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The Scattering of X-rays by N_2

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The wave function of Scherr has been employed to calculate the coherent X-ray scattering from N_2. Two alternative procedures are discussed, the first based on a three-centre representation of the of the charge cloud, the second based on a one-centre expansion in spherical harmonics following Banyard & March. It is found that the scattering obtained from Scherr's electron density differs only slightly from that given by forming the molecular density as a superposition of two N atoms.

The incoherent scattered intensity is estimated from Freeman's work on atoms and the final total intensity is compared with the experimental results of Gajewski. There is a large discrepancy and it is concluded that the wave function of Scherr leads to a density in which insufficient account of bonding is included.

1. Introduction

The wave function of Scherr (1957) for the nitrogen molecule, obtained by the procedure of Roothaan (1951), has been used to calculate the coherent X-ray scattering by gaseous nitrogen. The interest in this problem stems from the experimental results of Gajewski (1932) who measured the relative intensities of the total scattering from nitrogen gas at a number of scattering angles. He found his results to be in fair agreement with theoretical values obtained by superposing two atomic-nitrogen electron densities and using the scattering factors of Bragg & West (1928) to give the coherent component, the incoherent component being obtained by summing the contributions from two free N atoms. These free-atom scattering factors, which are based on a Thomas–Fermi electron density for the nitrogen atom, are known to be poor for such a light atom. If use is made of atomic scattering factors and incoherent intensities obtained from a Hartree–Fock description of the atom (Berghuis *et al.*, 1955) the agreement with Gajewski's results is much less satisfactory.

Although the superposition of Thomas–Fermi atomic densities gives quite good agreement with the experiments of Gajewski it does not follow that this superposition density is a good approximation to the molecular density. Indeed it should be noted that knowledge of the coherent scattering from randomly oriented scatterers is insufficient to give a unique electron density for molecules of the gas.

Therefore, the purpose of the present paper was to start from the molecular wave function of Scherr, which is the best available function for N_2, and to compare the predicted X-ray scattered intensities with Gajewski's measurements. Our main conclusion is that this wave function does not lead to good agreement with experiment.

The electron density, which may not be analysed into the sum of spherical distributions, obtained from this wave function has been used in the coherent scattering calculation in two ways:

(i) By expanding a part of the density in spherical harmonics about the mid-point of the N–N bond but retaining some 'atomic-like' density on the N nuclei.

(ii) By expanding the whole of the density as in (i), following Banyard & March (1957).

In the first method it is argued that a good approximation to the theoretical coherent scattering is obtained by including only the *s* and *d* terms in the expansion of the electron density. The second method is found to give results in agreement with the first, after again including only *s* and *d* terms in the density expansion. The result of terminating the expansions at the *s*-term is also considered.

An estimate of the intensity of the incoherent scattering is made by summing the contribution from two free nitrogen atoms, using the theoretical results of Freeman (1959). The total intensity, which agrees closely with that obtained by representing the molecular electron density as a superposition of Hartree-Fock atomic densities, differs considerably from the experimental results.

2. Formulation of the problem

The coherent scattering per electron of a free molecule may be written (see Pirenne p. 58)

$$I_{\text{coh}}/I_e = f^2(\varkappa) = N \iint \varrho(\mathbf{r}')\varrho(\mathbf{r}'') \frac{\sin \varkappa|\mathbf{r}'-\mathbf{r}''|}{\varkappa|\mathbf{r}'-\mathbf{r}''|}\, d\tau' d\tau''. \tag{1}$$

In equation (1), I_e is the Thomson scattering intensity for a single electron, $\varrho(\mathbf{r})$ is the electron density of the molecule normalized to unity, N is the number of electrons in the molecule and $\varkappa = (4\pi/\lambda) \sin(\frac{1}{2}\theta)$ where θ is the angle of scattering.

Although the Scherr wave function leads to a closed expression for $\varrho(\mathbf{r})$ it did not prove possible to perform the integration in (1) analytically. However, by expanding either the whole or part of $\varrho(\mathbf{r})$ about the bond centre in terms of spherical harmonics and performing numerical integrations, two estimates of the integral in (1) have been obtained. The principles involved in these two methods and the results obtained are outlined below.

3. Calculation of the coherent scattering

The Scherr density function separates into the sum of three distinct terms. Two of these are identical spherical distributions $\varrho'(r)$ centred on each of the two N nuclei, whilst the third part, $\varrho''(\mathbf{r})$, contributing about 12% to the total normalization, is of a more complex form. This final term may be expanded about the centre of the bond in terms of spherical harmonics Y_n^m (normalized to 2π);

$$\varrho''(\mathbf{r}) = 2^{\frac{1}{2}} \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \varrho''_{mn}(r) Y_n^m(\theta, \varphi) \,. \qquad (2)$$

We should perhaps stress that, owing to the orthogonality properties of the spherical harmonics, only the first term (s symmetry) contributes to the normalization in such a harmonic expansion. Thus, the total charge in the molecule is independent of the order at which the harmonic series is terminated.

$\varrho''(\mathbf{r})$ was tabulated as a function of r and θ, the origin of the co-ordinate system being taken as the centre of the bond and the line joining the two nuclei the z axis. By performing numerical integrations over θ ($\varrho(\mathbf{r})$ is independent of φ) the first two non-zero terms in the expansion (2) were obtained, these being $\varrho''_{00}(r)$ and $\varrho''_{20}(r)$.*

By using $\varrho'(r)$ and $\varrho''_{00}(r)$ in the expression

$$f(\varkappa) = 4\pi \int \varrho(r) j_0(\varkappa r) r^2 dr \ , \qquad (3)$$

where $j_0(\varkappa r) = \sin \varkappa r/(\varkappa r)$ is the zeroth order spherical Bessel function, the functions $f'(\varkappa)$ and $f''_{00}(\varkappa)$ were obtained respectively, the former in closed form and the latter in numerical form. These functions may be used to give a first approximation to the coherent scattered intensity.

Neglecting $\varrho''_{20}(r)$ and higher terms, the total electron density becomes the sum of three spherical distributions; $\varrho'(r)$ centred at each of the two nuclei and $\varrho''_{00}(r)$ placed at the centre of the bond. For this type of distribution the expression for the coherent scattered intensity is (see Pirenne p. 58)

$$I_{\text{coh}}/I_e = \sum_i \sum_j f_i(\varkappa) f_j(\varkappa) \frac{\sin \varkappa r_{ij}}{\varkappa r_{ij}} \ , \qquad (4)$$

where r_{ij} is the distance between the ith and jth centres and $f_i(\varkappa)$ is the scattering factor of the spherical distribution on the ith centre, given by (3). Thus neglect of $\varrho''_{20}(r)$ and higher terms leads to the expression,

$$f^2(\varkappa) = N\{2f'^2(\varkappa)[1 + (\sin 2\varkappa R/2\varkappa R)] + 4f'(\varkappa)f''_{00}(\varkappa) \sin \varkappa R/(\varkappa R) + f''^2_{00}(\varkappa)\} \ , \qquad (5)$$

for the coherent scattered intensity, where $2R(=2\cdot06$ Å) is the N–N bond length. This estimate of $f^2(\varkappa)$ is shown in curve 3 of Fig. 1.

Since $\varrho''(\mathbf{r})$ contributes only about 12% to the total normalization it was thought that the use of (5) might lead to a sufficiently accurate estimate of the integral in (1). However, to check this, $\varrho''_{20}(r)$ was retained and the appropriate generalization of (4) was obtained. To this higher order of approximation it was found that the term

$$N\{f''^2_{20}(\varkappa) + 4\sqrt{(5)} f''_{20}(\varkappa) j_2(\varkappa R)\} \ , \qquad (6)$$

where $f''_{20}(\varkappa) = 4\pi \int \varrho''_{20}(r) j_2(\varkappa r) r^2 dr$, must be added to (5). The results of this improved approximation are shown in curve 1 of Fig. 1.

The small difference between curves 3 and 1, together with the relatively small contribution of $\varrho''(r)$ to the normalization is taken to imply that there is sufficiently rapid convergence, over the range of $\varkappa$ considered, for curve 1 to be a good approximation to the coherent scattering from the Scherr electron density. To graphical accuracy these results are almost identical with those obtained by placing free-atom charge distributions at each nucleus and using the scattering factors of Berghuis *et al.* (1955) in conjunction with (4).

As a check on the above results the integral in (1) was re-estimated by direct application of the formulation of Banyard & March (1957) who showed that (1) may be reduced to the form

$$f^2(\varkappa) = N \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} |f_{nm}(\varkappa)|^2 \qquad (7)$$

where

$$f_{nm}(\varkappa) = 4\pi \int \varrho_{nm}(r) j_n(\varkappa r) r^2 dr \,. \qquad (8)$$

In (8) the j_n are the spherical Bessel functions and the $\varrho_{nm}(r)$ are defined through the equation

$$\varrho(\mathbf{r}) = 2^{\frac{1}{2}} \sum_{n=0}^{\infty} \sum_{m=-n}^{+n} \varrho_{nm}(r) Y_n^m(\theta, \varphi) \qquad (9)$$

where the Y_n^m are the spherical harmonics (normalized to 2π). Here, as in the previous calculations, there is an expansion in terms of spherical harmonics but this time it is the entire density which is expanded about the centre of the bond and not only a small fraction of it.

Scherr's density was tabulated as a function of r and θ, using the co-ordinate system of the previous calculation, and by performing numerical integrations over θ the first two non-zero terms, $\varrho_{00}(r)$ and $\varrho_{20}(r)$,

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* Owing to the symmetry of $\varrho(\mathbf{r})$ only the terms $\varrho''_{2l,0}(r)$ in expansion (2) are not identically zero.

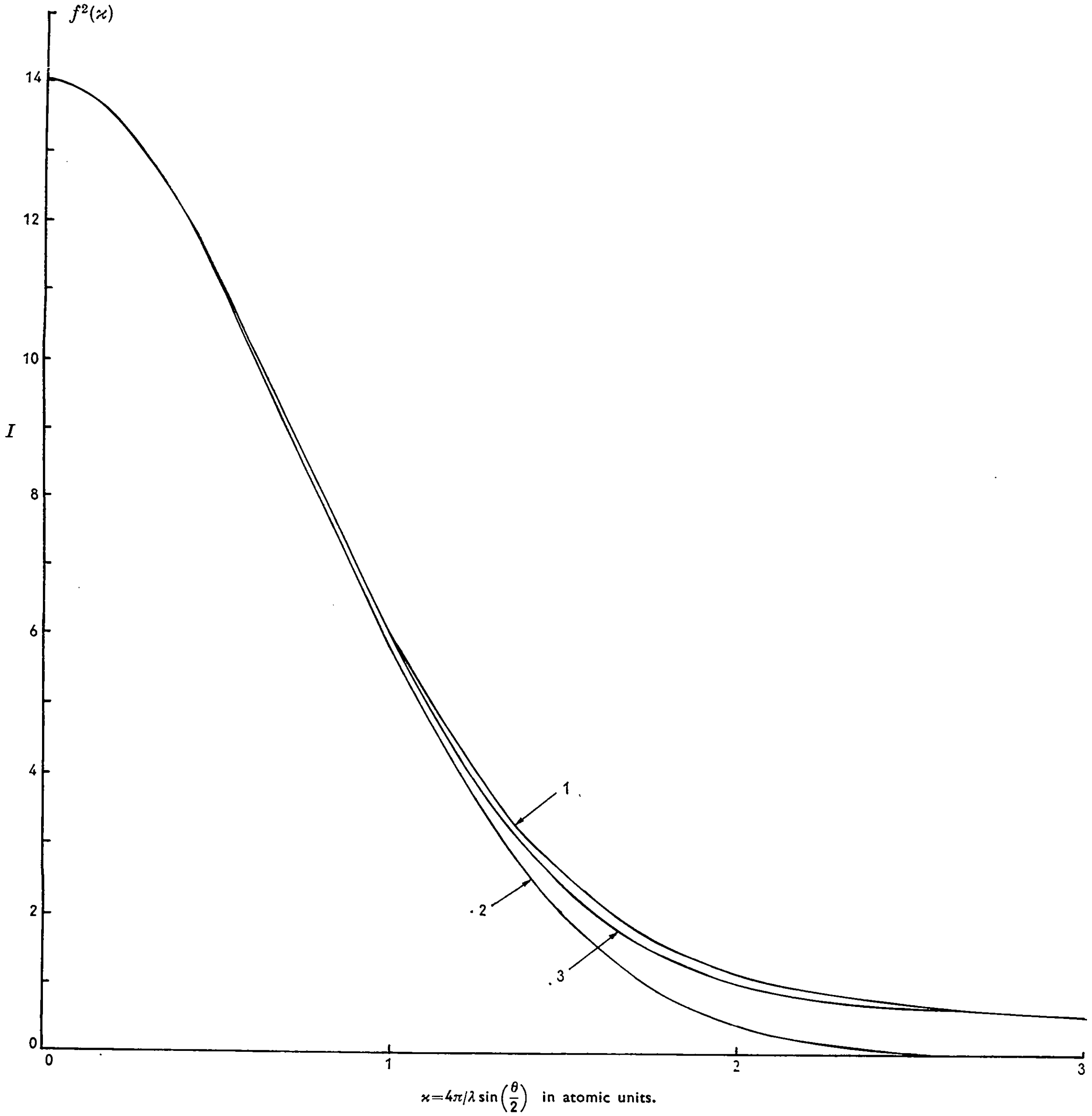

Fig. 1. Coherent scattering intensities for N_2.

Curve 1: From one and three centre expansions including the *d*-terms.
Curve 2: From one-centre expansion without the *d*-term.
Curve 3: From three-centre expansion without the *d*-term.

were obtained. Substitution of these in (8) and carrying through the integrations for a number of values of $\varkappa$ led to the tabulation of the functions $|f_{00}(\varkappa)|^2$ and $|f_{20}(\varkappa)|^2$.

Curve 2 of Fig. 1 shows the contribution of $|f_{00}(\varkappa)|^2$ to $f^2(\varkappa)$ and this may be compared with curve 1 which, to within graphical accuracy, also shows the sum of the contributions of $|f_{00}(\varkappa)|^2$ and $|f_{20}(\varkappa)|^2$. The results of the two calculations agree, and as (7) gives $f^2(\varkappa)$ as a summation over positive terms it follows that curve 1 of Fig. 1 will be a lower bound to $f^2(\varkappa)$.

If, as argued, the first calculation gives a good approximation to the coherent scattering from the Scherr electron density then we see that the series (7) of Banyard & March for $f^2(\varkappa)$ converges rapidly, even though the associated series (9) for the electron density requires the inclusion of many terms to give a good approximation to the density at any point. It follows that, over the range of $\varkappa$ considered, higher harmonics than the *d* term in the electron density make only a very small contribution to the coherent scattering from N_2.

4. Incoherent scattering and comparison with experiment

Before contact can be made with experiment some estimate of the incoherent scattered component is required. This estimate was made by assuming the incoherent intensity to be equal to that due to two free nitrogen atoms and using Freeman's (1959) calculation of the incoherent scattering based on a Hartree–Fock wave function. This incoherent component is shown in curve 3 of Fig. 2, whilst curve 1 of this figure shows the calculated total scattered intensity. The experimental curve of Gajewski is shown for comparison in curve 2. These measured intensities are relative values and so may be scaled to obtain the best fit with the theoretical curve, but, as the two curves cross one another, improving the agreement in one region will only increase the discrepancy in another.

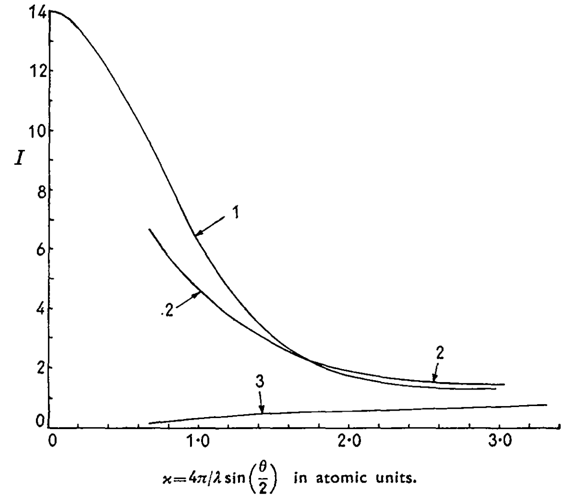

Fig. 2. Incoherent and total scattering intensities for N_2.
Curve 1: Theoretical results for total scattering.
Curve 2: Experimental results of Gajewski.
Curve 3: Freeman's theoretical results for the incoherent scattering for a free N atom.

5. Conclusion

It is seen that there is a marked discrepancy between the experimental results and the theoretical intensities obtained here. In attempting to localize the source of this discrepancy, it is unlikely that the estimate of the incoherent scattering will be greatly in error. However, even if this were so, an accurate estimate would hardly reduce the discrepancy, for in the region $\varkappa < 1{\cdot}5$ Å the incoherent intensity represents less than 20% of the total scattering. Also the discrepancy is increased by going to the limit of the combined atom and using the incoherent intensity as calculated for silicon.

Consideration of the molecular vibration will slightly reduce the coherent scattering from the 'rigid model' calculation but it is not expected to make any significant change in the results obtained. Only the zero-point vibration will be of any importance at normal temperatures (the separation of the vibrational levels being about $3300k$ where k is Boltzmann's constant) and the r.m.s. change of bond length for the ground state is about 0·03 Å, which is a little less than 3% of the internuclear distance. If one assumes the molecular electron density to be the superposition of two spherical densities which are centred on and move with the nuclei then it may be shown (Pirenne, 1946, p. 88, see especially equation (86)) that nowhere within the range of $\varkappa$ considered is the coherent scattering reduced by as much as 1% by consideration of the ground-state vibration. Although the electron density in N_2 may not be represented in this way it is not expected that this conclusion will be greatly in error.

The marked discrepancy between Gajewski's experimental results and the results of the fairly complete calculation of the X-ray scattering by N_2, described above, makes it difficult to escape the conclusion that acceptance of the measured intensities implies that the Scherr density is an inadequate representation of the true electron density in the nitrogen molecule, taking insufficient account of bonding.

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