factor in the form $-(\frac{1}{4})\sum_{ij} B_{ij}h_i h_j(\mathbf{a}_i^* . \mathbf{a}_j^*)$, where a factor $\frac{1}{2}$ must not be overlooked when going from the b_{ij} to the B_{ij} when $i \neq j$. Similarly, when $i=j$, $k=l$, each element of the covariance matrix cov (B_{ij}, B_{kl}) follows directly from the related element of cov (b_{ij}, b_{kl}), but when $i=j$ and $k \neq l$, or when $i \neq j$ and $k=l$ an additional factor $\frac{1}{2}$ must be used, and a factor $\frac{1}{4}$ when $i \neq j$ and $k \neq l$. In addition to transforming to main axes, we divide by $8\pi^2$, which yields the diagonal matrix U_{ij}. The values of the U_{ii} and of the directional cosines of these eigenvectors relative to the crystallographic axes are:

		a	b	c
$U_{11} = 0.02139$ Å^2	U_{11}	-0.0586	0.8801	0.0204
$U_{22} = 0.02285$	U_{22}	0.9359	-0.4692	0.3441
$U_{33} = 0.07161$	U_{33}	0.3474	0.0730	-0.9387

Note that these eigenvectors should form a right-handed system of axes for a proper connection with the sense of rotation around these eigenvectors.

The covariance matrix of the U_{ij} follows from that of the B_{ij} by equations (1) and (2). The result is given in the middle of Table 1. The final covariances between the V_i and V_j, the V_i and α_j, and the α_i and α_j, are shown in the bottom matrix of Table 1. The units for the different terms just enumerated are, respec-

tively, Å^4, Å^2.radian, and radian^2. Considering just the square roots of the diagonal terms of this matrix we find

$$V_1 = 0.0214 \pm 0.0006 \text{ Å}^2 \qquad \sigma(\alpha_1) = \pm\ 0.7°$$
$$V_2 = 0.0228 \pm 0.0007 \qquad \sigma(\alpha_2) = \pm\ 0.7$$
$$V_3 = 0.0716 \pm 0.0010 \qquad \sigma(\alpha_3) = \pm\ 19.$$

Of special note is the relatively large value of the standard deviation associated with α_3, which reflects the near equality of V_1 and V_2. We emphasize, however, that these standard deviations alone do not give the complete story, because the covariances are by no means negligible.

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The Crystal Structure of Benzamide

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The structure of benzamide has been refined using counter-measured intensity data (1037 planes). Libration corrections have been applied to the full-matrix least-squares refined parameters. The principal interatomic distances are C–C (mean benzene ring) 1·391 (5), C–O 1·249 (3), C–N 1·342 (3) and C–C (carboamide) 1·501(4) Å.

Previous work

Earlier determinations of the crystal structure of benzamide have been reported, by Penfold & White (1959) and Blake & Small (1959). Both of these were based upon two-dimensional photographically recorded data and are consequently, by present day standards, of limited accuracy. The results reported here are of a recent refinement making use of more extended experi-

mental data collected at the Chemistry Department, University of Birmingham.

Experimental

An evenly developed crystal of mean dimension 0·2 mm was grown from benzene solution and used for the experimental measurements. The crystal was mounted on the three-circle diffractometer of Small &

Table 1. *Observed and calculated structure factors*

Travers (1961) and the unit-cell dimensions were obtained from measurements of the θ values of all observable orders of 100, 010, 001, 101 and $10\bar{1}$ using Cu $K\alpha$ radiation ($\lambda = 1\cdot542$ Å). The following results were obtained:

$$a = 5\cdot607\ (2)\ \text{Å}$$
$$b = 5\cdot046\ (2)$$
$$c = 22\cdot053\ (8)$$
$$\beta = 90\cdot66\ (3)^{\circ}$$
$$D_{\text{obs}} = 1\cdot289\ \text{g.cm}^{-3}$$
$$\text{Space group } P2_1/c; \quad Z=4.$$

Using the same apparatus and radiation, 1037 integrated intensities were measured for which $\theta < 82^{\circ}$.

Refinement of the structural parameters

The starting point of the refinement was a set of positional parameters taken from one of the determina-

tions already referred to (Small & Blake, 1959). Isotropic B values of $3\cdot50$ Å^2 were used initially. These parameters were refined using the full-matrix anisotropic least-squares program *FMLS* of Bracher & Taylor (1967) which has been adapted for use on the ICL 1909 computer at Lancaster University. For these and all subsequent calculations, the atomic scattering factors listed in *International Tables for X-ray Crystallography* (1962) were used. At first the refinement included only carbon, nitrogen and oxygen atoms, but later an $F_o - F_c$ Fourier synthesis gave positions of all seven hydrogen atoms. Positional parameters and B values of $3\cdot50$ Å^2 for these hydrogen atoms were included but not refined in the next three least-squares cycles. Refinement of only the hydrogen positional parameters and individual isotropic B values was carried out for two cycles and finally, after two further cycles of refinement of the carbon, nitrogen and oxygen parameters, all parameter shifts were less than one twentieth of their estimated standard deviations. During the later cycles of refinement it had been noted that the calculated structure factor for $10\bar{4}$ was considerably greater (by 35%) than its observed value. As this was the most intense reflexion it was omitted from the refinement of the assumption that it was affected by extinction. The final R value was $0\cdot068$. A weighting factor $w = [1 + \{(F_o - 10\cdot0)/3\cdot0\}^2]^{-1/2}$ was used in the later stages of refinement. In Table 1 are listed the observed and calculated structure factors; the final positional parameters are recorded in Table 2 and the thermal vibration parameters in Table 3(a) and (b).

Table 2. *Fractional atomic co-ordinates and their standard deviations (in parentheses)* $\times 10^5$

	x	y	z
C(1)	82228 (53)	13046 (67)	19814 (14)
C(2)	65257 (60)	-6584 (66)	20369 (14)
C(3)	47837 (49)	-9500 (54)	15844 (13)
C(4)	47453 (42)	7294 (45)	10909 (11)
C(5)	64436 (52)	27025 (58)	10439 (13)
C(6)	84142 (53)	29596 (64)	14893 (16)
C(7)	28712 (44)	3114 (46)	6120 (11)
N	21997 (41)	24030 (42)	2826 (10)
O	19786 (36)	-19107 (34)	5309 (9)
H(1)	94496 (632)	15513 (717)	22906 (153)
H(2)	63774 (663)	81945 (748)	24069 (163)
H(3)	35705 (580)	76514 (652)	16391 (146)
H(4)	65244 (592)	37927 (698)	6838 (148)
H(5)	95051 (602)	43365 (744)	14257 (157)
H(6)	9287 (537)	23037 (631)	75 (136)
H(7)	25192 (553)	40960 (635)	4141 (139)

Interpretation of the thermal vibration parameters

On the assumption that the molecules in crystalline benzamide behave as rigid bodies, the thermal vibration may be described in terms of three tensors **T**, **ω** and **S**, as described by Schomaker & Trueblood (1968). The first two are, respectively, the translation and libration (angular vibration) tensors of Cruickshank (1956); the additional cross tensor **S** allows for the corre-

lation of translation and libration motions when the molecule is non-centrosymmetric.

The program *MGTL* of Gantzel & Trueblood (1970) was adapted for the ICL 1909 computer. With its aid the tensors **T**, ω and **S** were evaluated from the b_{ij} values of the final least-squares refinement. Values of these three tensors and their estimated standard deviations referred to orthogonal axes a, b, c^* are given in Tables 4, 5 and 6. The extent to which this rigid body model describes the atomic thermal vibration may be judged by converting the b_{ij} values from the least-squares refinement into the related U_{ij}'s and comparing these values with those calculated from the tensors **T**, ω and **S**, assuming rigid-body behaviour. The two sets of U_{ij} are given in Table 7. By comparison with the mean $\sigma(U_{ij})$ (0·0013 Å^2) calculated from the b_{ij} estimated standard deviations and the estimated standard deviation in U_{ij}'s calculated for the rigid-body model (0·0026 Å^2) it will be noted that the differences in the two sets of U_{ij} in Table 7 are not significant. The rigid-body model is therefore a reasonable description of the atomic thermal motion, and libration corrections to the atomic positions have been made; the corrected coordinates are given in Table 8.

Description and discussion of the structure

(a) Arrangement of molecules

The molecular arrangement is shown in Fig. 1. The hydrogen-bonding system consists of centrosymmetric pairs linked side by side to other pairs which are **b**-translation related. Infinite ribbons, two molecules wide, therefore extend along the **b** direction with the width of the ribbon roughly in the **c** direction. This type of

Table 4. *Rigid body translational tensor*

Elements ($T_{ij} \times 10^4$) of the mean square tensor (Å^2) and their standard deviations

11	22	33	12	13	23
441 (13)	346 (14)	515 (12)	15 (12)	−58 (12)	−68 (11)

Table 5. *Rigid body librational tensor*

Elements of ($\omega_{ij} \times 10^4$) the mean square tensor (rad^2) and their standard deviations

11	22	33	12	13	23
96 (9)	41 (4)	94 (9)	6 (3)	72 (8)	6 (3)

Table 6. *The cross tensor* **S**

Elements ($S_{ij} \times 10^6$)(rad. Å) and their standard deviations

1275 (770)	−332 (515)	−2790 (498)
−217 (302)	2121 (715)	−2094 (331)
567 (476)	3455 (536)	−3396 (2554)

hydrogen bonding in primary amides has been described by Leiserowitz & Schmidt (1969) as translation packing. In benzamide the hydrogen-bonded ribbons pack by stacking in an **a** translation sequence in one direction and by a **c** glide sequence in the other direction. Two ribbons, related by a screw axis parallel to their length, thus pass through each unit cell.

(b) Molecular dimensions and shape

The magnitudes and e.s.d.'s of the intramolecular distances and angles are given in Table 9 (based upon the coordinates in Table 8). In Table 10 are the deviations of the atoms from the 'best' plane defined by the

Table 3. *Temperature factors*

(a) b_{ij} values for C, N, and O atoms, exp $\{-10^{-5}(h^2b_{11}+k^2b_{22}+l^2b_{33}+hkb_{12}+hlb_{13}+klb_{23})\}$, with standard deviations (in parentheses).

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	3575 (99)	5010 (141)	287 (7)	345 (197)	−774 (43)	−423 (54)
C(2)	4606 (122)	4774 (143)	270 (7)	173 (215)	−690 (48)	196 (52)
C(3)	3540 (95)	3356 (105)	267 (7)	−319 (161)	−443 (40)	176 (43)
C(4)	2739 (77)	2756 (86)	204 (5)	338 (131)	−180 (31)	−304 (36)
C(5)	3675 (98)	4005 (117)	242 (6)	−1706 (173)	−184 (39)	−69 (44)
C(6)	3441 (102)	4824 (141)	320 (8)	−2107 (193)	−275 (45)	−480 (56)
C(7)	3002 (80)	2752 (89)	209 (5)	−49 (140)	−313 (33)	−134 (36)
O	3968 (86)	2826 (81)	240 (5)	−494 (132)	−632 (34)	39 (32)
H	4342 (78)	2466 (68)	305 (5)	−445 (115)	−931 (31)	−89 (30)

Table 3 (*cont.*)

(b) Isotropic B values (Å^2) for H atoms, with standard deviations (in parentheses).

	B
H(1)	4·103 (792)
H(2)	4·724 (836)
H(3)	3·342 (692)
H(4)	3·616 (723)
H(5)	4·459 (824)
H(6)	2·806 (635)
H(7)	3·384 (665)

seven carbon atoms. It will be noted that the benzene ring does not deviate significantly from planarity nor regularity and that the mean C–C distance, 1·391 Å, is quite typical of values found in other aromatic compounds. The deviations of the nitrogen and oxygen atoms from the plane of the seven carbon atoms indicate a relative twist of 24·6° of the amide group about the C(4)–C(7) bond relative to the benzene ring. In the carboamide group, the deviations of the atoms from the 'best' plane defined by C(4)C(7)ON show

Table 7. *Values of* $U_{ij} \times 10^4$ *(Å²) (a) from b_{ij} values, (b) from rigid body model*

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
C(1)	575	569	646	639	707	710	26	20	−251	−215	−119	−133
C(2)	622	660	616	616	665	671	12	7	−224	−244	55	33
C(3)	567	560	433	451	658	623	−23	−16	−147	−168	50	51
C(4)	438	442	356	339	503	510	25	13	−62	−55	−86	−65
C(5)	587	532	517	502	596	610	−122	−115	−65	−66	−19	−47
C(6)	550	559	622	647	788	762	−149	−136	−95	−148	−135	−98
C(7)	480	504	355	322	515	533	−3	1	−104	−100	−38	−43
N	637	678	365	378	591	583	−36	−37	−205	−171	11	25
O	696	677	318	334	751	770	−32	−34	−300	−286	−25	−29

Table 8. *Libration corrected atomic coordinates for C, N and O atoms* $\times 10^5$ *(referred to same origin and axes as Table 2)*

	x	y	z
C(1)	82317	13088	19838
C(2)	65250	−6702	20412
C(3)	47784	−9634	15874
C(4)	47452	7303	10908
C(5)	64538	27189	10422
C(6)	82290	29770	14889
C(7)	28658	3094	6105
N	21945	24192	2797
O	19697	−19301	5298

Table 9. *Bond distances and angles*

(a) Intramolecular distances (after libration correction) and their standard deviations in parentheses (Å).

C(1)–C(2)	1·390 (5)	C(1)–H(1)	0·96 (3)
C(2)–C(3)	1·400 (5)	C(2)–H(2)	0·99 (4)
C(3)–C(4)	1·389 (4)	C(3)–H(3)	0·98 (3)
C(4)–C(5)	1·392 (4)	C(5)–H(4)	0·96 (3)
C(5)–C(6)	1·398 (5)	C(6)–H(5)	1·00 (4)
C(6)–C(1)	1·378 (5)	N——H(6)	0·93 (3)
C(4)–C(7)	1·501 (4)	N——H(7)	0·91 (3)
C(7)–N	1·342 (3)		
C(7)–O	1·249 (3)		

(b) Bond angles (after libration correction) and their standard deviations in parentheses (°).

C(2)–C(1)–C(6)	121·1 (3)	H(1)–C(1)–C(2)	120 (2)
C(3)–C(2)–C(1)	119·2 (3)	H(1)–C(1)–C(6)	118 (2)
C(4)–C(3)–C(2)	120·1 (3)	H(2)–C(2)–C(3)	117 (2)
C(5)–C(4)–C(3)	120·1 (3)	H(2)–C(2)–C(1)	125 (2)
C(6)–C(5)–C(4)	119·8 (3)	H(3)–C(3)–C(2)	118 (2)
C(1)–C(6)–C(5)	119·7 (3)	H(3)–C(3)–C(4)	122 (2)
C(7)–C(4)–C(3)	118·2 (2)	H(4)–C(5)–C(4)	120 (2)
C(7)–C(4)–C(5)	121·7 (2)	H(4)–C(5)–C(6)	119 (2)
N——C(7)–C(4)	117·5 (2)	H(5)–C(6)–C(5)	118 (2)
O——C(7)–C(4)	120·5 (2)	H(5)–C(6)–C(1)	122 (2)
O——C(7)–N	122·1 (2)	H(6)–N——C(7)	121 (2)
		H(6)–N——H(7)	115 (3)
		H(7)–N——C(7)	120 (3)

Table 10. *Deviations of atoms from the 'best' plane defined by the carbon atoms (referred to orthogonal axes a, b, c*) (Å)*

$0·6015x - 0·6322y - 0·4884z = 0·1865$

C(1)	0·0047	H(1)	0·003
C(2)	−0·0023	H(2)	−0·089
C(3)	−0·0020	H(3)	−0·024
C(4)	−0·0109	H(4)	0·057
C(5)	−0·0160	H(5)	0·078
C(6)	0·0123	H(6)	−0·616
C(7)	0·0143	H(7)	−1·096
N	−0·5238		
O	0·5147		

Table 11. *Deviations of atoms from the 'best' plane defined by C(4), C(7), O and N (referred to orthogonal axes a, b, c*), (Å)*

$0·7167x - 0·2103y - 0·6649z = 0·2105$

C(4)	−0·006	N	−0·006
C(7)	0·0019	H(6)	−0·093
O	−0·0007	H(7)	−0·248

Table 12. *Hydrogen-bonded distances and angles (with standard deviations in parentheses)*

Distances (Å)

N^i···O^{iii}	2·933 (3)	H(6^i)···O^{iii}	2·01 (3)
N^i···O^{ii}	2·907 (3)	H(7^i)···O^{ii}	2·05 (3)

Angles (°)

N^i–H(6^i)–O^{iii}	176 (3)	C(7^{iii})–O^{iii}–H(6^i)	119 (2)
N^i–H(7^i)–O^{ii}	158 (3)	C(7^{ii})–O^{ii}–H(7^i)	148 (2)
		H(7^i)–O^{ii}–H(6^{iv})	88 (3)

The labelling code for the symmetry related atoms (see also Fig. 1) is:

Coordinates	Superscript
$x, \quad y, z$	i
$x, 1+y, z$	ii
$\bar{x}, \quad \bar{y}, \bar{z}$	iii
$\bar{x}, 1-y, \bar{z}$	iv

that apart from H(7), which is significantly out (0·25 Å), this group is planar.

The relative twists of the benzene ring and the amide group in the benzamide molecule may arise either from repulsion effects within the molecule or from repulsion between adjacent molecules brought close together by hydrogen bonding. Penfold & White (1959) consider the former effect to be predominant whilst

Lieserowitz & Schmidt (1969) attribute a large part of the rotation to the latter intermolecular effects. Both of these conclusions were based upon the results of the earlier two-dimensional determination of Penfold & White from which hydrogen-atom positions were not obtained. From the results of the present work, the internal close approach between hydrogen atoms H(4) and H(7) is 2·32 (5) Å whilst the shortest side to side distances between adjacent b-translated molecules are 2·86 (5) Å between H(3^{ii}) and H(5^i) and 3·26 (3) Å between H(3^{ii}) and C(5^i) (see Table 12 for nomenclature). The usual van der Waals distances to be expected in this type of compound are H$\cdots$H 2·10 Å and C$\cdots$H 2·85 Å (Bondi, 1964). The results obtained

here therefore support the view that the benzamide molecule is non-planar primarily on account of the repulsion between the amide hydrogen H(7) and the *ortho* hydrogen H(4).

The lengths of the C–N and C–O bonds within the amide group are separately within the range of values observed for these bonds in other amides. Although some variation in lengths of these bonds does appear to occur amongst the amide structures reported so far, a detailed comparison will be possible only when more extensive libration corrected data is available.

(*c*) *Hydrogen bonding*

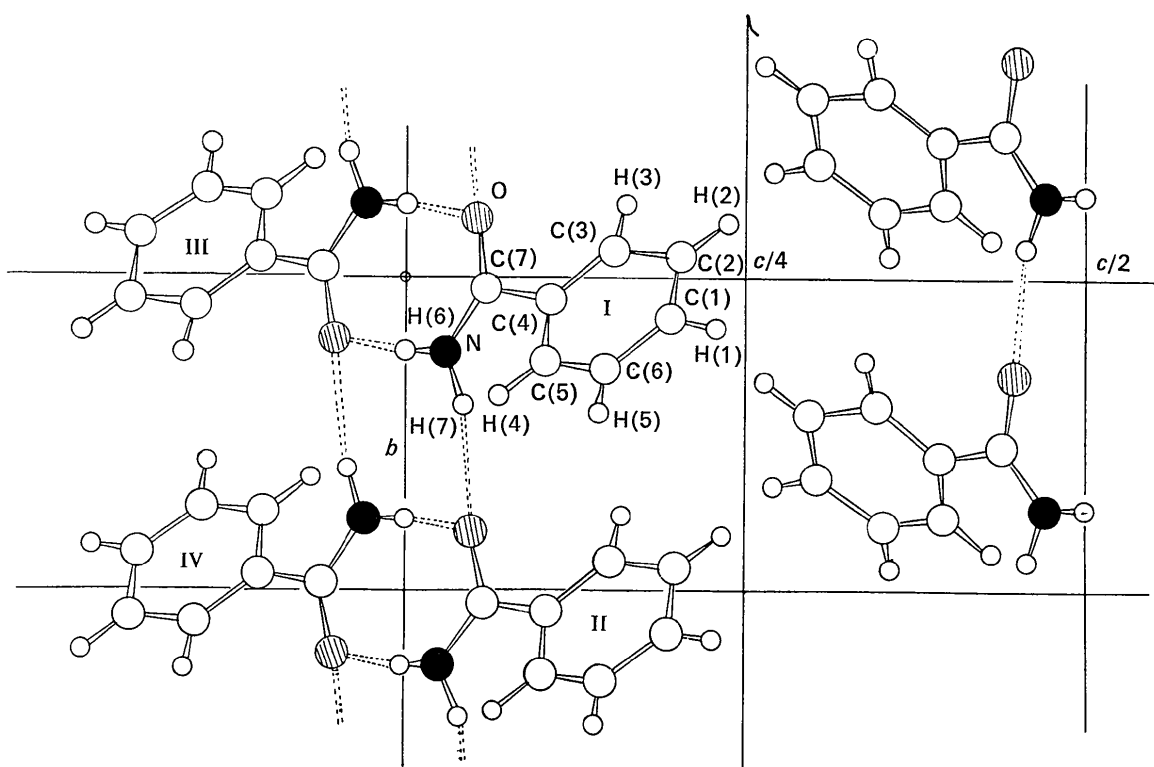The general features of the hydrogen-bonding system

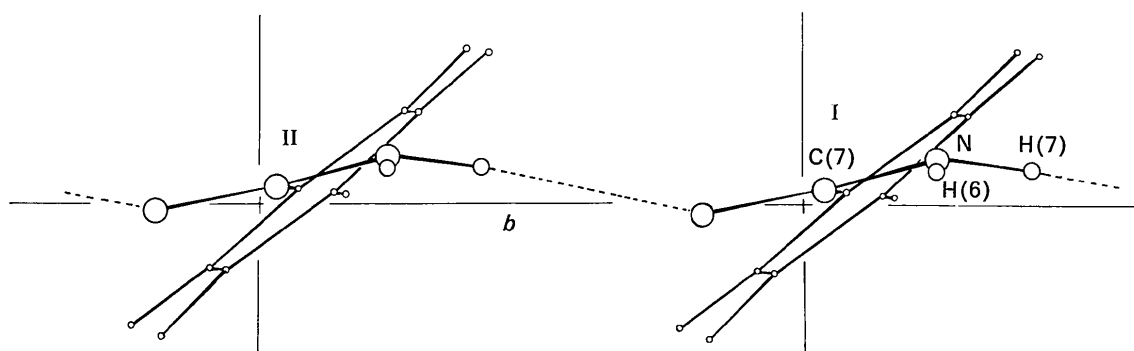Fig. 1. Molecular arrangement. Projection down *a* axis.

Fig. 2. Part projection down [10$\bar{4}$], centro-symmetric molecules omitted.

have already been described. The distances and angles involved in these bonds are summarized in Table 12. Hydrogen bonding across the centre of symmetry is nearly planar with a separation of the mean planes of the amide groups of 0·37 Å and the hydrogen bonds are effectively linear (Table 12). Between molecules related by b translation the bonding deviates markedly from planarity as shown in Fig. 2, the separation of the mean planes of the amide groups is 1·15 Å. This hydrogen bond is far from linear (Table 12). It is of interest to note from Fig. 2 that the bending of the hydrogen atom H(7) out of the amide plane (away from H(4) brings it more into line with the N^i-O^{ii} direction.

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The Effect of Molecular Vibrations on Apparent Bond Lengths. III. Diatomic Molecules

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A study is made of the effect of the nuclear vibrational motion on the charge density for the isoelectronic series BF, N_2, and CO. Although there are no measurable changes in the positions of the maxima in their dynamic charge densities, there is a reduction in the charge density at these maxima. A simple model for diatomic molecules is introduced to estimate the magnitude of any shift in position and thus any apparent change in bond length. The bond length here is taken to be the distance between the maxima in the charge density such as would be inferred from X-ray measurements. A test of this model on LiH gives a predicted shift of 0·018 a_0 whereas the convolution approximation gives a shift of 0·02 a_0. The variation of shift with vibrational amplitude is also investigated. In this approximation a method is suggested in which one could use the vibrational amplitude and the measured bond shortening to estimate the degree of asphericity in the charge density at the nucleus.

Introduction

In a previous paper (Coulson & Thomas, 1971, which henceforth will be referred to as I), it was shown that some of the differences between the bond lengths measured by X-ray and neutron diffraction methods (Coppens, 1970) can be accounted for by considering the effect of the vibrational motion on the static molecular charge density. Moreover, it was seen in I that a convolution approximation appeared to describe this dynamic charge density adequately near a nucleus. For simple covalent molecules involving hydrogen in

which the $1s$ electrons take part in bonding, the effect was significant. This was shown to be the case for diatomics such as H_2 and H_2^+ in I where bond shortenings of 0·1 a_0 were possible and also for simple polyatomics such as water (paper II, Thomas, 1971). However, in other diatomics such as N_2, the $1s$ electrons are not valence electrons and so are not involved in bonding to any great extent. Thus the asphericity in the charge density near the nucleus will be quite small. However, if one looks along the bond axis, there is considerable charge build-up over free spherical atoms both farther into the bond due to the bonding electrons and also farther out of the bond due to the lone pairs. This shows up quite clearly on the difference density map (Bader & Henneker, 1967). Thus it would be

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