The shared edges in $CsCu_2Cl_3$ are 3·76 and 4·00 Å, the unshared ones 3·71 and 3·94 Å. In $CsAg_2I_3$ the shared edges are: 4·58, 4·70, 4·84 Å, the unshared ones: 4·49, 4·54, 4·76 Å. Thus in both compounds there is no marked shortening of shared edges as is observed in ionic crystals (e.g. in TiO_2 and Al_2O_3) and also in SiS_2.

In $CsCu_2Cl_3$ the caesium ion is surrounded by six chlorine ions at the corners of a trigonal prism and two more chlorine ions on two lateral faces. On the third lateral face there are two chlorine ions at a distance only ±0·3 Å larger. In $CsAg_2I_3$ eight iodine ions surround the caesium ion, six at the corners of a trigonal prism and two on two lateral faces.

The Cl–Cl distances are all larger than twice the ionic radius of the chlorine ion. The I–I distances are also normal, except two distances of 4·08 and 4·11 Å (crystal radius of iodine ion = 2·16 Å).

Pauling's electrostatic valence rule (1939) is not strictly satisfied by these structures. The sum of the strength of the electrostatic bonds to Cl(I) is 0·9 and to Cl(II) is 1·20 (taking ten chlorine neighbours for the caesium ion). In $CsAg_2I_3$ these figures are 0·88 for I(I) and 1·25 for I(II) (taking eight iodine neighbours for the caesium ion). But of course these complexes do not strictly belong to the group of stable ionic compounds.

The optical behaviour of $CsCu_2Cl_3$ is as one would expect for a chain structure: the largest refractive index is in the chain direction. It is remarkable that in $CsAg_2I_3$ the smallest refractive index is in the chain direction. This may be a result of the rather small distances in the planes perpendicular to the z axis at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ between the iodine ions of different chains. Thus the highly polarizable iodine and caesium ions form rows in planes perpendicular to the chain direction.

We wish to thank Prof. Dr A. E. van Arkel and Prof. Dr C. H. MacGillavry for their interest in this study and the 'Organisatie voor Zuiver Wetenschappelijk onderzoek' for installing in this laboratory an X-ray diffraction apparatus which was used in this investigation.

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X-ray Scattering by Aggregates of Bonded Atoms. IV. Applications to the Carbon Atom

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The methods of previous papers are applied in the calculation of effective scattering factors for the carbon atom in diamond and in graphite, taking full account of the bonds. The factors are no longer isotropic, but the various extreme f-curves do not depart very greatly from that for the isolated atom; the differences may be significant for carbon, and for the other strongly bonded, light atoms common in organic molecules, but probably not elsewhere.

Further progress, and the full utilization of bonded-atom factors, would seem to demand a thorough investigation of thermal vibration and of 'temperature corrections'.

1. Introduction

In previous papers (McWeeny, 1951, 1952, 1953, hereafter referred to as I, II, III) the atomic scattering factors (f) for light atoms, as given by James & Brindley (1931), have been recalculated (I) using the best available analytical wave functions; the definition of such a factor has been extended to include the effect of bonding with neighbouring atoms (II); and a general approximate method of calculating certain 'bond scattering factors', which are then required, has been developed (III). It is now possible to calculate

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the *effective* factor (f^e) for a strongly bonded atom and thence to assess, with some precision, the nature and extent of the necessary corrections to the isolated-atom factor (I). Calculations of this kind will not, of course, be made very generally; but they should throw light on important fundamental issues, providing some justification for the almost universal practice of using *isolated-atom* factors for atoms in molecules and crystals and, consequently, indicating whether fairly precise calculations of such factors (along the lines of I) might usefully be extended.

Calculations on the carbon atom would be of particular value for various reasons: the effect of bonding should be particularly severe (of the six electrons in a carbon atom, four are actively engaged in the formation of strong bonds), the inadequacy of the James–Brindley f-curve has already been recognized (Brill, 1950; Franklin, 1950; Bacon, 1952) and the steady advance of organic structure analysis gives the carbon f-curve a growing importance. The desirability of using a basic f for the isolated atom *in its appropriate valence state* is already evident from I; and in this way it is possible to ascribe the main discrepancies between the observed intensities for diamond and those calculated using the James–Brindley factor to effects of *intra*-atomic origin (see Bacon, 1952). But it is necessary to go further; and in this concluding paper we shall investigate the essentially *inter*-atomic effects associated with the actual migration of charge from the carbon valence shell into the bond regions.

2. The bond factor for carbon

In dealing with carbon it is obviously necessary to distinguish two main bond types, associated respectively with saturated and unsaturated systems. In the first case all the bonds emanating from an atom are σ-bonds, but in the second case one of the bonds is of π-type and clearly raises quite new issues. We shall regard carbon in diamond and in graphite as typifying these two cases and attention will therefore be confined to C–C bonds; but it seems most unlikely that the general effects of bonding (in either given case) will be critically dependent upon what neighbours a carbon atom may have. It would not, for instance, be anticipated that the bond corrections for a (trigonal) carbon atom in an aromatic molecule would be very different from those for a similar (trigonal) carbon atom in graphite. The results of our calculations should therefore be fairly generally significant.

The wave functions we shall employ are based on the Slater (1930) atomic orbitals

$$(1s) = N_{1s}e^{-5\cdot690\,r},\quad (2s) = N_{2s}re^{-1\cdot625\,r},$$
$$(2p) = N_{2p}re^{-1\cdot625\,r}\cos\theta\,,$$

where $N_{1s} = 8\cdot3033$, $N_{2s} = 1\cdot0965$ and $N_{2p} = 1\cdot8992$: these are only slightly less accurate than the more cumbersome functions of Duncanson & Coulson (see I) and are in any case to be approximated by combinations of Gaussian terms (III). Now, the additivity of different one-electron contributions to f depends upon the mutual orthogonality of the orbitals employed and it is consequently necessary to construct an orbital $(2s)' = N'_{2s}[(2s)-A'(1s)]$, orthogonal to the inner shell $1s$ orbital[*]; $(2s)'$ then has an 'individual' significance, being an approximation to one of the Hartree–Fock orbitals upon which the calculation would ideally be based. It remains to calculate a σ-bond factor, (f_σ), and a π-bond factor (f_π).

Hybrid σ-bonds

The hybrid valence orbital involved in σ-bonding is generally

$$\varphi_\sigma(\lambda) = \frac{(2s)'+\lambda(2p)}{(1+\lambda^2)^{1/2}}\,;$$

this orbital is normalized and points in the (positive) direction of the $2p$ orbital. The hybrid C–C σ-bond results from the overlapping of two such orbitals, directed towards each other, and, in the notation of III, it follows easily that

$$\begin{aligned}f_\sigma = (\sigma|f|\sigma) = \frac{1}{S(1+\lambda^2)}\{&N'^2_{2s}S_{2s2s}(2s|f|2s)\\ &+2N'_{2s}\lambda S_{2p2s}\mathcal{R}(2p|f|2s)+\lambda^2S_{2p2p}(2p|f|2p)\}\\ -\frac{2N'_{2s}A'}{S(1+\lambda^2)}\{&N'_{2s}S_{1s2s}\mathcal{R}(1s|f|2s)+\lambda S_{1s2p}\mathcal{R}(1s|f|2p)\},\end{aligned} \quad (1)$$

where the hybrid orbital overlap integral is

$$\begin{aligned}S = \frac{1}{1+\lambda^2}\{&N'^2_{2s}S_{2s2s}+2\lambda N'_{2s}S_{2p2s}+\lambda^2S_{2p2p}\\ &-2N'_{2s}A'(N'_{2s}S_{1s2s}+\lambda S_{1s2p})\}\end{aligned}$$

in terms of those of the component orbitals. S_{1s1s} is completely negligible at C–C distances and is therefore omitted, together with a corresponding term which should, strictly, appear in (1). Indeed, only the first term in (1) is really significant: it represents the scattering from the body of the overlap charge which is essentially 'in the bond', whereas the second term arises from localized regions centred on the individual nuclei (effectively from a $1s$-type density, 'polarized' by the φ_σ factor from the other atom). On evaluating the various overlap integrals it becomes clear that the absolute contribution of the second term to the bond factor (for unit charge) is always less than $0\cdot02$: thus for all scattering angles for which the bond correction might be considerable the bond factor is quite accurately given by simply the first term of (1); this in turn amounts to saying that no serious error is committed by using the nodeless Slater $2s$ orbital

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[*] In the molecule there is a slight non-orthogonality between the *molecular* orbitals and the inner shells (arising from, for example, overlap between a $2s$ orbital on one atom and a $1s$ on another) but this is quite negligible for our purposes.

instead of the (more correct) orthogonalized orbital. This contention is confirmed by the complete calculation; and since it would be presumptuous to claim an absolute accuracy of the order 0·01 in the bond factor (which, in any case, occurs only in correction terms) we shall henceforth employ only the dominant first term of (1).

Fig. 1 shows the hybrid bond factor for a C–C bond in diamond (or a saturated molecule) based on a bond length $R = 2{\cdot}92$ a.u.* with $\lambda = \sqrt{3}$ (sp^3 hybridization), for two orientations of the scattering normal with respect to the bond, $\psi = 0$ and $\psi = \frac{1}{2}\pi$. Fig. 2 shows the factor for a C–C bond in graphite (or a conjugated molecule), based on a bond length $R = 2{\cdot}65$ a.u. (cf. 2·68 in graphite, 2·63 in benzene) with $\lambda = \sqrt{2}$ (sp^2 hybridization); for comparison purposes the valence shell contribution per electron, in the isolated atom, is added in each case. The relatively slow decay of f-values with increasing X is related to the fact that the main part of the bond charge is somewhat more compact than that associated with the atomic valence shell.

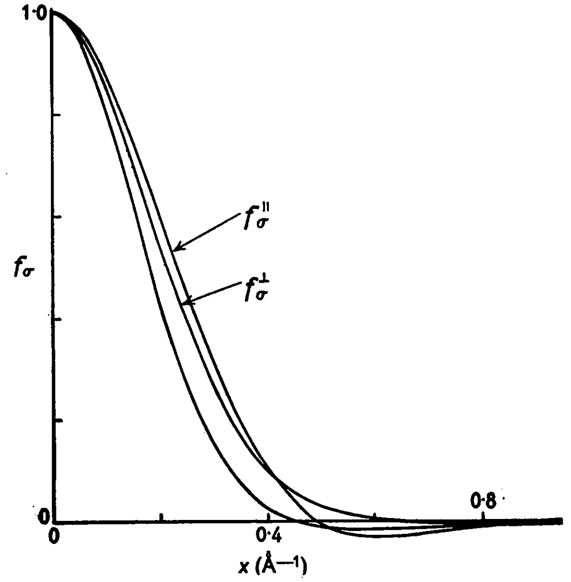

Fig. 1. σ-Bond factor (diamond) (with isolated-atom contribution/valence electron).

Although the formulae of III permit the calculation of bond factors for any orientation ψ, it is clear that they predict no *simple* angle dependence and that the anisotropy of the bond factor therefore raises considerable practical difficulties. Since, however, the anisotropy is not excessively large it may be supposed that a formula of the type

$$f_\sigma^\psi = \cos^2\psi f_\sigma^{\parallel} + \sin^2\psi f_\sigma^{\perp} \qquad (2)$$

would describe the angle dependence quite adequately, the extreme f-curves being regarded as 'principal factors', as in I. This formula would describe the scattering from the axially symmetrical charge distribution, developed in spherical harmonics as far as the term in $P_2(\cos\theta)$, and is therefore certainly a legitimate first approximation rather than an *ad hoc* interpolation formula. Numerical comparisons in the case of the hydrogen molecule confirm the adequacy of such an approximation*. For preliminary work a useful averaged bond factor might be

$$\bar{f}_\sigma = \tfrac{1}{3}(f_\sigma^{\parallel} + 2f_\sigma^{\perp}) \qquad \text{(cf. I, § 3).} \qquad (3)$$

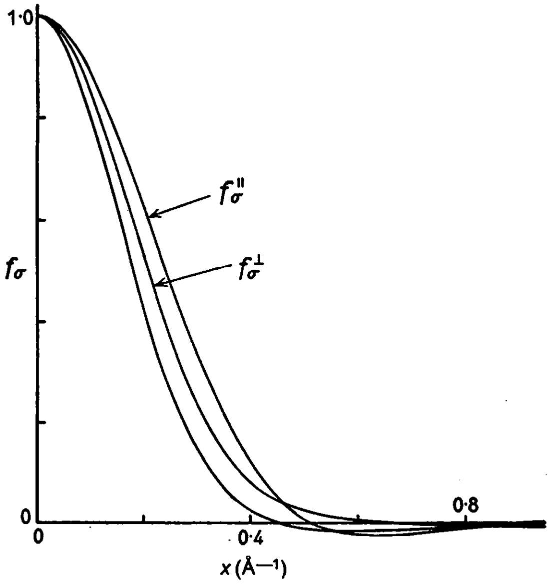

Fig. 2. σ-Bond factor (graphite) (with isolated-atom contribution/valence electron).

π-Bonds

The bond factor is in this case calculated directly from the formulae of III, f_π being a special case of the factor $(2p|f|2p)$, given for arbitrary orbital directions, occurring when the $2p$ orbitals are parallel to each other and normal to the bond. The dependence upon orientation is, however, very marked and much more complicated than in the σ-bond case, for f_π now depends on the inclination of the scattering normal **S** to both the bond axis and the $2p$ orbital directions. Fortunately, considerable reduction is possible. Denoting by φ the angle between the planes through the bond axis which contain, respectively, the vector **S** and the axes of the $2p$ orbitals, it is possible to proceed as for a single $2p$ orbital (I, § 3): it then follows (in this case rigorously) that $f_\pi^{\psi\varphi} = \cos^2\varphi f_\pi^{\psi 0} + \sin^2\varphi f_\pi^{\psi\pi/2}$. As for a σ-bond, the relatively small ψ-dependence may now be approximately described by a similar formula, giving finally

$$f_\pi^{\psi\varphi} = \cos^2\psi f_\pi^{\parallel} + \sin^2\psi\,[\cos^2\varphi f_\pi^{\perp 0} + \sin^2\varphi f_\pi^{\perp\pi/2}]\,, \qquad (4)$$

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* 1 a.u. = 0·5292 Å.

* For $\psi = \frac{1}{4}\pi$ the discrepancies are always less than 0·01.

where there are now *three* 'principal factors', one for **S** along the bond and two for **S** normal to it.

Our calculations relate to a bond length $R = 2{\cdot}65$ a.u., the three factors being shown in Fig. 3. Clearly the bond factor is not even approximately isotropic, behaving in much the same way as the atomic factor $f(2p)$.

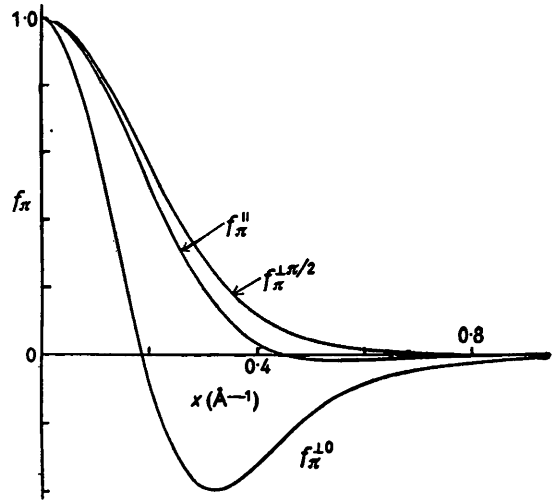

Fig. 3. π-Bond factor (graphite).

3. The effective atomic scattering factor

In order to illustrate the effects of bonding we shall calculate directly the effective factor f^e (defined in II), showing its extreme forms and comparing these results with the factor for the isolated atom in its appropriate valence state (I, § 3). In the notation of II, f^e for an atom 0 with neighbours 1, 2, ... is given by

$$f_0^e = f_{0c} + \sum_\tau f_0(\tau)\,,$$

where f_{0c} arises from the atom core, while $f_0(\tau)$ describes the scattering formally associated with atom 0, arising from the τth group of valence electrons. $f_0(\tau)$ is given by

$$f_0(\tau) = q_0^\tau f_0(\varrho_0^\tau) + \sum_n \tfrac{1}{2} q_{0n}^\tau f_0(\varrho_{0n}^\tau)\,,$$

where $f_0(\varrho_0^\tau)$ is the factor for a distribution $\varrho_0^\tau = \varphi_0^{\tau 2}$ and $f_0(\varrho_{0n}^\tau)$ is the bond factor, referred to 0 as origin, associated with a bond charge distribution $\varrho_{0n}^\tau = \varphi_0^\tau \varphi_n^\tau / S_{0n}^\tau$; the q's represent the actual amounts of charge contained in the atomic and bond regions so defined, and $Q_0^\tau = q_0^\tau + \sum_n \tfrac{1}{2} q_{0n}^\tau$ is the total amount *formally* associated with atom 0.

In diamond (and in saturated molecules) four effectively *localized* σ-bonds emanate from a carbon atom: there are four groups of two electrons (corresponding to $\tau = \sigma_1, \sigma_2, \sigma_3, \sigma_4$, say), and each makes unit contribution, $Q_0^{\sigma n} = 1$, to the formal charge associated with atom 0, the localized components being $q_0^{\sigma n} = 1/(1+S_{0n}^{\sigma n})$ 'on' the atom 0 and $q_{0n}^{\sigma n} = 2S_{0n}^{\sigma n}/(1+S_{0n}^{\sigma n})$ 'in' the bond 0–n (as in the hydrogen-molecule case, II, § 3). But in graphite (and in unsaturated or conjugated molecules) there are only three groups of *two* electrons (corresponding to $\tau = \sigma_1, \sigma_2, \sigma_3$, say), the fourth group ($\tau = \pi$, say) containing all the completely non-localized π electrons and contributing to the three 'partial' π-bonds: the calculation of Q_0^π and its component q's is no longer trivial and lies outside the scope of these papers. The effective factors for 'saturated' and 'unsaturated' carbon will now be considered individually.

Diamond

The four σ-bonds are similar and therefore give identical atom and bond charges. Using the numerical data of § 2 we find

$$q_0^{\sigma_1} = q_0^{\sigma_2} = \text{etc.} = 0{\cdot}6078\ (= q_0^\sigma),$$
$$q_{01}^{\sigma_1} = q_{02}^{\sigma_2} = \text{etc.} = 0{\cdot}7844\ (= q_{01}^\sigma)\,.$$

Thus $f(\sigma_n) = q_0^\sigma f_0(\varrho_0^{\sigma n}) + \tfrac{1}{2} q_{01}^\sigma f_0(\varrho_{0n}^{\sigma n})$ and the effective factor is

$$f_0^e = f_{0c} + q_0^\sigma \sum_{n=1}^{4} f_0(\varrho_0^{\sigma n}) + \tfrac{1}{2} q_{01}^\sigma \sum_{n=1}^{4} f_0(\varrho_{0n}^{\sigma n})\,, \tag{5}$$

where, it will be remembered, $f_0(\varrho_{0n}^{\sigma n})$ is the bond factor for the distribution $\varrho_{0n}^{\sigma n}$ of the nth σ-bond, referred to atom 0 as origin. If $\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \hat{\mathbf{r}}_3, \hat{\mathbf{r}}_4$ are unit vectors pointing along the bonds, it follows that

$$f_0(\varrho_{0n}^{\sigma n}) = \exp\,[2\pi i X R(\hat{\mathbf{S}}.\hat{\mathbf{r}}_n)] f(\varrho_{0n}^{\sigma n})\,,$$

where $f(\varrho_{0n}^{\sigma n})$ $(= f_\sigma)$ is the σ-bond factor calculated in § 2. It will be noticed that, according to I, § 3, $\sum_{n=1}^{4} f_0(\varrho_0^{\sigma n})$ is simply the valence-shell contribution (f_{0v}, say) for an *isolated* atom at 0; this *atomic* contribution remains isotropic in the bonded system because the four bonds are strictly equivalent and charge is therefore 'withdrawn' from the valence shell in a symmetrical fashion. The effective factor then consists of a dominant isotropic term $(f_{0c} + q_0^\sigma f_{0v})$, describing the scattering from a somewhat depleted but still spherical valence shell, together with an anisotropic term

$$\tfrac{1}{2} q_{01}^\sigma \sum_{n=1}^{4} f(\varrho_{0n}^{\sigma n}) \exp\,[2\pi i X R \hat{\mathbf{S}}.\hat{\mathbf{r}}_n]\,,$$

which describes the aspherical distortion associated with charge 'in the bonds'. Since $f(\varrho_{0n}^{\sigma n})$ depends on the orientation of the nth σ-bond with respect to **S**, the evaluation of this latter term is awkward; but simple expressions follow for some of the most important **S** vectors.

Thus, the bond contributions for the special **S** vectors indicated in Fig. 4 are:

$\hat{\mathbf{S}}_1$: $\tfrac{1}{2} q_{01}\, 4 \cos\,(2\sqrt{3}\pi X R/3) f_\sigma^\psi,\ \ \cos\psi = \sqrt{3}/3\,.$
$\hat{\mathbf{S}}$: $\tfrac{1}{2} q_{01} [2 \cos\,(2\pi X R \cos\psi_1) f_\sigma^{\psi_1} + 2 \cos\,(2\pi X R \cos\psi_2) f_\sigma^{\psi_2}],$

where

$$\cos\psi_1 = (\cos\alpha+\sin\alpha)/\sqrt{3},\quad \cos\psi_2 = (\cos\alpha-\sin\alpha)/\sqrt{3}\,,$$

extreme cases of the latter occurring for $\hat{\mathbf{S}}_2(\alpha = 0)$, when the contribution is clearly identical with that for $\hat{\mathbf{S}}_1$, and for $\hat{\mathbf{S}}_3(\alpha = \frac{1}{4}\pi)$.

$$\hat{\mathbf{S}}_3:\ \tfrac{1}{2}q_{01}[2\cos(2\sqrt{6}\pi XR/3)f_\sigma^\psi+2f_\sigma^\perp],\quad \cos\psi = \sqrt{6}/3\,.$$

$$\hat{\mathbf{S}}_4:\ \tfrac{1}{2}q_{01}[\cos(2\pi XR)f_\sigma^{\parallel}+3\cos(2\pi XR/3)f_\sigma^\psi],\qquad \cos\psi=1/3.^*$$

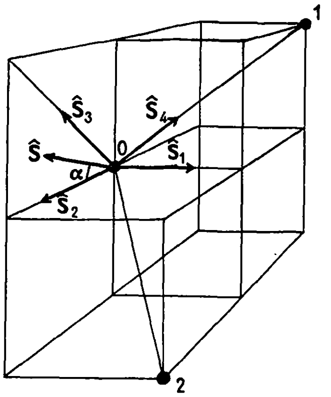

Fig. 4. Carbon atom (0) with two neighbours (1, 2) in the diamond structure, showing the directions $\hat{\mathbf{S}}_1$, $\hat{\mathbf{S}}_2$, $\hat{\mathbf{S}}_3$, $\hat{\mathbf{S}}_4$.

The effective atomic factors for $\hat{\mathbf{S}}_1$ (and $\hat{\mathbf{S}}_2$), $\hat{\mathbf{S}}_3$ and $\hat{\mathbf{S}}_4$ are shown in Fig. 5, being compared with the isolated-atom (valence state) factor (I).

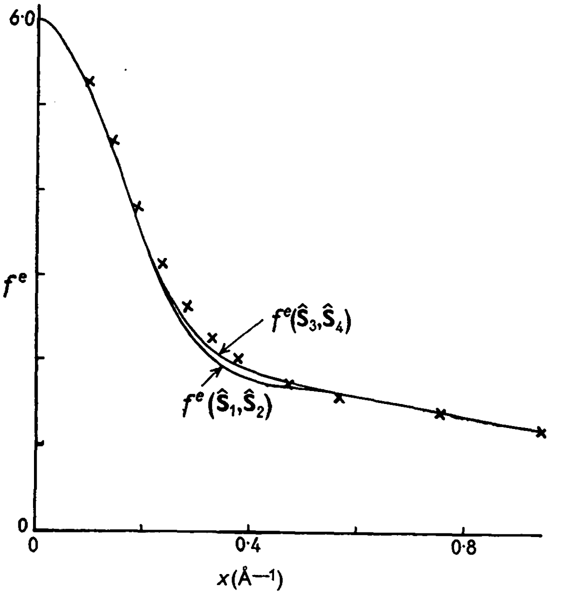

Fig. 5. The effective factor (diamond). Crosses indicate isolated-atom f-values.

Graphite

The three similar σ-bonds give, in this case, atom and bond charges $q_0^\sigma = 0{\cdot}5885$, $q_{01}^\sigma = 0{\cdot}8229$. The calculation of corresponding quantities for the π electrons of the infinite lattice is feasible only in the simple MO approximation (then involving an extension of the work of Coulson & Taylor (1952), using the methods introduced by Löwdin (1951)), but recent work (McWeeny, 1954) shows that in this approximation the π-electron bond charge is grossly over-estimated. For this reason we shall calculate the π-electron effect using two extreme estimates of the atom and bond charges: these will be taken as

$$\text{(i)}\ q_0^\pi = 0{\cdot}7510,\quad q_{01}^\pi = 0{\cdot}1660\ \text{(MO)},$$
$$\text{(ii)}\ q_0^\pi = 1{\cdot}0,\quad q_{01}^\pi = 0\,.$$

It is apparent that the effect of π-bonding is of a very different order of magnitude from that of σ-bonding, the charges 'in the bond' being respectively of the order of 10% and 80% of an electron: a π electron must therefore be described as nearly completely 'on' its atom (completely so in (ii)). This is in agreement with the findings of March (1952) who plotted π-electron densities in a system of this general type (benzene), showing that the actual π-electron density was insignificant (compared with that of the σ electrons) except immediately above and below each carbon atom.

The effective factor is

$$f_0^e = f_{0c}+\sum_{n=1}^{3}[q_0^{\sigma n}f_0(\varrho_0^{\sigma n})+\tfrac{1}{2}q_{0n}^{\sigma n}(\varrho_{0n}^{\sigma n})] + [q_0^\pi f_0(\varrho_0^\pi)+\sum_{n=1}^{3}\tfrac{1}{2}q_{0n}^\pi f_0(\varrho_{0n}^\pi)]\,. \quad (6)$$

As in the case of diamond, it is possible to extract a large isotropic term from the valence-electron contributions: thus, again using the results of I, § 3,

$$f_0^e = f_{0c}+q_0^\sigma f_{0v}+(q_0^\pi-q_0^\sigma)f_0(\varrho_0^\pi) +\tfrac{1}{2}q_{01}^\sigma\sum_{n=1}^{3}f(\varrho_{0n}^{\sigma n})\exp(2\pi iXR\hat{\mathbf{S}}.\hat{\mathbf{r}}_n) +\tfrac{1}{2}q_{01}^\pi\sum_{n=1}^{3}f(\varrho_{0n}^\pi)\exp(2\pi iXR\hat{\mathbf{S}}.\hat{\mathbf{r}}_n)\,. \quad (7)$$

This expression is of considerable interest. The first two terms represent, as in diamond, the scattering from a spherically symmetrical 'atomic' charge distribution. But now, in addition to the bond terms (representing both σ- and π-bonds), there is a *further* contribution of *intra-atomic* origin: this is associated with an *anisotropic* distortion of the atomic valence shell which arises because the electrons of the σ-bonds leave this shell to a far greater extent than that engaged in π-bonding. A contribution of this kind will always occur when the various bonds formed by the atom are not precisely equivalent.

Again, it is possible to give expressions for the f-curves for certain prominent types of reflexion. Owing

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* The contribution is in this case complex but, being small relative to the other terms in (5), it is sufficient to take the real part only, summation giving $|f_0^e|$ (see II, § 2).

to the complicated and very strong angle-dependence of f_π, however, the sums in (7) reduce to simple form only when S lies either in the plane of the carbon atom (($hk0$) reflexions) or normal to it (($00l$) reflexions). In the first case we may assume S makes an angle α with one bond: the total bond contribution is then periodic in α, with period $\frac{1}{3}\pi$, the relevant real part being

$$\begin{aligned}\tfrac{1}{2}[&\cos(2\pi XR\cos\alpha)(q^{\sigma}_{01}f^{\alpha}_{\sigma}+q^{\pi}_{01}f^{\alpha\,\pi/2}_{\pi})\\ &+\cos(2\pi XR\cos\beta)(q^{\sigma}_{01}f^{\beta}_{\sigma}+q^{\pi}_{01}f^{\beta\,\pi/2}_{\pi})\\ &+\cos(2\pi XR\cos\gamma)(q^{\sigma}_{01}f^{\gamma}_{\sigma}+q^{\pi}_{01}f^{\gamma\,\pi/2}_{\pi})]\,,\end{aligned}$$

where

$$\cos\beta=\tfrac{1}{2}(\cos\alpha+\sqrt{3}\sin\alpha)\quad\text{and}\quad\cos\gamma=\tfrac{1}{2}(\cos\alpha-\sqrt{3}\sin\alpha)\,,$$

with extreme values

$$\begin{aligned}&\hat{\mathbf{S}}_1(\alpha=0):\ \tfrac{1}{2}[\cos(2\pi XR)(q^{\sigma}_{01}f^{\|}_{\sigma}+q^{\sigma}_{01}f^{\|}_{\pi})\\ &\qquad+2\cos(\pi XR)(q^{\sigma}_{01}f^{\beta}_{\sigma}+q^{\pi}_{01}f^{\beta\,\pi/2}_{\pi})],\quad \cos\beta=\tfrac{1}{2};\\ &\hat{\mathbf{S}}_2(\alpha=\pi/2):\ \tfrac{1}{2}[(q^{\sigma}_{01}f^{\perp}_{\sigma}+q^{\pi}_{01}f^{\perp\,\pi/2}_{\pi})\\ &\qquad+2\cos(\sqrt{3}\pi XR)(q^{\sigma}_{01}f^{\beta}_{\sigma}+q^{\pi}_{01}f^{\beta\,\pi/2}_{\pi})],\quad \cos\beta=\tfrac{1}{2}\sqrt{3}\,.\end{aligned}$$

When S is normal to the plane the contribution is simply

$$\hat{\mathbf{S}}_3:\ \tfrac{3}{2}[q^{\sigma}_{01}f^{\perp}_{\sigma}+q^{\pi}_{01}f^{\perp 0}_{\pi}]\,.$$

The scattering factors for these three cases are shown in Fig. 6, again being compared with the isolated-atom factor of I. It is not possible, on this scale, to distinguish the cases $\alpha=0,\ \frac{1}{2}\pi$. The solid and broken curves refer, respectively, to the extreme approximations (ii) and (i), the former being almost certainly the more accurate.

4. Discussion

Figs. 5 and 6 provide a striking justification for the almost universal use of isolated-atom scattering factors in crystal-structure calculations. It is evident that factors calculated along the lines indicated in I, *for atoms in appropriate valence states*, would provide a sound basis even for quite refined analyses (except perhaps in the case of carbon and the other strongly bonded, light atoms commonly found in organic molecules—more particularly when the valence states involved are of less than maximum symmetry) for it is difficult to imagine other cases in which the relative effect of bonding might exceed that represented in the curves of Figs. 5 and 6. In the case of heavier atoms, for instance, the effect would be completely masked by the intense inner-shell scattering except in very-low-angle scattering.

There are two main effects of bonding. For an atom in a highly symmetrical environment (e.g. carbon in diamond, Fig. 5), the f-values are slightly reduced in low-angle scattering but closely approach those for the isolated atom at larger X values: this is due to a diminution of the valence-shell contribution (which is inappreciable in high-angle scattering), resulting from a symmetrical migration of charge into the more remote 'bond regions' where its effectiveness is reduced by interference. In such cases no extensive *anisotropy* is introduced and the usual assumption of a *spherical* atom may be fairly realistic. On the other hand, the atomic environment may be markedly asymmetrical (e.g. carbon in a graphite layer, Fig. 6) and in such cases a more significant anisotropy may arise: the bond charge distribution may then be no less compact *in certain directions* than that in the isolated atom, its effectiveness for scattering being preserved when S lies in such a direction (e.g. S normal to a graphite layer) but not otherwise (e.g. S in a graphite layer); and at the same time a comparable anisotropy may be introduced by the inherent distortion of the valence shell itself.

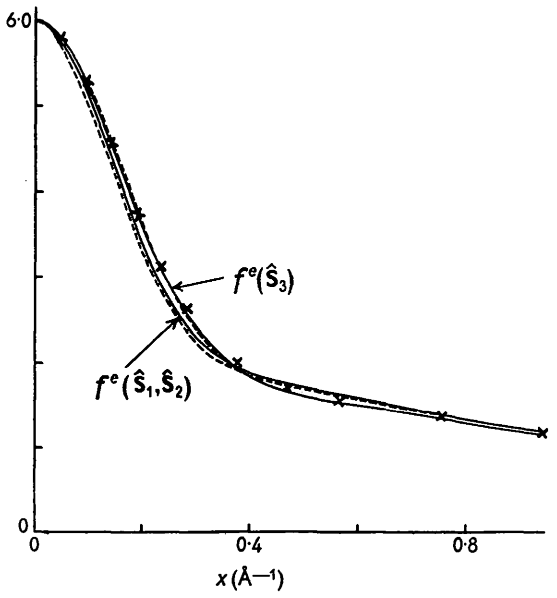

Fig. 6. The effective factor (graphite). Solid and broken curves correspond to different extreme approximations (solid curve more accurate). Crosses indicate isolated-atom f-values.

In our present state of knowledge of the best wave-function parameters for molecules, it does not seem possible to make any very reliable estimates of the absolute accuracy of the scattering factors given in this paper. But it will be appreciated that the bond correction *to the valence-electron scattering* is large and that its *gross features* may surely be predicted with some confidence; it is this drastic modification of the valence-electron scattering over a broad 'middle range' of X-values which is responsible for the small *net* bond effect represented in f^e. There is consequently little doubt that, in both magnitude and general character, the effects predicted are of real significance. The bond factors and extreme f^e-curves calculated in §§ 2 and 3 therefore seem worth recording and are collected in Table 1. The final f^e-curves may be of value in the most refined organic structure analyses, serving (probably in good approximation) to describe

Table 1

Isolated-atom factor (components)

X (a.u.)	0·00	0·05	0·10	0·15	0·20	0·25	0·30
Inner-shell	2·000	1·988	1·952	1·895	1·818	1·727	1·624
Valence-shell	4·000	3·283	1·850	0·734	0·180	−0·016	−0·058

X (a.u.)	0·40	0·50	0·60	0·70	0·80	0·90	1·00
Inner-shell	1·400	1·175	0·966	0·784	0·631	0·506	0·406
Valence-shell	−0·033	−0·005	0·007	0·011	0·010	0·009	0·008

σ-Bond factors

X (a.u.)		0·00	0·05	0·10	0·15	0·20	0·25	0·30	0·40	0·50
Diamond	$f_\sigma^{\parallel}$	1·00	0·89	0·63	0·35	0·14	0·02	−0·03	−0·01	0·00
	$f_\sigma^{\perp}$	1·00	0·87	0·57	0·30	0·12	0·04	0·01	0·00	0·00
Graphite	$f_\sigma^{\parallel}$	1·00	0·90	0·65	0·38	0·16	0·03	−0·02	−0·01	0·00
	$f_\sigma^{\perp}$	1·00	0·87	0·56	0·27	0·10	0·03	0·01	0·00	0·00

π-Bond factors

Graphite	$f_\pi^{\parallel}$	1·00	0·86	0·54	0·24	0·06	−0·01	−0·01	0·00	0·00
	$f_\pi^{\perp 0}$	1·00	0·65	−0·01	−0·37	−0·35	−0·21	−0·10	−0·03	−0·01
	$f_\pi^{\perp \pi/2}$	1·00	0·88	0·60	0·32	0·15	0·06	0·03	0·01	0·00

Effective factors

Diamond	$\hat{S}_1(\hat{S}_2)$	6·00	5·17	3·53	2·33	1·83	1·67	1·59	1·38	1·17
	$\hat{S}_3$	6·00	5·17	3·56	2·41	1·92	1·73	1·59	1·37	1·17
	$\hat{S}_4$	6·00	5·18	3·57	2·42	1·93	1·74	1·60	1·37	1·17
Graphite	$\hat{S}_1$	6·00	5·19	3·60	2·44	1·94	1·75	1·61	1·39	1·18
	$\hat{S}_2$	6·00	5·19	3·60	2·44	1·94	1·76	1·63	1·38	1·17
	$\hat{S}_3$	6·00	5·27	3·78	2·57	1·93	1·66	1·53	1·35	1·16

the carbon atom whenever there is any reasonable approach to tetrahedral or trigonal bonding.[*]

Finally, it is necessary to examine briefly the results of these papers in their more general context. The theoretical problem treated so far concerns the scattering by an aggregate of bonded atoms *at rest* and it must be appreciated that, however successfully this problem is solved, the situation is essentially hypothetical and that the introduction of thermal vibration will drastically modify the solution. Perhaps the most important result of the present work has been to establish fairly definite upper limits to the necessary 'bond corrections' to isolated-atom f-curves (as recalculated in I): it now appears that even the largest effects which can be expected are scarcely significant compared with those arising in thermal vibration and embodied in a 'temperature factor'. At the same time it is evident that bonding and vibration have a strongly differential action on the isolated-atom f-curve: bonding disturbs only the *outer* regions of the atomic charge cloud and therefore affects most significantly the *inner* part of the f-curve (Fourier transform), while vibration concerns primarily the *inner* regions (the inner-shell electrons being carried with the nucleus) and therefore affects most strongly the *outer* part of the f-curve. It is clear, for instance, that the bonding effect represented in Figs. 5 and 6 is quite insignificant for $X > 0{\cdot}8$ Å^{-1}. It follows that in high-angle scattering any discrepancies between theoretical and experimental f-curves cannot legitimately be dismissed as due to 'bond effects' and must, quite unambiguously, be attributed to an inadequate temperature factor. Indeed, bearing in mind the fact that temperature factors are often undisguisedly arbitrary while their effects heavily outweight those now associated with bonding, it would seem that, while every effort should be made to use isolated-atom factors for atoms in their appropriate valence states, future progress might well lie in the more detailed investigation of temperature factors rather than in further calculations of the effects of bonding.

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[*] Since f^e is not sensitive to the precise distribution of charge in a π-electron system, the factor for trigonal carbon should be essentially independent of the orders of the various π-bonds.