REVIEWS OF MODERN PHYSICS VOLUME 30, NUMBER 1 JANUARY, 1958

Some Electron Distribution Determinations by X-Ray Diffraction

W. Cochran
Cavendish Laboratory, Cambridge, England

1. MEASUREMENTS OF X-RAY INTENSITIES

THE measurements on which results reported in this paper are based were made using a counter diffractometer, and Cu or Mo characteristic radiations. Preliminary measurements were usually made photographically. The accuracy of the measurements is limited usually not by statistical fluctuations of counts recorded, but rather by extinction (especially in NH_4HF_2) and by double reflection (especially in LiH). It is thought however that the standard deviations of the values of $F^2(hkl)$ finally adopted did not exceed 4%, and were under 2% for the data from LiH. Measurements were put on an absolute scale by comparison of intensities from a cylindrical specimen of the material under investigation with intensities from a cylinder of NaCl. Balanced filters were used when necessary to cut out unwanted wavelengths. We are currently modifying the apparatus to use scintillation rather than Geiger counters. This will increase counting efficiency, practically eliminate corrections for nonlinear response, and should make it possible to dispense with filters (Calder, unpublished).

The first uses of this apparatus, made some six years ago, were made in order to determine the tautomeric forms of such molecules as adenine (Cochran, 1951)* and α-pyridone (Penfold, 1953) by locating hydrogen atoms in the crystal. It became clear that if the measured electron densities were to be given any but the most qualitative interpretation, the simplest molecules and crystals should be chosen for study. More recently therefore we have investigated the distributions in salicylic acid (Cochran, 1953), NH_4HF_2 (McDonald, unpublished), LiH (Calder and Cochran, unpublished), and potassium hydrogen maleate (Darlow and Cochran, unpublished). Results which have already been published will not be discussed here in any detail.

2. MEASUREMENTS ON NH_4HF_2

These were made using five different cylindrical crystals of diameters ranging from 0.16 mm to 0.37 mm. Counter measurements were made, using Cu radiation, of 169 independent reflections having $\lambda^{-1}\sin\theta \leqslant 0.55$. This range was extended by photographic recording, using Mo radiation.

Crystals of NH_4HF_2 are orthorhombic, space group *Pman*, with $a=8.408$, $b=8.163$, and $c=3.670$ A. The crystal structure was first determined by Pauling (1933), and a redetermination of atomic coordinates was made by Rogers and Helmholtz. The structure is completely determined by hydrogen bonds, with the ammonium ion making four bonds to neighboring fluorines of length 2.797 (twice) and 2.821 A (twice). The next nearest fluorines are at 3.028 and 3.106 A. These values have a standard deviation of 0.0025 A. There are two nonequivalent (FHF) ions in the unit cell, although they are not related by symmetry their environments are closely similar (Fig. 1). The FF bond lengths are 2.275 and 2.271 A with a standard deviation of 0.005 A. The electron density was investigated by calculating difference densities, that is, spherically symmetrical distributions corresponding to unbonded fluorine and nitrogen atoms were subtracted by calculating

$$\rho_0-\rho_c=\frac{1}{V}\sum_{hkl}(F_0(hkl)-F_c(hkl))\times\cos 2\pi(hx/a+ky/b+lz/c).$$

The difference density was made as flat as possible near the centers of nitrogen and fluorine atoms by choosing the atomic coordinates and anisotropic temperature factors with this aim in view. The temperature factor for nitrogen (Debye-Waller factor $=\exp(-B\lambda^{-2}\sin^2\theta)$) was found to be $B_N=1.88$ A^2. That of the attached hydrogens was guessed as $B_H=2.4$ A^2. The thermal vibrations of the fluorine atoms are markedly anisotropic. Calling the two fluorines not related by symmetry F_1 and F_2, the values of B corresponding to the principal axes of the ellipsoid of thermal vibration are

	B_1	B_2	B_3
F_1	1.88	1.71	3.70 A^2
F_2	1.94	1.78	3.76 A^2.

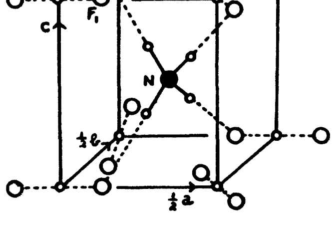


FIG. 1. Arrangement of atoms in NH_4HF_2. Hydrogen bonds dotted.

---

* See Bibliography at end of paper for references.

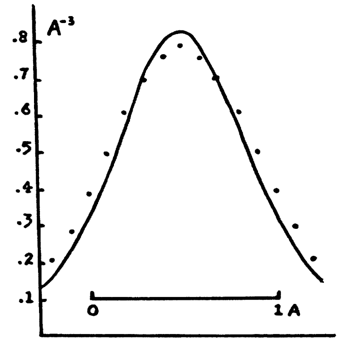


FIG. 2. A comparison of the electron distribution in the hydrogen atoms of the ammonium ion with that of an isolated (1*s*) hydrogen.

Each fluorine makes one hydrogen bond to fluorine, and two to nitrogen, and the three bonds are roughly coplanar. In each case a small value of $B(\sim 1.75)$ is associated with the FF direction, and a larger value (~ 3.73) with a direction perpendicular to the plane of the bonds.

The standard deviation of the electron density varies from about 0.06 A^{-3} in general positions to 0.11 A^{-3} in special positions. When the nitrogen distribution was subtracted, peaks of height 0.76 (twice) and 0.79 A^{-3} (twice) remained at distances of 0.879 and 0.875 A from the center of the nitrogen. These distances have a standard deviation of about 0.033 A, so the average is significantly less than the expected internuclear distance of 1.025±0.005 A (Gutowsky *et al.*, 1949). Apart from this inward movement of the charge distribution, the agreement with that expected for an isolated hydrogen (1*s*) distribution is remarkably close (Fig. 2), if one takes $B_H = 2.4\ A^2$. The hydrogen peaks lie (Fig. 3) on the lines NF within experimental error. The numbers of electrons within spheres of radii 1.1 A is 0.78 and 0.79 for the two ammonium hydrogens not related by symmetry; the corresponding figure for an unbonded atom is 0.757. The hydrogen peaks in the two unrelated (FHF) ions occur on centers of symmetry and are spherically symmetrical within the rather wide limits of error (Fig. 4). Their peak densities are 0.47 and 0.52 A^{-3} (standard deviation, 0.11 A^{-3}) so that the average is possibly significantly less than in an isolated hydrogen atom, but in the circumstances it is impossible to say what the value of B for hydrogen may be. The numbers of electrons within spheres of radii 1.1 A are 0.91 and 0.67, respectively (cf. 0.757 for an isolated hydrogen atom). Attempts to determine the state of ionization of the nitrogen and fluorine ions were not conclusive. The difference between an electron loosely associated with each (FHF) and the same number of electrons uniformly distributed through the unit cell must be below the limit of experimental error. This appeared to be confirmed by a rough calculation in which the F^- distributions were taken to be those appropriate to isolated atoms.

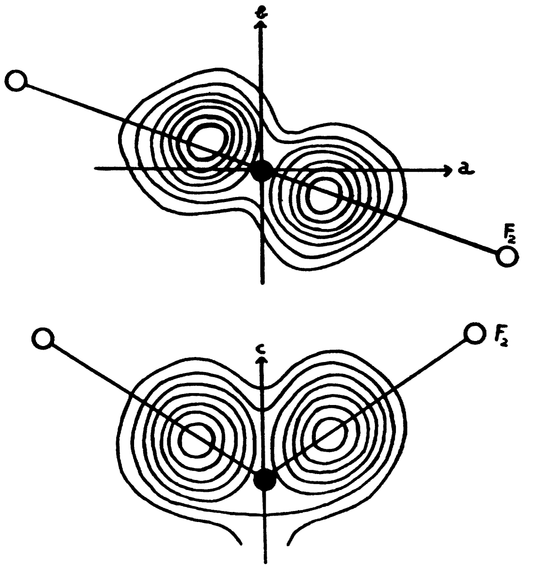


FIG. 3. Horizontal and vertical sections (relative to Fig. 1) through the electron distribution in the ammonium ion, with the nitrogen subtracted out. Contours every 0.1 A^{-3}.

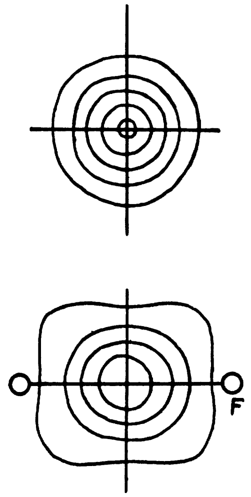


FIG. 4. Sections through the electron distribution in the bifluoride ion, with the fluorines subtracted out. Contours every 0.1 A^{-3}.

No calculation of the electron distribution in the $(FHF)^-$ ion has yet been made, but the experimental results obviously do not agree with the idea that the most important contributary resonance structure is $F^-\ H^+\ F^-$. That the ammonium ion is closely a superposition of spherically symmetrical nitrogen and hydrogen distributions contradicts the conclusions of Banyard and March (1956), who calculated the electron distributions in H_2O, NH_3, and CH_4 using central field analytic wave functions which correspond to neon-like configurations, and found that their results agreed quite well with experimental measurements of x-ray diffraction by these gases, measurements of doubtful accuracy however.

3. LITHIUM HYDRIDE

This has the rock-salt structure, with $a = 4.08$ A. Single crystals of suitable shape can be prepared, and have to be protected from the atmosphere by a thin layer of grease. Measurements were made on some half-dozen specimens, using Cu and Mo characteristic radiations. A number of x-ray studies of this substance have been made (see Ahmed, 1951) but in no instance was the accuracy of measurement great enough to justify the conclusions drawn. We realized at the outset that it was unlikely that the actual distribution could be described adequately by either of the classical pictures of ionized or un-ionized atoms; these however provide convenient models with which the measured distribution can be compared. The measured F values fell nicely on two smooth curves, and using the result

$$F_{\text{even indexes}} = f_{\text{Li}} + f_{\text{H}}$$

and

$$F_{\text{odd indexes}} = f_{\text{Li}} - f_{\text{H}},$$

empirical f-curves for Li and H were derived. That for lithium agreed excellently with that calculated from the Li electron distribution of Fock and Petrashen (1934), if B_{Li} was taken to be 1.00 A². The theoretical f curves for Li and Li^+ are virtually identical beyond $\lambda^{-1}\sin\theta = 0.2\,(\Delta f/f < 1\%)$, and whichever is used does not affect the derived value of B_{Li} appreciably. A difference density section in the (100) plane has been calculated, i.e., with the $\text{Li}(1s)^2$ distribution subtracted out. As anticipated, this density is everywhere greater than zero, so that no unambiguous division of the electrons between Li and H is possible. The peak density at the hydrogen nucleus is 1.20 A^{-3} (standard deviation 0.03 A^{-3}), falling to a minimum of 0.045 A^{-3} midway on the line joining adjacent hydrogens and having a slightly higher value of 0.07 A^3 at the lithium nucleus. Before one can say what charge has been transferred from lithium to hydrogen one must define the way in which the transfer is to be measured. We have done this in two ways:

TABLE I.

	Experimental	Isolated atoms	Isolated ions	E and S	L
N_{H}	1.46±0.01	1.35*	1.42	1.35	1.30
N_{Li}	0.54±0.01	0.65	0.58	0.65	0.70

(a) Equal volumes of $(2.04)^3$ A³ are associated with H and with Li, and the numbers of electrons (excluding $\text{Li}(1s)^2$) inside each cube evaluated. This can be done directly from the F's without calculating the electron density (see Table I). The results for "atoms" and "ions" were calculated assuming $B_{\text{H}} = B_{\text{Li}} = 1.0$ A², but are nearly independent of B values. (If, for example, one takes $B_{\text{H}} = B_{\text{Li}} = 0$, then 1.35* in Table I becomes 1.37.) The fourth column gives the results of Ewing and Seitz (1936), who obtained an approximate solution of the Hartree-Fock equations for the crystal. The fifth column gives the results of Lundquist (1954) who used the molecular-orbital approach.

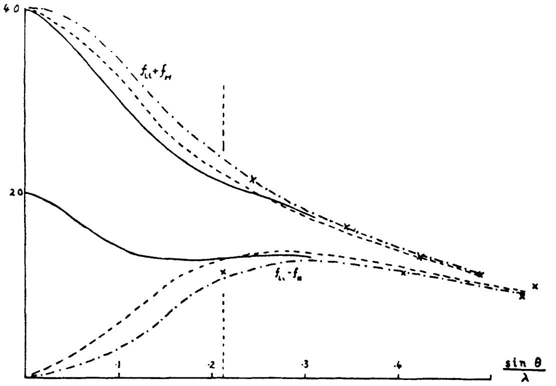


FIG. 5. Scattering factor curves for lithium hydride. Full line; neutral atoms. Broken line; complete ionization. Dotted line; complete ionization, overlap included. (From the calculations of Waller and Lundquist.) Crosses; experimental points. Vertical broken line denotes limit of experiment.

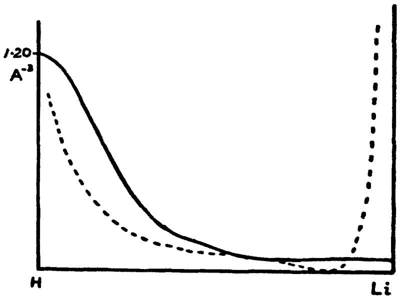
(b) The charge transferred can also be assessed from the density at the hydrogen nucleus. The density at this point calculated for the simple models is however dependent on the value of B_{H}. Metallic hydrides which have been studied by neutron diffraction (NaH, ZrH_2, ThH_2) show $B_{\text{H}} \simeq B_M$, and a value in LiH of B_{H} between 1.0 A² and 2.0 A² probably nearer the former, seems certain. (We hope to check this and other points by neutron diffraction.)

	Experimental	Isolated atoms		Isolated ions	
		$B_{\text{H}}=1.0$	$B_{\text{H}}=2.0$	$B_{\text{H}}=1.0$	$B_{\text{H}}=2.0$
$\rho =$	1.20±0.03 A^{-3}	1.14+0.09	0.89+0.09	0.98+0.03	0.76+0.03

(Corrections such as +0.09 allow for overlap of nearest neighbors.)

Clearly, from these two tables, the "atoms" or "ions" pictures fit the results equally well or equally badly. There are more electrons near the nucleus of H than for "atoms," but the peak density is higher than for "ions." This agrees qualitatively with the calculations of Waller and Lundquist (1953), in fact our measured F values agree quite well (Fig. 5) with their calculated ones if one takes $B_{\text{H}} = 1.0$ A². There is virtually no agreement (Fig. 6) between a line section through the measured density along a crystallographic axis and that calculated for this direction by Ewing and Seitz.

FIG. 6. Full line; section through the measured density in lithium hydride along (100), with lithium subtracted out. Broken line; corresponding result from the theory of Ewing and Seitz.



A recalculation of the density in LiH by self-consistent field methods would be of interest.

4. ELECTRON DISTRIBUTION IN BONDED HYDROGEN

McDonald (1956) has pointed out that the electron densities in the hydrogen atoms, not only of NH_4HF_2 but of a variety of organic compounds, agree rather well with that for a (1*s*) hydrogen. For example in salicylic acid the mean density at the center of a hydrogen attached to the benzene ring is 0.77 A^{-2} and the mean number of electrons within a circle of radius 1.1 A is 0.92. The corresponding values for an isolated hydrogen, with the same B as adjacent carbons, are 0.68 A^{-2} and 0.84. The writer has attempted to explain this and other features of the measured difference density by calculating a difference density for benzene using a molecular-orbital approximation (Cochran, 1956). Possible polarization of CH bonds was not allowed for, and effective nuclear charges in the molecule were taken to be the same as for Slater atomic orbitals. Temperature factor was allowed for only by having the molecule move as a rigid unit. Quite good agreement was obtained in this way with the measured difference density in salicylic acid. In particular the calculated peak density of hydrogen was closely the same as is observed, and the difference density at the center of a CC bond agreed with measured values (about 0.2 A^{-2}). There was some disagreement elsewhere, particularly at the center of the benzene ring for which experiment gives a difference density of -0.4 A^{-2} while calculation gives zero. However, neutron diffraction shows that hydrogens attached to a benzene ring have a considerably larger value of B than adjacent carbons (Bacon, private communication). The fact that despite this, x-ray diffraction gives a peak density in hydrogen, greater than for an isolated atom with the same B as the carbons, and about the same as a "molecular-orbitals hydrogen" with the same B as the carbons, is puzzling. It could be due to the effective nuclear charge of bonded hydrogen being considerably greater than unity, or to the electrons near the hydrogen nucleus not sharing fully the thermal movement of the latter when that of the adjacent nucleus is small. In calculating the electron density of such a molecule in the future, this is a point deserving investigation. There are advantages in presenting the results of such calculations in the form of a map of difference density; for one thing theory and experiment now agree that the molecular density differs by a comparatively small amount from a superposition of atomic densities.

BIBLIOGRAPHY

M. S. Ahmed, Phil. Mag. **42**, 997 (1951).
K. E. Banyard and N. H. March, Acta Cryst. **9**, 385 (1956).
W. Cochran, Acta Cryst. **4**, 81 (1951).
W. Cochran, Acta Cryst. **6**, 260 (1953).
W. Cochran, Acta Cryst. **9**, 924 (1956).
D. H. Ewing and F. Seitz, Phys. Rev. **50**, 760 (1936).
V. Fock and M. J. Petrashen, Physik. Z. Sowjetunion **8**, 547 (1935).
Gutowsky, Kistiakowsky, and Pake, J. Chem. Phys. **17**, 972 (1949).
S. O. Lundquist, Arkiv. Fysik **8**, 177 (1954).
T. R. R. McDonald, Acta Cryst. **9**, 162 (1956).
L. Pauling, Z. Krist. **85**, 380 (1933).
B. R. Penfold, Acta Cryst. **6**, 591 (1953).
I. Waller and S. O. Lundquist, Arkiv. Fysik **7**, 121 (1954).