Lawrence has germinated and developed and the resulting crop is being harvested in a variety of ways in many different laboratories.

We were both introduced to this fascinating field by Professor H. Lipson and we should like to express our gratitude to him; we also acknowledge the award of a grant from the Science Research Council for the development of the laser diffractometer.

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Analysis of Diborane X-ray Diffraction Data Utilizing Structure Factors Calculated from Molecular Wave Functions

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Crystal unit-cell structure factors for diborane, B_2H_6, have been calculated for four possible molecular geometries, using densities obtained from self-consistent field molecular wave functions. These structure factors were fitted for various B–H distances to the experimental X-ray data for B_2H_6 by varying the parameters of several thermal vibration models. B–H bond lengths so determined have values about 0·05 Å longer than those determined by the usual spherical atom analysis of the X-ray data. Consideration of additional factors, such as the X-ray B–H bond shortening due to rigid rotation of the molecule in the crystal, leads to the conclusion that the bond length correction given by this treatment accounts for about two-thirds of the observed discrepancy between X-ray and electron diffraction values for the B–H bond lengths in diborane.

Introduction

The increasing accuracy of X-ray data has led to an increased concern about the adequacy of the spherical atom model commonly used for data interpretation. One phenomenon generally attributed to such an inadequacy is the 'anomalous' shortening of B–H, C–H, and other (atom)–H bonds in some structures as elucidated by X-ray methods. The build-up of bonding density along the bond results in an aspherical density distribution around the atoms, especially hydrogen. Hence, it is supposed that the best fit to this true density, utilizing a spherical hydrogen density distribution, is obtained with the center of this spherical distribution displaced towards the B or C location from the true hydrogen nuclear location. Recently, Adrian & Feil (1969) observed this shortening phenomenon in N–H bonds when they obtained the crystal structure of NH_4F by both X-ray and neutron diffraction methods. Groenewegen & Feil (1969) then used several available molecular wave functions for NH_4^+ as a basis for calculating X-ray structure factors for NH_4F. For one of these functions, the only one with a multi-center basis, they obtained a fit to the experimental data superior to that obtained with a model based upon spherical atoms.

In the present study, B–H bond length differences in the structure of diborane, B_2H_6, as determined by X-ray (spherical atom model) and electron diffraction methods were investigated. This theoretical study was envisioned at the time the X-ray data were collected in this laboratory; for that reason, data well beyond that required for the structure determination alone were taken. These X-ray data were interpreted by using a model which fits the data with structure factors based on molecular densities obtained from self-consistent field (SCF) minimum basis set LCAO-MO wave functions for diborane. Such densities include effects of bonding. Unit-cell structure factors were calculated in this manner for several different choices of B–H bond lengths. For each choice of bond length the structure factors so obtained were fitted by least-squares to the experimental data by varying the parameters of several different thermal vibration models. For each such model, the weighted agreement factors for the various geometries were plotted as a function of bond lengths, and a parabolic fit was used to determine the set of bond lengths giving the optimum fit to the data. These lengths were then compared with the optimum lengths obtained by using spherical atom densities in corresponding vibrational treatments.

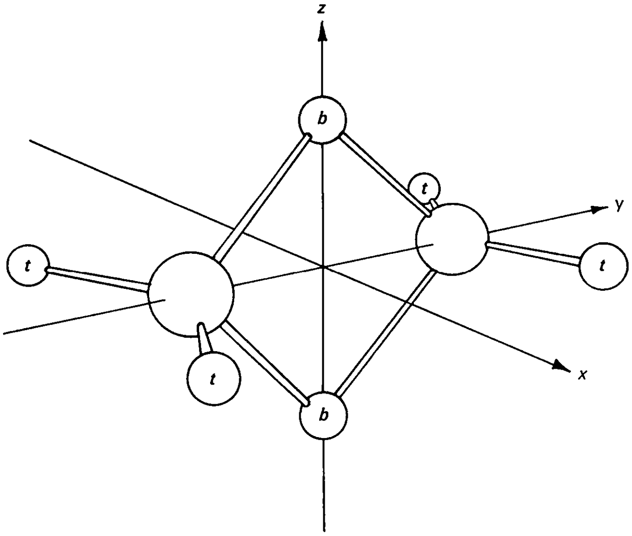

Fig. 1. Diborane structure with respect to the molecular Cartesian coordinate system. The molecular unit vectors **x**, **y** and **z** are related to unit vectors **X**, **Y** and **Z** in a unit cell Cartesian coordinate system through the rotation angles φ, θ and ϱ. The **X**, **Y** and **Z** vectors are defined as $\mathbf{X}=\mathbf{a}$, $\mathbf{Z}=\mathbf{c}$ and $\mathbf{Y}=\mathbf{Z}\times\mathbf{X}$, where **a**, **b** and **c** are unit vectors defining the unit cell monoclinic coordinate system, **c** unique.

1. Experimental information

Nitrogen temperature data for a single crystal of diborane taken in this laboratory (Smith, 1965; Smith & Lipscomb, 1965) established the space group as $P2_1/n$. There are two molecules per unit cell, the first of which is located at a symmetry center taken to be the origin of the unit cell, and the second of which is related to the first by a twofold screw axis. Structural parameters as determined by the usual spherical model treatment of 273 reflections are given in Table 1 (see Fig. 1). These parameters define a geometry not of D_{2h} symmetry. However, the parameter changes necessary to bring it into a symmetric geometry have values about the same size as the experimental errors in the parameters. Hence, we do not feel that there is any indication of a genuine departure from D_{2h} symmetry in the crystal. The observed structure factor magnitudes and their assigned errors are given in Appendix B.

The diborane structure has also been studied by gas-phase electron diffraction (Bartell & Carroll, 1965), a method which determines nuclear locations. The structural parameters so obtained are given in Table 1. In addition, Kuchitsu (1968) has used spectral data to obtain a refinement of the electron diffraction parameters of Bartell & Carroll.* The values reported by Kuchitsu are also given in Table 1. Throughout this paper, the term 'electron diffraction values' refers to the parameters of Bartell & Carroll. In the *Discussions and conclusions* section we discuss the question of which of these two sets of parameters is more appropriate for comparison with X-ray results. While the B–B bond lengths as determined by X-ray and electron diffraction methods differ by an amount on the order of experimental error,† the X-ray B–H bond lengths for the two types of bond, terminal ($\mathrm{B{-}H}_t$) and bridge

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* The work of Kuchitsu appeared after the calculations of the scattering factors, based on the parameters of Bartell & Carroll, were complete. We wish to thank a referee for calling this paper to our attention.

† As discussed later in detail, this difference is reduced if corrections are made in the X-ray length for the effects of rigid thermal motion of the molecule in the crystal.

Table 1. *Experimental structural parameters and standard errors*

	X-ray	Electron diffraction (Bartell & Carroll)	Spectroscopy (Kuchitsu)
B–B	$1{\cdot}76_2 \pm 0{\cdot}01$ Å	$1{\cdot}775 \pm 0{\cdot}003$ Å	$1{\cdot}77_0 \pm 0{\cdot}005$ Å
$\mathrm{B{-}H}_b$	$1{\cdot}24\ \pm 0{\cdot}02$	$1{\cdot}339 {}^{+0{\cdot}002}_{-0{\cdot}006}$	$1{\cdot}32_9 \pm 0{\cdot}005$
$\mathrm{B{-}H}_b'$	$1{\cdot}25\ \pm 0{\cdot}02$	$1{\cdot}339 {}^{+0{\cdot}002}_{-0{\cdot}006}$	$1{\cdot}32_9 \pm 0{\cdot}005$
$\mathrm{B{-}H}_t$	$1{\cdot}09\ \pm 0{\cdot}02$	$1{\cdot}196 {}^{+0{\cdot}008}_{-0{\cdot}006}$	$1{\cdot}19_2 \pm 0{\cdot}01$
$\mathrm{B{-}H}_t'$	$1{\cdot}06\ \pm 0{\cdot}02$	$1{\cdot}196 {}^{+0{\cdot}008}_{-0{\cdot}006}$	$1{\cdot}19_2 \pm 0{\cdot}01$
$\angle\mathrm{H}_t{-}\mathrm{B}{-}\mathrm{H}_t'$	$121{\cdot}6\ \pm 1^\circ$	$119{\cdot}0\ \pm 1{\cdot}8^\circ$	$121{\cdot}8\ \pm 3^\circ$

(B–H_b), are about 0·1 Å shorter than electron diffraction values. This discrepancy is five times the estimated error of 0·02 Å obtained in the X-ray work, and twelve times the largest estimated electron diffraction error.

2. Definition of geometry

Ideally, methods for fitting experimental data with structure factors based on molecular densities would allow for free variation of nuclear locations, just as fits with structure factors based on spherical atoms do. In fact, the computational complexity of obtaining molecular wave functions rules out this procedure. Thus, the molecular geometry must be fixed in advance of the fit. In addition, expense considerations severely limit the number of geometries that can be considered.

For this study, the B–B bond length and H_t–B–H_t angle were fixed at the electron diffraction values, which do not differ significantly from the X-ray values. Then the B–H_b and B–H_t lengths were varied to produce the following geometries:

(*a*) The 'short' geometry. The B–H_t and B–H_b lengths were obtained by averaging the two X-ray values for each of these bond types. Thus, this geometry is the X-ray geometry averaged to D_{2h} symmetry, with the H_t–B–H_t angle altered to the electron diffraction value.

(*b*) The 'electron diffraction' (ED) geometry. B–H_t and B–H_b lengths are those given by the electron diffraction study.

(*c*) The 'long' geometry. The B–H_t and B–H_b lengths are obtained by adding to the ED lengths for these bonds the difference between the ED and the 'short' geometry lengths for the bonds.

(*d*) The 'intermediate' ('Int.') geometry. B–H_t and B–H_b lengths are the averages of the ED and 'short' values for these bonds.

Parameters for these geometries are summarized in Table 2. It should be noted that the necessity for considering geometry (*d*) was not apparent until results were available for (*a*), (*b*) and (*c*).

Table 2. *Structural parameters for geometries upon which SCF structure factor calculations are based*

	Short	Int.	ED	Long
B–B	1·775 Å	1·775 Å	1·775 Å	1·775 Å
B–H_b	1·245	1·292	1·339	1·433
B–H_t	1·074	1·135	1·196	1·318
∠H_t–B–H_t	119·0°	119·0°	119·0°	119·0°

3. Structure factor calculations

(*a*) *Determination of density*

In order to obtain unit-cell densities it was first necessary to determine unambiguously the best orientation in the unit cell for a diborane molecule of D_{2h} symmetry. To this end, a least-squares program for spherical atoms was written which fitted the experimental data by rotating the rigid molecule about the fixed crystal–molecular symmetry center. Thermal parameters were treated according to the method suggested by Pawley (1964) (see also Schomaker & Trueblood, 1968) for rigid molecules. This method calculates the atomic anisotropic thermal parameters as a sum of two contributions, the first from translational motion of the center of mass of the molecule, and the second from librations of the molecule about its center of mass. Atomic form factors for boron were those of Ibers (1957), and the hydrogen atomic form factors were calculated from a hydrogen 1*s* orbital with an exponent of 1·2. This value is near that of the optimized H_t and H_b exponents obtained with the SCF calculations discussed below.

For treatment of the 'short' geometry, final orientation angles as defined by Scheringer (1963) were $\varphi = 14{\cdot}80°$, $\theta = 18{\cdot}08°$, and $\varrho = 29{\cdot}96°$ (see the legend of Fig. 1). The total atomic thermal parameters obtained were reasonable as compared with those obtained in the original X-ray study. However, when the tensor describing the librational motion was transformed to principal axes, the diagonal elements were 0·320, 0·986, and −0·214, in units of ($2\pi^2$ rad^2). The negative element indicates that this particular model is not totally appropriate in this case. In light of this result, two additional calculations of the orientation angles were made. In the first the rigid molecule was rotated, and variable isotropic temperature factors were assigned to each atom. Final φ, θ, and ϱ values obtained were 14·79, 18·16 and 29·57°. The second involved the calculation of 'average' orientation angles for the original X-ray structure, which was not of D_{2h} symmetry. The φ, θ and ϱ values thus calculated were 14·92, 18·12 and 29·82°. For each of the three sets of angles, the unit-cell coordinates of the atoms in the 'short' geometry molecule were calculated. The maximum difference between positions for the same atom as calculated from different sets was 0·001 fractional unit. Hence, we concluded that the differences among these sets of angles were inconsequential, and thus the angles as determined by Pawley's method were chosen.

The wave functions and molecular densities for each geometry were obtained from an optimized Slater minimum basis set SCF calculation for that geometry. [see Switkes, Stevens, Lipscomb & Newton (1969) for details of the calculation for the ED geometry.] The total unit-cell density is theoretically the sum of an infinite number of molecular contributions, but, in practice, a number of contributions were included such that the addition of still more contributions did not alter the value of the unit-cell structure factors by an amount greater than a preassigned uncertainty in these structure factors (*vide infra*). Thirteen different molecules made contributions to this unit-cell density. At any given point in the unit cell, however, an average of only four or five molecular contributions were required. This criterion led to a unit-cell density estimated to differ, at no point, by more than 0·5% from the infinite-sum limit. Although intermolecular forces will cause the total unit-cell density to differ from a simple sum of molecular contributions, errors generated by using the sum of molecular densities should be small compared with the uncertainties, detailed below, which are introduced by the thermal motion models.

(*b*) *Structure factor expressions*

The unit cell scattering factor, $F(h, k, l)$, is given by

$$F(h, k, l)=V\int_0^1 \mathrm{d}x\int_0^1 \mathrm{d}y\int_0^1 \mathrm{d}z\varrho(x, y, z) \times \exp\left[-2\pi i(hx+ky+lz)\right], \quad (3.1)$$

where x, y, and z are unit-cell coordinates in fractional units, V is the unit-cell volume, and $\varrho(x, y, z)$ is the unit-cell density at a point. The nature of the thermal motion treatments to be applied, however, dictates that the unit-cell scattering factor be written as a sum of two terms, each of which must be known separately. Thus,

$$F(h, k, l)=F_0(h, k, l)+F_s(h, k, l), \quad (3.2)$$

where $F_0(h, k, l)$ is the contribution to the total scattering factor by the molecule located at the origin, and $F_s(h, k, l)$ is the contribution by the screw-related molecule. F_0 and F_s are given by

$$F_0(h, k, l)=V\int_0^1 \mathrm{d}x\int_0^1 \mathrm{d}y\int_0^1 \mathrm{d}z\varrho_0(x, y, z) \times \exp\left[-2\pi i(hx+ky+lz)\right], \quad (3.3)$$

and

$$F_s(h, k, l)=V\int_0^1 \mathrm{d}x\int_0^1 \mathrm{d}y\int_0^1 \mathrm{d}z\varrho_s(x, y, z) \times \exp\left[-2\pi i(hx+ky+lz)\right], \quad (3.4)$$

where ϱ_0 is that part of the unit-cell density contributed by molecules related to the origin-located molecule by simple translations, and ϱ_s is that part contributed by molecules related to the origin molecule by simple translations plus a twofold screw operation. The symmetry properties of the unit cell can then be used to reduce (3.3) and (3.4) to the following forms. For details of the steps involved, see Jones (1969).

$$F_0(h, k, l)=V[I_1(h, k, l)-I_2(h, k, l)], \quad (3.5)$$

and

$$F_s(h, k, l)=\pm V[I_1(h, k, l)+I_2(h, k, l)], \quad (3.6)$$

where the sign is + for $(h+k+l)$ even and − for $(h+k+l)$ odd, and where

$$I_1(h, k, l)=2\int_0^1 \mathrm{d}x\int_0^{1/2} \mathrm{d}y\int_0^{1/2} \mathrm{d}z[\varrho_0(x, y, z)\pm\varrho_s(x, y, z)] \times[\cos 2\pi(hx+ky)\cos 2\pi(lz)], \quad (3.7)$$

and

$$I_2(h, k, l)=2\int_0^1 \mathrm{d}x\int_0^{1/2} \mathrm{d}y\int_0^{1/2} \mathrm{d}z[\varrho_0(x, y, z)\mp\varrho_s(x, y, z)] \times[\sin 2\pi(hx+ky)\sin 2\pi(lz)], \quad (3.8)$$

with the upper signs holding for $(h+k+l)$ even and the lower for $(h+k+l)$ odd. Note that integrals I_1 and I_2 need be evaluated over only one quarter of the unit cell.

(*c*) *Numerical integration*

Numerical three-dimensional Gaussian quadrature was used to evaluate the $I_1(h, k, l)$ and $I_2(h, k, l)$ integrals for all reflections. The necessary computing programs were not available and had to be written for these calculations. This section describes, first, a program test case based on spherical atom densities and, second, the calculation of the SCF structure factors. This latter computation involved the integration of the difference between SCF and spherical densities. For the test, the total unit-cell density was based on analytical spherical atom densities which yielded analytical expressions for the atomic form factors, so that exact values for unit-cell structure factors were available. For hydrogen, the form factors used for the unit-cell orientation study were adopted. The boron density was calculated from Duncanson & Coulson's (1944) atomic orbitals. McWeeny's (1951) analytical form factors for boron, also calculated from Duncanson & Coulson's orbitals, were used. Because of the rapid change in density near the nuclear centers, a much finer integration mesh was needed near these locations than in the remainder of the unit cell. In addition, because of the discontinuity of the first derivative of the density at the nuclear centers, it was necessary to devise a computing routine that would divide the unit cell into sub-volumes, in such a way that the nuclei were always located at a sub-volume 'corner', so that it was never necessary to integrate across the discontinuity (see Appendix A). We decided that values for the integrals with a relative accuracy of 0·1 % would be more than adequate for this study. Furthermore, we showed that a total of about 30,000 quadrature points, with about 9,000 of these points in fine-mesh volumes around the nuclei (comprising only 2% of the total integration volume) were sufficient. The ED geometry was chosen for the initial test integrations. With this quadrature, the maximum relative error encountered among 274 unit-cell scattering factors, $F(h, k, l)$, was 0·39 %, but the usual error was about 0·05 %. The usual values of the structure factors themselves were between 1 and 5. In fact, errors turned out to be fairly independent of scattering factor magnitude; these error values ranged from 0·00004 to 0·004, except for the density itself, which integrated to 31·989 instead of an exact 32·000 (relative error, 0·03 %). Additional spherical atom test calculations later showed that this mesh size and distribution were adequate for all geometries.

For the integration of the SCF densities, a convergence criterion was used to judge integral accuracy, since the only structure factor known exactly was the total density, $F(000)$. Expense considerations dictated that the convergence studies be limited to a set of representative structure factors, which were chosen as

000, 2 −1 3, 220, 218 and 012. The 220 reflection was the smallest encountered in the spherical atom test integrations, and should be especially sensitive to changes in the mesh size or distribution. It was soon discovered that the same mesh used for the test integrations was not satisfactory for the SCF density. Since the difference between the test and SCF cases was the aspherical nature of the latter, and since this asphericity is most marked along the B–H bonds, it was felt that the test mesh was inadequate mainly in the bonding regions. In an attempt to find an acceptable mesh without altering the total number of quadrature points, a 'difference density' technique was introduced, as follows. From the unit-cell SCF density we subtracted a spherical model density which was made up of atomic densities scaled to match the SCF density value at the nuclear centers. This difference density, $\Delta\varrho$, is given by

$$\Delta\varrho(x,y,z)=\varrho_{\mathrm{SCF}}(x,y,z)-\sum_{\substack{\text{B atoms,}\\ j}} S_{\mathrm{B}}\varrho_{\mathrm{B}j}(x,y,z) - \sum_{\substack{\text{H atoms,}\\ m}} S_{\mathrm{H},i}\varrho_{\mathrm{H}m}(x,y,z)\,, \qquad (3.9)$$

where

ϱ_{SCF} is the unit-cell density synthesized from SCF molecular densities,

ϱ_{B} is a spherical boron atomic density calculated from Duncanson & Coulson's orbitals,

ϱ_{H} is a spherical hydrogen atom density calculated from a 1s hydrogen orbital with an exponent of 1·2,

S_{B} is a scale factor such that ϱ_{SCF}(boron nucleus) $-S_{\mathrm{B}}\varrho_{\mathrm{B}}$(boron nucleus) $=0$,

$S_{\mathrm{H},i}$ is a scale factor such that ϱ_{SCF}(hydrogen nucleus) $-S_{\mathrm{H},i}\varrho_{\mathrm{H}}$(hydrogen nucleus) $=0$, $i=1$ for $\mathrm{H}=\mathrm{H}_t$, $i=2$ for $\mathrm{H}=\mathrm{H}_b$, and the summations are over all atoms included in the synthesis of ϱ_{SCF} from individual molecular densities.

This difference density varied much less drastically in the region of the atomic centers than did the total density. We hoped that, by integrating only this difference, some of the quadrature points massed around the nuclei in the test-case mesh could be shifted into the regions along the B–H bond axes. Accordingly, the fine-mesh volumes around the atomic centers were expanded to include the area along the bonds, without an alteration in the total number of points within these volumes. To further conserve funds, extensive calculations were done only on the 'long' geometry. This geometry was chosen because, of the four considered, it gave the smallest point-to-volume ratio within the fine-mesh volumes, and therefore provided the severest test of point distribution. Calculations were done first for a mesh of about 30,000 points, with about 9,000 of these in the fine-mesh volumes, and second for a mesh of about 50,000 points, with about 19,000 of these in the fine-mesh volume regions. Total unit-cell scattering factors, $F(h,k,l)$, were then obtained by adding the integration 'difference F' (ΔF) results to a spherical unit-cell scattering factor calculated from, and scaled in the same manner as, the spherical atoms which had been subtracted from the SCF density. The relations are

$$\begin{aligned}F(h,k,l)&=\Delta F(h,k,l)\\&+\sum_{\substack{\text{B atoms,}\\ j}} S_{\mathrm{B}}f_{\mathrm{B}}(h,k,l)\exp\left[-2\pi i(hx_{\mathrm{B}_j}+ky_{\mathrm{B}_j}+lz_{\mathrm{B}_j})\right]\\&+\sum_{\substack{\text{H atoms,}\\ m}} S_{\mathrm{H},i}f_{\mathrm{H}}(h,k,l)\\&\times\exp\left[-2\pi i(hx_{\mathrm{H}_m}+ky_{\mathrm{H}_m}+lz_{\mathrm{H}_m})\right]\,,\end{aligned} \qquad (3.10)$$

where

f_{B} is an atomic form factor calculated from ϱ_{B},

f_{H} is an atomic form factor calculated from ϱ_{H},

$(x_{\mathrm{B}_j}, y_{\mathrm{B}_j}, z_{\mathrm{B}_j})$ and $(x_{\mathrm{H}_m}, y_{\mathrm{H}_m}, z_{\mathrm{H}_m})$ give the locations of atoms B_j and H_m in unit-cell fractional coordinates,

the summations are over all atoms in the unit cell, and all other symbols are as defined in (3.9).

It is easy to see how (3.9) and (3.10) can be written in terms of ϱ_0, ϱ_s, F_0, and F_s.

The maximum relative difference between high and low-mesh values among the five scattering factors was 0·17% for 220, whose value was 0·090, and less than 0·05% for all others. All five agreed to within two digits in the fourth significant figure (third decimal place). In addition, these same meshes were used to integrate the full SCF density, and, although low and high-mesh values were not in good agreement, the agreement between high-mesh SCF values and the 'converged' difference technique values was within three digits in the fourth significant figure. Relative error here was 1·9% for 220 and less than 0·06% for the others.

These results indicated that the 30,000 point integration based upon this difference method yielded values which had converged to the desired accuracy. The 274 $I_1(h,k,l)$ and $I_2(h,k,l)$ integrals for the four geometries were calculated using this mesh, and final $F_0(h,k,l)$ and $F_s(h,k,l)$ values were then calculated from these integrals. For each geometry, about one hour of IBM 7094 computer time was required for density calculations, with an additional hour for integral evaluations.

4. Thermal motion models

In order to make valid comparisons with the results of spherical calculations, it was necessary to fit the SCF scattering factors using thermal vibration models as nearly akin as possible to those used in spherical atom fits. This section describes two basic types of thermal treatment. The first assumes that the thermal motion can be described as a translational motion of the entire molecule. The second treats the motion of individual atoms by utilizing a technique similar to that used for the difference density integrations.

Since the smallest entity recognized by the SCF model is the molecule, the only thermal parameter treatment which can be strictly applied to both spherical and SCF calculations is that which assigns a single temperature factor to the entire molecule. Taking this to be an anisotropic factor, the calculated structure factor, F_{calc}, based on the SCF model is given by

$$F_{\text{calc}}(h,k,l)=\text{SC}[F_0(h,k,l)\exp(-\sum_{i,j}\beta_{ij}s_is_j)$$
$$+F_s(h,k,l)\exp(-\sum_{i,j}\beta'_{ij}s_is_j)]\,, \qquad (4.1)$$

where

$s_1\equiv h,\ s_2\equiv k,\ s_3\equiv l$,

β_{ij} is an element of the anisotropic temperature tensor for the molecule located at the origin,

β'_{ij} is an element of the temperature tensor for the screw related molecule ($\beta'_{ij}=\beta_{ij}$ except for $\beta'_{13}=-\beta_{13},\beta'_{23}=-\beta_{23}$),

and SC is a scale factor.

An obvious objection to this treatment is that the boron atoms will dominate the fit, so that the hydrogen atoms, of chief interest here, will hardly be taken into account. In order to obtain a treatment which would both consider hydrogen atoms and be comparable with a spherical model treatment, a method parallel to the difference density integration technique was devised. 'Difference scattering factors', ΔF_0 and ΔF_s, were defined as

$$\Delta F_0(h,k,l)=F_0(h,k,l)$$
$$-\sum_{\substack{\text{B atoms,}\\ j}} S_{\text{B}}f_{\text{B}}(h,k,l)\exp[-2\pi i(hx_{\text{B}_j}+ky_{\text{B}_j}+lz_{\text{B}_j})]$$
$$-\sum_{\substack{\text{H atoms,}\\ m}} S_{\text{H},i}f_{\text{H}}(h,k,l)$$
$$\times\ \exp[-2\pi i(hx_{\text{H}_m}+ky_{\text{H}_m}+lz_{\text{H}_m})]\,, \qquad (4.2)$$

and similarly for $\Delta F_s(h,k,l)$ for the screw-related molecule. Note that (4.2) is just a rearrangement of (3.10), which was written in terms of the total scattering factor. All symbols are the same as those defined in (3.10), except that the summations extend only over atoms located in the origin-situated molecule for ΔF_0, and only over atoms in the screw-related molecule for ΔF_s. Thus, $(\Delta F_0+\Delta F_s)$ gives the scattering due to $\Delta\varrho$ (equation 3.9).

The expression for F_{calc} can then be written as

$$F_{\text{calc}}(h,k,l)=\text{SC}\{\Delta F_0(h,k,l)\exp(-\sum_{i,j}\beta_{ij}s_is_j)$$
$$+\Delta F_s(h,k,l)\exp(-\sum_{i,j}\beta'_{ij}s_is_j)$$
$$+\sum_{\substack{\text{atoms,}\\ m}}[f^0_m(h,k,l)\exp(-\sum_{i,j}B^m_{ij}s_is_j+f^s_m(h,k,l)$$
$$\times\ \exp(-\sum_{i,j}B'^m_{ij}s_is_j)]\}\,, \qquad (4.3)$$

where

β_{ij} is an element of the anisotropic temperature tensor for ΔF_0,

B^m_{ij} is an element of the anisotropic temperature tensor for atom m ($m=\text{H}$ or $m=\text{B}$),

$f^0_m(h,k,l)=S_mf_m(h,k,l)\exp[-2\pi i(hx_m+ky_m+lz_m)]$,

$f^s_m(h,k,l)=S_mf_m(h,k,l)\exp[-2\pi i(hx'_m+ky'_m+lz'_m)]$

with (x'_m,y'_m,z'_m) related to (x_m,y_m,z_m) by the twofold screw operation,

the β_{ij}, β'_{ij} and B^m_{ij}, B'^m_{ij} are related as in (4.1), the summation is over the atoms in the origin-situated molecule and the S_m are as defined in (3.9), and all other symbols are as defined in (4.2).

Note that if atoms m and m' are related by the inversion center operation, $f^0_m=f^0_{m'}$ and $f^s_m=f^s_{m'}$. Hence, there are only four unique atoms to be subtracted, corresponding to the four atoms in the asymmetric unit of the unit cell.

The essence of this treatment is that it assigns an anisotropic temperature factor to the difference density, $\Delta\varrho$, of (3.9), as well as to each of the subtracted atomic densities. It is emphasized that this density partitioning was motivated by the desire to obtain a thermal motion treatment as closely related as possible to the usual spherical atom treatment in which each atom is assigned an anisotropic tempertaure factor. No physical significance is claimed for the difference density part: indeed, it is negative at some points. The real significance of the difference density lies in the fact that this difference distinguishes the SCF model from the usual spherical model treatment. Since $\Delta\varrho$ measures the discrepancy between SCF and spherical atom densities for a given geometry, a $\Delta\varrho$ value of zero at all points would cause the SCF and spherical treatments (including thermal motion corrections) to coincide.* Because of the 'non-physical' nature of $\Delta\varrho$, the β_{ij} and β'_{ij} thermal parameters assigned to ΔF_0 and ΔF_s in (4.3) were held fixed in all but one of the least-squares fits described below. Each such set of fixed β and β' parameters was chosen in some 'reasonable' way.

5. Data fits

The least-squares fits of the SCF scattering factors to the experimental data utilized the weighting scheme originally used by Smith. The weights used are given by

$$w(h,k,l)=1/\sigma^2(h,k,l)\,,$$

where the $\sigma(h,k,l)$ are the assigned errors listed in Appendix B. The residual minimized and the weighted agreement factor calculated are given by

$$\text{Residual}=\Sigma\, w_{\text{obs}}(|F_{\text{obs}}|-|F_{\text{calc}}|)^2$$

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* This would be strictly true only if the S_{B} and S_{H} factors scaling the spherical atoms subtracted from the SCF density were all equal to one. However, we showed that, for a given choice of anisotropic thermal parameters for ΔF_0 and ΔF_s, the subtraction of unscaled spherical atoms and variation of atomic thermal parameters yielded nearly the same set of calculated structure factors as was obtained when scaled atoms were subtracted.

and

$$wR=\left[\frac{\Sigma\, w_{\rm obs}(|F_{\rm obs}|-|F_{\rm calc}|)^2}{\Sigma\, w_{\rm obs}|F_{\rm obs}|^2}\right]^{1/2}\times 100\,.$$

Six fits of the SCF scattering factors were carried out, one according to the model of (4.1), four according to the model of (4.3), and one according to a modification of (4.3). Each of these fits, described as *A* to *F* below, was made for all four molecular geometries.

(*A*) As in the model of (4.1), a single molecular anisotropic temperature factor and a scale factor were varied, for a total of seven parameters.

(*B*) This fit was made according to equation (4.3), except that only scaled boron atoms were subtracted, so that ΔF_0 and ΔF_s included all hydrogen atoms. Parameters which were varied included anisotropic thermal parameters assigned to ΔF_0 and ΔF_s. In this case these difference scattering factors do have a physically interpretable meaning. Variation of the scale factor and boron thermal parameters brought the number of parameters varied to thirteen.

(*C*) This fit was exactly as set forth in (4.3). The parameters which were varied included anisotropic temperature factors for each of the four subtracted atoms plus a scale factor, a total of twenty-five. The anisotropic thermal parameters assigned to ΔF_0 and ΔF_s were kept fixed, and, for each geometry, these were chosen to equal the final ΔF_0 and ΔF_s thermal parameters obtained in fit (*B*). This choice is a 'reasonable' one in the following sense: because the asphericity of hydrogen is much more marked than that of boron, $\Delta \varrho$ can be thought of as having mostly hydrogen

Table 3. *Weighted agreement factors for the spherical model least-squares fits to experimental data*

The number in parentheses after the minimum agreement factor gives the coordinate for this minimum. An asterisk indicates that the minimum was obtained from a parabolic fit to the three nearest data points.

Geometry coordinate	Model Molecular temp. factor	 B atom subtraction	 *ORFLS*
−0·10	10·40	9·21	8·62
−0·08	9·80	8·49	8·04
−0·06	9·34	7·88	7·54
−0·04	9·05	7·44	7·17
−0·02	8·95	7·18	6·94
0·00 (short)	9·07	7·15	6·89
0·02	9·38	7·34	7·03
0·04	9·89	7·74	7·36
0·06	10·55	8·30	7·83
0·08	11·34	8·99	8·41
Minimum	8·95 (−0·02)	7·14 (−0·0073)*	6·88 (−0·0047)*

Table 4. *Weighted agreement factors for the SCF model least-squares fits to experimental data*

The last line of the Table gives the coordinate at the minimum. An asterisk indicates that the minimum was obtained from a parabolic fit to the three nearest data points.

Geometry	Model					
coordinate	*A*	*B*	*C*	*D*	*E*	*F*
0·00 (short)	10·69	6·99	6·66	6·96	6·82	6·45
0·05 (Int.)	10·00	6·76	6·44	6·45	6·49	6·29
0·10 (ED)	10·47	7·54	7·19	6·90	7·10	6·45
0·20 (long)	13·00	10·80	9·51	8·83	9·11	7·17
Minimum	9·99*	6·72*	6·40*	6·45*	6·48*	6·29
Coordinate at minimum	0·055*	0·036*	0·036*	0·052*	0·043*	0·050

Table 5. *The shift to longer bond lengths between the minima obtained with the SCF models and corresponding spherical models*

The errors shown for the averages are standard deviations. The 'shift' is defined as (SCF minimum)–(spherical minimum) and is given in geometry coordinate units.

SCF model	*A*	*B*	*C*	*D*	*E*	*F*
Spherical model	Molecular	B atom subt.	FLS	FLS	FLS	FLS
Shift	0·075	0·043	0·041	0·057	0·048	0·055

Average of $C,D,E=0{\cdot}049\pm0{\cdot}008$.

Average of $B,C,D,E=0{\cdot}047\pm0{\cdot}007$.

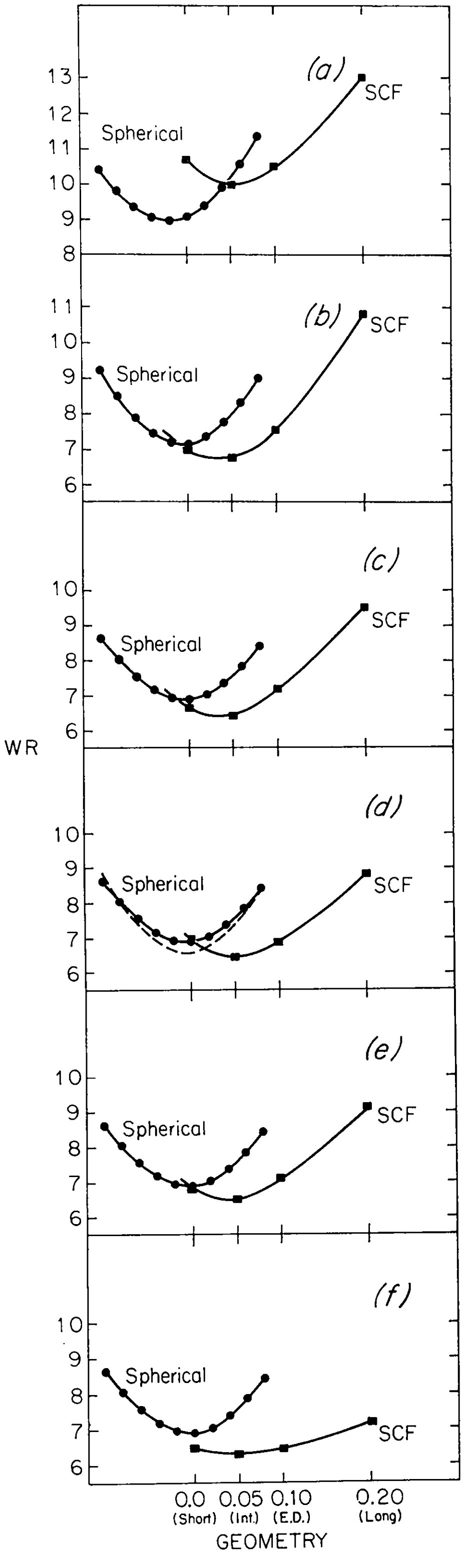

Fig. 2. Weighted agreement factors *vs.* B–H bond lengths for various treatments of diborane X-ray diffraction data.

character. Thus, temperature parameters appropriate to the total hydrogen density should be appropriate also to $\Delta\varrho$.

(*D*) This fit involved variation of the same twenty-five parameters as in (*C*). The fixed anisotropic thermal parameters assigned to ΔF_0 and ΔF_s were chosen, for each geometry, to equal the final thermal parameters for F_0 and F_s obtained in fit (*A*).

(*E*) Twenty-five parameters were varied, as in (*C*) and (*D*). In an attempt again to 'characterize' $\Delta\varrho$, it was felt that, since a large fraction of the difference lay in the bonding regions, the thermal motion of the difference might be thought of as being determined more by rigid body motions of the molecule than by internal vibrational motions. Accordingly, a set of ΔF_0 and ΔF_s thermal parameters was obtained by 'averaging' the atomic anisotropic thermal parameters which resulted from the thermal motion treatment of the orientation angle determination by Pawley's method. For each B–H bond the B and H parameters were averaged, and then these three sets of parameters were again averaged. Since the orientation angle study involved only one geometry ('short'), this single set of parameters was used for all four geometries.

(*F*) Thirty-one parameters were varied in the model of (4.3), including the scale factor, anisotropic thermal parameters for each of four atoms, and anisotropic parameters for the ΔF_0 and ΔF_s difference scattering factors.

In order to obtain spherical atom results with which the results of the above SCF calculations could be compared, the following three spherical atom fits were made. Each fit treated several geometries centered around the 'short' geometry. The atomic form factors used were as defined for equation (3.10).

(*A'*) The 'molecular temperature factor' fit. A scale factor and single anisotropic molecular temperature factor were varied. This corresponds exactly to SCF fit (*A*).

(*B'*) The 'boron subtraction' fit. The boron atom was assigned anisotropic thermal parameters, and the three hydrogen atoms were constrained to have identical anisotropic thermal parameters. Scale factor variation brought the number of adjustable parameters to thirteen. This fit corresponds to SCF fit (*B*).

(*C'*) The '*ORFLS*' fit. This is the usual spherical model treatment, varying a scale factor and independent anisotropic temperature factors on each of four atoms. This fit was done using a revised form of the *ORFLS* program of Busing, Martin & Levy (1962). Twenty-five parameters were varied.

6. Results

In Table 3 we list the weighted agreement factors for various geometries as determined by the three spherical model fits just discussed. Each unit of the 'geometry coordinate' represents a change of B–H_b and B–H_t bond lengths equal to ten times the difference between 'short' and ED values for these bonds. Each unit thus represents a 1·22 Å change in the B–H_t bond length and a 0·94 Å change in the B–H_b length. The 'short' geometry was arbitrarily assigned the coordinate zero. With these definitions, a geometry coordinate of g units represents a geometry with B–H bond lengths about g Å longer than the 'short' values for these bonds. Table 4 gives the weighted agreement factors for the six SCF fits discussed above, and Table 5 gives the differences between the coordinates at the minima of each SCF fit and its corresponding spherical atom fit. In Fig. 2 agreement factors are plotted *vs.* geometry coordinates for the six SCF and corresponding spherical atom fits as given in Table 5. Fig. 2(*a*) corresponds to SCF fit (*A*), *etc.**

Fig. 2(*a*) has the interesting properties: (*a*) the spherical model minimum is not at the 'short' geometry; (*b*) the minimum agreement factor for the SCF model is larger than that for the spherical model; (*c*) the SCF shift to longer bond lengths is about three-quarters of the observed 'anomalous' bond shortening.

Fig. 2(*b*), based on a thermal motion treatment including hydrogen atoms at a minimal level, gives a less pronounced shift to longer bond lengths, but the SCF optimum agreement factor is now lower than the best spherical model value. In addition, in Fig. 2(*b*) the spherical minimum falls much closer to the 'short' geometry than it does in Fig. 2(*a*).

Fig. 2(*c*), (*d*), and (*e*), representing SCF fits based on vibrational models most like the usual spherical atom models, have an appearance similar to that of Fig. 2(*b*), with the minimum SCF agreement factors 0·40 to 0·48 unit† lower than the spherical model minima. Shifts to longer bond lengths are around 0·05 Å, and the spherical minimum is consistently about 0·005 Å to the short bond-length side of the 'short' geometry. In the region of the minimum, the SCF and spherical curves are similarly shaped.

Fig. 2(*f*) is based on the vibrational treatment varying thirty-one parameters. A very shallow SCF curve is obtained, implying that the optimum bond lengths are not well determined.

7. Discussion and conclusions

All thermal vibration treatments give results indicating that use of the SCF model leads to B–H bond lengths longer than those obtained through use of the spherical model. The longest SCF model B–H lengths are obtained from fit (*A*), but the validity of these results must be seriously questioned for the following reasons: (*a*) this fit is severely limited in its ability to treat the motion of hydrogen atoms; (*b*) the spherical minimum is considerably displaced from its location in the remaining fits; (*c*) the SCF minimum agreement factor is larger than the best value for spherical atoms, a result also discordant with results of the remaining fits. Fits (*C*), (*D*), and (*E*) should be the 'best' treatments of thermal motion, in the sense that they are most like the usual spherical model treatments. For these three, and for (*B*), the SCF model does give better agreement factors than the corresponding spherical model, and the minima for spherical atoms are at more reasonable locations. The 0·005 unit difference between the '*ORFLS*' spherical minimum and the 'short' geometry is well below experimental uncertainty and is attributed to the effects of averaging the X-ray parameters to D_{2h} symmetry and altering the H_t–B–H_t angle to the ED value. Fit (*F*) is not considered a valid one for bond length determination, since the temperature factors assigned to a physically meaningless $\Delta\varrho$ were varied, but the results did serve as an additional indication of how serious an error might result from an incorrect choice for the temperature factor assigned to $\Delta\varrho$. The position of the SCF minimum here differed little from that of fits (*B*) through (*E*). The shallowness of the SCF curve occurred most probably because an additional six variable parameters were introduced.

Considering fits (*C*), (*D*), and (*E*) as the most nearly valid for bond length determination, an average SCF shift to longer bond lengths of about 0·05 ± 0·008 Å is obtained. (Inclusion of (*B*) as a fourth fit does not alter this value significantly.) The standard deviation of about 0·01 Å is a measure of the error introduced by choosing a set of ΔF_0 and ΔF_s thermal parameters different from some undefined 'best' set.

Another possible error source is the existence of random errors in the experimental data. The following test was devised to investigate the effects of such errors. A data set which was reasonably close to the experimental set, yet 'free' from any errors, was contrived by choosing as 'observed' data the calculated structure

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* After the original submission of this manuscript, we discovered that the '*ORFLS*' spherical atom fit would converge, for each geometry, on two different sets of thermal and scale parameters. Corresponding parameters in the different sets usually differed by no more than two standard deviations for that parameter. These newly-discovered sets yielded weighted agreement factors which, when plotted *vs.* geometry coordinate, gave a curve slightly steeper, and with a lower minimum, than the original '*ORFLS*' curve. This new curve is plotted as a dashed line in Fig. 2(*d*). The minimum of the new curve lies at −0·0039 geometry coordinate units, at virtually the same place as the minimum of the original curve (−0·0047 units). Hence, none of our conclusions regarding bond lengths are altered. A search was made, without success, for another agreement factor curve for SCF treatment (*D*). If such a curve did exist for any of the SCF treatments, we would not expect the position of its minimum to differ significantly from that of the original curve. Again, our conclusions about bond lengths would remain unaltered.

We considered the possibility that the three SCF points used to determine the minimum in each of the SCF curves might, in some case(s), actually belong on different curves. This possibility seems remote, however, in light of the fact that the curves for SCF treatments (*b*), (*c*), (*d*) and (*e*) are virtually superimposeable in the region of these three points. This is true, even though the treatments differ considerably among themselves.

† 0·16 to 0·24 units, if based upon the new spherical-model curve.

factors for the 'Int.' geometry of SCF fit (*D*). For this data set, fit (*D*) gave, of course, a minimum at the 'Int.' geometry (0·05 unit) and an agreement factor of 0·0. The spherical model ('*ORFLS*') gave a minimum, for these data, at −0·0045 unit, yielding a weighted agreement factor of 4·09. Note that this minimum falls at the same location as the spherical minimum based on the actual data. Ten data sets containing random errors (Gaussian) were then generated by adding 'errors' to the contrived scattering factors, $F_c(h,k,l)$, according to the formula

$$\mathrm{Error}(h,k,l) = R \times 0{\cdot}075 \times (\sigma_{\mathrm{rel}}/\overline{\sigma_{\mathrm{rel}}}) \times F_c(h,k,l)\,,$$

where R is a random number with standard deviation one, 0·075 is a normalizing factor selected so that fits to the random error data sets gave agreement factors of about the same size as those obtained in fits to the actual data, σ_{rel} is the relative error assigned to $F(h,k,l)$ in the actual data set, and $\overline{\sigma_{\mathrm{rel}}}$ is the average over all reflections of the relative errors assigned in the actual data set. Fits to these random error sets according to SCF method (*D*) gave minima with an average location 0·001 unit removed from the 'Int.' geometry, with a standard deviation from this average of 0·0069 unit. Spherical model ('*ORFLS*') treatment of these data sets gave an average minimum at −0·0045, identical to the minimum obtained with the contrived set without errors. The standard deviation from this average was 0·0051 unit. Of chief interest, however, is the error in the difference between SCF and spherical minima. For fits to the error-free data, this difference was 0·0546 unit. The average of the fits to the ten error-containing data sets gave exactly this value, with a standard deviation of 0·0027 unit. This indicated that random errors in the data can introduce an error in the SCF shift to longer bond lengths of about ±0·003 Å, a value well below both experimental uncertainties and the uncertainty, discussed above, inherent in the vibrational treatment. Hence it was concluded that, if the errors in the diborane experimental data are purely random, such errors will not significantly affect the results of this study.

Finally, the method of Cruickshank (1956) was applied to determine the magnitude of X-ray bond shortening caused by rigid thermal motion of the molecule. The tensor giving the mean-square amplitudes of libration was taken from the unit-cell orientation study described in § 3. The negative diagonal element present after the transformation to principal axes was set equal to zero for this calculation. Of the remaining diagonal elements, the larger corresponds to a root-mean-square oscillation of about 13° around an axis almost coincident with the B–B bond axis. The final diagonal element represents an oscillation of about 7°. An analysis showed a B–B bond shortening of 0·014 Å, and B–H_t and B–H_b shortenings of about 0·02 Å. While the negative oscillation angle originally present prevents us from accepting these figures as quantitative, we may still regard 0·01 to 0·02 Å as a reasonable value for shortening due to this effect.

What, then, may be finally concluded about the improvements gained by using an SCF model for X-ray data interpretation? Two separate questions can be asked. First, what X-ray bond length changes can be directly attributed to the use of the SCF scattering factors? Second, how do the B–H lengths based on the SCF model compare with the 'true' values? The answer to the second question must take into account errors in the X-ray thermal motion models, problems regarding the most appropriate parameters for comparison with X-ray results, *etc.* The first question, however, can be answered by considering only the matter of whether the effects of errors in the spherical-atom-model thermal-motion treatments are different from the effects of similar errors in the SCF-model thermal treatments. The spherical atom and SCF treatments were made as nearly alike as possible so that the bond length shift in going from spherical to SCF scattering factors would be relatively independent of such thermal model errors. For example, if both the spherical and SCF thermal treatments used here were modified to include anharmonic effects, we would expect the values of the B–H bond lengths as determined by the modified treatments to differ from those calculated here, but we would also expect the difference between the spherical atom and SCF bond lengths thus determined to remain very close to 0·05 Å.

The question of how our B–H lengths compare with the 'true' values is a much more complicated matter. If we knew exactly what thermal corrections to make in order to transform the static unit-cell density, a sum of molecular densities, into the true average cell density, then the molecular geometry upon which the static density was based would be an equilibrium geometry. The B–H lengths would then be r_e values. On the other hand, the Bartell & Carroll electron diffraction values are r_g values, representing 'the average value of an instantaneous internuclear distance' (Kuchitsu, 1968). Kuchitsu has used data from vibration and vibration-rotation spectroscopy to calculate 'r_z' values, which are 'distances between average positions of atoms with respect to a molecule-fixed coordinate system'. To go from either r_g or r_z to r_e ($r_g, r_z > r_e$) requires a detailed theoretical calculation to determine molecular vibrations, including anharmonic effects. Such calculations are not available for diborane, but calculations for CH_4 (Kuchitsu & Bartell, 1962) show that the value for $r_g - r_e$ for the C–H bond is about 0·02 Å. In this connection, the isotope effect for CH_4, $r_g(\mathrm{C{-}H}) - r_g(\mathrm{C{-}D})$, is 0·004 Å. For diborane, this effect, $r_g(\mathrm{B{-}H}) - r_g(\mathrm{B{-}D})$, is 0·006 Å for the bridge hydrogen atoms and −0·002 Å for the terminal hydrogen atoms (Kuchitsu, 1968).

We do have some information about the effects of the thermal motion model that has been applied in the X-ray case. The rigid rotation of an equilibrium geometry molecule in the crystal leads to X-ray lengths shorter than r_e values, necessitating the correction discussed above. We may also consider the anharmonicity present in the stretching of a B–H bond, and the error introduced by fitting such anharmonicity with a harmonic stretching function. If we fit, in the least-squares sense, the usual kind of anharmonic potential with a harmonic approximation, the minimum of the harmonic curve would then lie on the long bond-length side of the anharmonic minimum. Therefore, we might expect that X-ray B–H lengths, corrected for rotational shortening, would be somewhat greater than r_e values, but less than r_g values.

The accuracy of the wave functions used might also be considered as a possible source of error. It would seem, however, that the difference between the molecular SCF densities calculated in this study and the true molecular densities should be much less than the difference between the SCF densities and spherical atom densities. Even so, if the scattering factors were much more sensitive to changes in a density configuration very close to the true density than to changes in a configuration well removed from the true density, an improved wave function might give an additional bond lengthening on the order of hundredths of an Ångstrom. It would be desirable to investigate this possibility by carrying out additional SCF calculations with a balanced expanded basis set, in order to better account for density polarization around the hydrogen atoms. At present, however, such calculations are beyond our capabilities.

With our limited information about what X-ray bond lengths really represent, the r_z values of Kuchitsu would seem reasonable parameters for comparison. The r_z values are greater than r_e values but less than r_g values. For the B–H bonds, $r_g - r_z$ is about 0·01 Å. If we add 0·01 Å to the SCF bond lengths, to correct for rotational shortening, the discrepancy remaining between the X-ray and r_z values is about 0·03 Å. Thus, based on this comparison, we have accounted for about two-thirds of the observed 'anomalous' shortening. Of

Table 6. *Observed and calculated structure factors for diborane*

The four columns give, respectively, the *l* index, ten times the observed structure factor magnitude, ten times the calculated structure factor, and ten times the standard error. Asterisks in columns two and four indicate unobserved reflections.

	0 0 L		
2	1625	1674	17
4	316	291	9
6	***	16	**
8	***	-125	**
10	107	-112	3
	0 1 L		
1	1354	1289	14
2	796	-799	7
3	225	198	4
4	514	-517	5
5	***	18	**
6	335	-349	6
7	***	-63	**
8	175	-175	5
	0 2 L		
0	515	-540	5
1	490	-438	8
2	393	-414	5
3	634	-591	9
4	209	-180	4
5	473	-466	9
6	***	-40	**
7	298	-287	6
8	***	15	**
9	112	-107	3
	0 3 L		
1	649	-656	7
2	122	-99	2
3	367	-368	6
4	177	-165	3
5	***	-97	**
6	143	-129	3
	0 4 L		
0	512	-459	10
1	143	135	3
2	410	-373	8
3	207	217	4
4	192	-164	4
5	161	180	3
6	***	19	**
7	111	121	3
	0 5 L		
1	***	-41	**
2	250	245	5
3	***	-43	**
4	295	301	6
5	***	9	**
6	225	231	6
7	***	31	**
8	108	115	3
	0 6 L		
0	268	271	5
1	***	70	**
2	201	211	5
3	163	153	4
4	***	102	**
5	143	144	4
	0 7 L		
1	241	231	5
2	***	-10	**
3	138	139	4
	1 0 L		
1	1770	1992	10
2	117	114	2
3	626	603	8
4	58	-22	4
5	109	110	2
	1 1 L		
0	1131	1081	9
1	349	-358	4
2	343	302	5
3	558	-510	9
4	***	-37	**
5	412	-400	8
6	***	-48	**
7	244	-246	5
	1 -1 L		
0	1399	1353	22
1	409	395	5
2	954	909	9
3	486	527	9
4	300	285	6
5	407	415	8
6	***	9	**
7	263	253	5
	1 2 L		
1	***	-39	**
2	597	-581	8
3	221	-225	4
4	501	-474	10
5	***	-86	**
6	350	-341	7
7	***	-2	**
8	169	-168	5
	1 -2 L		
1	570	-599	4
2	311	307	5
3	174	-179	3
4	519	524	10
5	***	-66	**
6	406	404	8
7	***	4	**
8	201	191	5
	1 3 L		
0	504	-507	14
1	155	-152	3
2	423	-426	7
3	196	-182	4
4	219	-209	6
5	131	-125	4
	1 -3 L		
0	907	-891	17
1	101	-104	2
2	667	-644	13
3	83	81	2
4	295	-280	6
5	212	181	6
6	***	-12	**
7	128	98	3
	1 4 L		
1	454	-419	7
2	106	120	2
3	275	-246	5
4	164	176	3
5	***	-56	**
6	124	140	3
	1 -4 L		
1	437	-418	8
2	255	-234	5
3	329	-301	6
4	190	-202	4
5	***	-70	**
6	148	-156	4
	1 5 L		
0	***	-22	**
1	100	106	2
2	***	-14	**
3	231	240	4
4	***	11	**
5	***	230	**
6	***	31	**
7	140	145	4
	1 -5 L		
0	***	-24	**
1	149	-146	3
2	***	-52	**
3	296	-308	6
4	***	-21	**
5	288	-297	5
6	***	25	**
7	175	-185	5
	1 6 L		
1	198	213	4
2	98	100	3
3	122	134	3
4	129	130	3
	1 -6 L		
1	243	264	5
2	134	-134	4
3	156	170	4
4	181	-177	5
5	***	56	**
6	135	-130	4
	1 7 L		
0	206	196	6
1	***	-3	**
2	156	153	4
	1 -7 L		
0	281	272	5
1	***	5	**
2	232	217	6
3	***	14	**
4	109	95	3
	2 0 L		
0	786	735	15
1	***	-8	**
2	647	632	9
3	50	-30	3
4	275	262	4
5	***	-21	**
6	***	-26	**
7	***	-13	**
8	103	-111	3
	2 1 L		
1	480	450	4
2	304	-285	6
3	177	160	3
4	375	-370	6
5	***	4	**
6	266	-276	5
7	***	-73	**
8	139	-138	4
	2 -1 L		
1	682	687	9
2	163	171	3
3	516	508	8
4	354	372	7
5	121	104	2
6	299	301	6
7	***	-40	**
8	146	143	4
	2 2 L		
0	63	44	3
1	200	-225	4
2	77	-82	2
3	395	-395	6
4	100	-104	3
5	335	-338	6
6	***	-32	**
7	209	-206	6
	2 -2 L		
0	217	-253	3
1	***	5	**
2	93	-95	1
3	333	351	6
4	***	-38	**
5	441	451	8
6	***	6	**
7	261	265	5
	2 3 L		
1	416	-411	5
2	150	-152	3
3	299	-288	4
4	122	-115	3
5	87	-86	2
	2 -3 L		
1	716	-727	11
2	***	-8	**
3	478	-452	9
4	174	168	3
5	115	-121	3
6	154	134	4
	2 4 L		
0	354	-334	7
1	***	22	**
2	276	-260	5
3	***	100	**
4	135	-109	4
5	129	130	3
	2 -4 L		
0	459	-475	12
1	102	-106	3
2	447	-409	9
3	181	-191	3
4	204	-183	6
5	153	-174	4
	2 5 L		
1	***	2	**
2	135	131	4
3	***	20	**
4	187	188	5
5	***	32	**
6	151	147	4
	2 -5 L		
1	***	-44	**
2	231	-225	4
3	***	-16	**
4	303	-310	6
5	***	16	**
6	231	-238	6
7	***	18	**
8	116	-118	3
	2 6 L		
0	148	162	4
1	***	40	**
2	121	132	3
	2 -6 L		
0	240	263	6
1	***	-74	**
2	210	221	6
3	176	-169	5
4	***	111	**
5	167	-162	5
	2 7 L		
1	132	131	4
	2 -7 L		
1	271	257	7
2	***	6	**
3	169	162	5
	3 0 L		
1	442	429	5
2	65	-58	3
3	361	349	7
	3 1 L		
0	308	287	8
1	119	-111	2
2	263	262	4
3	260	-269	5
4	114	108	3
5	238	-251	5
6	***	-35	**
7	166	-154	4
	3 -1 L		
0	366	332	10
1	***	24	**
2	333	344	6
3	224	221	4
4	172	165	3
5	281	279	5
6	***	13	**
7	158	168	4
	3 2 L		
1	100	-105	2
2	202	-211	3
3	***	-90	**
4	270	-274	5
5	***	-56	**
6	183	-201	5
	3 -2 L		
1	50	-54	3
2	182	193	3
3	***	-37	**
4	360	362	7
5	***	11	**
6	289	285	6
7	***	42	**
8	128	138	3
	3 3 L		
0	326	-333	6
1	***	-51	**
2	270	-272	5
3	***	-96	**
4	132	-132	4
	3 -3 L		
0	539	-546	10
1	***	45	**
2	446	-445	9
3	***	124	**
4	194	-195	5
5	144	131	4
	3 4 L		
1	215	-205	6
2	***	42	**
3	130	-121	3
	3 -4 L		
1	484	-449	9
2	108	-108	3
3	283	-262	5
4	143	-161	4
5	***	-59	**
6	111	-121	3
	3 5 L		
0	***	0	**
1	***	43	**
2	***	10	**
3	***	109	**
4	***	23	**
5	127	120	3
	3 -5 L		
0	***	-81	**
1	***	-105	**
2	***	-34	**
3	246	-252	5
4	***	5	**
5	250	-248	7
6	***	3	**
7	141	-151	4
	3 -6 L		
1	213	225	6
2	121	-119	3
3	150	154	4
4	154	-158	4
	3 -7 L		
0	248	248	7
1	***	2	**
2	213	200	6
	4 0 L		
0	369	354	7
1	***	-20	**
2	298	309	6
3	***	-13	**
4	157	146	4
	4 1 L		
1	180	173	3
2	132	-139	4
3	121	125	3
4	173	-185	5
5	***	7	**
6	133	-138	4
	4 -1 L		
1	227	222	4
2	134	132	4
3	164	153	4
4	204	198	5
5	***	56	**
6	145	155	4
	4 2 L		
0	99	-114	3
1	***	-70	**
2	***	-90	**
3	153	-168	4
4	***	-55	**
5	154	-162	4
	4 -2 L		
0	***	-82	**
1	92	106	2
2	***	-63	**
3	248	240	5
4	***	-4	**
5	238	237	6
6	***	35	**
7	145	150	4
	4 3 L		
1	201	-205	5
2	***	-46	**
3	127	-126	3
	4 -3 L		
1	360	-355	7
2	***	90	**
3	211	-209	6
	4 4 L		
0	152	-136	4
	4 -4 L		
0	395	-361	8
1	***	-42	**
2	288	-272	6
3	***	-120	**
4	119	-110	3
5	95	-107	3
	4 -5 L		
1	***	-62	**
2	173	-150	5
3	***	-22	**
4	200	-205	5
	4 -6 L		
0	173	186	5
1	***	-52	**
2	147	154	4
	5 0 L		
1	230	224	6
	5 -1 L		
0	168	163	5
1	***	60	**
2	136	130	4
3	121	119	3
4	***	74	**
5	113	113	3
	5 -2 L		
1	***	-66	**
2	131	131	4
3	***	-20	**
4	164	164	4
5	***	20	**
6	131	130	4
	5 3 L		
0	124	-124	3
	5 -3 L		
0	230	-245	6
1	***	31	**
2	194	-190	5
	5 -4 L		
1	221	-216	6
2	***	-63	**
3	141	-128	4

this amount, about 0·05 Å can be attributed directly to the inadequacy of the spherical atom model for the interpretation of X-ray data.

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APPENDIX A

The computing routine used to divide the integration volume into subvolumes is a complicated one and may be of general use, so a brief description of it is given here.

The input data include (1) the limits of integration in each dimension, (2) the coordinates of each atomic center, (3) for each center, the dimensions of the special volumes to be constructed around that center and the integration mesh size for these volumes, and (4) the integration mesh size for the volume remaining after the special volumes have been removed.

The routine first generates the special volumes, then uses crystal symmetry operations to transform any special volumes protruding from the original integration volume to equivalent volumes within the original. Next a check is made to see if any special volumes overlap, then a set of volumes is generated to fill the space remaining after the special volumes are removed from the original integration volume. Output includes all volumes generated and the mesh sizes for these volumes.

Contribution of a revised version of this program to the Quantum Chemistry Program Exchange is planned.

APPENDIX B

The X-ray diffraction data originally taken for diborane (Smith & Lipscomb, 1965) were sufficient for the accurate determination of the crystal structure, but it was felt that a more complete data set was needed for this present work. Accordingly, additional data were taken, yielding the set of structure factor magnitudes given in Table 6 (Smith, 1965). Unobserved reflections are marked by asterisks in the columns giving the observed magnitudes and the standard errors. For observed reflections, the calculated structure factors are those of the 'Int.' geometry of SCF fit (*D*). The calculated magnitudes for the unobserved reflections are based on an '*ORFLS*' spherical atom calculation for the 'short' geometry. Because of expense considerations, no SCF scattering factors were calculated for these reflections. The spherical atom scattering factors thus calculated should differ from the corresponding SCF factors by much less than an order of magnitude.

The experimental data were taken by hand positioning a scintillation counter; the normal beam method was used, with a crystal of arbitrary orientation. These factors lead to three classes of unobserved reflections.*

(1) Below a sin θ value of 0·3, in the region where the original data were collected, all reflections were measured. Unobserved reflections in this region failed to give a count greater than background. (2) For values of sin θ greater than 0·3, reflection magnitudes were calculated using the structural parameters derived from the original data. Only those reflections having a calculated value beyond a predetermined limit were measured. (3) Some reflections were inaccessible because of the arbitrary orientation of the crystal and the design of the low temperature apparatus used.

The scale factor relating the calculated SCF structure factors as given in Table 6 and the calculated SCF structure factors on an absolute scale is 12·33.

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* We wish to thank Dr H. Waren Smith for a private communication giving these details.

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