Electron Population Analysis and Localization in Simple Molecules and Boron Compounds

Durward W. J. Cruickshank, Alexander Chablo, Miriam Eisenstein* and Paula L. Reidy

Chemistry Department, UMIST, Manchester M60 1QD, England

Cruickshank, D. W. J., Chablo, A., Eisenstein, M. and Reidy, P. L., 1988. Electron Population Analysis and Localization in Simple Molecules and Boron Compounds. – Acta Chem. Scand., Ser. A 42: 530–538.

The Roby projection-density method of population analysis is applied to two problems.

From 4-21G calculations on simple molecules it is shown that Roby shared populations s_{AB} may be regarded primarily as the shared populations of localized bonding orbitals. The relation $s_{AB} \approx 2\langle ah|bh\rangle$ interprets s_{AB} in terms of the overlap integral for the atomic hybrid orbitals defined by the LMO. For a multiple bond, s_{AB} is interpreted through the overlap integrals for the several banana bond LMO's. Shared populations for some bond types are correlated with bonding density peaks from X-ray electron-density difference maps.

For polyhedral boron hydrides and carboranes, localization may sometimes lead to valence structures whose chemical significance is uncertain. However, the Roby descriptions of a series of molecules show internal consistency with high two-centre shared populations (1.31–1.89) for every polyhedral edge and significant three-centre populations (0.49–0.59) for every face. The two-centre populations correlate well with the experimental bond lengths. The molecules considered are B_2H_6, B_4H_{10}, B_5H_{11}, B_6H_{10}, 4,5-$C_2B_4H_8$, 1,2-$C_2B_4H_6$, 1,6-$C_2B_4H_6$, $B_6H_6^{2-}$ and B_5H_9.

Dedicated to Professor Otto Bastiansen on his 70th birthday

The concepts of bond orders and shared populations go back to the earliest days of molecular orbital theory and have been developed by a number of authors. Mulliken's[1] methods of population analysis have proved particularly valuable, but as more sophisticated wave functions have become available certain drawbacks in Mulliken's procedures have become apparent.

Roby[2] has approached the problem of electron population analysis in a very different way. He introduced projection-density methods to calculate the electron populations of atoms and groups of atoms n_A, n_{AB}, n_{ABC},... The electron population shared between atoms A and B is then

$$s_{AB} = n_A + n_B - n_{AB}. \quad (1)$$

Similarly, the population shared between three atoms is

$$s_{ABC} = n_A + n_B + n_C - n_{AB} - n_{BC} - n_{AC} + n_{ABC}. \quad (2)$$

This expression and those for s_{ABCD}, etc., have no counterparts in the Mulliken procedures.

An extensive investigation of Roby's method has been made by Cruickshank and Avramides[3] (hereafter abbreviated to CA), and the calculations reported in this paper are based on the procedures described in detail by CA. In their development of Roby's method, atomic populations n_A are derived from a molecular wave function by projecting out with a set of *atomic SCF* functions. These SCF functions are obtained with

*Present address: Department of Structural Chemistry, The Weizmann Institute of Science, 76100 Rehovot, Israel.

the same basis functions as are used in the molecular calculations. The orthogonalised basis functions which remain after the atomic SCF functions have been abstracted from the basis are termed polarization functions. The projections are made in such a way as to ascribe maximum possible populations to the atomic SCF functions and minimum possible populations to the residual polarization functions. Polarization populations, which are usually small for first-row molecules, will be mentioned only incidentally in the present paper.

In the Roby method the atom population is

$$n_A = N\,\mathrm{tr}(\varrho P_A) = \Sigma\Sigma|\langle\mu|i\rangle|^2, \quad (3)$$

where N is the number of electrons in the molecule, tr denotes the trace, ϱ is the molecular one-density operator $(1/N)\Sigma|i\rangle\langle i|$ summed over the molecular orbitals $|i\rangle$, P_A is the atomic projector $\Sigma|\mu\rangle\langle\mu|$ summed over the SCF atomic orbitals $|\mu\rangle$, and $\langle\mu|i\rangle$ is the overlap integral between $|i\rangle$ and $|\mu\rangle$. For several centres

$$n_{ABC\ldots} = N\,\mathrm{tr}(\varrho P_{ABC\ldots}), \quad (4)$$

where the non-diagonal projector $P_{ABC\ldots}$ involves atomic orbitals on the several centres and an inverse overlap matrix.

In this paper we apply the CA development of the Roby method to two problems. We first consider simple molecules in which two-centre localized molecular orbitals (LMO's) can be formed rather satisfactorily, and we show that the shared populations s_{AB} are very simply related to the overlap integrals $\langle ah|bh\rangle$ defined by the atomic hybrid orbitals of the LMO's. The second problem concerns bonding in boron compounds. Here, both two- and three-centre bonding is involved. Calculations by Kleier *et al.*[4] for a set of boron hydrides and carboranes have led to LMO's whose chemical significance is sometimes uncertain. We show that the Roby method, independently of any localization of individual orbitals, leads to informative and consistent descriptions of the two- and three-centre shared populations in these boron compounds.

Localized molecular orbitals in simple molecules

CA[3] noted for a homopolar two-electron molecule in a minimum-basis calculation that there is an exact equation

$$s_{AB} = 2\langle a|b\rangle \quad (5)$$

for the shared population s_{AB} in terms of the overlap integral $\langle a|b\rangle$ between the atomic orbitals on each centre. The analysis is unaffected if the AO's are hybrids rather than pure s or p orbitals.

For multielectron molecules, s_{AB} is the sum of contributions from all molecular orbitals, and for canonical MO's these contributions may be large, small or negative (from anti-bonding MO's). However, the total Roby populations are invariant to unitary transformations among the MO's. CA observed that if it was possible to transform the canonical MO's to a set where just one localized molecular orbital (LMO) represented a two-electron bond between atoms A and B, then a good approximation for a homopolar bond might be

$$s_{AB} \approx 2\langle ah|bh\rangle, \quad (6)$$

where $\langle ah|bh\rangle$ is the overlap integral for the atomic hybrids defined through the coefficients of the LMO. For a heteropolar LMO, for which

$$|i\rangle = c_a|ah\rangle + c_b|bh\rangle, \quad (7)$$

CA showed that

$$s_{AB} = 2\langle ah|bh\rangle M(g), \quad (8)$$

where $g = c_b/c_a$ and

$$M(g) = M(1/g) = \{2g + (g^2+1)\langle ah|bh\rangle\}/\{(g^2+1) + 2g\langle ah|bh\rangle\}. \quad (9)$$

The multiplier function $M(g)$, which equals unity when $g = 1$, remains close to unity over appreciable ranges of g and positive $\langle ah|bh\rangle$; e.g. even for $g = 2$ and $\langle ah|bh\rangle = 0.5$, $M(g) = 0.93$. Thus, $2\langle ah|bh\rangle$ may be a rough approximation for s_{AB} for bonds which are not excessively heteropolar.

For a polyatomic molecule, eqn. (8) is exact only if the basis is minimal, if there are zero coefficients in the LMO for functions on other atoms, and if there are zero overlap integrals between each hybrid defined by the LMO and the remaining orthogonal atomic hybrids on the other centre.

CA were able only to explore the approximation $s_{AB} \approx 2\langle ah|bh\rangle$ for three diatomic molecules in [5,3] bases. For F_2 they showed that one LMO provided the main part, $s_{FF}(LMO) = 0.71$, of the shared electron population $s_{FF}(total) = 0.61$. For N_2 with $s_{NN}(total) = 2.93$, they showed that three banana bond LMO's each contributed 0.98, or equivalently that the σ-bond LMO contributed 1.55 and each of the two π-bond LMO's 0.69. The two lone pairs contributed only −0.010 each to $s_{NN}(total)$. Similar results were obtained for CO. Actually, CA only checked that suitable LMO(s) provided the main contribution(s) to s_{AB}, and that the implied overlap integrals were plausible. They did not calculate any hybrid overlap integrals, nor did they examine any polyatomic molecules. We now remedy these deficiencies.

Method. In the present work 17 molecules were examined, of which cyclopropane was the largest. Ground-state wave functions were calculated at or near experimental geometries with the TEXAS program with small but non-minimal 4-21G bases.[5] LMO's for each molecule were obtained by the Boys criterion,[6] which maximizes the sum of the squares of distances between orbital centroids. For a molecule such as H_2O_2, this method leads to LMO's which are well described as: oxygen inner shells, an O−O and two O−H single bonds, and two lone-pair orbitals on each oxygen. For multiple bonds, the Boys criterion leads to multiple banana bonds.

The LMOs were then expressed in terms of AO's and polarization functions, thus

$$|i\rangle = c_{as}|as\rangle + c_{ap}|ap\rangle + (\text{other atoms}) + (\text{inner shells}) + (\text{polarization functions}), \quad (10)$$

where the AO's were defined from atomic SCF calculations with the 4-21G basis, and $|as\rangle$ is the $2s$ AO on A and $|ap\rangle$ represents the combination of $2p$ AO's on A. In a bond LMO the sp^n hybrid on A is then the normalized form of

$$|ah\rangle = |as\rangle + \sqrt{n}|ap\rangle, \quad (11)$$

where $\sqrt{n} = c_{ap}/c_{as}$.

In the present calculations the total residual polarization populations ranged from 0.001 in F_2 to 0.118 in CO_2.

Table 1. Roby shared populations, s_{AB}, for single bonds and estimates from overlap integrals.

Bond type	Molecule	s_{AB}(total)	s_{AB}(LMO)	$2\langle ah\|bh\rangle$
C–H	CH_4	1.42	1.38	1.46
	C_2H_6	1.39	1.37	1.45
	C_2H_4	1.41	1.40	1.47
	C_2H_2	1.46	1.46	1.49
	C_3H_6	1.40	1.39	1.46
	H_2CO	1.32	1.38	1.46
	CH_3OH	1.38	1.37	1.45
	CH_3F	1.38	1.37	1.44
N–H	NH_3	1.32	1.26	1.36
	N_2H_4	1.29	1.22	1.35
O–H	H_2O	1.19	1.14	1.23
	H_2O_2	1.18	1.13	1.24
	CH_3OH	1.18	1.13	1.23
F–H	FH	1.04	1.01	1.08
C–C	C_2H_6	1.46	1.30	1.44
N–N	N_2H_4	1.10	1.09	1.16
O–O	O_2H_2	0.82	0.90	0.91
F–F	F_2	0.65	0.75	0.72
C–O	CH_3OH	1.20	1.10	1.20
C–F	CH_3F	1.03	0.97	1.06

Results. Table 1 summarises the results for molecules with conventional single bonds. The successive columns are the shared populations s_{AB}(total) from all MO's, s_{AB}(LMO) from the LMO corresponding to the bond, and 2<ah|bh>, the doubled overlap integral. For all the conventional bonds in this Table, s_{AB}(total) is well approximated by s_{AB}(LMO). The largest deviations are ±15 % and occur for C−C in C_2H_6, 1.46 vs. 1.30, and for F−F in F_2, 0.65 vs. 0.75. Overall, the results show that Roby shared populations in these molecules may be regarded primarily as the shared populations of localized bonding orbitals.

Table 1 also shows that s_{AB}(LMO) is well approximated by 2<ah|bh>, where <ah|bh> is the overlap integral for the hybrid AO's on A and B implied by the LMO. The largest difference is for C−C in C_2H_6, 1.30 vs. 1.44.

The multiplier function $M(g)$ for heteropolar LMO's was discussed above [eqns. (8) and (9)]. The most polar LMO's of Table 1 are for C−F in CH_3F and F−H in FH. These have g = 2.05 and 2.02, with $M(g)$ = 0.93 in both cases. In consequence, the differences between 2<ah|bh>$M(g)$ and 2<ah|bh> are not large, but as expected, the 2<ah|bh>$M(g)$ values for C−F and F−H, 0.99 and 1.01, are closer to the corresponding s_{AB}(LMO) values, 0.97 and 1.01.

By comparing the first and last columns of numbers in Table 1 it can be seen that the simple interpretation of s_{AB}(total) as roughly equal to twice the overlap, 2<ah|bh>, is a good working rule. In all cases except C−C in C_2H_6, s_{AB}(total) is slightly smaller than 2<ah|bh>; the largest deviation is for C−H in H_2CO, with 1.32 vs. 1.46.

Some multiple bonds are listed in Table 2. The Boys localization criterion leads to banana bonds rather than σ and π bonds. In ethene with its CC double bond, s_{AB}(total) = 2.31 is well approximated by contributions from two equivalent localized banana bonds, each with s_{AB}(LMO) = 1.09. Also, the latter is well approximated by 2<ah|bh> = 1.10. Similar results are obtained for the triple bonds in ethyne and nitrogen. For carbon monoxide, isoelectronic with N_2, s_{AB}(total) is again well approximated by contributions from three localized, but rather polar (g = 2.36), banana bonds.

For H_2CO, localization yields, as expected, two banana bonds for the C=O link and two lone pairs on oxygen. s_{AB}(total) = 2.04 is roughly approximated by twice s_{AB}(LMO) = 0.96, and s_{AB}(LMO) is roughly approximated by 2<ah|bh> = 0.92.

For CO_2, localization might again be expected to yield two banana bonds for each CO linkage, together with two lone pairs on each oxygen. However, the Boys method actually yields one axial lone pair on each oxygen, together with three banana bonds for each CO link. For each CO group, s_{AB}(total) = 2.15 is somewhat less than three times s_{AB}(LMO) = 0.80. The three banana bonds to the other oxygen and the two lone pairs all make small negative contributions to s_{AB}(total).

Table 2 also lists another banana bond, namely the bent CC single bond in cyclopropane. Here, s_{AB}(LMO) = 1.17 is 20 % less than s_{AB}(total) = 1.46 (the overlap approximation lies between them). The difference occurs because the LMO's are not completely localized. The LMO representing one CC bond also contributes shared populations of 0.12 to each of the other CC bonds. CA showed[3] that there is some three-centre sharing in cyclopropane (s_{CCC} = 0.38 in the [5,3] basis calculations), and it is this which prevents complete two-centre localization.

Table 2. Roby shared populations, s_{AB}, for multiple bonds and estimates from overlap integrals.

Bond type	Molecule	s_{AB}(total)	s_{AB}(LMO)	2<ah|bh>
C=C	C_2H_4	2.31	1.09 (×2)	1.10
C≡C	C_2H_2	3.30	1.08 (×3)	1.04
N≡N	N_2	2.92	0.98 (×3)	0.94
C=O	H_2CO	2.04	0.96 (×2)	0.92
C≡O	CO	2.58	0.87 (×3)	0.82
	CO_2	2.15	0.80 (×3)	0.87
C−C	C_3H_6	1.47	1.17	1.31

Discussion. As noted by CA, Roby shared populations s_{AB} are more consistent indicators of bond strengths than Mulliken overlap populations.[1] They are also more readily intelligible since the equation $s_{AB} \approx 2\langle ah|bh\rangle$ provides an approximate interpretation in terms of the overlap integral for the hybrid AO's of an LMO. The characterization of molecular wave functions can thus be closely linked to the long-established criterion of maximum overlapping and to the use of overlap integrals in discussions of the strengths of hybrid bonds (see e.g. Coulson[7]).

As one example consider the trend in s_{AB} values for the X−X single bonds listed in Table 1. The total shared population falls from 1.46 for C−C in C_2H_6 to 0.65 for F−F in F_2. The carbon hybrids for the C−C LMO are $sp^{1.79}$, so a high overlap of 1.44/2 = 0.72 is in accord with Maccoll's curve relating overlap and percentage *s* character.[7,8] In F_2 the AO's are distinctly more compact relative to the internuclear distance and the $sp^{8.74}$ hybrids have little *s* character, so the overlap integral is much smaller and the shared population behaves likewise.

This discussion is relevant to experimental electron-density *difference* maps obtained from accurate low-temperature X-ray analysis of organic compounds containing heteroatoms. Dunitz, Schweizer and Seiler[9,10] have shown that prominent "bonding density" peaks are found at or near the mid-points of C−C bonds, only weak accumulations at the centres of C−O, N−N and C−F bonds, and density deficits at the centres of O−O bonds. The respective ($\delta\varrho_{max}$, s_{AB}) values are C−C (0.42 eÅ^{-3}, 1.46), C−O (0.30 eÅ^{-3}, 1.20), N−N (0.22 eÅ^{-3}, 1.10), C−F (0.09 eÅ^{-3}, 1.03), O−O (−0.05 eÅ^{-3}, 0.82). There is a correlation between the electron density values and the shared populations. Thus, via the overlap integrals the decreasing electron density values in the series correlate with decreasing percentage *s* characters in the bonding LMO's. However, this is only part of the story. The $\delta\varrho_{max}$ can depend substantially on the subtracted model densities. In the studies of Dunitz *et al.*, spherical atoms are subtracted in each case. However, as shown for NF_3 by Cruickshank and Weaver[11,12] and for F_2 by Schwarz, Valtazanos and Ruedenberg,[13] there are major changes in the difference maps according to whether the F atoms subtracted are spherical p^5 or directionally prepared $p\sigma^1 p\pi^2 p\pi'^2$. In the latter case the central $\delta\varrho_{max}$ is more positive. There is a smaller change between the two possible states for oxygen atoms, but none for nitrogen or carbon where only spherical atoms, s^2p^3 or sp^3, are relevant. Schwarz *et al.* in their very thorough analysis also demonstrate the strong dependence of difference densities upon relative internuclear distances and the associated changes in overlap integrals. This aspect of their work is paralleled by our discussion of the dependence of s_{AB} on hybridization ratios.

Shared electron populations have been correlated with bond energies by Ehrhardt and Ahlrichs.[14] Their σ_{AB} are similar to our s_{AB} but are derived by projecting out, not with atomic SCF functions, but with Modified Atomic Orbitals determined after the molecular wave function has been found. They have shown that for covalent compounds there is a good linear relation between bond energies and the products of σ_{AB} and weighted ionization potentials. Their data span from Na_2 with ΔE = 75 kJ mol^{-1} to the C≡C bond in C_2H_2 with ΔE = 961 kJ mol^{-1}.

Boron hydrides and carboranes

Localized orbitals. We have now seen how the Roby method offers an interpretation of the shared populations in simple molecules in terms of the overlap integrals arising from two-centre LMO's. We now turn to a very different aspect of Roby population analysis and consider some boron hydrides and related carboranes. The structures and the understanding of the bonding in these molecules are particularly associated with Lipscomb.[15]

Molecules of type $B_nH_n^{2-}$ or $C_2B_{n-2}H_n$ adopt closed polyhedral structures with *n* framework atoms (C or B) at the vertices of the polyhedra. After discounting the C or B inner shells and one pair of electrons for one C−H or B−H bond at each vertex, there remain $n+1$ pairs of electrons for framework bonding. Molecules of type B_nH_{n+4} or $C_2B_{n-2}H_{n+2}$ show polyhedral structures with one vertex missing. They contain $n+2$ framework electron pairs. Molecules of type B_nH_{n+6} have two vertices missing and contain $n+3$ framework electron pairs.

Kleier, Halgren, Hall and Lipscomb[4] have presented an instructive set of LMO's for a number of boranes and carboranes. Diagrammatic forms of these molecules with the localized valence

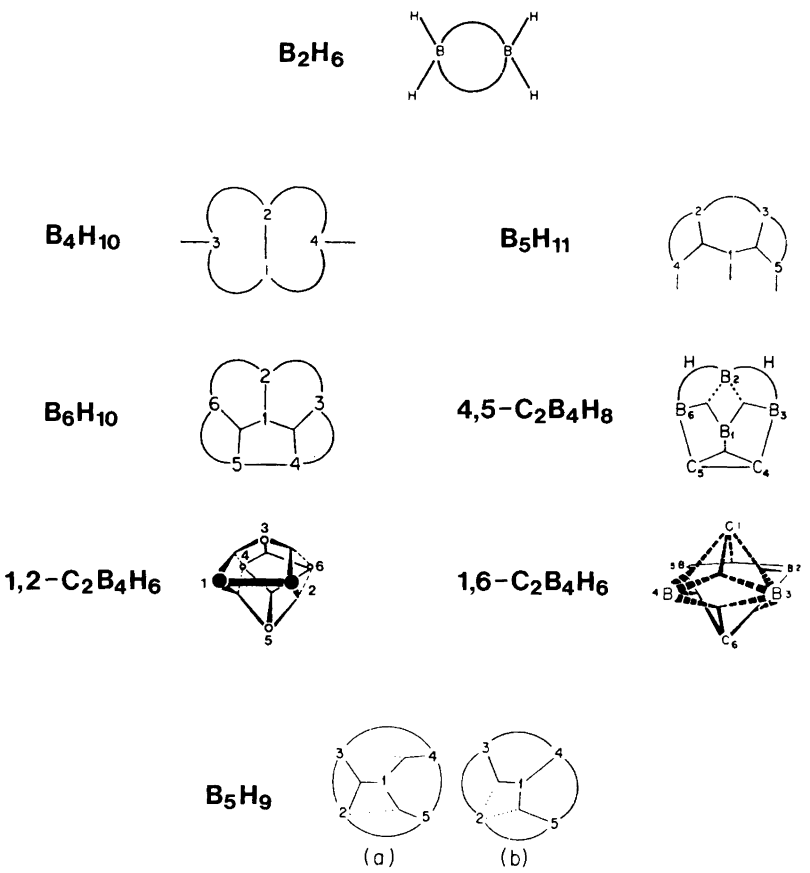

Fig. 1. Localized valence structures for boron hydrides and carboranes (adapted from Kleier *et al.*[4]).

structures found by Kleier *et al.* using the Boys criterion[6] are presented in Fig. 1.

For the simplest molecule B_2H_6, the Boys LMO's correspond to the expected B–H terminal bonds and B–H–B bridge bonds (represented by curved lines in Fig. 1).

For B_4H_{10} a B–B two-centre bond also emerges (in the diagram for this and subsequent molecules, one terminal hydrogen is omitted from each boron or carbon in the valence structure. Thus, the second B–H terminal bond is shown only for atoms B_3 and B_4. The 7 lines in the diagram for B_4H_{10} correspond to the 4+3 framework electron pairs which must be accounted for).

The compound B_5H_{11}, besides B–H terminal bonds and B–H–B bridge bonds, shows two B–B–B three-centre bonds. B_6H_{10} shows both B–B and B–B–B bonds. The isoelectronic molecule 4,5-$C_2B_4H_8$ loses two B–H–B bridge bonds and replaces them with C–B two-centre bonds. This molecule has not only a C–C two-centre bond, but also involves the carbons in a C–C–B three-centre bond. In addition there are two B–B–B fractional three-centre bonds, whose Mulliken atom populations are 0.75, 0.48 and 0.65 as compared with the more uniform 0.73, 0.65 and 0.57 for the three-centre bonds in B_6H_{10}.

Further variety is yet to come. The LMO's of octahedral 1,2-$C_2B_4H_6$ can be described as comprising a C–C bond, two B–B–B three-centre bonds and 4 C–B–B fractional three-centre bonds (with atom populations 1.07, 0.57 and 0.38). In the isoelectronic molecule 1,6-$C_2B_4H_6$, one apical carbon is involved in 4 C–B–B three-centre bonds, while the carbon at the opposite apex is involved in only 3 C–B–B bonds (with rather uneven atom populations).

Lastly, B_5H_9 may be mentioned. This molecule

has a four-fold symmetry axis passing through the apical B_1 atom. Geometrically there are 4 B–B–B faces, each edged equatorially by a B–H–B bridge bond. The localization procedure is then confronted with distributing 3 electron pairs (derived from canonical MO's of σ, π^2 symmetry) among 4 B–B–B faces and 4 B–B edges. Because of the geometrical symmetry there is no unique way of doing this, and a continuous range of localized descriptions can be generated, including *inter alia* (a) one B–B–B three-centre bond with two B–B–B fractional three-centre bonds, and (b) one B–B two-centre bond also with two B–B–B fractional three-centre bonds.

Faced with this variety, Kleier *et al.* concluded "In many instances, therefore, the framework bond LMO's cannot be said to have the level of chemical significance generally attributed, for example, to B–H_t and B–H_b–B bonds, which for many purposes can be viewed as independent entities".

Roby multi-centre shared populations. However, an analysis of the total wave functions of these molecules by Roby two-centre and three-centre shared populations reveals much similarity among the molecules. The shared populations s_{AB} and s_{ABC} are defined by eqns. (1) and (2). To anticipate the detailed results, in the set of molecules of Fig. 1 the ranges for the shared populations are: B–B edges 1.31–1.89, B–B–B faces 0.49–0.59, with similar values when carbon is involved. These numbers apply to *every* edge and *every* face. There are *no* B–B–B faces with shared populations below 0.49 electrons. The shared populations for B–H–B bridges lie in the range 0.57–0.80.

The calculations were carried out with 4-21G bases and with geometries fixed at literature values.

We consider the Kleier list in reverse order. In B_5H_9, as well as 4 B–H–B shared populations of 0.64 there are 4 shared populations of type B_1–B_2 of 1.69 and 4 B_2–B_3 of 1.53, together with 4 B_1–B_2–B_3 of 0.57. These shared populations from the total molecular wave function necessarily conform to the geometrical symmetry, but note that the B–B values are similar whether the edge is common to two B–B–B faces or lies between a face and a B–H–B bridge.

In octahedral $B_6H_6^{2-}$ (not considered by Kleier), the 12 B–B edges each share 1.66 electrons, and the 8 B–B–B faces each share 0.56. In this molecule the determination of LMO's for the 7 framework electron pairs would run into symmetry problems similar to those in B_5H_9.

In the isoelectronic 1,6-$C_2B_4H_6$, the 8 C_1–B_2 bonds each have 1.55 electrons, the 4 B_2–B_3 each have 1.49, and each of the 8 C_1–B_2–B_3 has 0.49.

In 1,2-$C_2B_4H_6$ the single C–C bond (picked out in the LMO's) has 1.48, the C–B have 1.44 (×4) and 1.50 (×2), and the B–B have 1.53 (×4) and 1.59 (×1). The two B–B–B faces have 0.58, the 4 C–B–B faces have 0.47, and the two C–C–B faces (not picked in the localization) have the slightly lower values of 0.41.

In 4,5-$C_2B_4H_8$ the two B–H–B each have 0.66. C_4–C_5 has 1.83, and the two C_4–B_3 have 1.79, while the two C_4–B_1 have 1.12 and the other B–B range from 1.42 (×2) for B_1–B_3, through 1.58 (×2) for B_2–B_3, to 1.65 for B_1–B_2. The two B–B–B faces have 0.57, the one C–C–B face has 0.40, and the two C–B–B faces (not picked out in the localization) have 0.38. Note that C_4–C_5 and B_3–C_4 have similar shared populations, both higher than appropriate for formal single bonds, whereas the valence structure suggested enhanced bonding only in C_4–C_5.

In the isoelectronic molecule B_6H_{10} there are 4 typical equatorial B_{eq}–H–B_{eq} populations. The unique B_1–B_2 of the LMO's has a shared population of 1.52, little different from the other B_1–B_{eq} of 1.52 (B_1–B_3) and 1.38 (B_1–B_4). The one B_{eq}–B_{eq} (B_4–B_5) which is not involved in any B_{eq}–H–B_{eq} bridge has a shared population of 1.89, rather higher than the other B_{eq}–B_{eq} of 1.53 (B_2–B_3) and 1.67 (B_3–B_4). The B_1–B_{eq}–B_{eq} faces have 0.55 (×2), 0.59 (×2) and 0.49, the latter involving the edge B_4–B_5 which has no bridging hydrogen. The localization picked out only two of these five faces for three-centre LMO's.

The shared populations for B_5H_{11} are 1.69 (B_2–B_4), 1.57 (B_1–B_2), 1.52 (B_2–B_3) and 1.31 (B_1–B_4). The two faces of type B_1–B_2–B_4 picked out by the LMO's each share 0.59 electrons, but the other face B_1–B_2–B_3 with 0.55 has almost as large a population.

In B_4H_{10} the 4 B–H–B have typical populations of 0.64, while the corresponding B–B populations are each 1.45. The other B–B (B_1–B_2), which is picked out in the localization, has the

slightly higher value of 1.58. Each of the B–B–B faces shares 0.51 electrons.

In diborane B_2H_6, each B–H–B shares 0.80, while B–B has 1.87. Or, in other words, the two borons share 1.87 electrons, and of these 0.80 are shared with one hydrogen and 0.80 with the other. The two B–H–B bridges of B_2H_6 seem rather separate so far as the hydrogens are concerned, for $s(H_bH_b') = -0.02$ and $s(BBH_bH_b') = -0.10$ are both small. The values $s(BH_b) = 1.16$ and $s(BH_t) = 1.51$ are fairly typical for the two kinds of B–H link. Thus, apart from the additional emphasis placed on the direct B–B sharing, the descriptions of diborane given by the Roby population analysis and by the LMO's are very similar. For a more detailed Roby analysis of B_2H_6 and a comparison with C_2H_4, see CA.[3]

Further remarks on Roby populations. The main result has been that all the molecules considered show significant B–B–B shared populations, 0.49–0.59, for every triangular face and substantial B–B shared populations, 1.31–1.89, for every edge.

When non-adjacent vertices are considered, the shared populations are small. Thus, in 1,2-$C_2B_4H_6$, $s(B_3B_5) = -0.02$ and $s(C_1B_6) = 0.00$, while $s(B_3C_1B_5) = 0.03$. The latter set appears in the Edmiston-Ruedenberg localization procedure[4] as an open three-centre bond. Similarly, in 1,6-$C_2B_4H_6$, $s(B_2B_4) = -0.03$ and $s(C_1C_6) = 0.04$, while $s(B_2B_3B_4) = 0.00$ and $s(C_1B_2C_6) = -0.01$. On the other hand, for sets of four atoms in a plane, the four-centre shared populations are just appreciable. In 1,6-$C_2B_4H_6$, $s(B_2B_3B_4B_5) = 0.21$ and $s(C_1B_2B_4C_6) = 0.13$. In B_5H_9, $s(B_2B_3B_4B_5) = 0.16$ and the five-centre shared population $s(B_1B_2B_3B_4B_5) = 0.12$. With non-planar sets of atoms, the four-centre shared populations are small, e.g. $s(B_1B_2B_3B_4) = 0.04$ in B_5H_9.

If we compare $B_6H_6^{2-}$, B_5H_9 and B_4H_{10}, we see that the B–B–B populations for the triangular faces 0.56, 0.57 and 0.51 are similar despite 0, 1 and 2 of the sides having bridging hydrogens. The slightly lower value for B_4H_{10} is related to its average triangular side of 1.81 Å being longer than the average 1.70 Å in each of the other molecules.

Correlation between bond lengths and populations. Not only are the two-centre B–B populations substantial for every edge, but also there is a good correlation between their individual values and the experimental bond lengths assumed in the calculations.

The shortest B–B bond in the series is B_4–B_5 in B_6H_{10}, which has a length of 1.60 Å with $s(BB) = 1.89$. The longest is B_1–B_4 in B_5H_{11}, with a length of 1.85 Å and $s(BB) = 1.31$. As it happens, these are the only two unshared edges in the series, i.e. edges which are not shared either between two faces or between a face and a B–H–B bridge. Nevertheless, on a length/population plot all the points for BB edges shared between the two B–B–B faces lie close to the straight line between these two points (1.60 Å, 1.89) and (1.85 Å, 1.31).

If one face is C–B–B, then for a given B–B population the B–B length is about 0.03 Å less than indicated by the line. In the case of a B–B edge in 1,6-$C_2B_4H_6$ which is shared between two C–B–B faces, the B–B length for the given population is perhaps 0.07 Å shorter than it would have been if shared between two B–B–B faces.

When a B–B edge is shared between a B–B–B face and a B–H–B bridge, the B–B length is about 0.04 Å longer than indicated by the above reference line. The extreme points of this type are (1.72 Å, 1.69) for B_2–B_4 in B_5H_{11} and (1.84 Å, 1.45) for B_1–B_3 in B_4H_{10}. The B–B point of (1.78 Å, 1.87) for B_2H_6, where two B–H–B bridges are involved, is perhaps 0.16 Å longer than for a bond of the same population involving two B–B–B faces.

The C–B bonds are of course shorter and show a roughly parallel correlation between lengths and s(CB) populations. The extreme points are both in 4,5-$C_2B_4H_6$ with (1.52 Å, 1.79) for C_4–B_3 and (1.76 Å, 1.12) for C_4–B_1. C–C bonds are shorter still, and the two C–C points from the carboranes interpolate well between points derived from the calculations mentioned earlier for ethane and ethene.

Discussion. The Roby descriptions of these boron compounds are consistent with the Boys LMO descriptions so far as the B–H_t and B–H_b–B features are concerned, though with an added emphasis on B–B sharing. The framework descriptions often differ considerably. For example, for B_6H_{10} the Roby method yields $s(B_2$–$B_3) = 1.53$ and $s(B_3$–$B_4) = 1.67$. These pairs of atoms are both involved in B–H–B bridges and

B−B−B three-centre shared populations. However, in the Boys localization the first pair of atoms is joined only by a B−H−B bridge, whereas the second pair of atoms is joined also by a three-centre B−B−B bond. A similar situation occurs in B_5H_{11}. If the Boys localizations were accurate shorthand summaries of the bonding, much larger differences in the s(BB) and in the bond lengths would be expected.

The essential difficulty is that the localized framework orbitals are actually somewhat delocalized beyond their shorthand descriptions implied by Fig. 1. For a molecular wave function, the total shared populations s(BB), s(BBB), etc. are the sums of contributions from all the LMOs. For the molecules with single bonds considered in the first part of this paper, the total shared population for a bond, s(XY), is approximately equal to the contribution s(XY) from one appropriate LMO. However, when, as in the boron compounds, there is no numerical match between the number of orbitals and the numbers of edges and faces, the derived LMO's must inevitably include some further delocalization so as to yield the correct total populations.

A comment on the magnitude of the S(BBB) values may be useful. CA[3] examined triangular two-electron H_3^+. With S as the overlap integral between hydrogen AO's, they showed s(HHH) $= 4S^2/(1+S)$. If we take $S = 0.55$, then s(HHH) $= 0.78$. Now a typical value for a borane face is s(BBB) $= 0.57$, but we have to remember that there are fewer than two framework electrons per face in the boron hydrides. Purely as a comparison, we note that the typical s(BBB) value is roughly the same as the three-centre shared population in a symmetric triangular MO containing, say, 1.4 electrons with overlap integrals of 0.55 between its constituent AO's.

Stone[16] has offered a general wave-mechanical explanation of the need to maximize the number of edges in borane structures, and hence as to why borane faces are triangular. The Roby descriptions with high s(BB) values for every edge and significant s(BBB) values for every face are consistent with Stone's reasoning.

Acknowledgements. We are grateful to SERC for financial support, and to Dr. P. Pulay and Prof. J. E. Boggs for the TEXAS program.

References

1. Mulliken, R. S. *J. Chem. Phys. 23* (1955) 1833.
2. Roby, K. R. *Mol. Phys. 27* (1974) 81.
3. Cruickshank, D. W. J. and Avramides, E. J. *Phil. Trans. Roy. Soc. London A 304* (1982) 533.
4. Kleier, D. D., Halgren, T. A., Hall, J. H. and Lipscomb, W. N. *J. Chem. Phys. 61* (1974) 3905.
5. Pulay, P., Fogarasi, G., Pang, F. and Boggs, J. E. *J. Am. Chem. Soc. 101* (1979) 2550.
6. Boys, S. F. *Rev. Mod. Phys. 32* (1960) 296.
7. Coulson, C. A. *Valence, 1st. ed.,* Clarendon Press, Oxford 1952.
8. Maccoll, A. *Trans. Faraday Soc. 46* (1950) 369.
9. Dunitz, J. D., Schweizer, W. B. and Seiler, P. *Helv. Chim. Acta 66* (1983) 123.
10. Dunitz, J. D. and Seiler, P. *J. Am. Chem. Soc. 105* (1983) 7056.
11. Cruickshank, D. W. J. and Weaver, R. F. *Abstracts, First European Crystallographic Meeting,* Bordeaux 1973.
12. Hinchliffe, A. and Dobson, J. C. *Chem. Soc. Rev. 5* (1976) 79.
13. Schwarz, W. H. E., Valtazanos, P. and Ruedenberg, K. *Theor. Chim. Acta 68* (1985) 471.
14. Ehrhardt, C. and Ahlrichs, R. *Theor. Chim. Acta 68* (1985) 231.
15. Lipscomb, W. N. *Science 196* (1977) 1047.
16. Stone, A. J. *Inorg. Chem. 20* (1981) 563.

Received January 26, 1988.