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The Electron Distribution in the Ammonium Ion

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Recent X-ray results of McDonald on the electron distribution in ammonium bifluoride may be summarized in terms of a model in which the electron density in the ammonium ion is represented to reasonable accuracy as a central spherical charge cloud containing six electrons around the N nucleus, plus four unperturbed hydrogen electron distributions centred not on the protons but inwards along the N–H bonds.

It is shown that the spherical average of the density in NH_4^+, calculated by Bernal & Massey (1954) in connection with their work on metallic ammonium, may be well represented by the above model. However, it appears necessary to place the hydrogen distributions at a distance from the N nucleus which is (0.76 ± 0.06) of the N–H separation, compared with McDonald's value of (0.86 ± 0.03).

1. Introduction

McDonald (1960) has recently reported results on the electron distribution in ammonium bifluoride, obtained by a three-dimensional X-ray analysis. From this work an electron distribution for the ammonium ion emerged, which may be described as follows. The N nucleus is surrounded by a spherical distribution of charge, but the 'atom' is electron-deficient, and in keeping with the findings of McDonald we shall take this distribution to contain very nearly six electrons. To this density, McDonald suggests that one should add four hydrogen atoms, with assumed unperturbed density distributions, but rather than centring these on the H nuclei, they should be moved inwards along the N–H bonds, to a distance of (0.86 ± 0.03) of the internuclear separation.

The object in this paper is to compare this model, which emerges from experiment, with available theoretical data. The present approach is closely connected with our earlier work on the series of 'neon-like' molecules Ne, H_2O, NH_3 and CH_4 (Banyard & March, 1956; see also later work by us on H_2O, 1957; by Carter, March & Vincent, on H_2, 1958, and by Banyard, 1960, on diamagnetism).

In this work, it was pointed out that, for scattering from gases of such molecules, all that could be obtained with the present experimental accuracy was information on the spherical average density. This, it was suggested, could be found theoretically in these molecules by averaging the nuclear field over angles before calculating the electronic wave functions. McDonald, in his work, has pointed out the interest in comparing the spherical average of the electron density obtained by such a method with his X-ray findings, and this is the aim of the present paper.

2. Theoretical results for spherical average of electron density in NH_4^+

For the electron distribution in the ammonium ion, there are at present two calculations, as far as we are aware, which make any claim to accuracy. These are an analytical treatment of Bernal (1953) and a Hartree field calculation of Bernal & Massey (1954), carried out as a preliminary step in the investigation of the properties of metallic ammonium. From comparable work on CH_4 (§ 5) it seems clear that the latter density is the more accurate, even though, unlike the analytical calculation, it is based on a product wave function rather than a determinantal one, and therefore neglects exchange effects. There is the further complication that the calculation of Bernal & Massey was carried out for an N–H distance of 0·97 Å, whereas McDonald quotes a figure of 1·025 Å in his work. Since it would be very laborious to repeat the self-consistent field calculation for another N–H distance, we shall content ourselves with an analysis of available results for this smaller internuclear separation. It seems clear, however, that it cannot markedly affect our essential findings.

The radial distribution given by the Hartree calculation is plotted in curve 1 of Fig. 1 and for comparison Bernal's density using analytical wave functions is also shown in curve 2.

3. Analysis of theoretical charge distribution

In the light of McDonald's findings, we begin the analysis by subtracting out of the Bernal–Massey density that due to a N atom with one $2p$ electron removed. This latter distribution (see curve 3 of Fig. 1) was obtained from the work of Hartree & Hartree

(1948) in which exchange is included and the results of the subtraction are plotted in curve 4 of Fig. 1. This distribution will now be compared with the spherical density contributed by four unperturbed hydrogen atoms, the position of the H atoms relative to the N nucleus being regarded, at this stage, as a parameter.

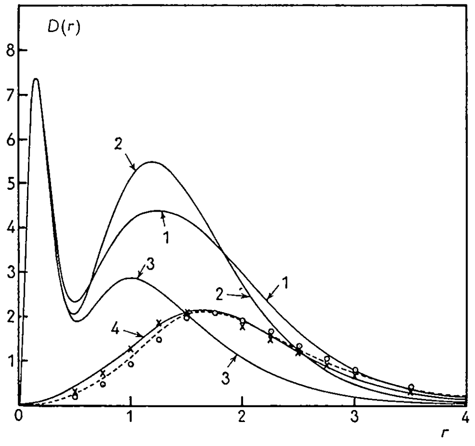

Fig. 1. Radial density distributions. Curve 1: Bernal–Massey results for NH_4^+. Curve 2: Bernal results for NH_4^+. Curve 3: Hartree density in N atom, after removal of one 2*p* electron. Curve 4: Density obtained by subtracting curve 3 from curve 1.

Hydrogen distributions are indicated as follows:

× $r_0 = 1{\cdot}3$. Broken curve $r_0 = 1{\cdot}4$. ⊙ $r_0 = 1{\cdot}5$.

The averaging of an electron density given in atomic units by

$$\pi^{-1} \exp(-2r)\,, \qquad (1)$$

about a new origin at a distance r_0 from the centre of this spherical charge cloud, may be achieved in closed form and the radial charge distribution $D_{4\mathrm{H}}(r)$ for the four H atoms is

$$D_{4\mathrm{H}}(r) = 2r/r_0[\{2(r-r_0)+1\} \exp\{2(r_0-r)\} - \{2(r+r_0)+1\} \exp\{-2(r_0+r)\}]\,, \qquad (2)$$
$$\text{for} \quad r > r_0\,.$$

For $r \leq r_0$, r and r_0 must be interchanged inside the square brackets.

Results for $r_0 = 1{\cdot}3$, $1{\cdot}4$ and $1{\cdot}5$ are shown in Fig. 1 for comparison with curve 4. It will be seen that there is remarkable agreement both in general shape and in the height of the maximum. Detailed inspection shows that for $r_0 = 1{\cdot}3$ the results fall very closely on curve 4 in the region of the maximum of the N 'ion' curve (~ 1 atomic unit).

4. N 'ion' density and McDonald's empirical scattering factor

So far, of course, our analysis has rested on the assumption of the N 'ion' density shown in curve 3 of Fig. 1. We must now consider whether this is acceptable in the light of the empirical scattering factor given by McDonald (see Table 5 of his paper). The theoretical scattering factor is obtained in terms of the electron density $\varrho(r)$ from the formula

$$f = \int_0^\infty 4\pi r^2 \varrho(r) \sin \varkappa r/\varkappa r\, dr : \varkappa = 4\pi \sin\theta/\lambda\,, \qquad (3)$$

θ being as defined by McDonald. The results are shown by the crosses in Fig. 2, together with McDonald's curve and that of Berghuis *et al.* (1955) for the neutral N atom (curve 2). In the region of the scattering curve ($\sin\theta/\lambda < 0{\cdot}15$) most sensitive to the distribution of the electrons around the maximum of the N 'ion' charge cloud, it will be seen that the theoretical results lie significantly below McDonald's curve and this is interpreted to mean that the Hartree N 'ion' density used is too diffuse.

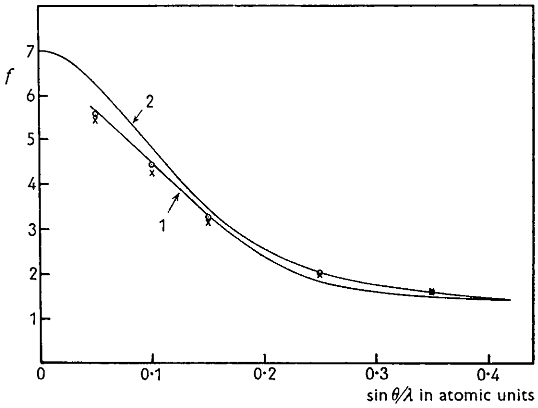

Fig. 2. Scattering factors for N 'ion'. Curve 1: McDonald's results. Curve 2: Berghuis *et al.* (1955) results for N atom. × Hartree N 'ion' results. ⊙ N 'ion' density corresponding to $r_0 = 1{\cdot}4$.

To proceed further, we have examined the less diffuse N 'ion' densities obtained by subtracting the results for the averaged H density for $r_0 = 1{\cdot}4$ and $1{\cdot}5$ from the Bernal–Massey distribution (the $r_0 = 1{\cdot}3$ results can be seen from Fig. 1 to lead to the Hartree N 'ion' density of curve 3 around the maximum at 1 atomic unit and will not therefore be considered separately). This procedure leads to significantly improved results for the scattering factor for $\sin\theta/\lambda < 0{\cdot}15$ as can be seen from Fig. 2, but at the expense of a slight difficulty which we must now consider. This difficulty arises because the fall-off of the H density given in equation (2) is, for large r, slower than that of the Bernal–Massey distribution for NH_4^+. The H densities for $r_0 = 1{\cdot}3$, $1{\cdot}4$ and $1{\cdot}5$ are found to cross the Bernal–Massey curve at 3·5, 3·2 and 3·0 atomic units respectively. To avoid the physical difficulty of negative density associated with the central atom, we have made the N 'ion' density zero outside these cross-over points; however the densities here are very small. Nevertheless, as a quantitative measure of this effect, we note that for $r_0 = 1{\cdot}3$, 1·4 and 1·5 the charge normalization of the N 'ion' densities obtained by this subtraction procedure is 6·05, 6·07 and 6·11 respectively. Exploratory calculations for $r_0 = 1{\cdot}6$ and 1·7 yield normalization factors of 6·18 and 6·28; McDonald quotes a figure of 6·1 electrons for the total charge in the central ion, by extrapolation of his scattering curve. This suggests that $r_0 = 1{\cdot}6$ and 1·7 should be excluded and this is confirmed below by further consideration of the scattering curve.

The density obtained from the $r_0 = 1{\cdot}4$ distribution was used to calculate the scattering factor and the values are shown by the circles in Fig. 2. For the density corresponding to $r_0 = 1{\cdot}5$, the scattering curve is lifted somewhat further and for $\sin\theta/\lambda = 0{\cdot}15$ lies slightly above the empirical curve. This would tend to support our neglect of $r_0 = 1{\cdot}6$ and 1·7.

However, none of the modifications we have made substantially changes the Hartree N 'ion' results for $\sin\theta/\lambda$ values of 0·25 and 0·35 and here a discrepancy between theory and experiment remains.

5. Conclusion

We agree that the available theoretical results on the spherical average of the electron distribution in NH_4^+ may be analyzed in terms of a model of the kind suggested by McDonald, although there is no uniqueness about our method of forming the spherical density. We find for the reduced internuclear distance of the theoretical calculation that we can obtain reasonable results by placing the hydrogen electron distributions at (1·4 ± 0·1) atomic units from the N nucleus. This figure, while not directly comparable with McDonald's because of the difference in the internuclear distances, seems to show that there is at least semi-quantitative agreement between theory and experiment. Thus, if we express both results as a fraction of their respective N–H separations, we obtain values of (0·86 ± 0·03) and (0·76 ± 0·06) from experiment and theory respectively.

In the light of these results it seems appropriate to comment on the deficiencies of the theoretical distribution assumed at the outset. There are obviously refinements which one should apply as follows:

1. Exchange should really be included in the calculation of the radial density distribution.
2. The effect on the radial charge distribution of including angular terms with the correct tetrahedral symmetry should be estimated.
3. The results of taking account of coulombic repulsions between electrons of antiparallel spin, not included in a determinantal wave function, should be considered.

On the first two points, some inferences can be drawn from existing work on the CH_4 molecule. Thus whereas Buckingham, Massey & Tibbs (1941) calculated a Hartree field for CH_4 after averaging the nuclear field over angles, a Hartree–Fock calculation has recently been made by Mills (1958). In order to show the general effect of exchange in a similar system, we have plotted these results in Fig. 3. The effect of exchange is essentially to contract the charge cloud.

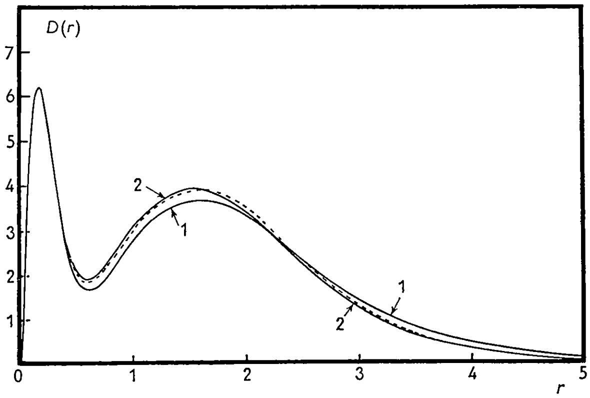

Fig. 3. Spherically averaged radial density in CH_4. Curve 1: Without exchange. Curve 2: With exchange. Broken curve shows influence of angular terms.

Mills has also made an estimate of the effect of including angular terms, and we indicate the influence of this on the spherical density by the broken curve in Fig. 3. The modification will be seen to be very small, but the resulting curve is more diffuse than the Hartree–Fock density.

The third point raised above is more difficult to deal with, and no final conclusion can be reached until much more accurate wave functions become available. However, the work of Carter, March & Vincent (1958) on H_2 (see especially Fig. 2 of their paper) suggests that the radial charge density in this case is still more contracted for a correlated wave function (the Gurnee & Magee function)* than for a Hartree product (or, what is equivalent in this two-electron case with opposed spins, a Hartree–Fock function). But the situations are clearly different, and probably no gross statement can be made, for the electron distribution could perhaps be influenced differently in different parts of the molecule.

Finally we wish to note that a more stringent test of McDonald's model would be provided by a theoretical calculation which included at least the first angular term (with *f* symmetry in this tetrahedral case) in the potential and density. For comparison, the appropriate angular terms could be extracted from McDonald's model using a result for the expansion of a hydrogen-atom density function given in equation (2) of Banyard & March (1957). Unfortunately, there is at present considerable practical difficulty in carrying through a calculation of angular terms from first

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* In view of McDonald's model discussed above, it is of interest to note that this wave function uses hydrogen orbitals centred inside the nuclei.

principles to an accuracy comparable with that already achieved for the spherical term.

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Estimation of a Crystallographic Orientation Relationship

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Two alternative procedures for obtaining the orientation relationship using the stereographic net and numerical methods are described. Their principal advantage over Mackenzie's method is the greatly increased speed achievable; the accuracy is commensurate with that of standard Laue photographs.

In a recent article, Mackenzie (1957) described a very elegant and precise method of determining the orientation relationship between the axes of two systems (structures) given the correspondence for an arbitrary set of two or more directions in the respective systems. However, the method which requires at least a desk calculator, is exceedingly lengthy.

Mackenzie points out that the conventional procedures using stereographic manipulations have limited accuracy and if high precision is required numerical methods are necessary at least in the final stages. No references were given to any such methods and no specific discussions of this topic could be found in the literature. In view of this, two methods (*A* and *B* below), employed successfully by the writer, (1960), are worth recording here. They are based on the well-known theorems of Euler & Rodrigues (Coe, 1938; Gibbs, 1943, 1948; Whittaker, 1944). The methods are a great deal faster than Mackenzie's, especially when a large number of directions such as are available from a Laue photograph have to be taken into consideration; in the one method no numerical computations need be made. The precision of the methods is in keeping with that obtainable from a standard Laue photograph, and compares favourably with Mackenzie's.

Method *A*

In manipulations with the stereographic net, any rotation not about the [001] axis (in the standard projection) or about an axis perpendicular to it can always be decomposed into two rotations θ_1 and θ_2, one of which is about the axis $[001]=\hat{\mathbf{n}}_1$ and the other about an axis $[x, y, 0]=\hat{\mathbf{n}}_2$ perpendicular to $\hat{\mathbf{n}}_1$. The procedure involves superimposing two pieces of tracing paper on a stereographic net, with the standard orientation (say) plotted on the one piece and the 'unknown' orientation on the other. The two tracing papers are then adjusted individually about the center point of the net until trial checks show that the correct position for $\hat{\mathbf{n}}_2$ and the correct values for θ_1, θ_2 have been found. Numerical substitution, in one of the equations below, to determine the axis $\hat{\mathbf{n}}_0$ and angle θ_0 of the equivalent single rotation is made at this stage. The value of $\hat{\mathbf{n}}_0$ may then be plotted on the original stereogram for a graphical presentation.

In general a rotation θ about the direction with unit vector $\hat{\mathbf{n}}=[n_1n_2n_3]$ (where n_i is a direction cosine) can be expressed by the 3×3 rotation matrix R with elements

$$r_{ii}=n_i^2(1-\cos\theta)+\cos\theta$$
$$r_{ij}=n_in_j(1-\cos\theta)-\delta n_k\sin\theta \quad (i\neq j)$$

(δ is $+1$ when the permutation is cyclic and -1 when anticyclic). $R_0=R_2R_1$ then gives the single rotation matrix necessary to bring one orientation into coincidence with the other, i.e. the orientation relationship.