X-ray Scattering by 'Neon-like' Molecules

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An attempt is made to interpret quantitatively the X-ray scattering results of Thomer for the series of 'neon-like' molecules Ne, H_2O, NH_3 and CH_4. For Ne and CH_4 wave functions calculated by the Hartree self-consistent-field method are available and the X-ray scattering factors can be obtained from these. For H_2O and NH_3 we have calculated new central-field analytical wave functions by setting up a total molecular wave function of determinantal form and applying the variational method. In both cases we have computed the scattering factors to be expected from the densities thus obtained.

In this way the general features of Thomer's experimental results are undeniably shown. The quantitative agreement for CH_4 is excellent and is still good for H_2O and NH_3. Everything points to the fact that if our central-field wave functions for H_2O and NH_3 were refined by making self-consistent-field calculations the agreement would be even better.

1. Introduction

Some years ago Thomer (1937) carried out an experimental investigation of the X-ray scattering from Ne, H_2O, NH_3 and CH_4, all in gaseous form. The comparison of such scattering curves is particularly interesting as all are ten-electron molecules and differences in the scattering functions as one goes through the series clearly reflect the changes which occur in the spatial distribution of electrons. (The other molecule, HF, needed to complete the series could not be included by Thomer in his experiments, for technical reasons.) Thomer's experiments reveal quite marked changes in the scattering functions, but as far as we are aware no theoretical interpretation of these results from a fundamental point of view has been attempted. In view of the interest attached to any rather direct experimental means of throwing light on the validity of approximations to molecular wave functions it seemed very worthwhile to attempt an analysis of Thomer's results, and in this paper we report our detailed findings.

2. Discussion of Thomer's results

Before going on to consider the fundamental theoretical treatment of the problem it is instructive to recall briefly the methods Thomer used to analyse his results and also some very interesting observations which he made concerning them. First of all, Thomer discussed methods of obtaining the incoherent part of the scattering, and concluded that the differences in the incoherent intensity scattered by the molecules H_2O, NH_3 and CH_4 are very small and that the Heisenberg–Bewilogua method is of sufficient accuracy for calculating this intensity. (For a discussion of the Heisenberg–Bewilogua method see, for example, Pirenne, 1946, p. 29.)

Thomer then considered two essentially different methods of analysing his results. The first of these, the so-called interference-like treatment (see Thomer's paper or Pirenne, 1946, chap. VI, for a detailed discussion) represents the H_2O molecule, for example, as a superposition of spherically symmetrical O and H atoms. Thomer's results, shown in Fig. 5 of his paper, make it clear that the curve calculated in this way is too steep to agree with experiment. The same situation exists in the other molecules.

The second method he adopted was quite different in principle. In this Thomer examined the possibility of explaining his results by regarding the electronic charge clouds of these molecules as spherically symmetrical. In this case, however, his method of analysis was largely empirical, the technique he adopted being to find whether, using the tables of James & Brindley (1931) and choosing the screening parameter s (introduced by James & Brindley in connection with their interpolation method) for the outer electrons appropriately, his experimental results could be fitted assuming a spherical distribution of charge. In each case he was able to obtain a reasonable fit. However, as Thomer pointed out, this is not a proof that the charge clouds in these molecules are even approximately spherical.

Nevertheless, these results are suggestive and it is this second interpretation of Thomer's experimental results that is of particular interest to us in this paper. For, as Buckingham, Massey & Tibbs (1941) have emphasized, for a molecule such as CH_4, which has quite high symmetry, it is probably not at all a bad first approximation to describe the electrons in the molecule by central-field wave functions. Using this approach, and calculating wave functions by the Hartree self-consistent-field method after averaging the nuclear field over all orientations about the central nucleus, they were able to show, by considering a

variety of experimental observations, that such an approximation seems to be scarcely less satisfactory than the usual Hartree self-consistent-field treatment for atoms. Of course, if one uses such central-field wave functions then one has simply a neon-like configuration $(1s)^2 (2s)^2 (2p)^6$, and thus, in this approximation, a spherical charge cloud. Thomer's finding that the X-ray scattering results for CH_4, in particular, can be explained on the assumption of a spherical charge cloud at least lends further support to these ideas, and it is clearly of interest to enquire whether the density obtained from the self-consistent-field treatment of CH_4 will yield a scattering factor which agrees quantitatively with Thomer's results. However, it might also be argued that Thomer's observations make it appear reasonable to try a similar method even for the much less symmetrical molecules NH_3 and H_2O. We have, therefore, calculated central-field wave functions for these molecules, using a total molecular wave function of determinantal form. To obtain as good an approximation as possible in terms of central-field wave functions we should really solve the Hartree–Fock equations after averaging the nuclear field over angles. In view of the labour involved in such calculations, and also bearing in mind the somewhat tentative application of such a method to molecules with much lower symmetry than CH_4, we have contented ourselves with one-electron wave functions of a simple analytical form which leaves tractable the handling of the variation problem thus presented.

The outline of the rest of the paper is thus as follows. In § 3 we discuss the results for Ne and CH_4, in which cases self-consistent-field wave functions have already been obtained. We then proceed in § 4 to describe the basic method we have used to calculate wave functions for NH_3. The method of obtaining the scattering factor from these is briefly described. In § 5 the results of applying similar methods to H_2O are described, whilst in § 6 we make a detailed comparison with Thomer's experimental results.

3. X-ray scattering factors for Ne and CH_4

As we have already remarked, self-consistent-field calculations have previously been made for both Ne and CH_4, and from these results we can obtain the total electron densities by squaring and adding the normalized wave functions. For a Ne configuration the density is spherical and thus we calculate the scattering factors from the usual formula

$$f = \int_0^\infty n(r) 4\pi r^2 \frac{\sin kSr}{kSr}\, dr \qquad (1)$$

where $k = 2\pi/\lambda$, $S = (2 \sin \tfrac{1}{2}\theta)/\lambda$, λ is the wavelength of the incident radiation, θ is the angle of scattering and $n(r)$ is the electron density. Very recently, results have been published for Ne (Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal, 1955) giving f calculated using the self-consistent-field wave

functions obtained by Brown (1933), and we show the results in curve (b) of Fig. 1. For CH_4 we have carried
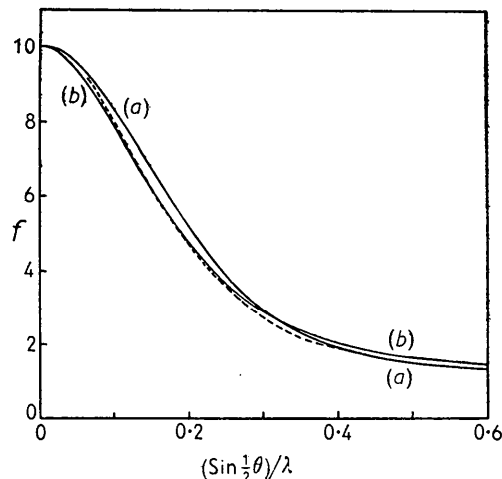

Fig. 1. X-ray scattering factor for Ne. (a) Results of McWeeny using analytical wave functions. (b) Results of Berghuis et al. using self-consistent-field wave functions.
Broken curve shows experimental results of Wollan.

out the necessary numerical integrations, using the tables of Buckingham et al., and the results we have thus obtained are indicated by the crosses in Fig. 2.

4. Approximate wave functions and X-ray scattering factor for NH_3

The case of NH_3 presents us with more difficulty as we have no suitable wave functions available. In accordance with the tentative approach outlined in § 2 we should really like to have the self-consistent-field
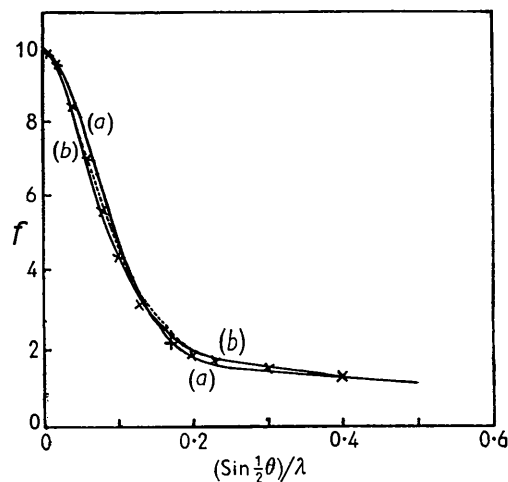

Fig. 2. X-ray scattering factor for CH_4. (a) Results using analytical wave functions. (b) Fitted curve given by Thomer, representing his experimental results.
Crosses indicate points calculated using self-consistent-field treatment. Broken curve gives rough estimate of deviations of experimental curve from fitted curve (b).

wave functions obtained by applying the procedure of Buckingham et al. to NH_3. In view of the labour involved we have decided instead to use the variational method, in conjunction with analytical wave functions. Bernal (1953) has previously calculated analytical wave functions for CH_4 and NH_4^+ and we shall follow his method of calculation closely in this work. We start from one-electron wave functions having radial factors $R(nl|r)$ given by

$$R(1s|r) = 2\alpha^{\frac{3}{2}}e^{-\alpha r},$$
$$R(2s|r) = \left(\frac{12\beta^5}{\alpha^2-\alpha\beta+\beta^2}\right)^{\frac{1}{2}}[1-\tfrac{1}{3}(\alpha+\beta)r]e^{-\beta r},$$
$$R(2p|r) = \left(\frac{4\gamma^5}{3}\right)^{\frac{1}{2}}re^{-\gamma r}. \qquad (2)$$

These are of the form used by Fock & Petrashen (1934) for Na^+ and utilized also by Bernal in his work. We form the total molecular wave function Ψ as a ten-electron Slater determinant from these one-electron functions combined with the spin functions. We then calculate the total molecular energy from the expression

$$E = \frac{\int \Psi^* H \Psi d\tau}{\int \Psi^* \Psi d\tau} + U_n. \qquad (3)$$

Here the integration is to be taken over the coordinates of all the electrons. The Hamiltonian H is given in atomic units (which we shall use throughout this paper) by

$$H = \sum_{i=1}^{10}(K_i + V_n(r_i)) + \sum_{i,j=1}^{10}\frac{1}{r_{ij}}, \qquad (4)$$

where

$$K_i = -\tfrac{1}{2}\nabla_i^2, \quad V_n(r_i) = -Z/r_i - N/r_0, \quad r_i \le r_0,$$
$$= -(Z+N)/r_0, \quad r_i > r_0,$$

and the second summation is to exclude terms $i \le j$. U_n is the nuclear–nuclear interaction energy, Z is the atomic number of the 'central' atom, N is the total number of remaining positive charges and r_0 is the distance between the 'central' and the outer atoms. Once one has decided to adopt central-field wave functions and is dealing with a configuration such as $(1s)^2 (2s)^2 (2p)^6$, for which the charge cloud is spherically symmetrical, then there is no additional approximation implied in using the Hamiltonian (4) in which the nuclear field is averaged over all orientations to evaluate the energy by the variational method. This was noted by Bernal in his work; the basic reason is that when the density is spherical the electron–nuclear interaction energy is solely determined by the first term in the expansion of the nuclear potential in spherical harmonics.

Many of Bernal's integrals can now be used in the evaluation of E from equation (3). The integrals which must be modified are those involving V_n, since Bernal

gave results for a general Z but $N = 4$. We of course require the special cases $N = 2\,(H_2O)$ and $N = 3\,(NH_3)$ in our work. These integrals, called $I(\alpha)$ in Bernal's notation*, are defined by

$$I(\alpha) = \int_0^\infty rR(\alpha|r)\left[-\frac{1}{2}\frac{d^2}{dr^2} + V_n(r) + \frac{l_\alpha(l_\alpha+1)}{2r^2}\right]rR(\alpha|r)\,dr. \qquad (5)$$

We then obtain the following results:

$$I(1s) = [Ne^{-\sigma}(\sigma+2)/2 - (Z\sigma/2) - N]/r_0 + (\sigma^2/8)/r_0^2,$$
$$I(2s) = [e^{-\omega}(B_3/6B_0) - (ZB_2/4B_0) - N]/r_0$$
$$\qquad\qquad + (B_1/24B_0)/r_0^2],$$
$$I(2p) = [e^{-\mu}(B_4/6) - (Z\mu/4) - N]/r_0 + (\mu^2/8)/r_0^2, \qquad (6)$$

where

$$\sigma = 2\alpha r_0, \quad \omega = 2\beta r_0, \quad \mu = 2\gamma r_0,$$

and

$$B_0 = \sigma^2 - \sigma\omega + \omega^2,$$
$$B_1 = 7\omega^4 - \sigma\omega^3 + \sigma^2\omega^2,$$
$$B_2 = 3\omega^3 - 2\sigma\omega^2 + \sigma^2\omega,$$
$$B_3 = \tfrac{1}{4}N[\omega^5 + 2\omega^4(\sigma-3) + \omega^3(\sigma^2+6) + 6\omega^2$$
$$\qquad \times(\sigma^2 - 2\sigma + 4) + 6\sigma\omega(3\sigma-4) + 24\sigma^2],$$
$$B_4 = \tfrac{1}{4}N[\mu^3 + 6\mu^2 + 18\mu + 24].$$

We have defined B_3 and B_4 as above so that they reduce to Bernal's quantities B_3 and B_4 when we put $N = 4$.

It should be noted that our results reduce to Bernal's when $N = 4$, with two exceptions. In $I(2s)$ Bernal has the second term in the square bracket as $-(ZB_2/B_0)$, i.e. the factor $\tfrac{1}{4}$ has been omitted, and in B_3 he gives the second term in the bracket as $-2\omega^4(\sigma-3)$ whereas the correct term is $+2\omega^4(\sigma-3)$. It appears, however, that these are misprints and that his calculations have been carried through using the correct formulae. Nevertheless it seemed to us essential to verify the remaining formulae in his paper in view of these misprints. This we have done and agree with all the other results as given.

We are now in a position to apply the method to NH_3. If Θ is the H–N–H angle and r_0 is the N–H bond length, then the nuclear–nuclear interaction energy may be written

$$U_n = \frac{21}{r_0}\left[1 + \frac{1}{14}\,\mathrm{cosec}\,\tfrac{1}{2}\Theta\right].$$

We have adopted the values $r_0 = 1\cdot91$, $\Theta = 106°\,46'$ (Mulliken, 1955). For these values we must now carry through the minimization of E with respect to the parameters in the wave function. (Of course, in our approximation, for a chosen r_0 there is no dependence of the parameters on Θ.) As in Bernal's work, we have pre-selected α and reduced the wave function Ψ to a two-parameter function. We have fixed α to have the

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* There is an obvious misprint in Bernal's equation for $I(\alpha)$.

value chosen by Bernal in his calculations on the ammonium ion. We found it possible to obtain a reasonable initial estimate of the parameters β and γ from various considerations, and we then proceeded to approach the best values by a method which was essentially trial and error. We concluded that with a good starting approximation this was simpler than using partly analytical methods. In this way we obtained the following results:

$$2\alpha = 13{\cdot}43, \quad 2\beta = 4{\cdot}30, \quad 2\gamma = 3{\cdot}06 ,$$

corresponding to a total molecular energy E of $-55{\cdot}26$. Thus the wave functions and the charge distribution are completely defined in this approximation. We can now obtain the X-ray scattering factor most simply by making use of the method developed by McWeeny (1951), who obtained atomic scattering factors resulting from analytical wave functions of a form similar to those used here. In McWeeny's method one calculates separately the contributions of the various groups of electrons to the total scattering factor, rather than starting from the total density $n(r)$ which is most convenient to use in purely numerical calculations. The contributions of the separate orbitals, when represented by wave functions compounded from exponential functions, can be expressed easily in terms of two functions

$$S_n(x) = \int_0^\infty t^n e^{-t} \sin xt\,dt, \quad C_n(x) = \int_0^\infty t^n e^{-t} \cos xt\,dt ,$$

which are conveniently made the basis of the calculations, as McWeeny has discussed. For these functions the following convenient recurrence relations have been given by him:

$$S_{n+1}(x) = \frac{n+1}{1+x^2}[S_n(x)+xC(x)] ,$$

$$C_{n+1}(x) = \frac{n+1}{1+x^2}[C_n(x)-xS_n(x)];$$

and, using these, the required functions may be built up from the results

$$S_0(x) = x/(1+x^2), \quad C_0(x) = 1/(1+x^2) .$$

In this way the scattering factor for NH_3 can be obtained from the wave functions we have calculated, and this is shown in curve (a) of Fig. 3.

Actually, in view of the fact that we have used relatively inflexible forms of the wave functions, as given by equation (2), it is of interest to try to obtain some estimate of the differences which would occur if we had applied the Hartree self-consistent-field method. To this end we have worked out also the scattering factor for CH_4 which the analytical wave functions of Bernal predict, and this is shown in curve (a) of Fig. 2. We have also plotted in curve (a) of Fig. 1 the results obtained by McWeeny for the scattering factor for Ne, using the analytical wave functions

introduced by Morse, Young & Haurwitz (1935; see also Duncanson & Coulson, 1944). It should be noted that for $(\sin \frac{1}{2}\theta)/\lambda < 0{\cdot}3$ for Ne and $< 0{\cdot}2$ for CH_4
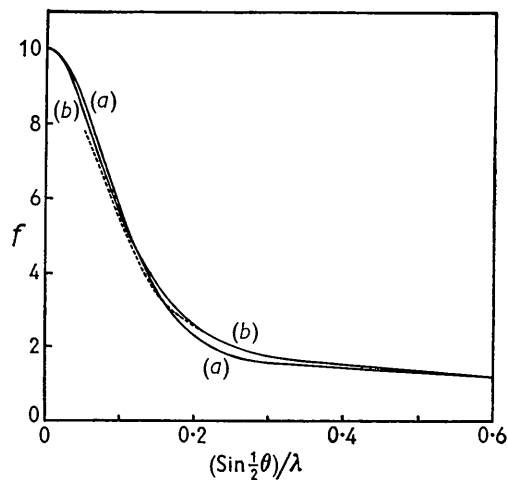

Fig. 3. X-ray scattering factor for NH_3. (a) Results using analytical wave functions. (b) Fitted curve given by Thomer, representing his experimental results.
    Broken curve gives rough estimate of deviations of experimental curve from fitted curve (b).

the scattering factors obtained from the analytical functions lie above those found from the self-consistent-field wave functions, although a cross-over occurs later. We shall see that this is a very pertinent point when we make a detailed comparison with experiment.

5. Results for H_2O

We have also carried out calculations for H_2O similar to those described in § 4, and we shall now summarize

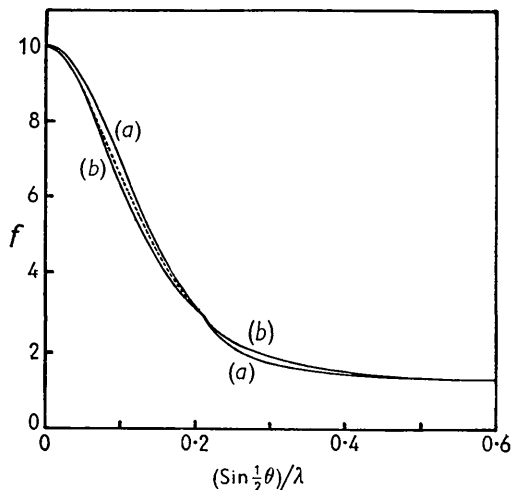Fig. 4. X-ray scattering factor for H_2O. (a) Results using analytical wave functions. (b) Fitted curve given by Thomer, representing his experimental results.
    Broken curve gives rough estimate of deviations of experimental curve from fitted curve (b).

the results we have obtained in this case. First, if r_0 is the O–H internuclear separation and Θ is the H–O–H angle, then we have

$$U_n = \frac{16}{r_0}\left[1+\frac{1}{32}\cosec \tfrac{1}{2}\Theta\right].$$

We have adopted the values $r_0 = 1{\cdot}81$, $\Theta = 105°$ (Ellison & Shull, 1953), and again we have pre-selected α. Carrying through the minimization we finally obtain

$$2\alpha = 15{\cdot}34,\quad 2\beta = 5{\cdot}26,\quad 2\gamma = 3{\cdot}77\ ,$$

corresponding to a total molecular energy E of $-75{\cdot}00$. Using McWeeny's method, the scattering factor has again been calculated and we show this in curve (a) of Fig. 4.

6. Comparison with experimental results

We have now reached the stage at which we can begin the detailed comparison with experiment. Unfortunately Thomer does not give tables of his results, and it is practically impossible to read off his diagrams with much accuracy. However, as we mentioned in § 2, he fitted his X-ray scattering results with reasonable success by making use of the tables of James & Brindley and by using the screening parameter s for the $2p$ electrons as an adjustable parameter. Since

he records the values he adopted for this parameter and states that he assumed for the $1s$ and $2s$ electrons the values given by James & Brindley for the 'central' atom in the molecule under consideration, it is possible to reconstruct these curves with fair accuracy. (It should perhaps be emphasized, in order to avoid misunderstanding, that the only use which has been made of the tables of James & Brindley in our work is to reconstruct reasonable approximations to Thomer's experimental curves. It is now known that the interpolation method used by James & Brindley is not entirely satisfactory and these tables have been largely superseded by the accurate Hartree results given for many atoms by Berghuis *et al.*) In each case it is clear from Thomer's curves just what kind of deviation there is between his fitted curves and his actual experimental results, and we can take a rough account of this (small) effect later when making a quantitative comparison. In this way we have constructed the fitted curves which represent Thomer's experimental results, and these are shown in curve (b) of Figs. 2, 3 and 4 for CH_4, NH_3 and H_2O respectively. In Fig. 5 we have collected together both the theoretical and the experimental results in order that the general trends in the scattering factors as one goes through the series can be readily seen. We have used for Ne the experimental results obtained by Wollan (1931) rather than those of Thomer. This is because for small angles Thomer's results are not entirely satisfactory owing
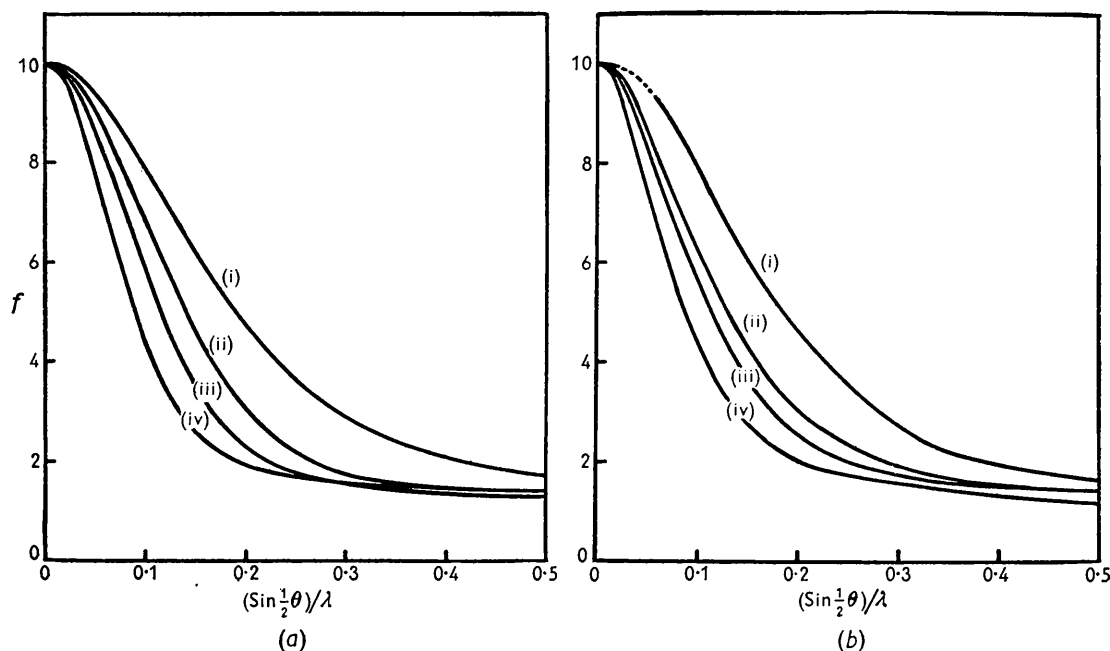

Fig. 5. X-ray scattering factors for 'neon-like' series.

(a) Theoretical results:
(i) Self-consistent-field results for Ne.
(ii) Results for H_2O using analytical wave functions.
(iii) Results for NH_3 using analytical wave functions.
(iv) Self-consistent-field results for CH_4.

(b) Experimental results:
(i) Results of Wollan for Ne.
(ii) Results for H_2O (fitted curve).
(iii) Results for NH_3 (fitted curve).
(iv) Results for CH_4 (fitted curve).

to the use of imperfectly monochromatized radiation for the scattering by Ne.

A study of Fig. 5 makes it apparent first of all that the general features of Thomer's results are reproduced satisfactorily by the present theoretical treatment. In addition, the agreement in each individual case is quite gratifying, as can be seen clearly from Figs. 1–4, and it is worthwhile to discuss the quantitative agreement in detail.

First we note that the agreement between the scattering factor using Hartree–Fock wave functions for Ne and Wollan's experimental results is excellent. This is rather as expected, for there is a good deal of independent evidence which points to the fact that the Hartree–Fock approximation gives a good account of the electron distribution in atoms. Concerning the theoretical curves for Ne it is apparent from a comparison of curves (a) and (b) of Fig. 1 that there are quite significant differences between the scattering factor calculated by McWeeny using the analytical wave functions of Morse et al. and that calculated from Hartree–Fock wave functions, as has already been noted by Berghuis et al. This is significant for the present work, first because it points out an essential restriction on the accuracy which one might hope to achieve with analytical wave functions, and secondly because it indicates the direction of the error. With regard to the latter point, the scattering factor obtained from analytical functions of the kind used in this paper is likely for small angles to lie above, and subsequently to lie below, that which would be obtained if self-consistent-field methods were used.

For CH_4 the most important conclusion is that the scattering calculated from the self-consistent-field treatment (indicated by the crosses in Fig. 2; we have not drawn the curve in order to avoid confusion of the diagram) is in truly excellent agreement with experiment. We have attempted to indicate very roughly by the broken curve the way in which Thomer's experimental curve deviates from the curve he fitted to his results (shown by our curve (b)). It is again interesting to know the accuracy which can be achieved with analytical functions, and this is demonstrated by curve (a) of Fig. 2, which shows the results obtained from Bernal's wave functions. The same conclusions can be drawn as in the case of Ne; the scattering factor lies above that obtained using Hartree wave functions for $(\sin \frac{1}{2}\theta)/\lambda < 0.2$, and crosses over later.

Passing on to the results for NH_3 we see that, as we would be inclined to expect from the above discussion, the theoretical scattering factor obtained from the variational wave functions we have calculated lies above the experimental curve at small angles and appears to cross it later. (Again we show in the broken curve the kind of deviation which occurs between Thomer's fitted curve and his actual experimental points. There is some indication that his experimental curve is somewhat low for the smallest angles, as in the case of Ne.) Nevertheless, the differences between theory and experiment are not large and it seems clear that if we were to use our results to obtain a starting field and then to carry through a Hartree self-consistent-field calculation we should improve the agreement significantly. Thus we feel that the results in this case make it appear plausible that even with the much lower symmetry of NH_3 compared with CH_4 it is still a useful first approximation to start with central-field wave functions, even though it seems certain that the necessary 'correction' terms which would have to be added to make these really good wave functions will be considerably more important here than for the case of CH_4. Such 'correction' terms will take us beyond the approximation of a spherical density to a more realistic form. We believe that the spherical density we have calculated here should be regarded as providing a reasonable approximation to the leading terms in an expansion of the actual density in the NH_3 molecule in spherical harmonics, or, put another way, to the actual density in the molecule, when this is averaged over angles. An even better approximation to this first term should be given by solving the Hartree–Fock equations to determine the central-field wave functions. That angular terms in the density are very significant for some purposes, however, is indicated by the magnitude of the dipole moment of NH_3; for the calculation of this quantity our present wave functions are quite inadequate.

Finally, for H_2O the same kind of situation exists and most of the previous remarks for NH_3 hold. Again it will clearly be of interest in the future to see how the use of Hartree–Fock wave functions would improve the agreement.

7. Conclusion

We have shown in this paper that the results of Thomer for the X-ray scattering by the series of ten-electron systems Ne, H_2O, NH_3 and CH_4 can be understood both from the point of view of the general trend through the series, and in each individual case from a quantitative point of view if one assumes that it is a reasonable first approximation to describe the electrons in the three molecules by central-field wave functions. This seems to be reasonably well established to be the case for CH_4 by the work of others, particularly that of Buckingham et al.; it is much less certain to be the case for H_2O and NH_3. However, we have presented central-field wave functions for these molecules which we have calculated by the variational method with a total molecular wave function of determinantal form, and the results we obtain are in satisfactory agreement with Thomer's findings. Further, it seems fairly well established that we could improve the agreement with experiment by refining the central-field wave functions by solving the Hartree–Fock equations. The success of our approach in

enabling Thomer's results to be reproduced rather faithfully suggests that it will be very worthwhile to carry this kind of approximation further, and we are now undertaking more detailed treatments of the H_2O and the NH_3 molecules, based on the results of this paper, in which angular terms will be included in the density. For H_2O we hope to make a detailed comparison of the method we are proposing with the LCAO self-consistent-field treatment (Roothaan, 1951) which has been worked out in detail for this case by Ellison & Shull (1953, see also Amako, 1954) whilst for NH_3 we hope to present calculations giving the total energy as a function of the N–H distance. A particularly interesting point in both cases will be to see whether one can calculate reasonably accurate dipole moments with only a few angular terms in the electron density. The results of these investigations will be published elsewhere at a later date.

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References

AMAKO, Y. (1954). *Sci. Rep. Tôhoku Univ.* (1), **38**, 77.
BERGHUIS, J., HAANAPPEL, I. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
BERNAL, M. J. M. (1953). *Proc. Phys. Soc.* A, **66**, 514.
BROWN, F. W. (1933). *Phys. Rev.* **44**, 214.
BUCKINGHAM, R. A., MASSEY, H. S. W. & TIBBS, S. R. (1941). *Proc. Roy. Soc.* A, **178**, 119.
DUNCANSON, W. E. & COULSON, C. A. (1944). *Proc. Roy. Soc. Edinb.* A, **62**, 37.
ELLISON, F. O. & SHULL, H. (1953). *J. Chem. Phys.* **21**, 1420.
FOCK, V. & PETRASHEN, M. J. (1934). *Phys. Z. Sowjet,* **6**, 368.
JAMES, R. W. & BRINDLEY, G. W. (1931). *Phil. Mag.* (7), **12**, 81.
MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
MORSE, P. M., YOUNG, L. A. & HAURWITZ, E. S. (1935). *Phys. Rev.* **48**, 948.
MULLIKEN, R. S. (1955). *J. Amer. Chem. Soc.* **77**, 887.
PIRENNE, M. H. (1946). *The Diffraction of X-rays and Electrons by Free Molecules.* Cambridge: University Press.
ROOTHAAN, C. J. (1951). *Rev. Mod. Phys.* **23**, 69.
THOMER, G. (1937). *Phys. Z.* **38**, 48.
WOLLAN, E. O. (1931). *Phys. Rev.* **37**, 862.

Electron-Diffraction Study of the Structure of Basic Lead Carbonate, 2 PbCO₃ . Pb(OH)₂

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Previously established techniques and some new techniques, including the use of modified Patterson functions and the derivation of three-dimensional Patterson functions by a 'stereoscopic' method, have been applied to the structure analysis of single crystals of basic lead carbonate by electron diffraction. The crystals have a disordered layer lattice and the structure was analysed by the 'distribution-function' method. The individual layers have a trigonal unit cell, $P31m$ with $a = b = 9.06$, $c = 8.27$ Å, and contain a $Pb(OH)_2$ sheet sandwiched between two $PbCO_3$ sheets. On the average the layers have approximate rhombohedral stacking, giving $c = 24.8$ Å, but the deviations from this are such that a fully-ordered structure would be triclinic, $P1$.

The modification of the intensities by the difference in phase of electrons scattered from light and heavy atoms is calculated, and its importance in structure analysis is assessed

Introduction

The structure of basic lead carbonate, better known as white lead, has not, as far as can be determined, previously been studied by diffraction methods. By X-ray diffraction, only powder patterns have been obtained. Because of the small crystal size of white lead, the powder patterns contain relatively few lines,

poorly defined, and do not form a suitable basis for a structure analysis.

The structure analysis based on single-crystal electron-diffraction patterns was undertaken as an exercise in the use of the techniques previously developed (Cowley, 1953a, b) and as a test for new techniques more recently devised. These include the use of a modified Patterson function (Cowley, 1956a) and the