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X-ray Scattering by Aggregates of Bonded Atoms. II. The Effect of the Bonds: with an Application to H_2

By R. McWeeny

Department of Physical Chemistry and Coke Research, King's College, Newcastle upon Tyne 1, *England*

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The X-ray scattering from an aggregate of *bonded* atoms can be dealt with in exactly the same way as when interactions are neglected, provided the atomic scattering factors (f) are replaced by *effective* scattering factors (f^e). The effective factor depends upon atomic environment and its precise definition involves the resolution of the non-localized charge cloud, which describes the bonding electrons, into formal 'atomic' components. f^e, which is generally a complex quantity, can be obtained from f by vector addition of a correction, Δf. The calculation of the correction involves the evaluation of a 'bond scattering factor'; the method of integration employed for this purpose is fully described.

Finally, the theory is applied to the case of a hydrogen atom in the hydrogen molecule. In this instance the correction required is large. f^e is found to depend strongly on the inclination of the scattering normal to the axis of the molecule: as this inclination decreases the pronounced asymmetry of the system introduces a considerable phase shift into the scattered beam. The correction is perhaps exceptionally large in this case; but the nature of the results throws some light on other problems involving 'anomalous reflexions'.

1. The effective scattering factor for a bonded atom

When interatomic distances are large the electrons associated with a number of atoms may conveniently be allocated to the various atoms, occupying orbitals which are essentially localised or *atomic* in character. The X-ray scattering from such an aggregate is then simply a sum of contributions, with appropriate phase factors, from the various atoms, each contribution (f) representing the scattering from a definite number of 'atomic' electrons.

When the atoms are united in a molecule or crystal, we shall naturally try to retain this *type* of description, replacing the atomic scattering factors (f) by *effective* atomic scattering factors (f^e). But there is one immediate difficulty: those electrons responsible for bonding now occupy orbitals which extend over at least two atoms and possibly over the whole molecule or crystal—the 'charge cloud' no longer falls naturally into localized regions, with a definite number of electrons 'on' each atom, and yet we wish to make such a division, describing the charge cloud as a superposition of modified 'atomic' contributions.

To a first approximation we assume, as is customary, that the electronic wave function of the whole many-electron problem is represented mainly by one configuration (i.e. by a single antisymmetrised product function); the one-electron functions may then be either atomic or molecular in character and, provided they are mutually orthogonal, the total electron density is simply a sum of one-electron contributions. Those contributions arising from the inner shell or atomic electrons (which occupy strict AO's) have been dealt with previously (McWeeny, 1951*a*—hereafter I). It is now necessary to allocate the mobile charge (i.e. that portion of the complete charge distribution which arises from the mobile or 'molecular' electrons) uniquely to the various atoms, distributing the charge allocated to each atom in such a way that superposition of these 'atomic' contributions yields the full mobile charge distribution. This may be achieved conveniently, in the molecular orbital (MO) approximation which we employ, by using the concepts of (mobile) atom and bond charges, q_μ and $q_{\mu\nu}$ (McWeeny, 1951*b*): these quantities measure, respectively, the amounts of mobile charge *on the atom* μ and *in the bond* μ—ν. More precisely, the mobile charge associated with a group of electrons occupying MO's $\psi_j = \sum_\mu x_{\mu j}\varphi_\mu$ may be divided out into localized amounts $q_\mu = \sum_j x_{\mu j}^2$ and $q_{\mu\nu} = 2S_{\mu\nu}\sum_j x_{\mu j}x_{\nu j}$, where $S_{\mu\nu}$ is the overlap integral between orbitals φ_μ, φ_ν and the summations extend over all electrons (a term being counted twice for a doubly filled orbital). These 'local' charges may conveniently be regrouped into 'formal' charges (Q_μ)* associated with the various atoms; we define Q_μ as

$$Q_\mu = q_\mu + \sum_\nu{}' \tfrac{1}{2}q_{\mu\nu}\,,^*$$

so that the formal charge comprises the atom charge plus half the charge in each bond† radiating from the

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* Q_μ replaces the q_μ of other authors (Chirgwin & Coulson, 1950); we now reserve small letters for the components of Q_μ, i.e. for the local charges.

* The prime indicates omission of the term $\nu = \mu$.

† Strictly, the summation includes all *atom-pairs* but only *adjacent* atoms possess a substantial $q_{\mu\nu}$.

atom. Summation of the formal charges (Q_μ) on one atom, associated with the various groups of molecular electrons (e.g. σ-bond electrons, π-bond electrons), gives roughly the number of valence electrons contributed by the atom; an appreciable difference implies ionic effects and is most marked when atoms with widely different electron affinities are bonded, while exact equality would imply uniform spreading of the mobile charge and, as might be expected, occurs only in special cases (see, for example, Coulson & Rushbrooke, 1940). It remains to determine the effective scattering factor for each atom with its appropriate share of mobile charge.

Now Q_μ arises from a charge density function

$$P_\mu = q_\mu \varrho_\mu + \sum_\nu{}' \tfrac{1}{2} q_{\mu\nu} \varrho_{\mu\nu} ,$$

where $\varrho_\mu = \varphi_\mu^2$ and $\varrho_{\mu\nu} = \varphi_\mu \varphi_\nu / S_{\mu\nu}$. The scattering factor computed using an appropriate P_μ for each group of molecular electrons may properly be called the *effective* scattering factor (f^e) for the atom in the given molecular environment. It is worth noting that, although their *extent* cannot be predicted without calculation, considerable insight into the *nature* of the modifications introduced by bonding can be gained from purely pictorial considerations. For the form of P_μ shows that valence electrons originally on atom μ may be regarded as 'pulled' into the bonds, 'knobs' appearing in these regions while the charge density nearer the nucleus is somewhat diminished: this picture will be found helpful in later discussions. It should, of course, be remembered that the *degree* of distortion it governed by the overlap integrals $S_{\mu\nu}$ and is therefore strongly dependent on the type of bond considered: in π-bonding, for example, the effect will probably be much less marked than in σ-bonding.

With the above definition, and with the notation of I, the contribution to f^e arising from the mobile charge Q_μ^τ associated with the τth group of MO's, is

$$f_\mu(\tau) = q_\mu^\tau \int \varrho_\mu^\tau \exp\{i\varkappa \mathbf{S}\cdot\mathbf{r}_\mu\} d\mathbf{r}_\mu + \sum_\nu{}' \tfrac{1}{2} q_{\mu\nu}^\tau \int \varrho_{\mu\nu}^\tau \exp\{i\varkappa \mathbf{S}\cdot\mathbf{r}_\mu\} d\mathbf{r}_\mu .$$

We write

$$f_\mu(\tau) = q_\mu^\tau f_\mu(\varrho_\mu^\tau) + \sum_\nu{}' \tfrac{1}{2} q_{\mu\nu}^\tau f_\mu(\varrho_{\mu\nu}^\tau) . \tag{1}$$

Then $f_\mu(\varrho_\mu^\tau)$ is simply the scattering factor for an electron in the AO φ_μ^τ and has been dealt with in I, while $f_\mu(\varrho_{\mu\nu}^\tau)$ may be called a 'bond scattering factor' for bond μ—ν, referred to atom μ. The coefficients, q_μ^τ, $q_{\mu\nu}^\tau$, may vary widely according to molecular environment; these coefficients, therefore, determine the effective scattering factor in any given environment in terms of $f_\mu(\varrho_\mu^\tau)$ and $f_\mu(\varrho_{\mu\nu}^\tau)$ which are, to a first approximation, *independent* of the mobile electronic structure. The effective atomic scattering factor is therefore

$$f_\mu^e = f_{\mu c} + \sum f_\mu(\tau) , \tag{2}$$

where $f_{\mu c}$ is the factor for the inner-shell or 'core' electrons, and the summation embraces all systems of molecular electrons.

Once the effective scattering factors, f^e, defined in this way, have been computed they may be used in the determination of structure factors in exactly the same way as the conventional f's; but now the effect of bonding is completely allowed for. Since, however, the definition and use of the f^e's presupposes considerable knowledge of the structure being determined (see also I) it is necessary (and would in any case be desirable) to make a preliminary analysis using much simpler and cruder f's.

2. The nature of the bond correction

In order to introduce the effect of bonding as a *correction* to existing isolated-atom factors (I), we write (1) in the form

$$f_\mu(\tau) = n_\mu^\tau f_\mu(\varrho_\mu^\tau) + [(q_\mu^\tau - n_\mu^\tau) f_\mu(\varrho_\mu^\tau) + \sum_\nu{}' \tfrac{1}{2} q_{\mu\nu}^\tau f_\mu(\varrho_{\mu\nu}^\tau)] ,$$

where n_μ^τ is the number of electrons originally on atom μ which go into the τth set of MO's. Now $f_{\mu c} + \sum_\tau n_\mu^\tau f_\mu(\varrho_\mu^\tau) = f_\mu$, the scattering factor for the isolated atom in the valence state, and we may therefore write, from (2),

$$f_\mu^e = f_\mu + \Delta f_\mu , \tag{3}$$

where the correction term is

$$\Delta f_\mu = \sum_\tau{}' [(q_\mu^\tau - n_\mu^\tau) f_\mu(\varrho_\mu^\tau) + \sum_\nu{}' \tfrac{1}{2} q_{\mu\nu}^\tau f_\mu(\varrho_{\mu\nu}^\tau)] . \tag{4}$$

Now the charge density with which f_μ^e is associated, as we have already seen, possesses generally neither centro-symmetry nor spherical symmetry about the centre μ. Apparently then, from elementary considerations, the correction Δf_μ must generally be complex, introducing a phase shift into the diffracted beam, and must be 'angle-dependent' in the sense that it will depend upon the orientation of the bonded atom with respect to the scattering normal S. (The uncorrected factor f_μ will, of course, itself exhibit angle-dependence if the isolated atom is non-spherical (see I) but the *bonding* effect considered here is quite general.) Δf_μ may therefore be written $\Delta f_\mu = |\Delta f_\mu| e^{i\delta}$, and the combination of f_μ and Δf_μ to give f_μ^e is conveniently indicated in a vector diagram (Fig. 1). If we assume, as in Fig. 1, that the correction is relatively small, then the phase factor introduced in the resultant f_μ^e is clearly likely to be of minor importance; but the phase factor in Δf_μ actually determines the *magnitude*

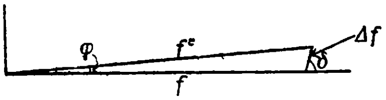

Fig. 1. Construction of the effective scattering factor f^e.

of f^e_μ. In fact, if the resultant phase shift is negligible, f^e_μ is an 'ordinary' real* scattering factor given by

$$f^e_\mu = f_\mu + |\Delta f_\mu| \cos \delta \, .$$

In certain cases δ may vanish, either for particular orientations (δ depends upon both scattering angle and orientation) or, more generally, in cases of centrosymmetry of the atomic site; f^e_μ is then certainly real. But the dependence of f^e_μ upon atomic orientation is universal, for no atomic site can possess spherical symmetry.

In a subsequent section, we shall study the hydrogen molecule, a case in which the correction Δf_μ is large and introduces great asymmetry and a considerable phase shift in f^e_μ; but we must remember that this is an extreme case. The importance of the correction will certainly be smaller for heavier atoms; a detailed judgement, however, must await the results of calculations at present in progress.

3. The bond scattering factor $f_\mu(\varrho_{\mu\nu})$

It remains simply to calculate the bond scattering factors $f_\mu(\varrho^\tau_{\mu\nu})$ which appear in (4). Before doing so, it should be emphasised that $f_\mu(\varrho^\tau_{\mu\nu})$ is calculated with reference to *point* μ as origin and represents the contribution per electron from the 'knob' $\varrho^\tau_{\mu\nu}$ (in the bond μ—ν) to the scattering factor to be associated with point μ, f^e_μ. This choice of origin is convenient mathematically, as well as formally, since the number of series expansions necessary in the integration is thereby kept to a minimum. $f_\mu(\varrho^\tau_{\mu\nu})$ can, of course, be subsequently referred to any other origin simply by introducing an appropriate phase factor. Thus, for example,

$$f_\nu(\varrho^\tau_{\nu\mu}) = f_\nu(\varrho^\tau_{\mu\nu}) = \exp\left(-i\varkappa \mathbf{S}\cdot\mathbf{R}_{\mu\nu}\right) f_\mu(\varrho^\tau_{\mu\nu}) \, ,$$

giving the bond contribution to be associated with atom ν at the other end of the bond μ—ν.

A rigorous calculation is extremely tredious but cannot be avoided if we are to provide the means of testing a method of approximation which will be introduced in a later paper. In view of the approximations inherent in the whole MO treatment and our lack of exact knowledge of the most suitable atomic valence orbitals (and since, indeed, we are calculating a 'correction factor') it would be foolish to include tentative refinements which would detract from the general utility of the treatment. For this reason we shall usually construct our MO's from the AO's appropriate to the isolated atoms (using variational approximations as in (I)) and shall assume a 'standard' bond length where possible; the effect of refinements will only be examined when satisfactory mathematical techniques have been developed.

Reduction of the integral

The bond scattering factor is

$$f_\mu(\varrho^\tau_{\mu\nu}) = \frac{1}{S_{\mu\nu}} \int \varphi^\tau_\mu(\mathbf{r}_\mu)\varphi^\tau_\nu(\mathbf{r}_\nu) \exp\{i\varkappa \mathbf{S}\cdot\mathbf{r}_\mu\} d\mathbf{r}_\mu \, . \qquad (5)$$

Taking the bond as an axis of polar co-ordinates, using the notation of Fig. 2 and putting $\varkappa' = \varkappa|S|$,

$$f_1(\varrho_{12}) = \frac{1}{S_{12}} \iiint \varphi_1(r_1\theta_1\varphi_1)\varphi_2(r_2\theta_2\varphi) \exp\{i\varkappa' r_1 (\cos\theta_1 \cos\psi + \sin\theta_1 \sin\psi \cos\varphi)\} r_1^2 \sin\theta_1 dr_1 d\theta_1 d\varphi \, .^*$$

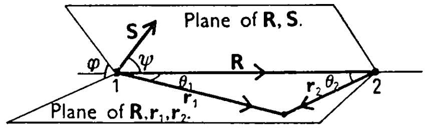

Fig. 2. Notation used in evaluation of $f_1(\varrho_{12})$.

The method of integration which we shall employ in this paper breaks down when the wave functions involve φ, in which case the problem becomes most unwieldy, but even with this restriction the method is applicable fairly generally (in particular, to molecular σ-bonding, where overlap is large and the effect of bonding is likely to be most marked).

$\varphi_1(r_1\theta_1)\varphi_2(r_2\theta_2)$ may be expressed as a sum of terms $r_1^{n_1} r_2^{n_2} e^{-c_1r_1-c_2r_2} (\cos\theta_1)^{m_1} (\cos\theta_2)^{m_2}$, where n_1, n_2, m_1, m_2 are usually integral, taking zero values in the simplest case (overlapping 1*s* orbitals).

The contribution of such a term to $f_1(\varrho_{12})$ will be denoted by $f_1(m_1m_2n_1n_2)$†; the φ-integration is then standard, giving

$$f_1(m_1m_2n_1n_2) = \frac{2\pi}{S_{12}} \iint r_1^{n_1} r_2^{n_2} e^{-c_1r_1-c_2r_2} (\cos\theta_1)^{m_1} (\cos\theta_2)^{m_2} \exp\{i\varkappa' r_1 \cos\theta_1 \cos\psi\} J_0(\varkappa' r_1 \sin\theta_1 \sin\psi) r_1^2 \sin\theta_1 dr_1 d\theta_1 \, .$$

In order to complete the integration it is necessary to express $r_2^{n_2} e^{-c_2r_2} (\cos\theta_2)^{m_2}$ in terms of the chosen variables r_1, θ_1. Expressing $(\cos\theta_2)^{m_2}$ in terms of $\cos\theta_1$, using $r_1 \cos\theta_1 = R - r_2 \cos\theta_2$, we may write all integrals (and hence, finally, $f_1(\varrho_{12})$) in terms of

$$J(klm) = \iint r_1^{l-1} r_2^{m-1} e^{-c_1r_1-c_2r_2} \cos^k\theta_1 \exp\{i\varkappa' r_1 \cos\theta_1 \cos\psi\} J_0(\varkappa' r_1 \sin\theta_1 \sin\psi) r_1^2 \sin\theta_1 dr_1 d\theta_1 \, . \qquad (6)$$

This is a generalization of an integral ($J(klm)$) considered by Barnett & Coulson (1951) (hereafter BC), whose notation we adopt, reducing to their case when $\varkappa' \to 0$. When $\varkappa' \neq 0$, the θ_1 integration is no longer straightforward, but provided k is small (as it is with

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[*] We assume here and in Fig. 1 that f_μ itself is real; in some atomic valence states f_μ may be complex (see I) but the requisite modifications are obvious.

[*] Here and elsewhere the integrations extend over the usual domains of the variables indicated.

[†] Only the numbers labeling a term are explicitly referred to; the dependence on the various parameters is not indicated.

the simpler wave functions) the following reduction is practicable. Making the usual expansion (BC),

$$r_2^{m-1}e^{-c_2r_2} = \sum_{n=0}^{\infty} \frac{2n+1}{(r_1R)^{\frac{1}{2}}} P_n(\cos\theta_1)\zeta_{mn}(c_2, R; r_1)\,, \quad (7)$$

we put, in the resultant integrand, $\cos^k\theta_1P_n(\cos\theta_1) = \sum_{n'} a_{n'}P_{n'}(\cos\theta_1)$ determining the several non-vanishing coefficients, $a_{n'}$, by standard methods. $J(klm)$ is now expressed as a sum of several (strongly convergent) infinite series, a typical term of which is

$$J_n(n'lm) = \iint r_1^{l-\frac{3}{2}}e^{-c_1r_1}P_{n'}(\cos\theta_1)\zeta_{mn}(c_2, R; r_1)$$

$$\exp\{i\varkappa' r_1\cos\theta_1\cos\psi\}\,J_0(\varkappa' r_1\sin\theta_1\sin\psi)r_1^2\sin\theta_1dr_1d\theta_1\,.$$

The θ_1 integration may now be performed using a result given by Gegenbauer (1877) (see also Watson, 1922):

$$\int\exp(iz\cos\theta\cos\psi)J_{\nu-\frac{1}{2}}(z\sin\theta\sin\psi)C_r^{\nu}(\cos\theta)\sin^{\nu+\frac{1}{2}}\theta d\theta$$
$$= \left(\frac{2\pi}{z}\right)^{\frac{1}{2}}(i)^r\sin^{\nu-\frac{1}{2}}\psi C_r^{\nu}(\cos\psi)J_{\nu+r}(z)\,.$$

Remembering $C_r^{\frac{1}{2}}(z) = P_r(z)$, we have

$$J_n(n'lm)$$
$$= \left(\frac{2\pi}{\varkappa'}\right)^{\frac{1}{2}}(i)^{n'}P_{n'}(\cos\psi)\int_0^{\infty} r_1^l e^{-c_1r_1}J_{n'+\frac{1}{2}}(\varkappa' r_1)\zeta_{mn}(c_2Rr_1)dr_1$$
$$= \left(\frac{2\pi}{\varkappa'}\right)^{\frac{1}{2}}(i)^{n'}P_{n'}(\cos\psi)Z_n(n'lm)\,, \text{ say}\,. \quad (8)$$

$Z_n(n'lm)$ is again a generalisation of an integral studied by Barnett & Coulson at a corresponding stage in their calculations. As these authors show, the ζ_{mn} are expressible as linear combinations of ζ_{on} functions, the latter being

$$\zeta_{on} = I_{n+\frac{1}{2}}(c_2r_1)K_{n+\frac{1}{2}}(c_2R)\,, \quad r_1 < R\,,$$
$$= I_{n+\frac{1}{2}}(c_2R)K_{n+\frac{1}{2}}(c_2r_1)\,, \quad r_1 > R\,.$$

The only types of integral remaining are now

$$\int_0^R r_1^l e^{-c_1r_1}J_{n'+\frac{1}{2}}(\varkappa' r_1)I_{n+\frac{1}{2}}(c_2r_1)dr_1 \quad \text{and}$$

$$\int_R^{\infty} r_1^l e^{-c_1r_1}J_{n'+\frac{1}{2}}(\varkappa' r_1)K_{n+\frac{1}{2}}(c_2r_1)dr_1\,.$$

It is convenient to introduce the variables $t = c_2r_1$, $x = \varkappa'/c_2$, $y = c_2R$, $c = c_1/c_2$, in which case we require only

$$\mathscr{I}(lmn) = \int_0^y t^l e^{-ct}J_{m+\frac{1}{2}}(xt)I_{n+\frac{1}{2}}(t)dt,$$
$$\mathscr{K}(lmn) = \int_y^{\infty} t^l e^{-ct}J_{m+\frac{1}{2}}(\varkappa t)K_{n+\frac{1}{2}}(t)dt\,. \quad (9)$$

The actual evaluation of these basic integrals will be considered in an Appendix. Simple numerical integration (used successfully in the BC integrals) is unfortunately out of the question at every stage in our calculations since the presence of the Bessel function makes the integrand oscillate strongly.

4. The hydrogen molecule

The bond factor $f_1(\varrho_{12})$ is, with

$$\varphi_1(r) = \varphi_2(r) = \varphi_{1s}(r) = N_{1s}e^{-\mu r},$$

$$f_1(\varrho_{12}) = \frac{1}{S_{12}}\iiint e^{-\mu(r_1+r_2)}\exp\{i\varkappa' r_1(\cos\theta_1\cos\psi$$
$$+\sin\theta_1\sin\psi\cos\varphi)\}r_1^2\sin\theta_1dr_1d\theta_1d\varphi\,.$$

In this case the reduction to $J(klm)$ is immediate, giving

$$f_1(\varrho_{12}) = \frac{2\pi N_{1s}^2}{S_{12}}J(011)\,,$$

where

$$J(011) = \iint e^{-\mu(r_1+r_2)}\exp\{i\varkappa' r_1\cos\theta_1\cos\psi\}$$
$$J_0(\varkappa' r_1\sin\theta_1\sin\psi)r_1^2\sin\theta_1dr_1d\theta_1\,.$$

Since $k = 0$, $n' = n$; and insertion of the expansion (7), followed directly by integration over θ_1, expresses $J(011)$ in terms of the Z-functions: thus, from (7) and (8),

$$J(011) = \frac{1}{R^{\frac{1}{2}}}\sum_{n=0}^{\infty}(2n+1)J_n(n11)$$
$$= \left(\frac{2\pi}{R\varkappa'}\right)^{\frac{1}{2}}\sum_{n=0}^{\infty}(2n+1)(i)^nP_n(\cos\psi)Z_n(n11)\,,$$

where

$$Z_n(n11) = \int_0^{\infty} r_1e^{-\mu r_1}J_{n+\frac{1}{2}}(\varkappa' r_1)\zeta_{1n}(\mu, R; r_1)dr_1\,.$$

Writing $\zeta_{1n}(\mu, R; r_1)$ as a combination of ζ_{0n}-functions, we find

$$\zeta_{1n}(\mu, R; r_1) = \frac{\mu Rr_1}{2n+1}\{\zeta_{0\overline{n-1}}(\mu, R; r_1) - \zeta_{0\overline{n-1}}(\mu, R; r_1)\}.$$

Finally, putting $\mu r_1 = t$, $\varkappa'/\mu = x$, $\mu R = y$,

$$Z_n(n11)$$
$$= \frac{y}{\mu^3(2n+1)}[K_{n-\frac{1}{2}}(y)\,\mathscr{I}(2n\overline{n-1}) - K_{n+\frac{3}{2}}(y)\,\mathscr{I}(2n\overline{n+1})$$
$$+ I_{n-\frac{1}{2}}(y)\mathscr{K}(2n\overline{n-1}) - I_{n+\frac{3}{2}}(y)\mathscr{K}(2n\overline{n+1})]$$

in terms of the basic integrals (9). The integrals are evaluated (see Appendix) using the correct bond length ($R = 1{\cdot}4$ atomic units) but, for reasons already discussed, with no 'screening constant' correction, i.e. taking $\mu = 1$. For small-angle scattering the series expansion converges fairly quickly and the integrals need be computed only for small n; but in computing the scattering curves (Figs. 3–5) for the higher angles ($x \sim 4$) as many as fourteen convergents are required in order to obtain four-figure accuracy.

Results and discussion

A very convenient check on the calculations is afforded by the centro-symmetry of the bond charge

ϱ_{12} about the mid-point. The associated scattering factor, referred to this origin, must consequently be purely real: and change of origin to atom 1 can only introduce a phase factor $\exp\{2\pi i\varkappa' R\cos\psi\}$. The factor $f_1(\varrho_{12})$ must therefore be of the form

$$f_1(\varrho_{12}) = |f_1(\varrho_{12})| \exp\{2\pi i\varkappa' R\cos\psi\}\,.$$

Comparing this with the results of our calculations,

$$f_1(\varrho_{12}) = A + iB\,,$$

we see that the ratio of the two infinite series, A, B, is completely determined by symmetry, whatever values ψ and the scattering angle may have; in fact, $B/A = \tan\{2\pi\varkappa' R\cos\psi\}$. Our calculations were continued until this equality was satisfied to at least five figures; the real factor $|f_1(\varrho_{12})|$ was then evaluated and all results were rounded off to four figures.

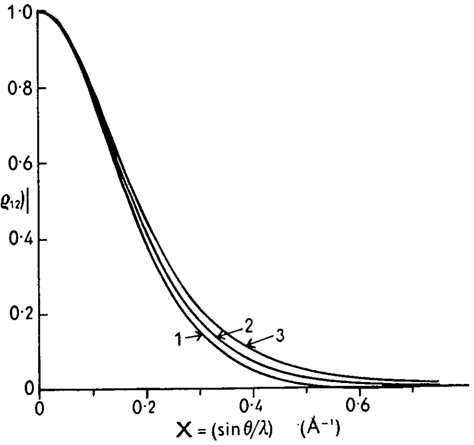

Fig. 3. Magnitude of the bond scattering factor $f_1(\varrho_{12})$. 1, 2, 3 refer to orientations $\psi = 0, \frac{1}{4}\pi, \frac{1}{2}\pi$.

In Fig. 3 $|f_1(\varrho_{12})|$ is drawn as a function of $X = (\sin\theta/\lambda)$ (as in I) for three inclinations of the scattering normal to the bond axis, $\psi = 0, \frac{1}{4}\pi, \frac{1}{2}\pi$. The marked departure from sphericity of the bond charge evidently has a very considerable effect upon the scattering; the curve for $\psi = 0$ shows a characteristic interference effect, crossing the X axis in the region $0{\cdot}5 < X < 0{\cdot}7$ Å.

Using (4), we now calculate the correction Δf which must be applied to the isolated-atom scattering factor, f. It is easily shown that in the hydrogen molecule, with our particular choice of wave functions,

$$q_1 = \frac{1}{1+S} = 0{\cdot}5705, \quad q_{12} = \frac{2S}{1+S} = 0{\cdot}8591\,.$$

Δf is of the form $|\Delta f|e^{i\delta}$ except when $\psi = \frac{1}{2}\pi$, in which case S is normal to a plane of symmetry and the phase δ vanishes. $|\Delta f|$ and δ are plotted in Fig. 4, again for the three cases $\psi = 0, \frac{1}{4}\pi, \frac{1}{2}\pi$. It is interesting to note that Δf always lies in the second or third quadrant, showing that the correction leads generally to a reduction in magnitude of the atomic scattering factor; this corresponds physically to the fact that charge has migrated away from the atom into the bond.

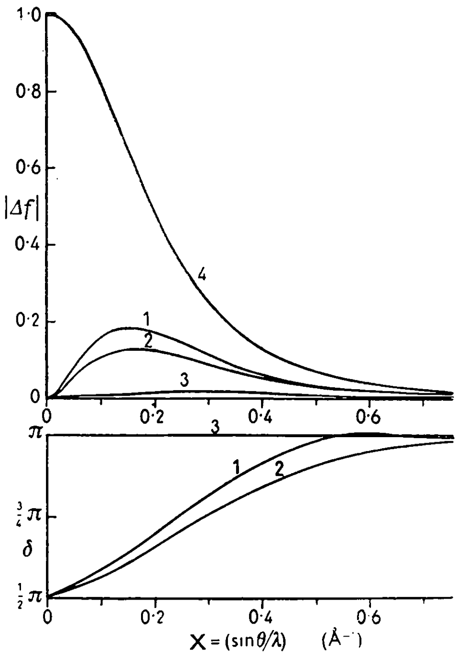

Fig. 4. Magnitude and phase of Δf for H in H_2. 1, 2, 3 refer to Δf with orientation $\psi = 0, \frac{1}{4}\pi, \frac{1}{2}\pi$. 4 is the scattering factor for the isolated atom.

Finally, the correction is applied to f, giving the effective factor f^e. Generally f^e is of the form $|f^e|e^{i\varphi}$; in Fig. 5 $|f^e|$ and φ are plotted for the three orientations considered. Comparison with the unmodified f curve shows that the correction is quite small when $\psi = \frac{1}{2}\pi$, i.e. when the bond lies in the plane of reflexion, but that the effect becomes more and more marked as ψ

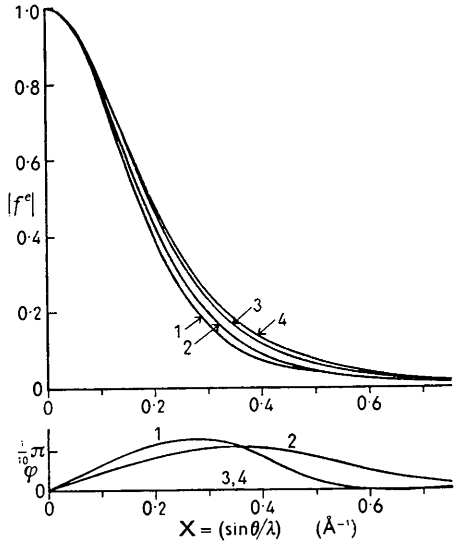

Fig. 5. Magnitude and phase of f^e for H in H_2. 1, 2, 3 refer to f^e with orientation $\psi = 0, \frac{1}{4}\pi, \frac{1}{2}\pi$. 4 refers to f, the scattering factor for the isolated H atom.

decreases, i.e. as the bond becomes normal to the plane of reflexion. Simple considerations, based upon the spread of charge, obviously support these conclusions; but the magnitude of the correction is perhaps alarming. It must, however, be emphasized that this particular case is an exceptional one in so far as the 'atomic' scattering factor arises entirely from *molecular* electrons.

These results may shed some light on a well known example of anomalous scattering. The intensities of reflexions from carbon in graphite cannot be reconciled with a single f curve and recent precise experimental work (Bacon, 1951) shows that the departures from such a curve (the valence state f curve given in I) are considerable. It now appears that the $(00l)$ reflexions, for which the bonds lie in the reflecting planes, may be roughly 'normal', lying near the isolated-atom f-curve; but the intensities of all other reflexions might be considerably depressed by the bond effect. This interpretation would certainly be consistent with the experimental results; a complete theoretical analysis will, it is hoped, appear shortly.

APPENDIX

The integrals (9) have been met with by other workers and, using the recurrence relations for $I_n(z)$ and $K_n(z)$, various recursion formulae have been listed (e.g. Duncanson, 1942). In principle it is possible to obtain all the integrals required in the hydrogen molecule calculations from the twelve integrals*

$$\mathscr{G}(10-1)\ \mathscr{G}(1-10)\ \mathscr{G}(100)\ \mathscr{G}(20-1)\ \mathscr{G}(2-10)\ \mathscr{G}(000)$$

and

$$\mathscr{K}(10-1)\ \mathscr{K}(1-10)\ \mathscr{K}(100)\ \mathscr{K}(20-1)\ \mathscr{K}(2-10)\ \mathscr{K}(000),$$

by repeated use of the appropriate formulae. It should be noticed that these formulae presuppose a knowledge of the Bessel functions $I_{n+\frac{1}{2}}(z)$, $K_{n+\frac{1}{2}}(z)$ for the z value $z = \mu R$; it was necessary to compute these functions accurately for $n = 0, 1, \ldots, 13$, no adequate tables at present existing. All the above integrals, apart from the last member of each set, can be evaluated in closed form, the Bessel functions reducing to circular or hyperbolic functions.

$\mathscr{G}(000)$, $\mathscr{K}(000)$ may be expressed as†

$$\mathscr{G}(000) = \frac{1}{\pi\sqrt{x}}(A-B), \quad \mathscr{K}(000) = \frac{1}{\sqrt{x}}C,$$

where

$$A = Si(xy),\ C = \tan^{-1}(\tfrac{1}{2}x)-B$$

and

$$B = \int_0^y \frac{e^{-2t}\sin xt}{t}\,dt.$$

Duncanson (1941) evaluates B by a series expansion but for our range of x values this is impracticable; it is then convenient to obtain B by numerical integration of the differential equation

$$\frac{dB}{dx} = \int_0^y e^{-2ct}\cos xt\,dt, \qquad (c=1)$$

the latter integral having been already tabulated as a function of x, in the calculation of $\mathscr{G}(1-10)$. This method is quite satisfactory in dealing with the $\mathscr{K}$'s, which increase fairly steadily in magnitude; but the $\mathscr{G}$'s, which are built up by repeated differencing of nearly equal quantities, rapidly becomes so inaccurate as to be quite useless. In this case it is necessary to evaluate the highest members of the required series of integrals and apply the various recurrence formulae *in reverse*: thus, in the calculation of the preceding section it was necessary to start with $\mathscr{G}(1, 14, 14)$, $\mathscr{G}(1, 13, 14)$, $\mathscr{G}(1, 14, 13)$, $\mathscr{G}(2, 13, 14)$, $\mathscr{G}(2, 14, 13)$. These integrals are evaluated by a double series expansion. Thus, we find,

$$\mathscr{G}(lmn) = \frac{(2x)^{m+1}}{\sqrt{(2\pi x)}}\sum_{r=0}^{\infty}(-x^2)^r A_m(r)\,\mathscr{G}(\overline{2r+m+l}, n),$$

where

$$\mathscr{G}(p, q) = \frac{2^{q+1}}{\sqrt{(2\pi)}}\sum_{s=0}^{\infty}A_q(s)F(p+q+1+2s),$$

$$A_m(r) = \frac{(m+r)!}{r!\,(2m+2r+1)!}$$

and

$$F(n) = \int_0^y t^n e^{-ct}\,dt \qquad \text{(an incomplete Gamma function)}.$$

Although these expansions are quite strongly convergent, it was necessary to tabulate the Gamma functions up to $F(50)$; again, in order to secure sufficient accuracy, it was necessary to build up the F's by working *downwards* from $F(50)$ using the recurrence formula,

$$F(n-1) = \frac{1}{n}\left[F(n)-y^n e^{-y}\right].$$

It is a pleasure to acknowledge the patience and skill of my wife, who is jointly responsible for many of the arduous calculations of this paper.

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* This choice is not an obvious one: but certain recurrence formulae break down for the starting values of l, m, n. It also seems advantageous, where possible, to evaluate first $\mathscr{G}(1mn)$, $\mathscr{K}(1mn)$. Once the integrals with $l = 1$ have been evaluated the $l = 2$ integrals follow very simply.

† In the case of interest $(c=1)$: more generally there are *two* integrals of type B.