

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 JONES, D. S., PAUTLER, D. & COPPENS, P. (1972). *Acta Cryst.* **A28**, 635–645.  
 KURKI-SUONIO, K. (1968). *Acta Cryst.* **A24**, 379–390.  
 LARSON, A. C. & CROMER, D. T. (1974). *J. Chem. Phys.* **60**, 185–192.  
 MCWEENY, R. (1951). *Acta Cryst.* **4**, 513–519.  
 SCHERINGER, C. (1977). *Acta Cryst.* **A33**, 588–592.  
 SCHERINGER, C. & REITZ, H. (1976). *Acta Cryst.* **A32**, 271–273.

STEWART, R. F. (1968). *J. Chem. Phys.* **48**, 4882–4889.  
 STEWART, R. F. (1969). *J. Chem. Phys.* **51**, 4569–4577.  
 STEWART, R. F. (1970). *J. Chem. Phys.* **53**, 205–213.  
 STEWART, R. F. (1972). *J. Chem. Phys.* **57**, 1664–1668.  
 STEWART, R. F. (1973). Charge densities from X-ray diffraction data in *Crystal Evaluation and Physical Structural Information*, NA Publ.  
 STEWART, R. F. (1976). *Acta Cryst.* **A32**, 565–574.  
 WANG, Y., BLESSING, R. H., ROSS, F. K. & COPPENS, P. (1976). *Acta Cryst.* **B32**, 572–578.

*Acta Cryst.* (1977). **B33**, 3816–3822

## A Simple Refinement of Density Distributions of Bonding Electrons. II. Bond Electron Density Distribution in Diborane

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Models for diborane are described in which valence electrons are included separately in the refinement. Values of  $R$  between 0.026 and 0.037 were obtained, compared with 0.047 for a spherical-atom model. The first model shows clearly the presence of the three-centre bond. Further models are described in which cores of two ( $1s^2$ ) electrons are used for the B atom; refinements with and without H cores are carried out. Charge clouds of valence electrons are represented in terms of probability ellipsoids.

### Introduction: description of the method

In this paper a new model for the bond electron density is described. Previous methods such as  $(\rho_X - \rho_N)$  maps give the deformation model, where spherical atomic form-factor curves are used in combination with positional and thermal parameters obtained from neutron diffraction data. In the model described here it is possible to obtain a dynamic electron density distribution (within the resolution allowed by the experimental data) which may be represented graphically.

Charges with given occupancy parameters are placed between atomic cores and the smearing of this bond density is simulated by allowing these charges anisotropic thermal parameters, defined in the usual way (Table 1).

The cores are also given occupancy parameters. They are assumed to have a spherically symmetrical electron distribution which may, however, possess anisotropy of thermal motion. In this case the anisotropic thermal parameters ideally contain only a contribution from thermal motion of the cores from neutron diffraction data, since these are true thermal parameters with no contribution from asymmetry in the electron density distribution. We have, however, obtained promising results from X-ray data alone, refining positional, thermal and occupancy parameters. The  $\beta_{ij}$  parameters of the valence electron charge clouds have

Table 1. *Positional and thermal parameters and dynamic bond-density distributions for various models of diborane*

(A) = spherical-atom model, Smith & Lipscomb (1965); (B) = spherical-atom model, this work.

(a) Positional parameters for cores

Atom/core	Model	$x$	$y$	$z$
B	(A)	0.002	0.146	0.042
	(B)	0.0016 (5)	0.1459 (3)	0.0420 (3)
	LQ1	0.0013 (4)	0.1454 (3)	0.0415 (3)
	LQ2	0.0009 (5)	0.1446 (4)	0.0423 (4)
	LQ3	0.0017 (3)	0.1450 (2)	0.0411 (2)
H(1)	LQ4	0.0018 (3)	0.1453 (2)	0.0413 (2)
	(A)	−0.194	0.166	0.140
	(B)	−0.196 (4)	0.169 (3)	0.140 (3)
	LQ1	−0.196 (4)	0.170 (4)	0.148 (4)
	LQ2	—	—	—
H(2)	LQ3	−0.235 (4)	0.158 (3)	0.140 (2)
	LQ4	−0.199 (3)	0.169 (2)	0.148 (2)
	(A)	0.196	0.294	−0.005
	(B)	0.202 (4)	0.295 (3)	−0.001 (2)
	LQ1	0.223 (5)	0.301 (3)	−0.001 (3)
H(3)	LQ2	—	—	—
	LQ3	0.239 (4)	0.307 (2)	−0.005 (3)
	LQ4	0.227 (3)	0.305 (2)	0.000 (2)
	(A)	0.104	−0.019	0.112
	(B)	0.110 (4)	−0.016 (3)	0.115 (3)
LQ1	LQ1	0.120 (4)	−0.013 (4)	0.120 (4)
	LQ2	—	—	—
	LQ3	0.115 (3)	−0.035 (2)	0.116 (3)
	LQ4	0.121 (3)	−0.014 (2)	0.122 (2)

Table 1 (cont.)

(b) Thermal parameters

$$T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})].$$

Atom/core	Model	$\beta_{11}$ (or $B$ )	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
B	(A)	0.050	0.020	0.019	0.010	-0.004	0.000
	(B)	0.0463 (10)	0.0207 (5)	0.0156 (3)	0.0113 (5)	-0.0039 (8)	-0.0009 (6)
	LQ1	0.0449 (7)	0.0200 (3)	0.0155 (3)	0.0103 (4)	-0.0031 (7)	-0.0006 (5)
	LQ2	0.0462 (9)	0.0205 (4)	0.0158 (4)	0.0104 (5)	-0.0030 (9)	-0.0015 (6)
	LQ3	0.0451 (5)	0.0208 (2)	0.0162 (2)	0.0109 (3)	-0.0018 (4)	-0.0009 (3)
LQ4	0.0455 (5)	0.0206 (3)	0.0160 (2)	0.0106 (3)	-0.0028 (5)	-0.0011 (3)	
H(1)	(A)	1.6	—	—	—	—	—
	(B)	0.036 (14)	0.005 (7)	0.016 (6)	0.011 (7)	0.012 (8)	-0.006 (5)
	LQ1	0.046 (15)	0.018 (8)	0.022 (7)	0.023 (9)	0.021 (9)	-0.008 (6)
	LQ2	—	—	—	—	—	—
	LQ3	0.107 (16)	0.043 (8)	0.039 (7)	0.039 (10)	0.022 (9)	-0.009 (6)
LQ4	0.059 (12)	0.018 (6)	0.025 (5)	0.028 (7)	0.019 (7)	-0.008 (5)	
H(2)	(A)	0.4	—	—	—	—	—
	(B)	0.041 (13)	0.005 (6)	0.003 (6)	0.009 (8)	-0.003 (7)	0.006 (4)
	LQ1	0.049 (14)	0.005 (7)	0.008 (7)	0.005 (8)	0.000 (7)	0.001 (5)
	LQ2	—	—	—	—	—	—
	LQ3	0.098 (13)	0.021 (7)	0.053 (7)	-0.013 (8)	0.008 (9)	-0.004 (6)
LQ4	0.045 (10)	0.009 (5)	0.018 (6)	0.000 (6)	0.001 (6)	-0.000 (4)	
H(3)	(A)	1.1	—	—	—	—	—
	(B)	0.023 (13)	0.016 (7)	0.011 (6)	-0.009 (9)	0.004 (7)	0.000 (6)
	LQ1	0.029 (13)	0.005 (6)	0.007 (6)	0.000 (8)	-0.004 (7)	0.001 (5)
	LQ2	—	—	—	—	—	—
	LQ3	0.038 (11)	0.024 (6)	0.050 (7)	0.008 (7)	-0.004 (7)	0.026 (5)
LQ4	0.029 (10)	0.002 (4)	0.011 (4)	0.002 (5)	-0.015 (5)	0.000 (3)	

(c) Positional parameters for bond charges

Charge	Model	$x$	$y$	$z$
B-H(1)	LQ1	-0.148 (14)	0.163 (6)	0.108 (6)
	LQ2	-0.185 (3)	0.163 (2)	0.130 (2)
	LQ3	-0.127 (3)	0.158 (3)	0.109 (2)
	LQ4	-0.123 (4)	0.150 (5)	0.100 (3)
B-H(2)	LQ1	0.096 (8)	0.220 (9)	0.017 (5)
	LQ2	0.153 (4)	0.259 (2)	0.014 (2)
	LQ3	0.102 (4)	0.241 (2)	0.019 (2)
	LQ4	0.106 (4)	0.235 (3)	0.021 (3)
B-H(3)	LQ1	0.078 (12)	-0.015 (16)	0.079 (7)
	LQ2	0.093 (2)	-0.015 (3)	0.091 (2)
	LQ3	0.067 (5)	0.030 (5)	0.075 (2)
	LQ4	0.074 (14)	0.066 (7)	0.058 (8)
B-H(3')	LQ4	-0.054 (6)	0.079 (7)	-0.059 (6)

(d) Dynamic bond-density distributions ( $\beta_{ij}$ )

$$T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})].$$

Charge	Model	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
B-H(1)	LQ1	0.372 (71)	0.082 (14)	0.066 (14)	0.053 (27)	-0.041 (25)	-0.001 (11)
	LQ2	0.347 (17)	0.193 (9)	0.144 (7)	0.126 (10)	0.045 (9)	-0.006 (6)
	LQ3	0.191 (9)	0.136 (7)	0.146 (8)	0.035 (7)	0.026 (7)	0.012 (6)
	LQ4	0.226 (16)	0.134 (9)	0.100 (7)	0.035 (10)	0.025 (7)	-0.001 (6)
B-H(2)	LQ1	0.191 (32)	0.192 (32)	0.051 (10)	0.141 (28)	-0.049 (14)	-0.062 (15)
	LQ2	0.416 (20)	0.182 (8)	0.115 (5)	0.149 (11)	-0.013 (9)	-0.030 (6)
	LQ3	0.263 (16)	0.135 (7)	0.105 (5)	0.079 (9)	-0.022 (8)	-0.006 (5)
	LQ4	0.200 (12)	0.108 (7)	0.106 (7)	0.036 (8)	-0.021 (9)	-0.012 (6)
B-H(3)	LQ1	0.067 (31)	0.099 (38)	0.014 (13)	0.029 (28)	0.002 (13)	-0.003 (14)
	LQ2	0.211 (12)	0.206 (9)	0.149 (8)	0.093 (9)	0.030 (7)	0.010 (7)
	LQ3	0.251 (17)	0.192 (12)	0.089 (7)	0.086 (13)	0.005 (7)	-0.003 (7)
	LQ4	0.272 (43)	0.083 (14)	0.080 (13)	0.082 (21)	0.009 (23)	0.006 (12)
B-H(3')	LQ4	0.143 (15)	0.108 (19)	0.065 (8)	0.007 (14)	-0.018 (10)	0.014 (13)

contributions from thermal motion of the molecules as well as a smearing effect related to the static distribution of the bonding electrons. Positional, thermal and occupancy parameters for cores and bond density may be refined by least-squares calculations. Finally, the bond density distribution may be represented by thermal ellipsoids and drawn with *ORTEP* (Johnson, 1965).

### Refinement and results

A single-crystal X-ray diffraction study of diborane at 90 K was carried out by Smith & Lipscomb (1965). They give the space group as  $P2_1/n$  with  $a = 4.40$ ,  $b = 5.72$ ,  $c = 6.50$  Å,  $\gamma = 105.1^\circ$ . An extended set of X-ray intensities was collected by Smith (see Jones & Lipscomb, 1970), but no further structure refinement was published.

In this work, the fuller data set of Smith was taken and the structure refined by least-squares calculations, with spherically symmetrical atoms. All atoms were given anisotropic temperature factors and  $R$  for 273 observed reflexions was 0.047. The same data set was used for the refinement of the models in which bond electron density distributions were included.

In this paper four different models are described, designated LQ1 to LQ4. In LQ1 the core occupancies were refined along with those of the bond charges, while in LQ2 to LQ4 the B core occupancy was kept fixed at 2 e. An additional charge cloud for the B atom was introduced in the refinement.

#### (a) Model LQ1

For the starting model all charges were placed at the mid-points of bonds and He form factors were used for the bond-density sites. Occupancy factors were set arbitrarily at 2 e for the terminal H bonds and 1.5 e for the bridging H bonds. Large shifts were shown for the B–H(3) (bridging) bond charge. The core occupancies appeared to be too low and those for the charges in the bond too high.

A further model was tried in which all charges were adjusted to have occupancies of the order of magnitude indicated in the previous refinement. The bridging bond density was placed, in accordance with the idea of a three-centre bond, on a line joining the two bridging atoms, H(3), H(3'), and half-way between H(3) and the B–B axis [Fig. 1(a)]. In addition, all charges in the bonds were given a point-charge form factor independent of  $\sin \theta$ .

The first stages of the refinement were carried out with all core parameters fixed. In the final stages, all parameters were refined. During the refinement the site occupancies of charges and cores were also refined, but independently of the thermal parameters. The final  $R$  was 0.037. The significance test of Hamilton (1965) shows that this decrease in  $R$  is significant at the 0.005 level. Table 1 gives positional and thermal parameters for all models described in this paper.

The model obtained in this way gives the dynamic density distribution for the bond charges. With the program of Scheringer (1977) approximate thermal parameters may be calculated and hence the static density distribution obtained in the form of parameters

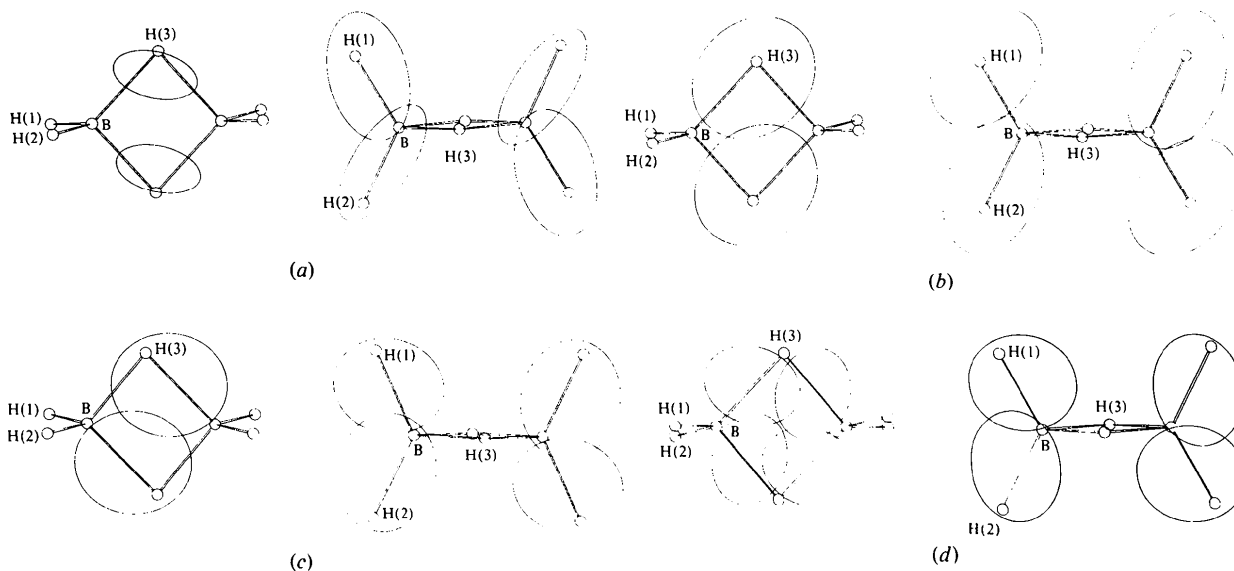


Fig. 1.  $B_2H_6$  molecule showing the nature of the density distributions of the  $\sigma$  bonds in two planes through the molecule (50% probability ellipsoids). (a) LQ1, (b) LQ2, (c) LQ3, (d) LQ4. Left: B–HB. Right: B–HT.

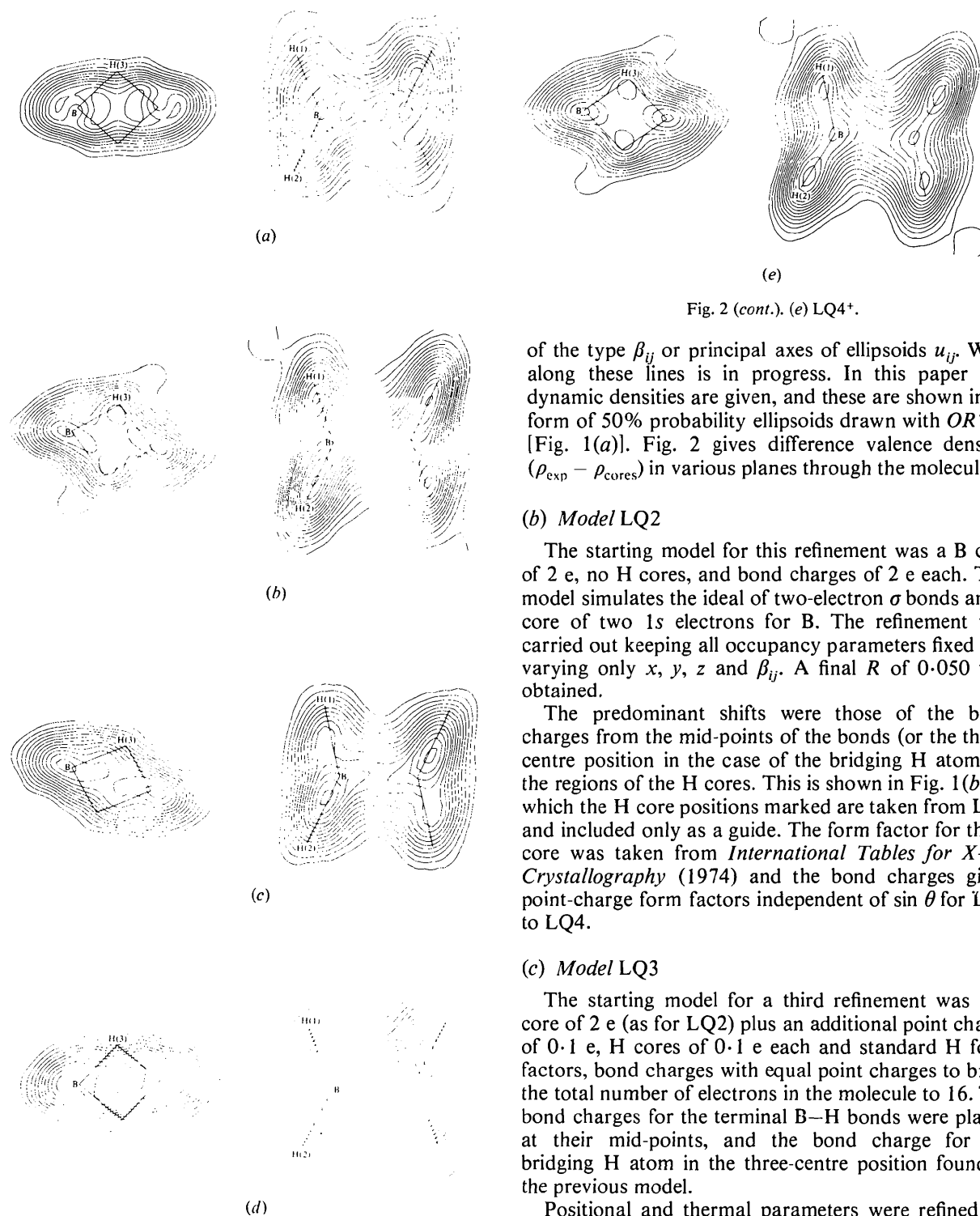


Fig. 2. Difference density maps ( $\rho_{\text{exp}} - \rho_{\text{cores}}$ ) showing dynamic bonding (valence) electron density in planes through the  $\text{B}_2\text{H}_6$  molecule (contours at  $0.05 \text{ e } \text{\AA}^{-3}$ , no negative contours, first line zero). For (a), (c), (d) B and H cores are subtracted; for (b), (e) only the two  $1s^2$  electrons of the B core. (a) LQ1, (b) LQ2, (c) LQ3, (d) LQ4. Left: B-HB. Right: B-HT.

Fig. 2 (cont.). (e) LQ4<sup>+</sup>.

of the type  $\beta_{ij}$  or principal axes of ellipsoids  $u_{ij}$ . Work along these lines is in progress. In this paper only dynamic densities are given, and these are shown in the form of 50% probability ellipsoids drawn with ORTEP [Fig. 1(a)]. Fig. 2 gives difference valence densities ( $\rho_{\text{exp}} - \rho_{\text{cores}}$ ) in various planes through the molecule.

#### (b) Model LQ2

The starting model for this refinement was a B core of 2 e, no H cores, and bond charges of 2 e each. This model simulates the ideal of two-electron  $\sigma$  bonds and a core of two 1s electrons for B. The refinement was carried out keeping all occupancy parameters fixed and varying only  $x$ ,  $y$ ,  $z$  and  $\beta_{ij}$ . A final  $R$  of 0.050 was obtained.

The predominant shifts were those of the bond charges from the mid-points of the bonds (or the three-centre position in the case of the bridging H atom) to the regions of the H cores. This is shown in Fig. 1(b), in which the H core positions marked are taken from LQ1 and included only as a guide. The form factor for the B core was taken from *International Tables for X-ray Crystallography* (1974) and the bond charges given point-charge form factors independent of  $\sin \theta$  for LQ2 to LQ4.

#### (c) Model LQ3

The starting model for a third refinement was a B core of 2 e (as for LQ2) plus an additional point charge of 0.1 e, H cores of 0.1 e each and standard H form factors, bond charges with equal point charges to bring the total number of electrons in the molecule to 16. The bond charges for the terminal B-H bonds were placed at their mid-points, and the bond charge for the bridging H atom in the three-centre position found in the previous model.

Positional and thermal parameters were refined for both core and bond charges. In the early stages cores and bond charges were refined separately. All occupancy parameters were refined except for the two 1s electrons of the B core. While the positional and thermal parameters of these electrons were free to vary, the occupancy was constrained to 2 e.

Table 2. Bond and atom populations in various diborane models (e) and comparison of different basis sets

(a) Bond and atom populations

Charge	LQ1	LQ2	LQ3	LQ4	Snyder & Basch (1972) overlap populations
	$R_w = 0.043$ $R = 0.037$	$R_w = 0.062$ $R = 0.050$	$R_w = 0.033$ $R = 0.029$	$R_w = 0.031$ $R = 0.026$	
B	4.76 (2)	2.00	2.00	2.00	—
H(1)(terminal)	0.82 (2)	—	0.88 (3)	0.86 (2)	—
H(2)(terminal)	0.81 (2)	—	0.92 (3)	0.85 (2)	—
H(3)(bridging)	0.79 (2)	—	0.89 (3)	0.83 (2)	—
B—H(1)	0.30 (2)	2.00	1.05 (2)	0.88 (2)	0.8634
B—H(2)	0.28 (1)	2.00	1.04 (2)	0.87 (1)	0.8634
B—H(3)	0.08	2.00	1.02 (2)	0.45 (1)	0.3643
B—H(3')	—	—	—	0.43 (1)	0.3643

Table 2 (cont.)

(b) Comparison of different basis sets [bond and atom populations in electrons,  $B = 3.5 \text{ \AA}^2$  (after Coppens, 1972)]

	Theoretical*	Exact STO†	Standard STO	HF‡
B	3.54	3.77 (2)	3.98 (2)	3.4 (2)
HT <sub>1</sub>	0.70	0.68 (1)	0.62 (1)	0.6 (1)
HT <sub>2</sub>	0.70	0.68 (1)	0.61 (1)	0.5 (1)
HB	0.66	0.66 (1)	0.63 (1)	1.0 (1)
B—HT <sub>1</sub>	0.82	0.74 (1)	0.70 (2)	1.1 (1)
B—HT <sub>2</sub>	0.82	0.74 (1)	0.71 (2)	1.0 (1)
B—HB <sub>1</sub>	0.39	0.37 (1)	0.38 (2)	0.3 (1)
B—HB <sub>2</sub>	0.39	0.36 (1)	0.37 (2)	0.2 (1)
Scale factor		0.995 (1)	0.986 (1)	1.043 (5)
R		0.006	0.011	0.047
R <sub>w</sub>		0.007	0.013	0.060

\* Jones &amp; Lipscomb (1970).

† STO = Slater-type orbitals.

‡ HF = Hartree-Fock orbitals.

The predominant shift from the starting positions was that of the B—H bridging bond density from the three-centre position to the mid-point of the B—H bond, giving a strongly asymmetric bridge.

The charge of 0.1 for the H cores increased markedly to values between 0.65 and 0.85. The charge of 0.1 additional to the two core electrons of the B atom decreased to zero. The bond charges decreased to values between 0.8 and 1.0. The total number of electrons in the molecule was found to be about 13% below the expected total of 16. At this stage the occupancy parameters for the H cores and bond charges were averaged for the three bonds and scaled to give the required total of 16 e. Refinement was continued to a final  $R$  of 0.029.

## (d) Model LQ4

In this model charges were placed at the mid-points of all four B—H bonds, removing the symmetry of the bridging H bonds and simulating  $sp^3$  hybridization for

the B atom. In LQ3, in comparison, only one charge was present for the H-bridge. The core positions in the starting model were those obtained in the LQ1 refinement.

In the first stages the positional parameters were kept fixed and only temperature factors and occupancies were refined. An  $R$  of 0.035 was obtained. Refinement was continued, allowing the positional parameters to shift, and  $R$  fell to 0.026. The core and charge populations were closely similar to those obtained before the positional parameters were allowed to shift. The final electron population for the molecule was 14.34, which is about 90% of the ideal total of 16.

Core and bond-charge parameters ( $x, y, z, \beta_{ij}$ ) and populations are given for all models in Tables 1 and 2(a).

## Comparison and discussion of results

Diborane was investigated in terms of quantum mechanical models by Lipscomb (1972) and Laws, Stevens & Lipscomb (1972). In these calculations, both a minimum basis set and extended Slater orbital wave functions were used to obtain a model for the bonding electrons. It was found that, while minimum basis set calculations gave reliable results for several molecular properties and the total electron density, extended Slater orbitals were required to obtain correct difference densities (*i.e.* molecular density minus the sum of the spherical-atom densities).

In particular, the occurrence of the special case of the three-centre bond is apparent in both LQ1 [Fig. 1(a)] and Lipscomb's model.

Further investigations were made by Jones & Lipscomb (1970) with various geometrical models. The X-ray analysis (Smith & Lipscomb, 1965) gave B—H bonds which were shorter than those obtained by electron diffraction (Bartell & Carroll, 1965) by about 0.1 Å. Jones & Lipscomb (1970) considered four possible geometries: bond lengths from X-ray analysis ('short'), bond lengths averaged from X-ray and

electron diffraction results ('intermediate'), bond lengths determined by electron diffraction, and bond lengths which were longer than those found from electron diffraction analysis by the difference between the electron diffraction and 'short' bond lengths. For each of these geometries, six models were considered, based on two expressions for the SCF structure factors. Firstly the usual structure factor expression was used and secondly so-called 'difference structure factors' were calculated in which the structure factor expression is separated into contributions from the B atoms and the remaining density, so that the dominance of the B atoms is reduced.

Jones & Lipscomb (1970) considered six models built up from these two expressions by varying the number of anisotropic thermal parameters and by subtracting the B atoms in some of the models by use of the difference structure factors. For the various models, weighted agreement factors ranging from 6 to 13% were obtained. It was found that 0.05 Å of the 0.1 Å bond shortening observed in the X-ray results could be attributed to the inadequacy of the spherical-atom model in interpreting the X-ray data. This corresponds to the 'intermediate' model of Lipscomb.

Jones, Pautler & Coppens (1972) and Coppens (1972) have compared calculations for diborane with different basis sets, *i.e.* exact and standard Slater-type orbitals (STO) and Hartree-Fock (HF) orbitals. Structure factors calculated on the basis of these orbitals were compared with the theoretical SCF structure factors of Jones & Lipscomb (1970). The

same positional parameters were used as in the SCF structure factor calculation. Agreement factors,  $R = \Sigma |F_{\text{SCF}}| - |F_{\text{STO/HF}}| / \Sigma |F_{\text{SCF}}|$ , between the SCF and STO or HF orbitals were calculated. The exact STO was found to give the best  $R$  [Table 2(b)].

In LQ2, LQ3 and LQ4, attempts were made to examine the behaviour of the refinement with respect to the presence or absence of H cores. When no H cores are included (LQ2), the shifts of the bond charges compensate for this [Fig. 1(b)]. LQ1 and LQ4 may be considered as 'final' models, whereas LQ2 and LQ3 are important only from the point of view of testing the behaviour of the refinement procedure.

Table 2(a),(b) gives the electron populations for bond charges and cores for our models, and for those of Jones & Lipscomb (1970), Coppens (1972) and Snyder & Basch (1972). Mulliken populations are compared in Table 3, and those of LQ1 and the Snyder & Basch model are in good agreement. In LQ4 the Mulliken population of the B core is lower, and of the H cores higher, than the values given either by Coppens (1972) or Snyder & Basch (1972).

In Table 4 peak heights from difference maps ( $\rho_{\text{exp}} - \rho_{\text{B+H cores}}$ ) are compared with quantum mechanical results of Lipscomb (1972).

In Table 5 a comparison is made of B-H lengths in our models, in the spherical-atom model and the electron diffraction results of Bartell & Carroll (1965). The B-H lengths in the spherical-atom model are of the order of 0.1 Å shorter than those obtained by electron diffraction. In both LQ1 and LQ4 the B-H

Table 3. Mulliken populations for diborane: models LQ1-LQ4 (Coppens, 1972; Snyder & Basch, 1972)

Atom	LQ1	LQ2	LQ3	LQ4	Coppens (1972)				Snyder & Basch (1972)
					Theoretical*	Exact STO†	Standard STO	HF‡	
B	5.09	5.0	3.56	3.31	4.75	4.88	5.06	4.7	5.2384
H(1)(terminal)	0.97	1.0	1.41	1.30	1.11	1.05	0.97	1.1	0.9162
H(2)(terminal)	0.95	1.0	1.44	1.28	1.11	1.05	0.97	1.1	0.9162
H(3)(bridging)	0.83	1.0	1.40	1.05§	1.05	1.03	1.01	1.2	0.9292

\* Jones & Lipscomb (1970).

† STO = Slater-type orbitals.

‡ HF = Hartree-Fock orbitals.

§ Mean value for H(3), H(3').

Table 4. Dynamic valence electron densities,  $\rho_{\text{exp}} - \rho_{\text{B+H cores}}$ , compared with the static electron density of Lipscomb (1972) ( $\text{e } \text{Å}^{-3}$ )

Bond charge	Lipscomb (1972)*	LQ1 $R = 0.037$	LQ2† $R = 0.050$	LQ3 $R = 0.029$	LQ4 $R = 0.026$	LQ4+†
B-H(1)(terminal)	0.344	0.48	0.66	0.55	0.49	0.70
B-H(2)(terminal)	0.344	0.59	0.76	0.62	0.57	0.70
B-H(3)(bridging)	0.108	0.50	‡	‡	0.45	0.50
B-H(3')(bridging)		0.52			0.51	0.50

\* Static electron density.

† LQ4':  $\rho_{\text{exp}} - \rho_{\text{B+H}}$ , H cores not subtracted. In LQ2 no H cores are present in the refinement and are therefore not subtracted.

‡ In LQ2 and LQ3 no peaks occur in the B-H bonds. Density maxima in this plane are about 0.55 in both cases [Fig. 2(b),(c)].

Table 5. B—H lengths (Å) in various diborane models

Bond	Spherical-atom model*	Bond-density models*			Electron diffraction†
		LQ1	LQ3	LQ4	
B—H (terminal)	1.09 (2)	1.17 (3)	1.24 (2)	1.16 (2)	1.196 (8)
	1.11 (2)	1.14 (3)	1.24 (2)	1.19 (2)	
B—H (bridging)	1.24 (2)	1.27 (3)	1.35 (2)	1.28 (2)	1.339 (6)
	1.28 (2)	1.32 (3)	1.24 (2)	1.33 (2)	

\* Present work (LQ2 omitted; no H cores included in refinement).

† Bartell & Carroll (1965).

distances increase to values which are about 0.05 Å longer than the spherical-atom results. This corresponds well with the predictions of Jones & Lipscomb (1970).

### Summary

This investigation of diborane shows that there are at least two quite different models for describing the electron distribution of the molecule in the crystal (LQ1 and LQ4).

There are two basic points of agreement between our models and the results of Lipscomb *et al.* Firstly, in LQ1 there is a charge cloud centred at the 'three-centre' position (Lipscomb, 1972). Secondly, both LQ1 and LQ4 give bond lengths in agreement with those of Jones & Lipscomb (1970). In LQ1 the atom population for B is extremely high (4.76 e). For the terminal H(1) and H(2), the values of 0.82 and 0.81 respectively, and for the bridging H(3) the value of 0.79, seem reasonable. Extremely low bond populations of 0.30, 0.28 and 0.08 are found [Table 2(a)]. For LQ4 ( $R = 0.026$ ) with  $sp^3$  hybridization for the valence electrons the results are in contrast to LQ1. The atom population for B is extremely low at 2.0 e (3.54, Jones & Lipscomb, 1970); for H the values lie between 0.83 and 0.86 (0.66–0.70). Populations for the bonds are [values of Jones & Lipscomb (1970) and Snyder & Basch (1972) respectively in parentheses] B—HT, 0.87 and 0.88 (0.82; 0.8634) and B—HB, 0.43 and 0.45 (0.39; 0.3643), which show good agreement. The atom populations however differ and this is also seen in the Mulliken population analysis (Table 3).

Fig. 2 gives the dynamic valence density distributions in the various models. The B—HT densities are 0.48 and 0.59  $e \text{ \AA}^{-3}$  in LQ1 and 0.49 and 0.57  $e \text{ \AA}^{-3}$  in LQ4. The B—HB densities are 0.50 and 0.52 (LQ1) and 0.45 and 0.51  $e \text{ \AA}^{-3}$  (LQ4). Both models thus show closely similar experimental valence densities.

$R$  for LQ4 (0.026) is significantly lower than for LQ1 (0.037), although only nine additional parameters

were used in the refinement of the former. For these reasons, LQ4 is thought to be an important alternative model.

In a third paper in this series (Scheringer, Mullen & Hellner, 1978) static deformation densities calculated from our models will be compared with the static densities obtained by Lipscomb (1972) from quantum mechanical calculations.

For these refinements only relative intensities could be used; therefore the occupation factor  $n = 2$  and the form factor  $B^{3+}$  have been used as an internal standard. The sum of the electrons in the molecule has been found to be about 10% less than the total of 16 expected for  $B_2H_6$ . A similar effect has been found by Stewart (1969) for refinement in which the charge density was split into separate parts for the  $K$  and  $L$  shells.

In the fourth paper of this series, form factors of the charge clouds of bonding (valence) electrons in the cyanuric acid and  $B_2H_6$  molecules will be discussed and a comparison made with the results of Fritchie (1966), Hirshfeld & Rabinovich (1967) and Stewart (1969).

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### References

- BARTELL, L. S. & CARROLL, B. L. (1965). *J. Chem. Phys.* **42**, 1135–1139.
- COPPENS, P. (1972). *Trans. Am. Crystallogr. Assoc.* **8**, 93–111.
- FRITCHIE, C. J. (1966). *Acta Cryst.* **20**, 27–36.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- HIRSHFELD, F. L. & RABINOVICH, D. (1967). *Acta Cryst.* **23**, 989–1000.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- JONES, D. S. & LIPSCOMB, W. N. (1970). *Acta Cryst.* **A26**, 196–207.
- JONES, D. S., PAUTLER, D. & COPPENS, P. (1972). *Acta Cryst.* **A28**, 635–645.
- LAWS, E. A., STEVENS, C. M. & LIPSCOMB, W. N. (1972). *J. Am. Chem. Soc.* **94**, 4461–4467.
- LIPSCOMB, W. N. (1972). *Trans. Am. Crystallogr. Assoc.* **8**, 79–92.
- SCHERINGER, C. (1977). *Acta Cryst.* **A33**, 426–429, 430–433.
- SCHERINGER, C., MULLEN, D. & HELLNER, E. (1978). *Acta Cryst.* Submitted for publication.
- SMITH, H. W. & LIPSCOMB, W. N. (1965). *J. Chem. Phys.* **43**, 1060–1064.
- SNYDER, L. C. & BASCH, H. (1972). *Molecular Wave Functions and Properties Tabulated from SCF Calculations in a Gaussian Basis Set*. New York: Wiley-Interscience.
- STEWART, R. F. (1969). *J. Chem. Phys.* **51**, 4569–4577.