C1s–F1s	1.522	−0.018	−0.014	−0.014
C1s–G1s	1.112	−0.176	−0.178	−0.178
G1s–G1s	1.000	−0.593	−0.593	−0.593
G1s–H1s	1.134	−0.217	−0.206	−0.206

	B. BH_3	
Element[g]	I	III[h]
1s–1s	−7.677	−7.706
1s–2s	−1.719	−1.728
1s–H	−0.584	−0.585
2s–2s	−0.969	−1.081*
2s–H	−0.569	−0.592
2p–2p	−0.345	−0.337
2p–H	−0.406	−0.423
H–H	−0.465	−0.464
H–H′	−0.176	−0.173

[a] Sign convention for p orbitals is positive lobe pointing in positive direction along coordinate axis. [b] Differences from the SCF of ≥0.04 au are starred. [c] The atomic centers A–H are identified in Table I. [d] This small ZO element is neglected in II–IV. [e] The 2s–2p ZO element is obtainable from eq 2, using $K^{ZO} = 0.35$ and $\alpha_{2p} = -0.337$. [f] Since the overlap integral for this pair of orbitals is negligibly small, K_{ij} is arbitrarily taken as 1.00. [g] H and H′ refer to hydrogen 1s-orbitals on different centers. 2p denotes one of the two occupied 2p orbitals. [h] For BH_3, calculations II, III, and IV become identical.

Table III. Parameters

A. α's and Exponents		
Orbital	Exponent	α
B1s	4.700	−7.706
B2s	1.300	−1.081
B2p	1.300	−0.337
H (terminal)	1.200	−0.464
H (bridge)	1.200	−0.593

B. Mulliken Approximation Coefficients			
One-center			
K_{1s-2s}	0.66		
Two-center			
K_{1s-1s}	1.00	K_{2s-H}	1.04
K_{1s-2s}	0.81	$K_{2p-2p,\sigma}$	1.13
K_{1s-2p}	0.82	$K_{2p-2p,\pi}$	1.14
K_{1s-H}	0.81	K_{2p-H}	1.05
K_{2s-2s}	1.05	K_{H-H}	1.13
K_{2s-2p}	1.11		

C. Zero–Overlap Coefficient

$K^{ZO} = 0.35$

anisotropies, there are some other kinds of closely related interactions in B_2H_6 which generate different coefficients. The *K* values for the interaction of 2s on boron with two adjacent terminal H atoms ($K = 1.03$), two distant terminal H atoms ($K = 1.05$), and two bridge H atoms ($K = 1.04$) have also been averaged according to the procedure outlined in ref 3. Good results can be expected when the *K*'s are so nearly the same. To complete the choice of parameters listed in Table III for B_2H_6, we add that the K^{ZO} is chosen to fit exactly the correct SCF result for the 2s–2p one-center element for B_2H_6.[20]

Four different calculations are now outlined so that we can examine how well our method reproduces the SCF B_2H_6 wave function, how well the parameters from B_2H_6 reproduce the SCF BH_3 function, how much the former results are influenced by the anisotropies of theF_{ii}'s and F_{ij}'s, and how the assumption $K^{ZO} = 0$ for the 2s–2p interaction affects the results for all boron hydrides considered. These four calculations are as follows (results are in Table IV).

Table IV. Eigenvalues

	A. Diborane			
	I	II	III[a]	IV
b_{1g} = HFMO	−0.487	−0.493	−0.437	−0.437
a_g	−0.535	−0.555	−0.497	−0.506
b_{3u}	−0.560	−0.592	−0.599	−0.599
b_{1u}	−0.576	−0.596	−0.661*	−0.661
b_{2u}	−0.656	−0.668	−0.665*	−0.683
a_g	−0.900	−0.886	−0.880	−0.876
b_{2u}	−7.708	−7.708	−7.708	−7.708
a_g	−7.708	−7.708	−7.708	−7.708
$\Sigma\epsilon_i^m$	−19.130	−19.207	−19.146	−19.179

	B. BH_3	
	I	III
e′	−0.510	−0.521
	−0.510	−0.521
a_1′	−0.713	−0.778
a_1′	−7.679	−7.708
$\Sigma\epsilon_i^m$	−9.412	−9.529

	C. Ionization Potentials		
	IP_{exptl}	HFMO III	HFMO IV
BH_3		−0.521	−0.521
B_2H_6	−0.441[b]	−0.437	−0.437
B_4H_{10}	−0.382[b]	−0.415	−0.420
B_5H_9	−0.386[b]	−0.387	−0.367
$B_{10}H_{14}$	−0.404[b] −0.393[c]	−0.402	−0.385

[a] Differences from the SCF of ≥ 0.04 au are starred. [b] Reference 23. [c] Reference 24.

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(19) For example, see K. S. Pitzer, *J. Am. Chem. Soc.*, **67**, 1126 (1943).

(20) See footnote *e* of Table II.

Calculation I. The SCF results are taken from ref 4.

Calculation II. Anisotropic. Here, the correct SCF values for B_2H_6 are given to $\alpha(2p_x)$, $\alpha(2p_y)$, $\alpha(2p_z)$, $F(2p_x\text{–}2p_x)$, $F(2p_y\text{–}2p_y)$, and $F(2p_z\text{–}2p_z)$, while eq 1 and 2 are used with our averaged values of K[21] for the other matrix elements. This is an intermediate type of calculation not yet readily extendable to the other boron hydrides until methods for introducing local anisotropies are developed, but when compared to I and III it serves to isolate the effects of anisotropies of the p orbitals. The main problem which arises from the averaging of K's performed in this calculation is that the p_x interactions with adjacent terminal and bridge hydrogen atoms are 0.042 au high and 0.050 au low, respectively (Table II; starred values differ from SCF results by 0.04 au or more).

Calculation III. This is the general method. The SCF parameters of Table III for B_2H_6 are used in conjunction with eq 1 and 2. The results for B_2H_6 yield six matrix elements which differ by 0.04 au or more from the SCF values (Table IIA). Use of these same parameters in a calculation of matrix elements for BH_3 yields the results shown in Table IIB. Here, the only appreciable error is the overestimation of $\alpha(2s)$ by 0.112 au. The average value of $\alpha(2p)$ works out well for BH_3, as do the off-diagonal matrix elements.

Calculation IV. $K^{ZO} = 0$. In order to study the effect of ignoring zero-overlap elements, these elements have been set equal to zero in a calculation that is otherwise like III. Results are also given for this method on B_4H_{10}, B_5H_9, and $B_{10}H_{14}$. Note that the threefold axis of BH_3 causes this element to vanish.

Results. The eigenvalues obtained from the approximate Hamiltonian matrices II, III, and IV fit the SCF results surprisingly well (Table IV). The inversion of the order of eigenvalues for the b_{1u} and b_{2u} molecular orbitals in calculation III is mostly associated with the assumption of isotropic atoms, but in any case both eigenvalues are very close. Also given in Table IV are the sums of eigenvalues, which are used below to obtain binding and total energies. Calculated vertical ionization potentials, which are given for a closed-shell molecule by the energy of its highest filled molecular orbital (HFMO) provided that the same set of MO's may be used for both ionized and un-ionized states,[22] are also tested. These values for ionization potentials compare well with experiment[23,24] (Table IV).

Molecular binding energy A relative to individual atoms, neglecting correlation and relativistic energies and assuming the quantity Δ[25] $= \Sigma(E_i^{\mathrm{m}} - E_i^{\mathrm{a}})/2] + N$ to be zero (N = nuclear repulsion energy), is

$$A = (\Sigma\epsilon_i^{\mathrm{m}} - \Sigma\epsilon_i^{\mathrm{a}})/2 \qquad (3)$$

while the total energy is

$$E_{\mathrm{tot}} = (\Sigma\epsilon_i^{\mathrm{m}} + \Sigma E_i^{\mathrm{a}})/2 \qquad (4)$$

where ϵ_i and E_i are molecular (m) or atomic (a) orbital eigenvalues and core energies, respectively, and sums are taken over electrons i.[26] Because we are dealing with minimum basis sets of wave functions, appropriate reference atoms are Clementi's best single ζ atoms,[16b] for which $\Sigma\epsilon_i^{\mathrm{a}}(\mathrm{H}) = -0.250$, $\Sigma\epsilon_i^{\mathrm{a}}(\mathrm{B}) = -8.312$, $\Sigma E_i^{\mathrm{a}}(\mathrm{H}) = -0.250$, and $\Sigma E_i^{\mathrm{a}}(\mathrm{B}) = -16.186$ au. In Table V we summarize binding and total energies, obtained from these equations, for the boron hydrides. The agreement with experimental values,[27] also shown in Table V, is surprisingly good. Furthermore, the values of E_{tot} from eq 4 of -53.002 for B_2H_6 and -26.338 au for BH_3 are in reasonably good agreement with the respective SCF values of -52.678 and -26.338 au. Thus, further use of eq 3 and 4 (based upon the $\Delta = 0$ approximation) is probably reasonable for predicting binding and total energies in the higher hydrides. Finally, the dissociation energy of B_2H_6 into $2BH_3$ is calculated to be only 0.003 au by SCF methods, while calculations III and IV give 0.078 and 0.121 au, respectively, from eq 3. Experimental values are ≤ 0.088,[28] <0.061,[29] and 0.045.[30] Chemical energies of this magnitude cannot be predicted reliably from a minimum basis framework, even when correlation energies tend to cancel, but we do find B_2H_6 stable with respect to $2BH_3$. The approximate virial theorem[31] is examined in Table V, where the total kinetic energy calculated from the coefficients of the wave functions and the kinetic energy integrals over the atomic basis sets is compared to the total molecular energy. The results from calculations III and IV actually satisfy the virial theorem almost as well as do unscaled SCF wave functions.[32]

Table V. Energies

		$\frac{1}{2}(\Sigma\epsilon_i^{\mathrm{m}} + \Sigma E_i^{a})$	E_{kinetic}	$\frac{1}{2}(\Sigma\epsilon_i^{\mathrm{m}} - \Sigma\epsilon_i^{a})$	A_{exptl}
B_2H_6	I	−53.002	+52.254	−1.006	−0.917
	II	−53.079	+52.264	−1.083	
	III	−53.018	+52.255	−1.022	
	IV	−53.051	+52.245	−1.055	
BH_3	I	−26.338	+26.178	−0.350	−0.428[a]
	III	−26.465	+26.275	−0.467	
B_4H_{10}	III	−104.751	+103.558	−1.758	−1.670
	IV	−104.812	+103.540	−1.820	
B_5H_9	III	−128.886	+127.925	−1.896	−1.800
	IV	−128.956	+127.554	−1.966	
$B_{10}H_{14}$	III	−255.547	+252.604	−3.567	−3.311
	IV	−255.634	+252.312	−3.654	

[a] Assuming D_0 ($B_2H_6 \rightarrow 2BH_3$) = 0.061 au (ref 29).

The atomic charges, as given by Mulliken's method,[33] are sensitive to the parametrization (Table VI). The net Mulliken charges (NMC) on bridge (0.099) and terminal (0.092) hydrogens are the same in the SCF calculation, but this near-equality is no longer true

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(21) Listed in Table III.

(22) F. Koopmans, *Physica*, 1, 104 (1934); R. S. Mulliken, *J. Chim. Phys.*, **46**, 497 (1949).

(23) T. P. Fehlner and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 581 (1964).

(24) W. S. Koski, T. T. Kaufman, C. F. Packuki, and F. J. Shipko, *ibid.*, **80**, 3202 (1958).

(25) Values of Δ for the SCF wave functions of ref 4 are given in Appendix III of Paper III (ref 18).

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Table VI. Charge Distribution

		NMC I	NMC II	NMC III	NMC IV
B_2H_6	B1	−0.283	−0.306	−0.206	−0.297
	H1	+0.092	+0.073	+0.004	+0.093
	H_{BR}	+0.099	+0.161	+0.197	+0.112
BH_3	B	−0.171		−0.404	−0.404
	H	+0.057		+0.135	+0.135

	Atom	NMC III	NMC IV	FC III	FC IV	3-C
B_4H_{10}	B1	+0.12	−0.14	+0.13	+0.04	0.
	B2	−0.20	−0.32	−0.13	−0.04	0.
	H1	−0.12	+0.08			
	H2	0.00	+0.09			
	H2′	−0.06	+0.08			
	H_{BR}	+0.13	+0.11			
B_5H_9	B1	+0.20	−0.33	−0.07	−0.28	−0.78
	B2	+0.11	−0.08	+0.02	+0.07	+0.20
	H1	−0.27	+0.05			
	H2	−0.18	+0.07			
	H_{BR}	+0.09	+0.08			
$B_{10}H_{14}$	B1	+0.32	0.00	+0.15	+0.05	−0.03
	B2	+0.18	−0.14	−0.06	−0.14	−0.46
	B5	+0.12	−0.02	−0.04	0.00	+0.10
	B6	+0.10	+0.03	−0.01	+0.09	+0.29
	H1	−0.17	+0.04			
	H2	−0.24	0.00			
	H5	−0.19	−0.01			
	H6	−0.19	0.00			
	H_{BR}	+0.07	+0.06			

Table VII. Bond Overlap Populations (OP)

	Bond	Distance, A	OP (I)	OP (II)	OP (III)	OP (IV)	3-C bond order
B_2H_6	B1–B2	1.775	0.291	0.456	0.429	0.384	1.00
	B1–H1	1.196	0.864	0.832	0.817	0.815	
	B1-H_{BR}	1.339	0.400	0.391	0.419	0.429	
BH_3	B–H	1.19	0.837		0.803	0.803	

	Bond	Distance, A	OP (III)	OP (IV)	3-C bond order
B_4H_{10}	B1–B2	1.84	0.44	0.37	0.50
	B1–B3	1.71	0.58	0.59	1.00
	B1–H1	1.19	0.78	0.82	
	B2–H2	1.19	0.76	0.78	
	B2–H2′	1.19	0.78	0.82	
	B1–H_{BR}	1.33	0.41	0.44	
	B2–H_{BR}	1.33	0.34	0.34	
B_5H_9	B1–B2	1.66	0.51	0.57	0.84
	B2–B3	1.77	0.40	0.35	0.61
	B1–H1	1.21	0.72	0.83	
	B2–H2	1.20	0.72	0.82	
	B2–H_{BR}	1.35	0.39	0.41	
$B_{10}H_{14}$	B1–B2	1.79	0.47	0.44	0.73
	B1–B3	1.71	0.48	0.48	0.73
	B1–B5	1.78	0.51	0.46	0.74
	B2–B5	1.78	0.45	0.47	0.75
	B2–B6	1.72	0.44	0.51	0.76
	B5–B6	1.77	0.45	0.40	0.68
	B5–B10	1.80	0.49	0.48	0.70
	B1–H1	1.16	0.70	0.81	
	B2–H2	1.25	0.69	0.81	
	B5–H5	1.28	0.70	0.79	
	B6–H6	1.28	0.71	0.79	
	B5–H_{BR}	1.32	0.38	0.39	
	B6–H_{BR}	1.46	0.39	0.40	

when the average of coefficients is made in calculation II, or when the anisotropy of 2p orbitals is removed in calculation III. The better agreement when the zero-overlap elements are omitted in calculation IV must be fortuitous. In the higher hydrides the negative charges on H atoms of BH units seem excessive, but those on H atoms of BH_2 units are more nearly neutral. A comparison of these charges with those from three-center resonance theory,[5] which assumes that H atoms are neutral, is possible if we define boron framework charges (FC) as

$$\mathrm{FC(B)} = \mathrm{NMC(B)} + \Sigma\mathrm{NMC(H\ terminal)} + {}^1/_2\Sigma\mathrm{NMC(H\ bridge)}$$

where the sums are taken over all immediately bonded H atoms. These three-center charges apparently correlate with chemical evidence obtained from Friedel–Crafts methylation of $B_{10}H_{14}$,[34] which can be interpreted to yield the decreasing amount of negative charge in the order B2, B1, B5, and B6. We note that the framework charges from calculation III are not in good agreement, although those from calculation IV are more consistent with this order of charges. We recall that the previous extended Hückel calculations, in which zero-overlap elements were also omitted, were likewise in qualitative agreement with three-center theory and with indications from experiments. It is disturbing that these zero-overlap elements have so much influence on the charge distribution, especially since they have been omitted in earlier molecular orbital studies of complex molecules. Equation 2 guarantees that these elements will increase with increasing asymmetry of the environment of the atom. Boron atoms having one terminal hydrogen atom are predicted to have larger zero-overlap Hamiltonian elements (0.24 au for $F(2s\text{–}2p_z)$ for B1 in B_5H_9) than will boron atoms having two terminal hydrogen atoms (0.10 au for $F(2s\text{–}2p_x)$ for B1 in B_2H_6). These zero-overlap elements tend to transfer negative charge out to the terminal H atoms.

With respect to this unsatisfactory turn of events we can only offer alternatives in order of probable validity. (1) If there is less anisotropy in the higher hydrides than in B_2H_6, we may be overestimating these zero-overlap elements, and hence calculation IV may be more nearly correct than calculation III for these higher hydrides. (2) The fortuitous cancellation of errors observed in calculation IV for B_2H_6 may be maintained in the higher hydrides, but if so we may hope for further theoretical developments which will explain or remove this cancellation. (3) Future SCF calculations could corroborate calculation III, and hence require both a future development and revision of the three-center valence theory. At any rate, exact SCF calculations involving boron atoms in polyhedral environments will be necessary to resolve this question.

Overlap populations[33] (Table VII) show reasonable agreement between calculations I and III for B_2H_6 and BH_3, except for the comparison of 0.291 and 0.429, respectively, for the B–B bond in B_2H_6. Overlap populations of bonds between B and H (bridge) or H (terminal) remain in the reasonable ratio of 1 to 2 in all calculations, and at least in the higher hydrides the B–B overlap populations tend to parallel those from three-center resonance theory. The main effect of excluding

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zero-overlap elements in calculation IV is to give slightly higher overlap populations for B–H (terminal) bonds.

Molecular dipole moments are sometimes[35] in disagreement with experiment by as much as a factor of 2 when a minimum basis set is used in SCF calculations; moderate extension of the basis set can be expected to improve calculation of this ground-state, one-electron property considerably. Not only can our results be expected to be no better than the SCF results, but the lack of an iterative procedure for self-consistency can leave an exaggerated charge distribution in a molecular calculation parametrized by SCF results on a simpler molecule. Here, we compute atomic, bond, and total molecular dipole moments[36] from the complete LCAO wave function, not simply using the Mulliken point charges,[33] which we find to yield dipole moments lower by a factor of 2 or 3 than those given by the complete wave function. The origin-invariant partitioning method[36] yields an analysis of the result in terms of Mulliken point charges (referred to as the classical dipole), but there are also other terms due to polarization of each atom, and of each bond. It is interesting to examine these latter terms in a molecule such as B_2H_6, for which the total molecular dipole moment is zero by symmetry (Table VIII). Bond, atomic and classical dipole terms for B_4H_{10}, B_5H_9, and $B_{10}H_{14}$ are also given in Table VIII for components along the symmetry (Z) axis, from calculations with and without zero overlap. Calculations for other neutral boron hydride species and derivatives are summarized elsewhere.[6] The relative trends of dipole moments of these compounds are very reasonable and believed to give the direction of the dipole moment correctly: the negative pole points outward from the imaginary center of a polyhedral fragment. Nevertheless, the magnitudes of the dipole moments are consistently overestimated with respect to the experimental results[37–39] (Table VIII). The differences between calculations with and without zero-overlap elements are striking, especially if we compare changes in the individual terms rather than in the resultant. The classical component of the B_5H_9 moment, for example, is -5.16 D. for III and -1.78 D. for IV. The inclusion of zero-overlap elements generally has the effect of reducing the atomic polarization terms. In diborane, the SCF wave function gives an atomic term of -1.13 D., but III gives only -0.51 D., while IV yields -1.57 D. This reduction of atomic polarization components is then not necessarily in accord with SCF results. In general, calculations without zero-overlap elements give moments that are somewhat less exaggerated, and also predict the experimental order $B_4H_{10} < B_5H_9 < B_{10}H_{14}$. Bridge hydrogen bonds have large bond dipole moments in a direction opposing the Mulliken charges. In the case of B_5H_9, the eight-bond moments from the bridges contribute $+3.20$ (III) and $+5.20$ (IV), respectively, in *opposition* to the net molecular dipole moment.

Table VIII. Dipoles (Debye Units)

B_2H_6		I	II	III	IV
Atom A:	(X axis)	−1.13	−0.80	−0.51	−1.57
Bond AC:	X axis	−0.20	−0.39	−0.61	−0.26
	Y axis	−1.40	−1.36	−1.32	−1.32
	Total	1.41	1.41	1.45	1.34
Bond AG:	X axis	+0.26	+0.18	+0.34	+0.22
	Z axis	−0.70	−0.75	−0.75	−0.75
	Total	0.75	0.77	0.82	0.78

Atomic moments (z components)

		III	IV
B_4H_{10}	B1	+0.33	+1.16
	B2	+0.03	−0.48
B_5H_9	B1	+0.27	−1.74
	B2	−0.53	−0.35
$B_{10}H_{14}$	B1	+0.06	+1.36
	B2	+0.09	+0.85
	B5	+0.59	+0.48
	B6	+0.68	−0.60

Bond moments (z components)

	Bond	III	IV
B_4H_{10}	B1–B2	0.13	0.37
	B1–B3	0.37	−0.93
	B1–H1	0.91	0.51
	B2–H2	−1.30	−1.36
	B2–H2′	0.56	0.91
	B1–H_{BR}	−0.20	−0.48
	B2–H_{BR}	−0.09	−0.06
B_5H_9	B1–B2	−1.02	−0.75
	B2–B3	+0.18	−0.53
	B1–H1	−0.82	−0.55
	B2–H2	−0.08	−0.15
	B2–H_{BR}	+0.40	+0.65
$B_{10}H_{14}$	B1–B2	+0.73	+0.57
	B1–B3	+0.95	+0.60
	B1–B5	−0.13	+0.06
	B2–B5	+0.20	+0.13
	B2–B6	+0.02	−0.01
	B5–B6	−0.10	+0.25
	B5–B10	−0.34	−0.13
	B1–H1	+0.40	+0.30
	B2–H2	+0.42	+0.47
	B5–H5	+0.07	−0.31
	B6–H6	−0.51	−0.36
	B5–H_{BR}	−0.54	−0.48
	B6–H_{BR}	−0.33	−0.42

		$\mu_{classical}$	μ_{atom}	μ_{bond}	μ_{total}	μ_{exptl}
B_4H_{10}	III	1.54	0.73	0.42	2.69	0.56[37]
B_4H_{10}	IV	0.14	1.35	0.29	1.78	
B_5H_9	III	−5.16	−1.86	−1.46	−8.48	2.13[38]
B_5H_9	IV	−1.78	−3.15	−1.10	−6.03	
$B_{10}H_{14}$	III	2.15	4.00	0.95	7.11	3.52[39]
$B_{10}H_{14}$	IV	2.07	5.13	0.03	7.23	

In summary, the ability of our method to predict energies (binding, total, and kinetic energies, eigenvalues, and ionization potentials) for large molecules appears far superior to earlier methods. However, the general situation with respect to charge distribution, at least for boron hydrides, is less satisfactory, particularly because of the restrictions of atomic anisotropy in molecules, which have largely been unrecognized in previous approximate treatments.

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